

Extinction Coefficients of Triplet-Triplet Absorption Spectra of Organic Molecules in Condensed Phases: A Least-Squares Analysis

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A global least-squares technique is developed to assist in the critical evaluation of data consisting of large sets of measurements. The technique is particularly designed to handle sets of data where many of the measurements are relative measurements. A linearization procedure is used to reduce the inherently nonlinear problem to a traditional multivariate linear regression. The technique developed here is used to evaluate extinction coefficients, ϵ 's, of triplet-triplet absorption (TTA) spectra of organic molecules in condensed phases. A previous assumption, that there are no solvent effects on the TTA spectra, is investigated and modified so that a group of compounds measured in benzene is treated separately. The set of 445 ϵ 's obtained from the global least-squares fit, including these solvent effects, is presented in the accompanying tables. How these least-squares results can be used in a hierarchy of TTA ϵ standards is discussed. Further solvent effects such as the separation of polar and nonpolar media and the influence of temperature are probed.

Key words: condensed phase; data compilation; extinction coefficients; least-squares method; solution; statistical analysis; triplet states; triplet-triplet absorption.

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1. Introduction

Most of what is known about the microworld of physics and chemistry has been revealed by a variety of scattering experiments.¹ The fundamental quantity obtained from scattering experiments is a cross section for the process under investigation. In light absorption such cross sections are commonly obtained from the integrated form of Beer's law,²

$$I(\lambda) = I_0(\lambda)e^{-\sigma(\lambda)\eta l}, \quad (1)$$

where I is the intensity of light transmitted through the sample, I_0 is the incident intensity, $\sigma(\lambda)$ is the absorption cross section at the wavelength, λ , under investigation, η is the concentration of absorbers (in molecules/cm³), and l is the path length in cm. An equivalent statement of Beer's law, which is more convenient for condensed phase work, is given by

$$I(\lambda) = I_0(\lambda)e^{-2.3\epsilon(\lambda)cl}, \quad (2)$$

where c is the concentration of the absorber in mol/L and ϵ is the molar extinction coefficient. The extinction coefficient then contains the same information as the cross section for absorption. Because of its direct relationship to the cross section, the extinction coefficient is of fundamental importance for the characterization of systems interacting with light.

However, from a more practical point of view, a knowledge of the extinction coefficient is desired for two different reasons. First, ϵ as a function of λ can be used as a fingerprint of the species under study, and second ϵ , along with Beer's law Eq. (2), gives a means of measuring concentrations. Both of these uses for extinction coefficients are extremely important in the study of short-lived transients, which is the subject of this work.

In this work we will be evaluating the location and extent of the absorbance of a class of metastable excited states of organic molecules in solution. The excited states under study are the triplet states of these molecules. In a previous work,³ we concentrated mainly on characterizing the spectra of these transients by compiling all the λ_{\max} of the known triplet-triplet absorption (TTA) spectra. We also touched on evaluating the extinction coefficients themselves, and developed tentative standards. In the current paper, we will look in more detail at the evaluation of the triplet-triplet extinction coefficients.

The preliminary evaluation of the measured extinction coefficients in our previous work³ started with the observation that for a given compound, the scatter in the data was in general as large as, or larger than, the scatter between measurements in different solvents and/or at different temperatures. This observation was put to a series of statistical tests using the data on anthracene, which was by far the most studied compound. The measurements on anthracene afforded a wide variety of opportunities to look at extinction coefficients measured in different environments such as polar versus nonpolar, low versus high temperature, and various combinations of these categories. The categories were initially tested pairwise, using t -tests,⁴ to see whether the hypothesis, "the extinction coefficients from the two environments are the same," was false. In all the categories of

environment tested, the hypothesis was not seen to be violated at conventional (5% or 1%) levels of statistical significance.

Furthermore, a similar hypothesis was tested by doing an Analysis of Variance⁴ (ANOVA) on many of the same categories of the anthracene data. Although the ANOVA procedure has some restrictions that are not shared by a series of t -tests,⁵ it has the advantage of dealing with all the environmental categories at once. The basic idea of ANOVA is to test the hypothesis concerning whether or not there is a statistical difference between M groups of measurements by looking to see whether the variation *between* the groups is larger than the variation of the measurements *within* the groups. If the variation between groups is larger (by an amount determined by an F distribution), then an hypothesis that there is no difference between the groups would be rejected. When an ANOVA was done on the groups of anthracene³ ϵ 's corresponding to different environments, no statistical differences were found between the groups at the traditional levels of significance.

These statistical results on anthracene show that, for the data available in the literature, there are no statistically significant solvent and temperature effects. This result was generalized in our previous work³ to apply to all the compounds. This assumption will be further investigated in the present work and will be shown to be in need of modification if the data are to be adequately represented. The advantage of this assumption is that, if it can be made, a whole series of statistical procedures can be brought to bear on the measurements.

2. General Methodology

In general, the primary physical quantities whose values are to be obtained are not directly accessible to measurement. The quantities actually measured are often secondary physical quantities which can be complicated functions of the primary physical quantities. For example,

$$F_q(\xi_1, \xi_2, \dots, \xi_p) = A_q, \quad q = 1, n \quad (3)$$

might represent the measurement of a secondary quantity A_q that is a complicated function of the set of primary quantities $\{\xi_j\}$ whose values are unknown but desired. One useful form that F_q can take is that of a product of the primary physical quantities, each raised to some power, i.e.,⁶

$$F_q(\xi_1, \xi_2, \dots, \xi_p) = \prod_{j=1}^p \xi_j^{\alpha_{jq}}, \quad q = 1, n. \quad (4)$$

The exponents α_{jq} in Eq. (4) represent the power of the j th physical quantity in the q th measurement. This form of Eq. (4) is appropriate for the problem of choosing the best ϵ 's because their equations will involve products of the unknown ϵ 's raised to the powers of 1, 0, and -1 .

To complete a formalism of measurements, some account must be made of errors in real measurements. The experimental error in the q th measurement must be a function of the difference between F_q , which is a function of the true physical quantities, and A_q , which is a result of a real measurement. For the single-product form of F_q , the error can be represented as

$$\prod_{j=1}^p \xi_j^{\alpha_j} = A_q (1 - r_q), \quad q = 1, n, \quad (5)$$

where A_q is a number resulting from the q th measurement and r_q is the relative fractional error in A_q . There are p parameters $\{\xi_j\}$ in the set of primary physical quantities whose values are unknown.

Mathematically the general problem can be stated as how can the values for the p physical quantities $\{\xi_j\}$ be obtained starting with the n measured A_q 's? If some set of measured values for $\{\xi_j\}$ is put into the left-hand side of Eq. (5), the result will not give A_q in general. To make Eq. (5) acceptable, r_q must be added to make the equation valid. In fact the set of equations represented by Eq. (5) would likely be inconsistent without the r_q 's. As long as $n > p$ and all of the r_q 's are zero, the set of equations, represented by Eq. (4), is overdetermined.

One common method used to deal with such mathematical problems, where the original problem is overdetermined, is a technique of Legendre called the Method of Least Squares. It has been derived from many principles and has been presented in many forms.⁷ The derivation that illustrates the statistical assumptions best starts with the Principle of Maximum Likelihood, which states that the r_q 's are such that the probability,

$$P(r_1, \dots, r_n) = \prod_{q=1}^n P_q \quad (6)$$

is maximum. If it can be assumed that the r_q 's can be characterized by a Gaussian probability distribution with a mean of zero,

$$P_q(r < r_q < r + dr) = [\exp(-r_q^2/2\sigma_q^2)/\sigma_q\sqrt{2\pi}] dr, \quad (7)$$

and if the Principle of Maximum Likelihood is invoked, then it is easy to see that this will be true when the exponent in

$$P(r_1, \dots, r_n) = \exp\left(-\sum_{i=1}^n \frac{r_i^2}{2\sigma_i^2}\right) / \prod_{i=1}^n \sigma_i \sqrt{(2\pi)^n} \quad (8)$$

is a minimum. This leads directly to the least-squares condition for

$$Q = \sum_{i=1}^n \frac{r_i^2}{\sigma_i^2} \quad (9)$$

to be a minimum.

2.1 Statement of Extinction Coefficient Problem

For extinction coefficients there are two general types of measurements. One type is absolute, where the extinction coefficient is measured directly, as in the total depletion method.³ For absolute measurements, Eq. (5) reduces to the simple form of

$$\epsilon_a = \epsilon_{ai}(1 - r_{ai}), \quad \text{for all } ai \text{ absolute}, \quad (10)$$

where the ϵ_a 's are the unknown extinction coefficients and the ϵ_{ai} 's are the measured extinction coefficients of compound a in the i th experiment. The ϵ_a 's are the quantities to be determined and are the physical quantities $\{\xi_j\}$ in Eq. (5). The ϵ_{ai} 's correspond to the A_q 's in Eq. (5) for the absolute measurements of extinction coefficients.

The other type of measurement gives relative values of

extinction coefficients. The set of equations in this case is given by

$$\frac{\epsilon_a}{\epsilon_b} = T_{ai,bj}(1 - r_{ai,bj}), \quad \text{for all relative } ai, bj. \quad (11)$$

Equation (11) holds for all sets of molecules a and b and for all measurements i of molecule a and all measurements j of molecule b . $T_{ai,bj}$ is the ratio of the optical densities, OD, between the unknown a and the reference b in the i th measurement of compound a . Here, we recover the experimental $T_{ai,bj}$'s from the reported extinction coefficient of a in the i th measurement ϵ_{ai} and from the reference extinction coefficient of b used in the experiment, ϵ_{bj} .

$$T_{ai,bj} = \epsilon_{ai}/\epsilon_{bj}. \quad (12)$$

In other words ϵ_{bj} is usually from a different work than the paper reporting the estimation of ϵ_{ai} . The $T_{ai,bj}$'s are the basic measured quantities in the relative technique for the estimation of ϵ 's. They are the A_q 's in Eq. (5) for relative measurements.

The set of Eqs. (10) and (11) form the total set of extinction coefficient measurement equations analogous to the general measurement Eq. (5). In this work we will choose the variances σ_i^2 (or weights) in the least-squares equation, Eq. (9) to be equal. Some justification for this is given in the statistical tests of Ref. 3. With the choice of equal σ_i^2 's and with the r_{ai} 's from Eq. (10) and the $r_{ai,bj}$'s of Eq. (11), the Q in Eq. (9) can be formed. This Q has only to be minimized to obtain the least-squares equations.

The minimization is not straightforward in the case of the extinction coefficients because of the nonlinear dependence of the r 's on the ϵ 's. Several methods can be used. First, Q can be differentiated with respect to each member of the set $\{\epsilon_j\}$, and the resulting derivatives can be set to zero. It is easy to show that the resulting equations are nonlinear equations in the set of variables $\{\epsilon_j\}$. Such equations make this approach unattractive as a general rule. However this result does show that the least-squares equations cannot be interpreted as self-consistent averages of the set $\{\epsilon_j\}$, since self-consistent averages must be linear functions of the set $\{\epsilon_j\}$. The second approach is to make a logarithmic⁸ transformation of Eqs. (10) and (11). This technique was used in our previous work.⁹ The third method, which is the method used here, is to expand the ratios of the physical quantities such that only the linear terms are kept in the end.

2.2. Derivation of the Normal Equations

Rather than do a formal expansion, a simple algebraic exercise can lead to the desired equations. The procedure is first to define three new types of quantities,

$$z_c = \frac{\epsilon_c - \epsilon_c^0}{\epsilon_c^0}, \quad (13)$$

$$S_{ci} = \frac{\epsilon_{ci} - \epsilon_c^0}{\epsilon_c^0}, \quad (14)$$

$$S_{ci,dj} = \left(\frac{\epsilon_{ci}}{\epsilon_{dj}} - \frac{\epsilon_c^0}{\epsilon_d^0} \right) / \frac{\epsilon_c^0}{\epsilon_d^0}, \quad (15)$$

all of which are expected to be small. Then after a few steps of algebra, Eqs. (10) and (11) can be written in terms of these three types of quantities and in terms of the relative errors. The results are

$$z_a = S_{ai} - r_{ai} - r_{ai}S_{ai} \quad (16)$$

for Eq. (10) and

$$z_a = z_b + S_{ai,bj} - r_{ai,bj} + z_b S_{ai,bj} - r_{ai,bj}z_b - r_{ai,bj}S_{ai,bj} - r_{ai,bj}z_b S_{ai,bj} \quad (17)$$

for Eq. (11). No approximations have yet been made.

From the definitions of the parameters (z , S , and r) in these equations, it is to be expected that they are small if the set $\{\epsilon^0\}$ is properly chosen. The assumption is thus made that the five types of quantities, z_c , S_{ci} , $S_{ci,dj}$, r_{ci} , and $r_{ci,dj}$, are all much smaller than one. It is then possible to simplify Eqs. (16) and (17). The terms having two or more factors can be ignored giving

$$r_{ai} = S_{ai} - z_a \quad (18)$$

for Eq. (16) and

$$r_{ai,bj} = S_{ai,bj} - z_a + z_b \quad (19)$$

for Eq. (17).

These "linearized" expressions can be put back into the sum-of-the-squares expression, Eq. (9), giving

$$Q = \sum_{ai} (S_{ai} - z_a)^2 + \sum_{ai,bj} (S_{ai,bj} + z_b - z_a)^2. \quad (20)$$

There are n terms in Eq. (20), one for each separate measurement. The set $\{z_c\}$ that minimizes Q is found by setting to zero each of the p derivatives of Q with respect to z_c . The resulting set of p equations is given by a general expression

$$N_c z_c = \sum_i S_{ci} + \sum_{i,bj} (S_{ci,bj} + z_b) + \sum_{bj,i} (-S_{bj,oi} + z_b), \quad \text{for all } c. \quad (21)$$

This is the set of *normal equations* for the least-squares method. In Eq. (21), the second sum is over all relative measurements of c (represented by i,bj), where c was explicitly used as the unknown. The third sum is over all relative measurements of c (represented by bj,i) where c was used as the standard. N_c is the total number of all these measurements of c .

The set of equations represented by Eq. (21) is a set of p linear equations for the variables z_c . It should also be noted, first, that the linear equations represented by Eq. (21) cannot easily be interpreted as a self-consistent average for the z_c 's. Also at the end of Sec. 2.2.1. we sketched a proof that the normal equations cannot be interpreted as self-consistent averages of the ϵ_c 's. This contrasts to the singlet oxygen case⁹ where the equations can be interpreted as a self-consistent average of the logarithms of the data items. Second, it should again be noted that the sum-of-the-squares expression, Eq. (20), involves a sum over all measurements. This means every relative measurement will contribute a term to

two different equations in the set of equations represented by Eq. (21). This is because it is possible to consider that a molecule b is being measured even when it is used as a standard.⁹ However, this principle can be seen to follow directly from the derivation of Eq. (21). Any attempt to eliminate a term in the set of equations represented by Eq. (21) may be appropriate if a self-consistent set of averages is being calculated, but interpreting the results of such a calculation as a least-squares solution is then not possible.

2.3. Numerical Solution to the Normal Equations

Equation (21) is the basic set of equations that was used to obtain the least-squares extinction coefficients. The set of equations can be rearranged

$$N_c z_c - \sum_b N_b z_b = \sum_i S_{ci} + \sum_{i,bj} S_{ci,bj} - \sum_{bj,i} S_{bj,ci}, \quad \text{for all } c, \quad (22)$$

and written in a matrix notation,

$$\mathbf{Nz} = \mathbf{a}, \quad (23)$$

which is more suggestive for obtaining a solution. In Eq. (23) the matrix \mathbf{N} has diagonal elements equal to the total number of measurements of compound c . These include absolute measurements, relative measurements where compound c is the standard, and relative measurements where compound c is the unknown. The matrix \mathbf{N} is symmetric, and its off-diagonal elements, $N_{b,c}$, are equal to the negative of the number of relative measurements for compounds b and c . This counting of relative measurements is independent of whether b or c was used as the standard. Only off-diagonal elements corresponding to pairs of compounds measured relative to one another have nonzero elements. The c th component of the z vector in Eq. (23) is given by z_c in Eq. (13), and the c th component of the a vector is given by the right-hand side of Eq. (22).

The set of equations represented by Eqs. (22) or (23) is a set of p linear equations for the p unknown z_c 's, which are directly related to the least-squares estimators of the extinction coefficients. Here, $p \sim 450$ and the solution was obtained by matrix factorization techniques.¹⁰ Inversion of the matrix \mathbf{N} was later necessary to generate confidence intervals.

Preliminary to a solution of the normal equations of the least-squares problem, a large amount of data processing had to be done in order to fill in the matrix elements of \mathbf{N} and the vectors z and a . Since the information on extinction coefficients was already in a file that was being used in the Radiation Chemistry Data Center Database,¹¹ only some modifications to existing programs in the database management system had to be made. One important part of the preprocessing was to choose the set $\{\epsilon_c^0\}$ to compute the components of the z vector in Eq. (13) and the components of the a vector, given by the right-hand side of Eq. (22). Initially the set $\{\epsilon_c^0\}$ was chosen so that each ϵ_c^0 was the average of all the reported measurements on compound c . Another important item of preprocessing involved dropping terms in the normal equations that corresponded to self-relative measurements. These terms fail to appear because of the linearization proce-

cedure adopted. Other items dropped in the preprocessing were ϵ measurements deemed as involving systematic errors,³ heterogeneous systems, and mixed crystals. For the purpose of this analysis, measurements that violated³ Chauvenet's criterion¹² were considered as systematic errors.

The solutions that were obtained from the linear equation solver after such preprocessing were such that most components of the z vector were much less than unity, which is the criterion for the linearization procedure to be valid. When the linearization method was used on the fundamental constant of physics, the components of the z vector were of the order of parts per thousand or less.⁶ In that application the normal equations were set up once and solved once. However, since the components of the z vector from the TTA project are of the order of 0.1 for most compounds, following the above procedure, it was deemed necessary to introduce an iterative process to correct for the neglect of nonlinear terms [terms ignored in Eqs. (16) and (17)] in the process of obtaining the normal equations. The iterative scheme was to use the solution (the z vector) to the normal equations to compute the best-fit ϵ 's via Eq. (13) and to use these best-fit ϵ 's as the new set $\{\epsilon_i^0\}$. This set $\{\epsilon_i^0\}$ was then used to form the new normal equations, and these normal equations were solved using the linear equation solver.

On the second pass through the procedure there was some change in the individual z_i 's. However, on successive passes the solutions quickly converged with the individual components of the z vector reaching values much less than unity. It was found that it only took about five passes through the process for all of the individual components to become sufficiently small. Even after two iterations only a few components of the z vector remained of the order of 0.1.

As the iterations were performed, checks were implemented to make sure that the procedures were running smoothly. The sum of the squares of differences in extinction coefficients was checked to ensure that it was in fact decreasing. The measure used for this test was the sum of the squares of the components of the z vector, namely, the square of the norm of the vector. The overall drift in values on successive iterations was also investigated. For this check a global average of the p extinction coefficients at the end of each iteration was used as a measure of this drift. No such drift was found.

3. Results and Discussion

3.1. Treatment of Benzophenone Ketyl Radical

Before the least-squares computation on the TTA could be run, a preliminary decision had to be made on how to handle reference extinction coefficients that are not in the set of TTA ϵ 's. The most important example of reference ϵ 's for species not in this set is the benzophenone ketyl radical. The absorption of this radical was used as the nominal reference in 36 measurements and was the primary standard in the Bensasson and Land (BL) measurements.¹³

3.1.1. Preliminary Least-Squares Calculations

Two ways to deal with these extra standards were tried. The first way was to treat the ϵ for the ketyl radical on an

equal footing with the TTA extinction coefficients and let it float in the fitting procedure. When this was done, under the assumption of no solvent effects, the best fit for benzophenone ketyl radical was $4320 \text{ L mol}^{-1} \text{ cm}^{-1}$. Other results from this fit for four of the most important standards were 61 500, 9160, 32 600, and $22\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ for anthracene, benzophenone, biphenyl, and naphthalene triplets, respectively. The second treatment of the benzophenone ketyl radical was to use its ϵ as a fixed standard,¹³ $3700 \text{ L mol}^{-1} \text{ cm}^{-1}$. To implement such a procedure, all of the relative measurements using benzophenone as a standard were renormalized, if necessary, to the 3700 value, and the resulting measurements were treated as though they were absolute measurements. The least-squares fit with this second treatment of the ϵ for the ketyl radical gave roughly the same results as the first treatment for most of the triplet states. For example anthracene, biphenyl, and naphthalene were 59 700, 32 000, and $21\,300 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. As expected, these frequently used standards showed larger changes, in general, than compounds with fewer measurements. Another commonly used reference, the benzophenone triplet, showed a particularly large change, going to $8760 \text{ L mol}^{-1} \text{ cm}^{-1}$.

3.1.2. Fixed versus Floating ϵ for Ketyl Radical

Based on several considerations, it was decided to fix the ketyl radical at $3700 \text{ L mol}^{-1} \text{ cm}^{-1}$. First, using both treatments of the ketyl radical gave the best-fit ϵ 's much higher than expected for the benzophenone triplet^{13,14} (7630 and 7220), but letting the ketyl radical's value float gave the poorer result of the two treatments. Second, we could not explicitly identify which (and how many) BL¹³ values really used the value of 3700 for the benzophenone ketyl radical as a reference. Bensasson and Land used a least-squares procedure for obtaining extinction coefficients of a limited set of compounds that they measured over a number of years.^{13,15,16} From their papers it is possible to follow their network of relative measurements to a large extent, but they published no details of their least-squares procedure. For this reason their network of relative values was incompletely specified for our purpose, and we chose to treat some of their major results as absolute measurements. The measurements so treated are the ones listed in Table 6 of Ref. 3 as being relative to benzophenone ketyl radical.¹³ In summary, choosing $3700 \text{ L mol}^{-1} \text{ cm}^{-1}$ for the benzophenone ketyl radical gives better results for the benzophenone triplet and is consistent with treating some of the BL values as pseudoabsolute measurements.

Implicit in the judgments of the preceding paragraph, there is a non-numerical weighting scheme. In Ref. 3, we took the $7220 \text{ L mol}^{-1} \text{ cm}^{-1}$ value¹⁴ for benzophenone triplet and certain BL values as the tentative standards. In the following analysis, we continue to use these values as guides in evaluating results of the least-squares procedures. These particular standard ϵ values were measured in the spirit of obtaining benchmarks for TTA extinction coefficients, and from our assessment of the experimental works, we have no reason at this time to say that the authors failed in their goal.

3.2. Solvent Effects

From the results of the statistical tests on the data reported in our previous work³ and summarized in Sec. 1, there was reason to believe that solvent effects could be ignored in arriving at a least-squares fit to the data. When such a calculation is done using the assumption of no solvent effects, the partial results are given in Sec. 3.1.1. The results are quite reasonable, in general, and roughly agree with the simple averages in Table 5 of Ref. 3, in which no attempt was made to correct relative measurements with uniform standards. The moderate success of the calculation shows that the method is not limited by the large size of the matrices involved in this problem.

3.2.1. Criticism of the No-Solvent-Effect Assumption

However, once the feasibility of the computations was assured, a more critical look at the results was necessary. The biggest problem with the least-squares procedure, used in conjunction with the assumption of no solvent effect, is that the best-fit ϵ for the benzophenone triplet is much too high. The value of 8700 L mol⁻¹ cm⁻¹ does represent a value that might be interpreted as a general purpose number as opposed to the values of 7220¹⁴ and 7630¹³ L mol⁻¹ cm⁻¹ which are specifically for benzene. A closer look at the benzophenone triplet measurements shows that the majority of measurements of its TTA ϵ are in benzene. It would be expected that the best fits would thus approach the benzene value.

The reason that it fails to approach this value is that in the benzophenone measurements the reference compounds, generally aromatic hydrocarbons, have best-fit ϵ values which are artificially too high for benzene. The source of this problem is the systematic variation in certain aromatic hydrocarbons that have broader TTA (and hence, smaller ϵ 's) in benzene than many other common solvents, in particular, cyclohexane.¹⁵ Since the least-squares ϵ 's are roughly an average over solvents, the reference ϵ 's are higher than expected for measurements in benzene. However these high values are, in effect, used to calibrate all relative measurements, whether in benzene or not. This leads to high values for compounds that have been measured predominately in benzene and relative to the aromatic hydrocarbons. Such is the case with benzophenone triplets.

3.2.2. Test Calculation on a Small Sample of Benzene-Only Results

These considerations suggest that it will not be possible to treat the TTA ϵ 's as totally solvent independent because of the particular network of connected relative measurements in the TTA data. The results in benzene play too central a role in this network and the variations of the benzene results are too systematic, implying that the results in benzene should be separated from results in other solvents. In order to test the extent of the benzene solvent effects, a separate calculation was done to see whether reasonable least-squares fits could in fact be obtained for the benzene data alone. This was done in an attempt to isolate the source of the high benzophenone triplet values. There are nearly 50 reported measurements that use benzophenone triplet as a reference, and any group of these could be causing the high values.

In order to perform the calculation, ϵ results in benzene were taken from a selected group of compounds. The compounds chosen were ones that had a total of five or more measurements in any solvent. (This core of ϵ values in benzene was chosen with the view that they might be used for more extended calculations on the whole set of TTA measurements.) The least-squares calculation was carried out on the limited set of measurements of ϵ in benzene, and the results are listed in the 3rd column of Table 1. There were 20 compounds in all, with 46 measurements. The agreement with the BL values¹³ in benzene, listed in the 6th column of Table 1 is quite satisfactory. In particular the value of the benzophenone triplet is 7320 L mol⁻¹ cm⁻¹, compared to their value of 7630 L mol⁻¹ cm⁻¹. The agreement between the values in columns 3 and 6 is not too surprising since the BL values in benzene form a large subset of all the benzene measurements used to obtain the results in column 3. However, it does show that the procedure works and supports the speculation that benzene needs to be segregated.

3.2.3. Correlation Analysis

Another way to investigate the influence of measurements throughout the complex of a network of relative measurements is to do a correlation analysis. The simplest way to do this is to compute the correlation coefficients for each pair of compounds. This can be done using the inverse of the N matrix defined in Eq. (23). The linear correlation coefficient is given by⁶

$$r_{b,c} = \frac{(N^{-1})_{b,c}}{\sqrt{[(N^{-1})_{b,b}(N^{-1})_{c,c}]}} \quad (24)$$

Even in these benzene-only calculations, benzophenone is correlated to other measurements (see the results in column 3 of Table 2). For example, the largest correlation coefficients of benzophenone with other compounds were +0.53, +0.41, +0.33, +0.32, +0.23, and +0.23 for naphthalene, anthracene, 9,10-diphenylanthracene, triphenylene, benz[*a*]anthracene, and phenanthrene, respectively. Any outside measurement that raises any of the ϵ 's of these compounds, especially naphthalene, could have a large upward effect on benzophenone also.

3.3. Least-Squares Estimators of ϵ 's—the Global Fit

Since the core of the network of relative measurements depended so heavily on measurements in benzene, it was decided to separate out just those measurements treated above in the benzene-only trial run. Those compounds, listed in Tables 1 and 2, were treated as separate compounds—one compound if they were in benzene and another compound if they were in a nonbenzene solvent. The output from the least-squares procedure is given for the selected compounds in column 4 of Table 1, for the benzene results, and column 5 of Table 1, for the nonbenzene results. Correlation coefficients of these same 20 compounds with respect to benzophenone/benzene are also given in columns 4 and 5 of Table 2 for benzene and nonbenzene solvents, respectively. All 445 of the ϵ values from the global fit are listed in Table 3.

As usual the extinction coefficients are computed from the final z vector using Eq. (13). In order to obtain the val-

TABLE 1. Comparison of least-squares fits of TTA extinction coefficients (ϵ , L mol⁻¹ cm⁻¹) to reference standards

No.	Compound ($\lambda_{\text{nominal}}/\text{nm}$)	ϵ (benzene set)	ϵ (global-fit, benzene set)	ϵ (global-fit, nonbenzene set)	ϵ (BL, benzene)	ϵ (BL, cyclohexane)
1	Acridine (440)	25400 ± 5140	25400 ± 8160	23800 ± 4720	24300	31500
2	Anthracene (430)	50000 ± 7010	49800 ± 8370	61900 ± 6160	45500	64700
3	Benzophenone (525)	7320 ± 860	7870 ± 1200	6250 ± 1250	7630	—
4	Biphenyl (360)	25100 ± 4270	25000 ± 4410	37000 ± 4300	27100	42000
5	Naphthalene (415)	13200 ± 2130	14400 ± 2900	24100 ± 2780	13200	24500
6	Benz[a]anthracene (490)	19700 ± 5010	19800 ± 6790	26200 ± 4880	20500	28800
7	Phenanthrene (490)	15100 ± 3840	15600 ± 6270	26800 ± 4680	15700	25200
8	Pyrene (415)	20900 ± 7310	20900 ± 11600	37700 ± 12100	20900	30400
9	Triphenylene (430)	5760 ± 2120	6190 ± 3570	13500 ± 2660	—	—
10	3-Carboxypsoralen (450)	6950 ± 2700	6910 ± 4030	3730 ± 860	—	—
11	β -apo-Carotenal (480)	119000 ± 41600	114000 ± 77800	116000 ± 46000	—	—
12	9,10-Diphenylanthracene (445)	13900 ± 3170	14500 ± 4990	15600 ± 5240	—	—
13	1,4-Diphenylbutadiene (390)	45000 ± 15700	45000 ± 25000	54500 ± 15100	—	—
14	1,6-Diphenylhexatriene (420)	104000 ± 27300	105000 ± 32200	114000 ± 27300	—	—
15	1,8-Diphenyloctatetraene (440)	169000 ± 44200	178000 ± 60000	198000 ± 50900	—	—
16	Duroquinone (490)	7050 ± 1530	7030 ± 2330	6310 ± 1610	6950	5330
17	C ₁₇ -aldehyde (440)	64700 ± 16900	58300 ± 25300	52000 ± 15600	—	—
18	<i>all-trans</i> -Retinal (450)	62000 ± 16200	58400 ± 24100	69300 ± 11700	—	—
19	TMPD (620)	12200 ± 4270	12200 ± 6780	17000 ± 4000	—	12200
20	Zinc(II) phthalocyanine (480)	51000 ± 17800	51000 ± 28400	28900 ± 8030	—	—

TABLE 2. Correlation coefficients of benzophenone/benzene with respect to some other compounds

No.	Compound ($\lambda_{\text{nominal}}/\text{nm}$)	r_{ij} (benzene set)	r_{ij} (global-fit, benzene set)	r_{ij} (global-fit, nonbenzene set)
1	Acridine (440)	0.00E+00	0.00E+00	3.07E-02
2	Anthracene (430)	4.12E-01	3.07E-01	8.69E-02
3	Benzophenone (525)	—	—	8.78E-04
4	Biphenyl (360)	1.18E-01	6.93E-02	2.01E-02
5	Naphthalene (415)	5.30E-01	5.21E-01	1.09E-02
6	Benz[a]anthracene (490)	2.30E-01	1.80E-01	6.56E-03
7	Phenanthrene (490)	2.30E-01	1.91E-01	4.71E-04
8	Pyrene (415)	0.00E+00	0.00E+00	0.00E+00
9	Triphenylene (430)	3.17E-01	2.65E-01	0.00E+00
10	3-Carboxypsoralen (450)	5.15E-02	2.10E-02	7.63E-04
11	β -apo-14'-Carotenal (480)	0.00E+00	1.71E-03	2.94E-03
12	9,10-Diphenylanthracene (445)	3.26E-01	2.62E-01	6.59E-02
13	1,4-Diphenylbutadiene (390)	0.00E+00	0.00E+00	0.00E+00
14	1,6-Diphenylhexatriene (420)	3.83E-02	1.18E-02	3.78E-03
15	1,8-Diphenyloctatetraene (440)	3.83E-02	1.29E-02	3.39E-03
16	Duroquinone (490)	1.20E-01	6.41E-02	1.64E-02
17	C ₁₇ -aldehyde (440)	3.83E-02	1.69E-02	8.04E-03
18	<i>all-trans</i> -Retinal (450)	3.83E-02	1.64E-02	7.95E-03
19	TMPD (620)	0.00E+00	0.00E+00	1.88E-03
20	Zinc(II) phthalocyanine (480)	0.00E+00	0.00E+00	0.00E+00

ues listed in Table 3, extinction coefficients had to be chosen for three species that were outside of the compiled set of TTA extinction coefficients.³ These were the extinction coefficient for benzophenone ketyl radical, methyl viologen radical cation, and naphthalene disulfonate triplet state. These three initial values are listed first in Table 3.

3.3.1. Coupling Between Fits in Benzene and Nonbenzene Solvents

There are several features of note in these results. Comparing the benzene-only results in column 3 of Table 1 with the benzene results from the global fit in column 4 of Table 1 shows that the global-fit results got somewhat worse, compared to the BL benzene results of column 6 of Table 1. This is particularly true for benzophenone and naphthalene, two of the most important standards. [It is also true that these two compounds in benzene still have a correlation coefficient, computed by Eq. (24), of +0.52 even in the global fit, see column 4 of Table 2.] Since the number of measurements in the benzene group is the same as in the benzene-only group, it is somewhat surprising that the two benzene values shift upwards so much.

In fact when the whole set of TTA ϵ 's are considered, it is not possible to totally isolate the results in benzene. This is due to relative actinometry measurements³ and to another set of relative measurements that are based on the principle that the same band in different solvents has equal oscillator strength.³ Both types of measurements can be done using two separate optical cells. For example a relative actinometry measurement might be done on a compound dissolved in cyclohexane, using an actinometer dissolved in benzene. The best-fit ϵ of the actinometer in benzene should be used to calibrate the experiment, thus coupling the best-fit ϵ 's in benzene with those in nonbenzene solvents. Xanthone provides an example of an analogous coupling and has a correlation coefficient with benzophenone/benzene of +0.19.

In addition there are other compounds measured in benzene which couple the two sets of measurements. In our scheme, a compound is not split into two species (one for benzene and one for nonbenzene) if the compound has less than a total of five ϵ measurements—irrespective of solvent. If such a compound in benzene was measured via a single-cell, relative method, then the measurement provides a coupling between the benzene and nonbenzene sets. This type of coupling between the benzene and nonbenzene results is artificial but is left in to help the statistics. If all the measurements in benzene were chosen for the benzene set, then the statistics might degrade for both the benzene and nonbenzene sets due to examples of compounds having only one measurement in both classes of solvents, see below. Some representative correlation coefficients of benzophenone in benzene with compounds in nonbenzene solvents are given in the last column of Table 2. Most of the correlations are small but nonzero.

3.3.2. Relationship of Global Fit to Other Standards

Another feature of the results in columns 6 and 7 of Table 1 is that the benzene results are generally larger than the benzene results of Bensasson and Land.¹³ On the other hand, the nonbenzene results are somewhat less than the

cyclohexane results of Bensasson and Land. It is possible that the results are artificially being pulled together by the couplings between the results in benzene and the results in nonbenzene solvents. This is possible because, as was seen above, when the benzene results were totally decoupled from the nonbenzene results (see column 3 of Table 1), BL benzene results were obtained.

3.4. Characterization of Error Distributions

Before the analysis can be carried further, it is important to know something of the distribution of errors, r_{ai} in Eq. (10) and $r_{ai,bj}$ in Eq. (11). In the above derivation, which is based on the Principle of Maximum Likelihood, it was assumed the errors were distributed normally. However Cohen *et al.*⁶ showed that the normal equations, Eq. (23), can be obtained without assuming normality. Thus the analysis, to this point, is independent of the distribution of errors; further analysis depends on the distribution.

The first question about the distribution is whether the errors in the relative measurements $r_{ai,bj}$ are from the same distribution as the errors in the absolute measurements, r_{ai} . For the sake of data processing the residuals, both of absolute, R_{abs} and relative, R_{rel} measurements,

$$R_{ai} = S_{ai} - z_a, \quad \text{for all } ai \text{ absolute} \quad (25)$$

and

$$R_{ai,bj} = S_{ai,bj} - z_a + z_b, \quad \text{for } ai,bj \text{ relative}, \quad (26)$$

are transformed in each case as

$$R' = 1000 + 1000R. \quad (27)$$

Thus it is expected that the new residuals will have a mean of ~ 1000 and a variance of $10^6\sigma^2$ since the old residuals of Eqs. (25) and (26) are expected to have a mean of zero and a variance of σ^2 . The sample mean and sample variance of the residuals of the absolute measurements are 1000 and 57 600, respectively. The corresponding quantities for the residuals of the relative measurements are 1015 and 52 900. In these statistics described and in the following tests described in this section (3.4), compounds that have only one ϵ measurement, total, will be excluded from the samples.

One way to check whether the distributions of errors from relative and absolute measurements are the same is to check whether the means and variances are the same. In order to check the means, we did an Analysis of Variance (ANOVA)^{4,17} on the two sets. From the F -test it was found that the hypothesis that "the means of the two distributions are the same" could not be rejected at traditional levels of significance.

A second test that was used to compare the two distributions was an F -test to see whether the variances of the distributions were equal. The test statistic for this hypothesis was

$$F = s_{abs}^2 / s_{rel}^2, \quad (28)$$

where s_{rel}^2 and s_{abs}^2 are the estimates of the variance of the relative and absolute distributions, respectively. The F statistic defined by Eq. (28) is equal to 1.089 for the two distributions in question. For 359 and 172 degrees of freedom, the

F statistic falls at about the 70% fractile of the F distribution.¹⁸ Thus the hypothesis that "the variances of the two distributions are the same" cannot be rejected at the conventional levels of significance.

Finally, a Kolmogorov–Smirnov two-sample test^{4,19,20} was used to test whether the two distributions (360 absolute vs 173 relative) were the same. This test²⁰ involved computing the differences between the cumulative frequency distributions of the two samples in question. The maximum difference D is then compared to the sampling distribution.²⁰ In our case, the test¹⁷ gave D as 0.054 which shows that the hypothesis would not even fail at the 10% level of significance, where D would have to be as large as 0.12 (computed by formulas in Table M of Siegel²⁰). This result indicates that the two distributions are not different. The tests of the equalities of the means and variances of the distribution assume a normal distribution (discussed below), but the Kolmogorov–Smirnov test is independent of such an assumption.

Since none of the above tests could find any significant differences between the distributions of the errors from the relative and absolute measurements, the next step was to put the distributions together and to test whether the combined values were drawn from a normal distribution. In order to test this hypothesis it was again convenient to use the Kolmogorov–Smirnov test. To accomplish this the combined (533) residuals from the relative and absolute measurements were compared to a normal distribution. The normal distribution was cut up into 200 separate areas, and the probability distribution assigned to each area was computed using an approximation given by Hastings.²¹ A maximum difference of 0.099 was found.¹⁷ Again using the formulas in Siegel²⁰ this value is just smaller than the "critical value" of 0.101 for rejection of the hypothesis "the distribution of residual is normal" at the 10% level of significance. Thus the combined collection of residuals cannot be rejected as being normal at conventional levels of significance.

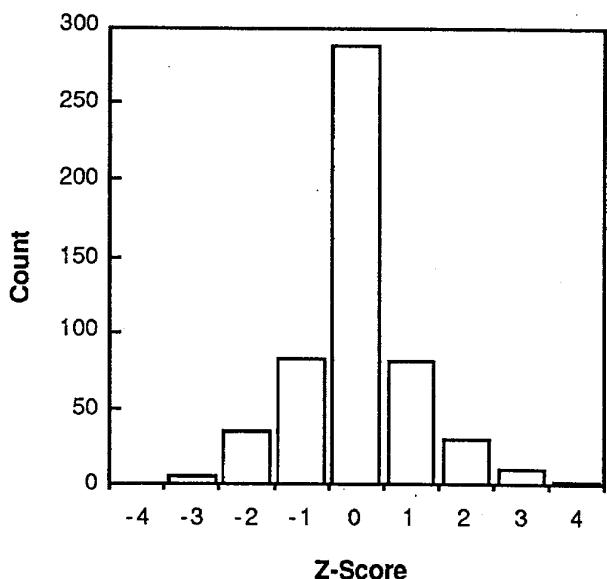


FIG. 1. Histogram of transformed residuals of global fit.

This Kolmogorov–Smirnov test was used to compare several other sets of values to normal distributions. Among the sets of results tested were sets of self-consistent averages of the logarithms⁹ of the ϵ 's. One such test, comparing values from the relative measurements to a normal distribution, failed at the 5% level of significance. The analogous test for relative measurements using the linearized least-squares method did not fail the test. These results indicate that the relative differences, $\{z_c\}$, of extinction coefficients are more likely to be distributed according to a normal distribution than are the logarithms of the ϵ 's.

Another aspect of the distribution of errors can be seen in Fig. 1 where the Z scores of the residuals are plotted as a histogram. Two different types of Z scores were used, one,

$$Z_{ai} = (R'_{ai} - \mu_{res})/s_{res}, \quad (29)$$

for absolute measurements and one,

$$Z_{ai,bj} = (R'_{ai,bj} - \mu_{res})/s_{res}, \quad (30)$$

for relative measurements. The parameters μ_{res} and s_{res} are defined by

$$n\mu_{res} = \sum_{ai} R'_{ai} + \sum_{ai} R'_{ai,bj} \quad (31)$$

and

$$s_{res}^2 = \frac{\sum_{ai} (R'_{ai} - \mu_{res})^2 + \sum_{ai} (R'_{ai,bj} - \mu_{res})^2}{(n - 1)}. \quad (32)$$

R'_{ai} and $R'_{ai,bj}$, in these last four equations are the transformed [see Eq. (27)] residuals that were originally defined in Eqs. (25) and (26). Using the sample mean (1005) and sample standard deviation (237) computed for the distribution of Z scores of all the residuals, a plot is shown in Fig. 2 for a normal distribution. A comparison of Figs. 1 and 2 shows that there are systematic deviations of the histogram of the residuals from the normal histogram. The center is sharper, and the wings are more spread for the histogram of the residuals. This is also reflected in the results of the Kol-

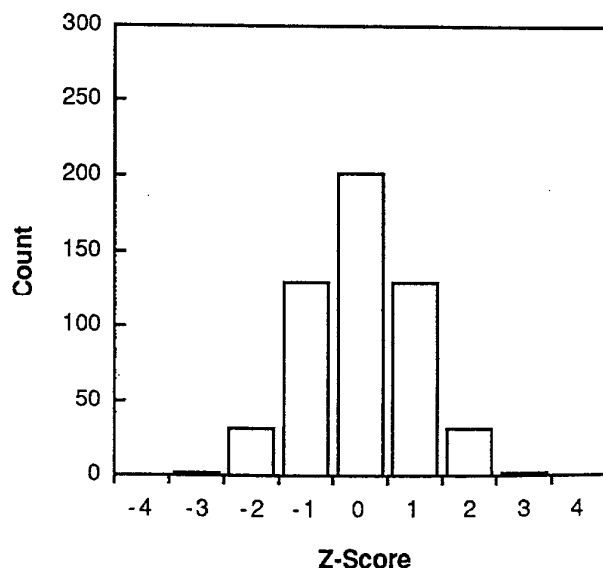


FIG. 2. Histogram of a normal distribution of equal total counts.

mogorov-Smirnov tests which indicated that the distributions of residuals were approaching the point where they could not be considered as normal. However, neither these tests nor the histograms rule out the distribution as normal, and it is convenient for the rest of the analysis to assume normality.

The sharper than normal distribution was also observed in the kinetic data for singlet oxygen⁹ and is also present in the data on the rate constants²² of OH and H in aqueous solution. The cause of this systematic deviation from normality is unknown, but open to speculation. It could be due to the sociology of scientific measurement,²³ or it could be due to repeated measurements of certain compounds by single research groups or by different groups using the same method. Compounds that have been measured repeatedly by the same group or methods would be less susceptible to fluctuations caused by systematic errors between research laboratories and techniques, respectively.

3.5. Confidence Intervals

It is possible to make an estimate of the confidence intervals of the extinction coefficients by establishing the connection of the least-squares analysis given above with the traditional multivariate linear regression analysis. This connection can be made by looking at Eqs. (18) and (19) for the measured values S_{ai} and $S_{ai,bj}$, respectively. (Note that these equations have already been linearized.) These equations have the traditional form for multivariate linear regression⁴

$$Y_i = \sum_j \beta_j X_{ji} + \delta_i, \quad (33)$$

where Y_i is an individual measurement of the response or dependent variable, the β_j 's are the parameters to be estimated, X_{ji} is the value of the independent variable X_j in the i th measurement of Y , and δ_i is the error in the i th measurement. The correspondence between Eq. (33) and Eqs. (18) and (19) can be made by relating the measured values S_{ai} and $S_{ai,bj}$ to the Y_i 's and by relating the unknown parameters to be fit, the z 's, to the β_j 's of Eq. (33). The correspondence can be completed by noting that the independent variables, the X_j 's, in the TTA least squares are control variables which equal one, minus one, or zero depending on whether the j th compound was used as the unknown, was used as the reference, or was not included in a particular measurement, respectively.

Once the connection to the traditional multivariate linear regression is made, traditional error analysis can be used. Since the assumption is made that the distribution is normal, confidence intervals can be calculated. They are listed in Table 3 and computed from the formula⁴ for 95% confidence intervals, $\Delta_{95\%z_c}$,

$$\Delta_{95\%z_c} = z_c \pm t_{0.975(n-p)} s_{z_c}, \quad (34)$$

where z_c is the least-squares estimator, $t_{0.975(n-p)}$ is Student's t factor for 95% confidence intervals with $n-p$ degrees of freedom, and $s_{z_c}^2$, the estimate of the variance of z_c , is given by

$$s_{z_c}^2 = (\mathbf{N}^{-1})_{c,c} Q / (n-p). \quad (35)$$

In Eqs. (34) and (35), n is the total number of measurements and p is the total number of compounds. Q in Eq. (35) is given by Eq. (20). $Q/(n-p)$ is the estimate of the variance of the error δ in the individual measurements. In forming Q , it is important to note two points. First, each square in the sum stands for one measurement. Second, in relative measurements, the z_b that an author uses as a reference appears with a plus sign; whereas the z_a that an author claims to be measuring appears with a minus sign. Again the factor $(\mathbf{N}^{-1})_{c,c}$ in Eq. (35) is the c th diagonal element of the inverse of the \mathbf{N} matrix defined in Eq. (23). Since the $p \times p$ matrix \mathbf{N} has $p \sim 450$, some care had to be taken in computing the inverse.¹⁰ A check was done to make sure that $\mathbf{N} \times$ the resulting inverse gave the unit matrix.

Since compounds with only one ϵ measurement do not contribute to the least-squares estimates of the best fits,⁹ there could be some concern that their confidence intervals are listed in Table 3. However, the results in Table 3 were obtained under the assumption that the variance [estimated by $Q/(n-p)$] of the errors for an isolated ϵ measurement are the same, irrespective of the compound, method of measurement, or laboratory where the measurement was performed. Furthermore, this assumption has been checked in Ref. 3 and also in Sec. 3.4. Thus the extension of the assumption to compounds with only one measurement seemed to be justifiable.

3.6. Other Environmental Effects

3.6.1. Influence of Low-Temperature Results on Global Fit

Since it is not possible to treat satisfactorily the TTA ϵ 's as being totally independent of solvent, environmental effects, other than benzene effects, were also investigated. The prime candidates responsible for the high ϵ values are the low-temperature measurements. All of these measurements are absolute, and low-temperature spectra tend to be sharp (high ϵ 's). The combination of fixed (i.e., nonrelative) and high ϵ 's should cause the global fits to be pulled up to high values also. To test the trends, two new pseudospecies, anthracene/low temperature and naphthalene/low temperature, were pulled out of the species listed in Table 3. For anthracene this amounted to six measurements out of 33, for naphthalene ten low-temperature results out of 15 measurements total. From the calculation of the best-fit ϵ 's using the extra species, the benzene results for anthracene, benzophenone, and naphthalene were 49 300, 7830, and 14 400 $\text{L mol}^{-1} \text{cm}^{-1}$, respectively. The values for the nonbenzene, nonlow-temperature ϵ 's for these three compounds were 59 700, 6200, and 23 700 $\text{L mol}^{-1} \text{cm}^{-1}$, respectively. The least-squares estimators for the low-temperature results were 71 000 $\text{L mol}^{-1} \text{cm}^{-1}$ for anthracene and 24 600 $\text{L mol}^{-1} \text{cm}^{-1}$ for naphthalene.

Thus the low-temperature results do not have much effect on the high results in benzene. In fact it can be seen from Table 1 that only phenanthrene and pyrene have nonbenzene values in column 5 that are higher than the BL cyclohexane values in column 7. Only these values could be considered as pulling up the best fits in an unjustifiable fashion. In fact there is quite a scatter in the low-temperature

results.³ Many of these results were done with weak exciting sources and thus had low signal-to-noise ratios. In addition if care was not taken to use narrow slits in the monochromators, the sharp spectra could be broadened resulting in artificially low ϵ 's.²⁴ Moreover, it is really the anthracene and naphthalene values in benzene that are responsible for the overly high values for benzophenone when no solvent effects are taken into account.

3.6.2. Further Solvent Effects: Benzenelike, Nonpolar, and Polar

Since the global fit improved so markedly when the small group of measurements in benzene was treated separately, the question arose whether further improvement was possible by further segregation of solvents. In other words, could subtleties, such as those uncovered with the benzene results, remain hidden from all of the statistical tests used so far. In order to check this we did a three-part classification of measurements, isolating measurements in benzenelike solvents from other nonpolar solvents, and further isolating these two sets of measurements from those in polar solvents.

The treatment was carried through and the results were not significantly better than the results presented in Table 3. The sum of the squares of the deviations, Q in Eq. (20), decreased somewhat from 30 to 22, but the degrees of freedom, $n - p$, also decreased from 371 to 312. This led to a marginally better overall fit, measured by $Q/(n - p)$, of 0.08 to 0.07. On the other hand, the least-squares estimators of the ϵ values for individual compounds are less certain in many important cases in the expanded treatment of solvents. An example is the case of anthracene in nonbenzenelike solvents. Its extinction coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$) goes from $61\,900 \pm 10\%$ in the restricted solvent-effect scheme reported in Table 3 to $62\,100 \pm 15\%$ in nonpolar and $60\,600 \pm 13\%$ in polar solvents in the benzene nonpolar-polar scheme. This increase in the confidence intervals is largely due to the reduced number of measurements that go into a determination of an individual compound's ϵ since the same number of actual measurements are spread over three possible solvent categories instead of two. The inverse matrix element, $(\mathbf{N}^{-1})_{c,c}$, will in general be larger for a smaller number of measurements which will make the estimate, s_c^2 in Eq. (35), of the variance of the errors of the ϵ 's for individual compounds larger. In addition Student's t factor will be larger for a smaller number of degrees of freedom. Both of these factors will tend to increase the 95% confidence intervals, Eq. (34), for the individual ϵ 's. Thus there is a tradeoff when the solvents are further segregated: On one hand the overall fit improves slightly, but on the other, the individual confidence intervals increase slightly.

It appears from these considerations that there are no further solvent effects that can be removed profitably to enhance the fits. In fact as a crude test for further solvent effects, we ran several unranked sign tests⁴ on the benzene nonpolar-polar results. Again the hypothesis that there are no differences between the groups could not be overturned.

All of these considerations lead us to suspect that other sources of fluctuations between various measurements of ϵ 's are as important as or even more important than solvent effects for the data under study. The only exceptions are the

limited number of measurements in benzene. The sources of the extra fluctuations are likely due to systematic errors between laboratories and methods. Errors in the methods themselves were already discussed.³

3.7. Recommended Values

The tentative standards for extinction coefficients of TTA, given in our previous work,³ were a hierarchy of values starting with the value of benzophenone in benzene on Level 1 with a recommended value¹⁴ of $7220 \text{ L mol}^{-1} \text{cm}^{-1}$. On the Level 2 the values of Bensasson and Land were recommended for values they measured in Ref. 13 in cyclohexane or benzene. Finally, on Level 3 there were a small number of extinction coefficients for compounds, some of which were already on Levels 1 or 2, which were to be used in any situations where Level 1 or 2 did not apply. The values in Level 3 were found by taking averages of the reported ϵ 's of compounds having five or more measurements (none of which violated Chauvenet's criterion¹²). Solvent effects were ignored in the averages, but only those compounds with 95% confidence intervals $< 30\%$ of the compound average were taken as standards.

As mentioned in Sec. 1, there was no convenient way to calibrate the relative measurements that went into the averages for the Level 3 values.³ Also because of the restriction of only five measurements (to get good statistics from Chauvenet's criterion¹²), the number of recommended values was very small. This restriction had the further disadvantage of not including measurements of some of the prominent reference values when they were used as standards for compounds having less than five measurements. In order to circumvent these problems, we chose to do the least-squares fit. The least-squares procedure automatically chooses the best values to renormalize the measurements so that the output gives the least-squares estimators directly. Also since the fit is global, it is possible to get meaningful statistics because of the large number of measurements.

One point about the Level 3 standards from Ref. 3 can be noted. In these standards some account of the appropriate reference ϵ 's for relative measurements was taken in individual numbers going into the averages by the individual authors. Thus many of the simple averages gave reasonable results because some authors had already corrected their results by using either reference ϵ 's from measurements in benzene or nonbenzene as appropriate. As a result even though the reference ϵ 's were not uniformly applied, the simple averages turned out to be better, in certain critical cases like benzophenone, than the global-fit ϵ values without any solvent effects.

However once the global fit was modified to account for the benzene results, reasonable ϵ 's were again obtained for the least-squares calculation. By scanning Table 3, it can be seen that the 95% confidence intervals are quite large for many compounds. We would not recommend that ϵ 's with 95% confidence intervals of $> 30\%$ to be taken seriously as standards. On the other hand, ϵ 's with 95% confidence intervals $< 30\%$ of the best-fit value should replace the ϵ 's of Table 5, Ref. 3, as the Level 3 standards. We still recommend the Level 1 and Level 2 standards to be used whenever they are appropriate.

One final point should be made concerning the use of the values in Table 3 as standards. The value for *all-trans*-retinol should not be used, but $80\,000\text{ L mol}^{-1}\text{ cm}^{-1}$ seems to be appropriate for a large number of solvents.^{25,26} There are several reasons that the global fit gave such a poor value for this widely used standard. First, the retinol measurements form an almost closed subset of experiments. The members of this subset are only weakly linked (have small linear correlation coefficients) to the main body of measurements. Second, most of the measurements in the retinol subset are relative measurements, making the retinol value very sensitive to the small number of absolute measurements in

the set. (There are several relative, electron-transfer measurements which are treated as absolute in the current procedure because we do not put in the ϵ 's of the radical ions formed.) It happens that all of these absolute (and pseudoabsolute) measurements give ϵ 's that are all significantly lower than the relative measurements. Based on the previous analysis,^{3,27} low values are not unreasonable from these particular methods. We therefore would put more trust in the higher values obtained from the energy-transfer method.^{25,26} Third, there are two values²⁸ around $57\,000\text{ L mol}^{-1}\text{ cm}^{-1}$. Both are measured by the energy-transfer method, but we feel the later measurements^{25,26} should supersede them.

TABLE 3. Global least-squares fit of TTA ϵ 's

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
1	1,5-Naphthalene sulfonic acid disodium salt	fixed standard	445	9900	—
2	Benzophenone ketyl radical	fixed standard	530	3700	—
3	Methyl viologen radical cation	fixed standard	440	580	—
<i>Measurements Outside the Special Set of Compounds in Benzene</i>					
4	Acenaphthene	(1, 0)	430	6000	± 3340 (56%)
5	2'-Acetonaphthone	(1, 0)	430	10500	± 5840 (56%)
6	Acetone	(0, 1)	300	600	± 470 (79%)
7	Acetophenone	(2, 2)	330	7160	± 2120 (30%)
8	9-Acetylanthracene	(1, 0)	426	20000	± 11100 (56%)
9	4-Acetylbiphenyl	(1, 0)	435	130000	± 72300 (56%)
10	<i>N</i> -(2-Acetylphenyl)acetamide	(1, 0)	450	8900	± 4950 (56%)
11	<i>N</i> -(2-Acetylphenyl)formamide	(1, 1)	450	7240	± 2870 (40%)
12	<i>N</i> -(2-Acetylphenyl)- <i>N</i> -methylacetamide	(0, 2)	430	1130	± 460 (41%)
13	<i>N</i> -(2-Acetylphenyl)- <i>N</i> -methylformamide	(0, 2)	430	960	± 390 (41%)
14	Acridine	(3, 6)	440	23800	± 4720 (20%)
15	Acridine- <i>d</i> ₉	(1, 0)	440	26000	± 14500 (56%)
16	Acridine Orange, conjugate monoacid	(3, 0)	540	9570	± 3070 (32%)
17	Acridine Orange, free base	(3, 0)	410	39600	± 12700 (32%)
18	Acridine, conjugate acid	(1, 1)	490	7840	± 3300 (42%)
19	9(10 <i>H</i>)-Acridone	(0, 1)	620	41400	± 24000 (58%)
20	Acriflavine cation	(1, 0)	620	8600	± 4780 (56%)
21	Amiloride	(0, 1)	400	6790	± 4010 (59%)
22	1-Amino-4-anilinoanthraquinone	(1, 0)	550	27000	± 15000 (56%)
23	1-Aminoanthraquinone	(0, 1)	550	2190	± 1290 (59%)
24	2-Aminoanthraquinone	(0, 1)	599	7800	± 4610 (59%)
25	2-Aminofluorene	(1, 0)	426	10600	± 5890 (56%)
26	1-Amino-4-hydroxyanthraquinone	(1, 0)	500	28000	± 15600 (56%)
27	4-Amino-4'-hydroxybiphenyl	(1, 0)	425	24000	± 13300 (56%)
28	2-Amino-3-(4-methoxy-6-benzothiazolyl)propionate ion	(1, 1)	370	6940	± 3240 (47%)
29	1-Amino-4-(<i>N</i> -methylamino)anthraquinone	(1, 0)	575	27000	± 15000 (56%)
30	7-Amino-4-methylcarbostyryl	(0, 1)	600	38100	± 21500 (56%)
31	3-Amino- <i>N</i> -methylphthalimide	(1, 0)	495	1100	± 610 (56%)
32	4'-Aminomethyl-4,5',8-trimethylpsoralen	(1, 0)	460	24200	± 13500 (56%)
33	1-Amino-4-nitronaphthalene	(1, 0)	440	28000	± 15600 (56%)
34	2-Amino-4-[3 <i>H</i>]pteridinone	(1, 0)	360	4700	± 2610 (56%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
35	Anthracene	(19, 29)	430	61900	± 6160 (10%)
36	Anthracene- <i>d</i> ₁₀	(2, 0)	425	95000	± 37300 (39%)
37	1-Anthrol	(0, 1)	440	29100	± 19900 (68%)
38	Anthrone	(1, 0)	341	74000	± 41100 (56%)
39	1-(2-Anthryl)-2-(2-naphthyl)ethylene	(0, 1)	635	57100	± 33300 (58%)
40	1-(2-Anthryl)-2-phenylethylene	(0, 1)	455	55300	± 32200 (58%)
41	1-(2-Anthryl)-2-(2-thienyl)ethylene	(0, 1)	630	43300	± 25300 (58%)
42	Azulene	(0, 1)	360	4140	± 2390 (58%)
43	Azure A cation	(1, 0)	840	10000	± 5560 (56%)
44	Bacteriochlorophyll	(3, 0)	620	16900	± 5430 (32%)
45	Benz[<i>b</i>]acridin-12(5 <i>H</i>)-one	(0, 1)	590	53600	± 30200 (56%)
46	Benz[<i>a</i>]anthracene	(7, 2)	490	26200	± 4880 (19%)
47	Benzene	(1, 0)	235	11000	± 6110 (56%)
48	Benzidine	(2, 0)	460	35500	± 14000 (39%)
49	Benzo[<i>a</i>]coronene	(5, 0)	570	22300	± 5540 (25%)
50	Benzoic acid	(1, 0)	320	1000	± 560 (56%)
51	Benzo[<i>ghi</i>]perylene	(4, 0)	465	39300	± 10900 (28%)
52	Benzo[<i>c</i>]phenanthrene	(1, 0)	517	4800	± 2670 (56%)
53	Benzophenone	(5, 9)	525	6250	± 1250 (20%)
54	Benzo[<i>e</i>]pyrene	(2, 0)	555	17000	± 6660 (39%)
55	Benzo[<i>b</i>]triphenylene	(2, 0)	450	29900	± 11800 (39%)
56	Benzoylamino-2- Δ^2 -thiazoline	(0, 1)	551	7090	± 4020 (57%)
57	2-Benzoyl- <i>N</i> -methyl- β -naphthiazoline	(1, 0)	640	16000	± 8890 (56%)
58	Benzyl 9-anthroate	(1, 0)	430	63000	± 35000 (56%)
59	3-Benzyl-3,4,5-triphenyl-2(3 <i>H</i>)-furanone	(0, 1)	375	14500	± 8360 (58%)
60	Biacetyl	(1, 3)	315	4580	± 1460 (32%)
61	Bifluorenylidene	(1, 0)	440	110000	± 61100 (56%)
62	Bilirubin	(0, 1)	500	8110	± 4730 (58%)
63	Biliverdin	(0, 1)	700	21800	± 12400 (57%)
64	Biliverdin, dimethyl ester	(0, 1)	400	50700	± 29500 (58%)
65	1,1'-Binaphthyl	(0, 1)	615	12400	± 7140 (58%)
66	2,2'-Binaphthyl	(0, 1)	450	24800	± 14300 (58%)
67	Biphenyl	(5, 49)	360	37000	± 4300 (12%)
68	Biphenyl- <i>d</i> ₁₀	(1, 0)	365	7000	± 3890 (56%)
69	Biphenylene	(1, 1)	350	10500	± 4250 (41%)
70	2-Biphenylphenylbenzoxazole	(1, 0)	560	4500	± 2500 (56%)
71	2-(4-Biphenyl)benzoxazole	(1, 0)	460	2500	± 1390 (56%)
72	1-(2-Biphenyl)-1-phenylethylene	(1, 0)	370	17000	± 9450 (56%)
73	2-(4-Biphenyl)-5-phenyloxazole	(2, 0)	535	66300	± 26000 (39%)
74	2,5-Bis(5- <i>tert</i> -butyl-2-benzoxazolyl)thiophene	(1, 0)	520	160000	± 88900 (56%)
75	4,4'-Bis(dimethylamino)thiobenzophenone	(0, 1)	335	14900	± 8560 (58%)
76	1,4-Bis(methylamino)anthraquinone	(1, 0)	550	20000	± 11100 (56%)
77	<i>trans</i> -1,2-Bis(1-naphthyl)ethylene	(0, 1)	530	30200	± 20700 (69%)
78	<i>trans</i> -1,2-Bis(2-naphthyl)ethylene	(0, 1)	430	20100	± 13800 (69%)
79	Bonellin	(1, 0)	625	40000	± 22200 (56%)
80	Brilliant Sulfaflavine anion	(1, 0)	575	1800	± 1000 (56%)
81	9-Bromoanthracene	(1, 2)	430	47500	± 16000 (34%)
82	Bromo(methanol)(phthalocyaninato)rhodium(III)	(1, 0)	590	22000	± 12200 (56%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
83	1-Bromonaphthalene	(1, 0)	425	11500	± 8390 (56%)
84	2-Bromotriphenylene	(1, 0)	430	8000	± 4450 (56%)
85	2- <i>tert</i> -Butyl-4-methylindazole	(2, 0)	409	8000	± 3140 (39%)
86	Cadmium(II) tetraphenylporphyrin	(1, 0)	490	57000	± 31700 (56%)
87	Carbazole	(5, 1)	425	14000	± 3180 (23%)
88	3-Carbethoxypsoralen	(5, 1)	450	3730	± 860 (23%)
89	4-Carboxybenzophenone	(0, 1)	535	6810	± 3920 (58%)
90	11- <i>cis</i> - β - <i>apo</i> -14'-Carotenal	(1, 0)	470	90000	± 50000 (56%)
91	β - <i>apo</i> -14'-Carotenal	(1, 2)	480	116000	± 46000 (40%)
92	β - <i>apo</i> -8'-Carotenal	(1, 0)	520	223000	± 124000 (56%)
93	15,15'- <i>cis</i> - β -Carotene	(0, 1)	515	216000	± 123000 (57%)
94	β -Carotene	(1, 4)	515	187000	± 53500 (29%)
95	ζ -Carotene	(0, 1)	445	70000	± 39700 (57%)
96	Chloranil	(1, 4)	510	6990	± 1940 (28%)
97	Chloroaluminum phthalocyanine	(2, 0)	490	26600	± 10500 (39%)
98	1-Chloroanthracene	(0, 2)	438	50700	± 21400 (42%)
99	Chlorobenzene	(0, 1)	300	6150	± 3490 (57%)
100	4-Chlorobenzophenone	(0, 1)	320	23100	± 14500 (63%)
101	(2'-Chlorobenzoyl)amino-2- Δ^2 -thiazoline	(0, 1)	557	11400	± 6480 (57%)
102	(4'-Chlorobenzoyl)amino-2- Δ^2 -thiazoline	(0, 1)	563	16600	± 9440 (57%)
103	Chloroindium(III) phthalocyanine	(1, 0)	490	23000	± 12800 (56%)
104	Chloro(methanol)(phthalocyaninato)rhodium(III)	(1, 0)	590	22000	± 12200 (56%)
105	1-Chloronaphthalene	(0, 1)	420	29500	± 17800 (60%)
106	1-(2-Chlorophenyl)naphthalene	(1, 0)	495	9500	± 5280 (56%)
107	1-(4-Chlorophenyl)naphthalene	(1, 0)	505	32500	± 18100 (56%)
108	Chlorophyll <i>b</i>	(3, 0)	450	24300	± 7810 (32%)
109	Chrysene	(6, 1)	580	29800	± 6280 (21%)
110	Coproporphyrin III	(2, 0)	401	115000	± 45200 (39%)
111	Coproporphyrin III, tetramethyl ester	(1, 1)	440	25400	± 10200 (40%)
112	Coproporphyrin I, tetramethyl ester	(1, 1)	440	28200	± 11400 (40%)
113	Coronene	(3, 0)	480	15000	± 4820 (32%)
114	Coronene- <i>d</i> ₁₂	(2, 0)	480	17200	± 6740 (39%)
115	Coumarin	(0, 1)	400	10100	± 5910 (58%)
116	α -Crocecin	(0, 3)	445	83300	± 41700 (50%)
117	Croconate Blue dianion	(2, 0)	590	22500	± 8840 (39%)
118	9-Cyanoanthracene	(0, 1)	435	8490	± 5020 (59%)
119	1,3-Cyclohexadiene	(1, 0)	303	2300	± 1280 (56%)
120	2-Cyclohexen-1-one	(0, 1)	270	2170	± 1250 (58%)
121	2-Cyclopentenone	(0, 1)	270	1970	± 1130 (58%)
122	Deuteroporphyrin, dimethyl ester	(1, 1)	440	23900	± 9630 (40%)
123	1,4-Diaminoanthraquinone	(1, 0)	575	22000	± 12200 (56%)
124	Dibenz[<i>a,h</i>]anthracene	(4, 1)	580	25100	± 6260 (25%)
125	5 <i>H</i> -Dibenzo[<i>a,d</i>]cycloheptene	(1, 0)	426	20000	± 11100 (56%)
126	2,5-Di(4-biphenyl)oxazole	(1, 0)	560	110000	± 61100 (56%)
127	9,10-Dibromoanthracene	(0, 2)	425	46300	± 21300 (46%)
128	Dibromofluorescein dianion	(1, 0)	506	18000	± 10000 (56%)
129	1,5-Dichloroanthracene	(0, 2)	445	50700	± 21400 (42%)
130	9,10-Dichloroanthracene	(0, 4)	425	42500	± 13700 (32%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
131	4,4'-Dichlorobenzophenone	(0, 1)	320	23300	± 14600 (63%)
132	4,4'-Dichlorostilbene	(1, 0)	359	28000	± 15600 (56%)
133	4-(4,6-Dichloro-1,3,5-triazin-2-yl)- <i>N,N</i> -diethylaniline	(2, 0)	490	31000	± 12200 (39%)
134	9,10-Dicyanoanthracene	(0, 1)	440	9180	± 6220 (68%)
135	1,4-Dicyanonaphthalene	(0, 1)	455	6730	± 3980 (59%)
136	<i>all-trans</i> -3',4'-Didehydro- β,ψ -16'-carotenal	(1, 0)	580	363000	± 202000 (56%)
137	7-Diethylamino-4-methylcoumarin	(0, 1)	620	17800	± 10100 (56%)
138	1,1'-Diethyl-6-bromo-2,2'-cyanine iodide	(1, 0)	651	33800	± 18800 (56%)
139	1,1'-Diethyl-2,2'-carbocyanine chloride	(1, 0)	635	58000	± 32200 (56%)
140	1,1'-Diethyl-4,4'-carbocyanine iodide	(0, 1)	778	35600	± 20200 (57%)
141	1,1'-Diethyl-2,2'-cyanine iodide	(1, 0)	635	31000	± 17200 (56%)
142	1,1'-Diethyl-2,2'-dicarbocyanine iodide	(0, 1)	780	69300	± 39400 (57%)
143	1,1'-Diethyl-6-iodo-2,2'-cyanine iodide	(1, 0)	600	28500	± 15800 (56%)
144	3,3'-Diethyl-2,2'-oxadibocyanine iodide	(0, 1)	650	81400	± 46200 (57%)
145	3,3'-Diethyl-2,2'-thiadibocyanine iodide	(0, 1)	1	161000	± 91400 (57%)
146	3,2'-Diethyl 2,2' thiatricarbocyanine iodide	(0, 1)	900	173000	± 97500 (56%)
147	4',5'-Dihydro-3-carbethoxypsoralen	(1, 0)	550	10000	± 5560 (56%)
148	7,7'-Dihydro- β -carotene	(0, 1)	448	363000	± 206000 (57%)
149	10,11-Dihydro-5,7:14,16-dietheno-8 <i>H</i> ,13 <i>H</i> -diindeno[2,1- <i>h</i> :1',2'] $\{$ [1,4]dioxacyclotridecin	(1, 0)	385	21200	± 11800 (56%)
150	5,10-Dihydro-5,10-dimethylphenazine	(0, 1)	450	62900	± 35500 (56%)
151	5,10-Dihydro-5,10-diphenylphenazine	(0, 1)	444	99400	± 56200 (56%)
152	5,10-Dihydro-5-methyl-10-phenylphenazine	(0, 1)	444	95400	± 53900 (56%)
153	5,12-Dihydro-5-methylquino[2,3- <i>b</i>]acridine-7,14-dione	(1, 0)	710	15300	± 8510 (56%)
154	9,10-Dihydrophenanthrene	(1, 0)	365	26000	± 14500 (56%)
155	1,2-Dihydro-3-phenyl-naphthalene	(1, 0)	384	40000	± 22200 (56%)
156	4',5'-Dihydro-psoralen	(0, 1)	500	14500	± 8430 (58%)
157	3,6-Dihydroxyphthalimide	(1, 0)	440	2900	± 1610 (56%)
158	4,4'-Dimethoxybenzophenone	(0, 1)	350	14100	± 8830 (63%)
159	2,3-Dimethoxy-1,4-benzoquinone	(0, 2)	430	4750	± 1950 (41%)
160	2,5-Dimethoxy-1,4-benzoquinone	(0, 2)	440	4620	± 1890 (41%)
161	5,7-Dimethoxycoumarin	(0, 1)	450	10500	± 6120 (58%)
162	2,3-Dimethoxy-5-methyl-1,4-benzoquinone	(0, 2)	430	5660	± 2320 (41%)
163	4,4'-Dimethoxythiobenzophenone	(0, 1)	295	20500	± 11800 (58%)
164	<i>trans</i> -1-(4-Dimethylaminophenyl)-2-nitroethylene	(1, 0)	440	35000	± 19500 (56%)
165	<i>N,N</i> -Dimethylaniline	(0, 1)	465	8370	± 4750 (57%)
166	9,10-Dimethylanthracene	(0, 2)	435	35300	± 14900 (42%)
167	<i>cis</i> -2,3-Dimethyl-2,3-di-(2-naphthyl)oxirane	(0, 1)	425	10300	± 5950 (58%)
168	<i>trans</i> -2,3-Dimethyl-2,3-di-(2-naphthyl)oxirane	(0, 1)	425	12400	± 7140 (58%)
169	3,9-Dimethyl- <i>trans</i> -fluorenone	(1, 0)	481	93500	± 52000 (56%)
170	1,3-Dimethylindazole	(2, 0)	420	8350	± 3280 (39%)
171	<i>N,N</i> -Dimethyl-4-nitroaniline	(1, 0)	390	20600	± 11500 (56%)
172	<i>N,N</i> -Dimethyl- <i>p</i> -phenylenediamine	(1, 0)	530	23000	± 12800 (56%)
173	(<i>E,E,E,E,E,E</i>)-7,11-Dimethyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8,10,12-tridecahexaenal	(2, 0)	505	169000	± 66200 (39%)
174	1,3-Dimethyluracil	(1, 0)	380	8000	± 4450 (56%)
175	2,5-Di(1-naphthyl)-1,3,4-oxadiazole	(2, 0)	600	7130	± 2800 (39%)
176	<i>cis</i> -2,3-Di-(2-naphthyl)oxirane	(0, 1)	430	10300	± 5950 (58%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
177	<i>trans</i> -2,3-Di-(2-naphthyl)oxirane	(0, 1)	430	8250	± 4760 (58%)
178	Diphenylamine	(3, 0)	540	23300	± 7490 (32%)
179	9,10-Diphenylanthracene	(0, 3)	445	15600	± 5240 (34%)
180	1,4-Diphenyl-1,3-butadiene	(4, 0)	390	54500	± 15100 (28%)
181	1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxy-1,4-dihydronaphthalene	(0, 1)	490	5460	± 3150 (58%)
182	1,0-Diphenyl-1,3,5-hexatriene	(4, 3)	420	114000	± 27300 (24%)
183	1,4-Diphenylnaphthalene	(1, 0)	444	32500	± 18100 (56%)
184	1,5-Diphenylnaphthalene	(1, 0)	538	22800	± 12700 (56%)
185	1,8-Diphenyl-1,3,5,7-octatetraene	(4, 1)	440	198000	± 50900 (26%)
186	2,5-Diphenyl-1,3,4-oxadiazole	(1, 0)	425	980	± 540 (56%)
187	2,5-Diphenyloxazole	(0, 2)	500	14800	± 5930 (40%)
188	<i>N,N'</i> -Diphenyl- <i>p</i> -phenylenediamine	(1, 0)	615	26800	± 14900 (56%)
189	<i>N,N'</i> -Diphenyl- <i>p</i> -phenylenediamine, conjugate acid	(1, 0)	600	67000	± 37200 (56%)
190	Duroquinone	(1, 4)	490	6310	± 1610 (25%)
191	Eosin	(1, 5)	580	10200	± 2790 (27%)
192	Ergosterol	(1, 0)	305	2800	± 1560 (56%)
193	Erythrosin dianion	(2, 0)	525	19000	± 7470 (39%)
194	10-Ethyl-9(10 <i>H</i>)-acridinone	(1, 0)	580	14600	± 8120 (56%)
195	<i>N</i> -Ethylcarbazole	(0, 3)	420	21600	± 7440 (34%)
196	β -Ethylstyrene	(0, 1)	325	3520	± 2000 (57%)
197	Fluorene	(4, 0)	380	22700	± 6300 (28%)
198	Fluoren-9-one	(1, 7)	425	6040	± 2420 (40%)
199	2-Fluorenyl phenyl ketone	(1, 0)	525	18600	± 10300 (56%)
200	4-Fluorobenzophenone	(0, 1)	315	21900	± 13700 (63%)
201	3-Formylfurochromene	(0, 1)	440	18100	± 10900 (60%)
202	2-Formyl-5'-methylfurobenzene	(0, 1)	540	9040	± 5450 (60%)
203	3-Formyl-2-methylfurochromene	(0, 1)	450	32000	± 19300 (60%)
204	3-Formyl-8-methylfurochromene	(0, 1)	450	14200	± 8570 (60%)
205	D-Glucose phenylosazone	(1, 1)	460	110000	± 46700 (42%)
206	Hematoporphyrin IX	(2, 0)	395	98200	± 38600 (39%)
207	1,1,1,5,5,5-Hexafluoroacetylacetone	(1, 0)	390	1000	± 560 (56%)
208	10,11,13,14,16,17-Hexahydro-5,7:20,22-dietheno-8 <i>H</i> ,19 <i>H</i> -diindeno[2,1- π :1',2'- σ][1,4,7,10]tetraoxacyclononade	(1, 0)	383	17100	± 9510 (56%)
209	9,10,11,12,13,14-Hexahydro-5,7:15,17-dietheno-2,20-heptano- <i>H</i> -cyclotetradeca[1,2- α :1,14- α']diindene	(1, 0)	465	35000	± 19500 (56%)
210	Indole	(0, 2)	430	4260	± 1710 (40%)
211	Iodo(methanol)(phthalocyaninato)rhodium(III)	(1, 0)	590	22000	± 12200 (56%)
212	β -Ionone	(1, 0)	330	85300	± 47400 (56%)
213	Isopsoralen	(0, 1)	450	4330	± 2530 (58%)
214	Isoquinoline	(2, 0)	418	11900	± 4660 (39%)
215	Kynurenic acid	(0, 1)	570	28500	± 16200 (57%)
216	Lumiflavine	(3, 1)	650	6090	± 1700 (28%)
217	Lumiflavine, conjugate monoacid	(1, 1)	425	6850	± 2710 (40%)
218	Lumiflavine, negative ion	(1, 0)	350	11000	± 6110 (56%)
219	<i>all-trans</i> -Lutein	(1, 0)	518	40000	± 22200 (56%)
220	<i>all-trans</i> -Lycopene	(0, 2)	525	406000	± 163000 (40%)
221	Magnesium(II) octaethylporphyrin	(0, 1)	440	100000	± 78600 (79%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
222	Magnesium(II) phthalocyanine	(2, 0)	480	32300	± 12700 (39%)
223	Magnesium(II) tetraphenylporphyrin	(1, 0)	485	72000	± 40000 (56%)
224	Mercury(II) tetraphenylporphyrin	(1, 0)	495	86000	± 47800 (56%)
225	Mesoporphyrin, dimethyl ester	(1, 1)	440	30700	± 12400 (40%)
226	4-Methoxyacetophenone	(0, 1)	360	8840	± 5230 (59%)
227	4-Methoxybenzophenone	(0, 1)	335	10100	± 6340 (63%)
228	(<i>R</i>)-4-Methoxydinaphtho[2,1- <i>d</i> :1',2'- <i>f</i>][1,3,2]dioxaphosphepin 4-oxide	(1, 0)	420	11100	± 6170 (56%)
229	1-Methoxynaphthalene	(0, 1)	440	9980	± 6020 (60%)
230	2-Methoxynaphthalene	(0, 1)	435	21400	± 12900 (60%)
231	<i>cis,cis</i> -1-(3'-Methoxy-5'-nitro-2'-oxo-3',5'-cyclohexadienyl)-3,4-dimethyl-1,3-pentadiene	(1, 0)	330	12000	± 6670 (56%)
232	4'-Methoxypropiophenone	(0, 1)	390	13300	± 7870 (59%)
233	5-Methoxypsoralen	(1, 1)	450	9450	± 3810 (40%)
234	8-Methoxypsoralen	(2, 1)	370	17700	± 5830 (33%)
235	8-Methoxy-2,2,3-trimethyl-6-nitro-2 <i>H</i> -chromene	(1, 0)	330	10000	± 5560 (56%)
236	4-Methylacetophenone	(0, 1)	331	9340	± 5520 (59%)
237	9-Methylacridine	(1, 0)	452	30000	± 16700 (56%)
238	10-Methyl-9(10 <i>H</i>)-acridinethione	(1, 3)	520	8790	± 2830 (32%)
239	2-Methylanthracene	(1, 0)	431	73000	± 40600 (56%)
240	9-Methylanthracene	(0, 3)	430	45900	± 16300 (35%)
241	4-Methylbenzophenone	(0, 1)	315	21100	± 13200 (63%)
242	(2'-Methylbenzoyl)amino-2- Δ^2 -thiazoline	(0, 1)	550	7280	± 4140 (57%)
243	(4'-Methylbenzoyl)amino-2- Δ^2 -thiazoline	(0, 1)	550	9450	± 5360 (57%)
244	3-Methyl-5-deazalumiflavine	(1, 0)	700	3600	± 2000 (56%)
245	<i>N</i> -Methyldiphenylamine	(1, 0)	540	26000	± 14500 (56%)
246	Methylene Blue cation	(4, 3)	420	14400	± 3210 (22%)
247	Methylene Blue cation, conjugate monoacid	(4, 0)	370	13800	± 3820 (28%)
248	α -Methyl- β -ethylstyrene	(0, 1)	325	4020	± 2280 (57%)
249	1-Methylindole	(0, 1)	460	5460	± 3230 (59%)
250	1-Methylnaphthalene	(2, 9)	420	20200	± 5850 (29%)
251	2-Methylnaphthalene	(1, 1)	420	30600	± 12600 (41%)
252	2-Methyl-1,4-naphthoquinone	(1, 0)	400	6600	± 3670 (56%)
253	<i>N</i> -Methylphenothiazine	(0, 1)	465	22600	± 12900 (57%)
254	<i>all-trans</i> -Methyl retinoate	(0, 1)	435	82000	± 47800 (58%)
255	(<i>E,E,E</i>)-5-Methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienal	(2, 2)	440	52000	± 15600 (30%)
256	(<i>E,E,E</i>)-6-Methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3,5,7-octatrien-2-one	(1, 0)	0	52000	± 28900 (56%)
257	(<i>E,E,Z</i>)-6-Methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3,5,7-octatrien-2-one	(1, 1)	0	49000	± 19500 (40%)
258	(<i>E,Z,E</i>)-6-Methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3,5,7-octatrien-2-one	(1, 1)	0	36900	± 14700 (40%)
259	(<i>E,Z,Z</i>)-6-Methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3,5,7-octatrien-2-one	(1, 0)	0	23000	± 12800 (56%)
260	(<i>E,E</i>)-3-Methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal	(2, 1)	385	32300	± 10400 (32%)
261	(<i>E,Z</i>)-3-Methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal	(1, 1)	0	14500	± 5780 (40%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
262	(<i>Z,E</i>)-3-Methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal	(1, 1)	0	19100	± 7590 (40%)
263	(<i>Z,Z</i>)-3-Methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal	(1, 1)	0	17600	± 6980 (40%)
264	3-Methyl-3,4,5-triphenyl-2(3 <i>H</i>)-furanone	(0, 1)	370	11400	± 6570 (58%)
265	2-Naphthalenamine, conjugate acid	(1, 0)	410	8960	± 4980 (56%)
266	Naphthalene	(12, 41)	415	24100	± 2780 (12%)
267	Naphthalene- <i>d</i> ₈	(6, 0)	415	23500	± 5340 (23%)
268	2-Naphthol	(0, 1)	435	6680	± 4560 (68%)
269	1-Naphthyl acetate	(1, 0)	405	1400	± 780 (56%)
270	2-(1-Naphthyl)benzoxazole	(1, 0)	530	24200	± 13500 (56%)
271	<i>trans</i> -1-(1-Naphthyl)-2-(2-naphthyl)ethylene	(0, 1)	500	19100	± 13100 (69%)
272	<i>trans</i> -1-(1-Naphthyl)-2-phenylethylene	(0, 1)	490	17100	± 11700 (69%)
273	<i>trans</i> -1-(2-Naphthyl)-2-phenylethylene	(0, 1)	395	8060	± 5520 (69%)
274	2-(2-Naphthyl)-5-phenyl-1,3,4-oxadiazole	(1, 0)	413	14000	± 7780 (56%)
275	2-(1-Naphthyl)-5-phenyloxazole	(1, 0)	550	100000	± 55600 (56%)
276	Neo-alloocimene	(0, 1)	315	1720	± 1170 (68%)
277	Neomethylene Blue cation	(1, 0)	840	4000	± 2220 (56%)
278	<i>all-trans</i> -Neurosporene	(0, 1)	489	237000	± 134000 (57%)
279	Neutral Red cation, conjugate diacid	(1, 0)	680	12000	± 6670 (56%)
280	5-Nitroacenaphthene	(1, 0)	370	7100	± 3950 (56%)
281	5-Nitro-2-furoic acid	(5, 0)	490	20700	± 5150 (25%)
282	2-Nitronaphthalene	(1, 0)	360	3600	± 2000 (56%)
283	4-Nitro- <i>p</i> -terphenyl	(1, 0)	340	38500	± 21400 (56%)
284	2-Nitrothiophene	(4, 0)	545	9930	± 2760 (28%)
285	Octaethylporphyrinatotin(IV) dichloride	(1, 0)	418	18000	± 10000 (56%)
286	8,9,10,11,12,13,14,15-Octahydro-5,7:16,18-dietheno-2,21-octanocyclopentadeca[1,2- α :1,15- α']diindene	(1, 0)	397	35900	± 20000 (56%)
287	Orotate ion	(1, 0)	315	22000	± 12200 (56%)
288	Orotic acid	(1, 0)	280	14000	± 7780 (56%)
289	7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene	(0, 1)	410	5840	± 3370 (58%)
290	7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hept-2-ene	(0, 1)	450	2800	± 1610 (58%)
291	Oxonine cation	(1, 0)	750	15000	± 8340 (56%)
292	Oxonine cation, conjugate monoacid	(1, 0)	650	16000	± 8890 (56%)
293	Palladium(II) etioporphyrin I	(1, 0)	410	70000	± 38900 (56%)
294	Palladium(II) tetrakis(4- <i>N</i> -methylpyridyl)porphyrin	(1, 0)	450	52000	± 28900 (56%)
295	Palladium(II) tetrakis(<i>p</i> -sulfonatophenyl)porphyrin	(1, 0)	460	28000	± 15600 (56%)
296	Palladium(II) tetraphenylporphyrin	(2, 0)	450	47400	± 18600 (39%)
297	Pentacene	(2, 0)	305	595000	± 234000 (39%)
298	Pentaphene	(1, 0)	493	45900	± 25500 (56%)
299	Perylene	(1, 4)	485	13400	± 5300 (40%)
300	Phenanthrene	(9, 3)	490	26800	± 4680 (17%)
301	Phenanthrene- <i>d</i> ₁₀	(4, 0)	490	28700	± 7970 (28%)
302	Phenazine	(2, 0)	355	37700	± 14800 (39%)
303	Phenothiazine	(1, 0)	460	27000	± 15000 (56%)
304	9-Phenylacridan	(1, 0)	520	10000	± 5560 (56%)
305	9-Phenylanthracene	(0, 1)	428	14600	± 9040 (62%)
306	1-Phenylcyclohexene	(0, 1)	325	4420	± 2510 (57%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
307	2,2'-(1,4-Phenylene)bisbenzoxazole	(1, 0)	480	18600	± 10300 (56%)
308	O-(2-Phenylethyl) 4-(dimethylamino)benzenecarbothioate	(1, 0)	450	20000	± 11100 (56%)
309	1-Phenylnaphthalene	(1, 1)	490	21700	± 8920 (41%)
310	2-Phenylnaphthalene	(1, 1)	430	43000	± 17300 (40%)
311	N-Phenyl-2-naphthylamine	(1, 0)	292	21500	± 12000 (56%)
312	2-Phenyl-2-norbornene	(0, 1)	325	18000	± 10200 (57%)
313	9-Phenylproflavine, conjugate monoacid	(1, 0)	280	47500	± 26400 (56%)
314	Pheophytin a	(1, 0)	407	62800	± 34900 (56%)
315	Pheophytin b	(1, 0)	423	71200	± 39600 (56%)
316	Photoprotoporphyrim isomer "A", dimethyl ester	(1, 1)	475	35800	± 14400 (40%)
317	Photoprotoporphyrim isomer "B", dimethyl ester	(0, 1)	475	34100	± 19900 (58%)
318	Phthalazine	(1, 0)	421	4450	± 2470 (56%)
319	Phthalocyanine	(4, 0)	480	29900	± 8300 (28%)
320	15- <i>cis</i> -Phytoene	(0, 1)	320	22000	± 15100 (69%)
321	<i>all-trans</i> -Phytoene	(0, 1)	320	19700	± 11200 (57%)
322	Picene	(4, 0)	630	45500	± 12600 (28%)
323	2-Piperidinoanthraquinone	(0, 1)	581	15700	± 9300 (59%)
324	Poly(2-vinylnaphthalene)	(0, 4)	426	11100	± 3640 (33%)
325	21H,23H-Porphine	(1, 0)	419	98600	± 54800 (56%)
326	Proflavine	(2, 1)	550	9510	± 3120 (33%)
327	Proflavine, conjugate monoacid	(2, 2)	550	8270	± 2500 (30%)
328	Psoralen	(1, 3)	450	11200	± 3570 (32%)
329	4',5'-Psoralen-thymine photo adduct	(0, 1)	500	5490	± 3310 (60%)
330	Purine	(1, 0)	390	4100	± 2280 (56%)
331	Pyranthrene	(0, 1)	500	20600	± 11700 (56%)
332	Pyrazine	(3, 0)	260	3600	± 1160 (32%)
333	Pyrene	(3, 0)	415	37700	± 12100 (32%)
334	Pyrene- <i>d</i> ₁₀	(3, 0)	415	40700	± 13100 (32%)
335	1-Pyrenecarboxaldehyde	(10, 0)	440	18400	± 3240 (18%)
336	Quinoline	(2, 0)	425	6750	± 2650 (39%)
337	11- <i>cis</i> -Retinal	(3, 3)	450	45300	± 10600 (23%)
338	13- <i>cis</i> -Retinal	(1, 3)	450	42400	± 12300 (29%)
339	9- <i>cis</i> -Retinal	(1, 2)	450	42400	± 14000 (33%)
340	<i>all-trans</i> -Retinal	(7, 5)	450	69300	± 11700 (17%)
341	<i>all-trans</i> -Retinoic acid	(0, 1)	440	63100	± 35800 (57%)
342	<i>all-trans</i> -Retinol ^b	(2, 19)	405	51600	± 12100 (23%)
343	Retinyl acetate	(2, 1)	405	65400	± 21100 (32%)
344	N-11- <i>cis</i> -Retinylidene- <i>n</i> -butylamine	(0, 1)	1	43200	± 24500 (57%)
345	N- <i>all-trans</i> -Retinylidene- <i>n</i> -butylamine	(1, 2)	435	74900	± 24700 (33%)
346	N- <i>all-trans</i> -Retinylidene- <i>n</i> -butylamine, conjugate acid	(1, 0)	570	150000	± 83400 (56%)
347	Rhodamine 6G	(3, 1)	620	16000	± 4460 (28%)
348	Rhodamine 6G dimer	(2, 0)	620	13300	± 5210 (39%)
349	Riboflavine, conjugate monoacid	(0, 1)	415	7560	± 4270 (56%)
350	Rubrene	(0, 4)	495	26500	± 10300 (39%)
351	Safranin cation	(1, 0)	420	10000	± 5560 (56%)
352	Safranin cation, conjugate diacid	(1, 0)	660	21500	± 12000 (56%)
353	Safranin cation, conjugate monoacid	(1, 0)	800	15500	± 8620 (56%)
354	Selenine cation	(1, 0)	770	17000	± 9450 (56%)

TABLE 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
355	Selenine cation, conjugate monoacid	(1, 0)	650	15500	± 8620 (56%)
356	<i>all-trans</i> -Spheroidene	(0, 1)	510	267000	± 152000 (57%)
357	<i>all-trans</i> -Spheroidenone	(0, 1)	550	52400	± 29700 (57%)
358	<i>all-trans</i> -Spirilloxanthin	(0, 1)	560	79500	± 45100 (57%)
359	<i>trans</i> -Stilbene	(1, 0)	378	34000	± 18900 (56%)
360	<i>trans</i> -Stilbene- <i>d</i> ₁₂	(1, 0)	378	28000	± 15600 (56%)
361	Styrene	(0, 1)	325	2210	± 1250 (57%)
362	<i>m</i> -Terphenyl	(1, 0)	436	3900	± 2170 (56%)
363	<i>p</i> -Terphenyl	(3, 0)	460	72700	± 23300 (32%)
364	<i>p</i> -Terphenyl- <i>d</i> ₁₄	(1, 0)	460	12900	± 7170 (56%)
365	4-(4- <i>p</i> -Terphenylmethyl)benzophenone	(1, 0)	480	110000	± 61100 (56%)
366	2-([1,1':4',1''-Terphenyl]-4-ylmethyl)triphenylene	(1, 0)	471	100000	± 55600 (56%)
367	Tetracene	(3, 0)	465	57900	± 18600 (32%)
368	<i>N,N,N',N'</i> -Tetraethyloxonine cation	(1, 0)	820	24000	± 13300 (56%)
369	<i>N,N,N',N'</i> -Tetraethyloxonine cation, conjugate monoacid	(1, 0)	700	28000	± 15600 (56%)
370	6,7,8,9-Tetrahydro-4-hydroxythiazolo[4,5- <i>h</i>]isoquinoline-7-carboxylate ion	(0, 1)	370	8890	± 6650 (75%)
371	Tetrakis(2,6-dimethyl-4-sulfonatophenyl)porphine	(1, 0)	780	3200	± 1780 (56%)
372	Tetrakis(2- <i>N</i> -methylpyridyl)porphine	(1, 0)	790	2600	± 1450 (56%)
373	Tetrakis(3- <i>N</i> -methylpyridyl)porphine	(1, 0)	840	3200	± 1780 (56%)
374	Tetrakis(2-pyridyl)porphine	(1, 0)	790	2600	± 1450 (56%)
375	Tetrakis(3-pyridyl)porphine	(1, 0)	790	3600	± 2000 (56%)
376	Tetrakis(4-pyridyl)porphine	(1, 0)	790	3800	± 2110 (56%)
377	Tetrakis(trimethylaminophenyl)porphine	(1, 0)	800	3200	± 1780 (56%)
378	<i>N,N,N',N'</i> -Tetramethylbenzidine	(3, 0)	475	38700	± 12400 (32%)
379	1,1',3,3'-Tetramethyldianthrone	(2, 0)	485	26000	± 10200 (39%)
380	<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine	(2, 8)	620	17000	± 4000 (24%)
381	3,3,4,5-Tetraphenyl-2(3 <i>H</i>)-furanone	(0, 1)	365	13500	± 7760 (58%)
382	<i>meso</i> -Tetraphenylporphine	(2, 0)	785	6000	± 2360 (39%)
383	1,3,6,8-Tetraphenylpyrene	(1, 0)	510	19700	± 11000 (56%)
384	Thiobenzophenone	(0, 1)	400	4950	± 2850 (58%)
385	Thionine cation	(3, 0)	770	10900	± 3490 (32%)
386	Thionine cation, conjugate monoacid	(4, 0)	650	18000	± 5000 (28%)
387	Thiopyronine cation	(3, 0)	660	4370	± 1400 (32%)
388	4-Thiouridine	(0, 2)	520	32300	± 14800 (46%)
389	9 <i>H</i> -Thioxanthene-9-thione	(0, 1)	505	2580	± 1400 (58%)
390	Thioxanthene-9-one	(0, 2)	650	26200	± 10600 (41%)
391	Thymidine	(0, 1)	370	2320	± 1400 (60%)
392	Thymidine 5'-monophosphate	(1, 1)	370	3290	± 1350 (41%)
393	Thymine	(0, 2)	340	2580	± 1180 (46%)
394	<i>s</i> -Triazine	(1, 0)	245	6000	± 3340 (56%)
395	4-(Trifluoromethyl)acetophenone	(0, 1)	455	2290	± 1350 (59%)
396	4-(Trifluoromethyl)benzophenone	(0, 1)	320	22400	± 14000 (63%)
397	4,4,4-Trifluoro-1-phenyl-1,3-butanedionatosodium	(1, 1)	620	11400	± 4530 (40%)
398	4,5',8-Trimethylpsoralen	(0, 1)	470	25700	± 16100 (63%)
399	Triphenylamine, conjugate acid	(1, 0)	546	9900	± 5500 (56%)
400	Triphenylene	(8, 0)	430	13500	± 2660 (20%)

TABLE 3: Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
401	Triphenylene- <i>d</i> ₁₂	(1, 0)	430	12000	± 6670 (56%)
402	3,3,5-Triphenyl-2(3 <i>H</i>)-furanone	(0, 1)	330	13500	± 7760 (58%)
403	Tris(2,2'-bipyridine)osmium(II) ion	(1, 0)	365	17700	± 9840 (56%)
404	Tris(2,2'-bipyridine)ruthenium(II) ion	(5, 0)	370	27600	± 6860 (25%)
405	Tris(1,10-phenanthroline)rhodium(III) ion	(0, 1)	490	4430	± 2560 (58%)
406	Tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)lanthanum(III)	(1, 1)	620	23300	± 9250 (40%)
407	Tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)lutetium(III)	(1, 1)	620	27800	± 11000 (40%)
408	Tryptophan	(1, 0)	460	5000	± 2780 (56%)
409	Dl-Tryptophan	(1, 0)	485	3700	± 2060 (56%)
410	L-Tryptophan	(1, 0)	450	8000	± 4450 (56%)
411	Ubiquinone 30	(0, 3)	440	8370	± 2820 (34%)
412	Uracil	(0, 2)	350	1730	± 790 (46%)
413	Uridine	(0, 1)	370	4130	± 2490 (60%)
414	Uridine monophosphate	(0, 1)	390	5810	± 3500 (60%)
415	Uroporphyrin I, octamethyl ester	(1, 1)	440	27700	± 11200 (40%)
416	2-Vinylnaphthalene	(0, 1)	426	12200	± 7090 (58%)
417	9 <i>H</i> -Xanthene-9-thione	(0, 1)	345	15900	± 9160 (58%)
418	Xanthone	(0, 2)	605	6480	± 2620 (40%)
419	Zinc(II) etioporphyrin I	(1, 0)	440	99000	± 55000 (56%)
420	Zinc(II) phthalocyanine	(4, 0)	480	28900	± 8030 (28%)
421	Zinc(II) tetrabenzoporphyrin	(1, 0)	490	74000	± 41100 (56%)
422	Zinc(II) tetrakis(2,6-dimethyl-4-sulfonatophenyl)porphyrin	(1, 0)	830	6000	± 3340 (56%)
423	Zinc(II) tetrakis(3- <i>N</i> -methylpyridyl)porphyrin	(1, 0)	440	57000	± 31700 (56%)
424	Zinc(II) tetrakis(4- <i>N</i> -methylpyridyl)porphyrin	(2, 0)	1020	7200	± 2830 (39%)
425	Zinc(II) tetrakis(trimethylaminophenyl)porphyrin	(1, 0)	840	5000	± 2780 (56%)
<i>Special Set of Measurements in Benzene</i>					
426	Acridine/Benzene	(3, 0)	440	25400	± 8160 (32%)
427	Anthracene/Benzene	(3, 12)	430	49800	± 8370 (17%)
428	Benzophenone/Benzene	(5, 46)	525	7870	± 1200 (15%)
429	Biphenyl/Benzene	(1, 33)	360	25000	± 4410 (18%)
430	Naphthalene/Benzene	(1, 19)	415	14400	± 2900 (20%)
431	Benz[<i>a</i>]anthracene/Benzene	(1, 2)	490	19800	± 6790 (34%)
432	Phenanthrene/Benzene	(1, 1)	490	15600	± 6270 (40%)
433	Pyrene/Benzene	(1, 0)	415	20900	± 11600 (56%)
434	Triphenylene/Benzene	(0, 1)	430	6190	± 3570 (58%)
435	3-Carbethoxy psoralen/Benzene	(0, 1)	450	6910	± 4030 (58%)
436	β - <i>apo</i> -14'-Carotenal/Benzene	(0, 1)	480	114000	± 77800 (68%)
437	9,10-Diphenylanthracene/Benzene	(0, 3)	445	14500	± 4990 (34%)
438	1,4-Diphenylbutadiene/Benzene	(1, 0)	390	45000	± 25000 (56%)
439	1,6-Diphenylhexatriene/Benzene	(1, 3)	420	105000	± 32200 (31%)
440	1,8-Diphenyloctatetraene/Benzene	(1, 2)	440	178000	± 60000 (34%)
441	Duroquinone/Benzene	(1, 2)	490	7030	± 2330 (33%)
442	C ₁₇ -aldehyde/Benzene	(0, 2)	440	58300	± 25300 (43%)
443	<i>all-trans</i> -Retinal/Benzene	(0, 2)	450	58400	± 24100 (41%)

Table 3. Global least-squares fit of TTA ϵ 's — Continued

No.	Compound	Number of measurements (abs., rel.)	λ (nominal) /nm	ϵ /L mol ⁻¹ cm ⁻¹	95% Confidence Interval ^a
444	<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine/Benzene	(1, 0)	620	12200	± 6780 (56%)
445	Zinc(II) phthalocyanine/Benzene	(1, 0)	480	51000	± 28400 (56%)

^a Confidence intervals for compounds with only one measurement are based on the assumption that the estimate of the variance $Q/(n-p)$ for multiply-measured compounds is the same as that for singly-measured compounds. $Q/(n-p)$ is the estimate of the variance of the underlying distribution of the errors in individual determinations of extinction coefficients.

^b Use 80000 L mol⁻¹ cm⁻¹ for retinol in hexane, see Section 3.7.

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5. References

- ¹P. Roman, *Advanced Quantum Theory* (Addison-Wesley, Reading, MA, 1965), p. 143.
- ²J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley, London, 1970).
- ³I. Carmichael and G. L. Hug, *J. Phys. Chem. Ref. Data* **15**, 1 (1986).
- ⁴B. Ostle and R. W. Mensing, *Statistics in Research*, 3rd ed. (Iowa State University, Ames, IA, 1975).
- ⁵*SAS User's Guide: Statistics, 1982 Edition* (SAS Institute, Cary, NC, 1982).
- ⁶E. R. Cohen, K. M. Crowe, and J. W. M. DuMond, *Fundamental Constants of Physics* (Interscience, New York, 1957).
- ⁷E. Whittaker and G. Robinson, *The Calculus of Observations*, 4th ed. (Blackie, London, 1944).
- ⁸M. S. Bartlett, *Biometrics* **3**, 39 (1947).
- ⁹W. P. Helman, in Appendix II of paper by F. Wilkinson and J. G. Brummer, *J. Phys. Chem. Ref. Data* **10**, 809 (1981).
- ¹⁰Modified from routines in LINPACK, see J. J. Dongarra, J. R. Bunch, C. B. Moler, and G. W. Stewart, *LINPACK Users' Guide* (Soc. Indust. Appl. Math., Philadelphia, PA, 1979).
- ¹¹W. P. Helman, G. L. Hug, I. Carmichael, and A. B. Ross, *J. Chem. Inf. Comput. Sci.* **26**, 99 (1986).
- ¹²A. G. Worthing and J. Geffner, *Treatment of Experimental Data* (Wiley, New York, 1943).
- ¹³R. Bensasson and E. J. Land, *Trans. Faraday Soc.* **67**, 1904 (1971).
- ¹⁴J. K. Hurley, N. Sinai, and H. Linschitz, *Photochem. Photobiol.* **38**, 9 (1983).
- ¹⁵E. J. Land, *Proc. R. Soc. (London) Ser. A* **305**, 457 (1968).
- ¹⁶E. J. Land, *Trans. Faraday Soc.* **65**, 2815 (1969).
- ¹⁷D. Feldman and J. Gagnon, *StatView: A Graphic Statistics Utility for the Macintosh* (BrainPower, Calabasas, CA, 1985).
- ¹⁸A. Hald, *Statistical Tables and Formulas* (Wiley, New York, 1952).
- ¹⁹M. Kendall and A. Stuart, *The Advanced Theory of Statistics*, 4th ed. (Macmillan, New York, 1977), Vol. 2, pp. 476 and 530.
- ²⁰S. Siegel, *Nonparametric Statistics for the Behavioral Sciences* (McGraw-Hill, New York, 1956).
- ²¹C. Hastings, Jr., *Approximations for Digital Computers* (Princeton University, Princeton, NJ, 1955).
- ²²G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross (in preparation).
- ²³L. Branscomb, *Am. Sci.* **73**, 421 (1985).
- ²⁴C. A. Parker, *Photoluminescence of Solutions* (Elsevier, Amsterdam, 1968).
- ²⁵R. Bensasson, E. A. Dawe, D. A. Long, and E. J. Land, *J. Chem. Soc. Faraday Trans. I* **73**, 1319 (1977).
- ²⁶K. Bhattacharyya and P. K. Das, *Chem. Phys. Lett.* **116**, 326 (1985).
- ²⁷I. Carmichael and G. L. Hug, *J. Phys. Chem.* **89**, 4036 (1985).
- ²⁸T. Rosenfeld, A. Alchalel, and M. Ottolenghi, in *Excited States of Biological Molecules*, edited by J. B. Birks (Wiley, New York, 1976), p. 540.