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Optical Limiting Chromophores. Correlation Effects in Computing Triplet−Triplet Absorption Energies of Organic Molecules

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The computation of molecular triplet−triplet absorption wavelengths for a series of organic chromophores potentially useful in reverse saturable absorption and photodynamic therapy has been systematically investigated using the semi-empirical INDO/S model Hamiltonian. The effect of parameters defining the model and of the level of configuration interaction on the computed triplet absorption have been explored in detail. From eight different models which vary in the INDO/S model Hamiltonian parameters and the level of excited configurations used in the CI, a reliable model that estimates the triplet absorption of organic π-conjugated systems has been deduced. The model that employs Zerner's suggested triplet parameters and uses a MRD-CI level of configuration interaction reproduces the experimentally observed triplet absorption to reasonable accuracy. While this model performs exceptionally well in the case of acenes (fused unsubstituted ring systems) and α,ω-diphenyl polyene systems, it performs somewhat less well for organic molecules substituted with polar functional groups. The total RMS deviation in the computed triplet absorption $\lambda_{\max}$ of 100 organic molecules is 58 nm with a correlation coefficient of 0.85 for the entire set, 56 nm (correlation coefficient = 0.93) in the case of acenes, and 56 nm (correlation coefficient = 0.96) for α,ω-diphenyl polyenes.

I. Introduction

Molecule-based materials that exhibit strong triplet absorption in the same spectral region where they exhibit weak singlet absorption are of great current interest in the area of optical limiting, especially using the reverse saturable absorption (RSA) mechanism.[1−6] To date, the design of chromophores for RSA applications has been largely empirical, and it would be of interest to develop efficient and accurate computational approaches to predicting and understanding molecular triplet−triplet absorption features. Another area where reliable estimates of organic molecule triplet absorption wavelengths would be of great utility is in photodynamic therapy (PDT).[7−10] PDT, a dye-sensitized photo-oxidation of biological matter, wherein a sensitizer molecule is introduced into the organism followed by exposure of the sensitizer to light of appropriate wavelength, is an innovative and attractive approach to treating tumors.[7,9] The tumor is destroyed either by radical products generated via resonant energy transfer reactions or through reactive singlet oxygen. For a detailed description of energy transfer reaction mechanisms, see ref 11.

RSA is a widely used approach to optical limiting.[2] While there exist a number of other optical limiting mechanisms, such as nonlinear refraction[12] or free carrier absorption,[13] RSA[3−5,14] and two-photon absorption (TPA)[15,17,18] have received the greatest attention in the context of organic chromophores. RSA occurs in molecules where the excited-state absorption cross-section exceeds that of the ground state. In principle, the excited state exhibiting a larger absorption cross-section could be either a singlet or a triplet excited state. However, molecules exhibiting larger triplet absorption cross-sections are currently of greater interest since triplet-state temporal characteristics are compatible with longer laser pulses. Thus, one of the primary requirements in modeling materials for the above applications is to devise reliable computational models for estimating triplet−triplet absorption and the associated oscillator strengths.

Accurate, efficient computational models provide an opportunity to expeditiously survey large numbers of candidate chromophores and provide useful guidance to both synthetic and spectroscopic experimentalists. Such computational tools have been successfully employed in understanding, modeling, and designing molecular-based chromophores for a wide variety of optical applications. In addition to the importance of understanding triplet absorption in molecules active for PDT and RSA, there are numerous other photophysical and photochemical processes that require quantitative estimation of triplet absorption. For example, it has been postulated by Garito et al. that some organic molecules may exhibit far larger non-linear optical (NLO) responses in excited states than in the ground state.[19] Preliminary NLO response studies of organic molecules in the first excited singlet state (2^1A_g) and of excited triplet states of finite polyenes, indeed indicate that the excited-state responses are an order of magnitude larger than the ground state, as reported by Garito et al.[20] Resonant energy transfer from the T_1 state of organic molecules to suitable acceptor molecules has also been extensively studied.[21] Such resonant energy transfer is accepted as one of the mechanisms of PDT and characterization provides useful information for the design of new PDT chromophores.[7,9]

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While there have been a number of reports on ab initio[22−24] and semi-empirical methods for estimating organic molecule singlet absorption spectra, there are only a few reports on the corresponding computation of triplet absorption.[25−27] The majority of these studies have been carried out using semi-empirical model Hamiltonians with configuration interaction (CI), the subspace of which spans mainly singly excited configurations, and using parametrization chosen for the specific molecular system under examination. For example, Despres et al.[25] used an INDO/CIPSI (intermediate neglect of differential overlap/configuration interaction by perturbative selected iterations) procedure with screening factors of $k_{\sigma\sigma} = 1.0$, $k_{\sigma\pi} = 0.75$, and $k_{\pi\pi} = 0.6$ to study the resonant energy transfer and triplet−triplet absorption characteristics of diphenyl carbene. Ochsner[26] employed an INDO/CIS (configuration interaction with singles) approach with a $k_{\pi\pi}$ value of 0.68 to study the electronic structure and triplet absorption of zinc(II) phthalocyanine. Bredas et al.[27] used an INDO/MRD-CI (multi reference double-configuration interaction) approach to estimate the triplet excitation energies of oligothiophenes and oligo(phenylene-vinylene) systems. Although the INDO/MRD-CI approach overestimates the triplet excitation energies, it reproduces the correct conjugative pathlength dependence of oligothiophene and oligo(phenylenevinylene) response. Apart from a few studies on specific systems, no general models have been developed for the reliable estimation of the triplet absorption of organic molecules.

In this contribution, we present a reliable and computationally efficient model for computing triplet absorption wavelengths for a broad class of organic molecules. We have computed the vertical triplet−triplet absorption of 100 typical chromophores, the absorption energies of which span the entire visible region, using a semi-empirical INDO/S model Hamiltonian with CI levels that vary from singles only to full CI. In Section II we present the details of the computational approach, and in Section III the results.

II. Computational Details

Triplet absorption spectra of organic molecules can be computed using either ab initio or semi-empirical methods. While ab initio methods are expected to reproduce experimental properties to high accuracy, they can be applied only to small or medium-sized molecules.[23,24] Semi-empirical model Hamiltonians, specifically INDO/S,[29] have been employed to describe linear and nonlinear optical properties of numerous organic[32] and organometallic chromophores.[33] Semi-Empirical approaches offer an attractive alternative to ab initio methods in that they can be applied to large molecules and to a large extent still retain the accuracy of the ab initio methods. While semi-empirical methods may not reproduce experimental observables to the highest degree of accuracy, they do reproduce qualitative and quantitative trends, which can be invaluable for elucidating response mechanisms, assaying a wide range of molecules for specific applications, or for designing novel molecular architectures with attractive materials properties.

A number of factors such as basis set, vibrational interactions, environment, electron correlation, and spin−orbit interactions influence the computed photophysical properties of organic molecules. A detailed description of how these effects influence molecular linear and nonlinear optical properties has been recently presented.[34] While inclusion of extended basis sets, vibrational,[35] solvent,[36] and spin−orbit[37] effects does improve the accuracy of computed photophysical properties, neglecting electron correlation leads to results that differ both qualitatively and quantitatively from models that include electron correlation. Inclusion of electron correlation to a high degree of accuracy (performing complete active space perturbation theory (CASPT2), coupled-clusted, or higher excited CI such as multi-reference CI (MRCI), or full CI) is a significant computational hurdle even in semi-empirical models for large systems. Nevertheless, model exact calculations (calculations performing full CI within a chosen model Hamiltonian) on moderately large systems have been performed.[28] In addition, extensive literature demonstrates the applicability of semi-empirical models in reliably computing organic molecule linear and nonlinear response.[32−34] Thus, in the present investigation, we employ the INDO/S model Hamiltonian with CI calculations of varying degrees of accuracy to investigate the effect of electron correlation on computed organic molecule triplet absorption $\lambda_{\max}$ and thereby to develop a reliable and efficient computational model for estimating these absorption maxima.

The triplet state geometries of the 50 test chromophores chosen in this study were fully optimized using the restricted open shell Hartree-Fock/Austin Model 1 (ROHF/AM1) model Hamiltonian[39] as implemented in the Gaussian 94 package[40] with no symmetry restrictions. Using these AM1 geometries, triplet−triplet vertical absorption $\lambda_{\max}$ were computed using the various levels of parametrization and configuration interaction described below. The molecules chosen in this study span a wide range of absorption $\lambda_{\max}$ and architectures, so that a model reproducing absorption energies within this set should be of value for describing organic molecule triplet absorption spectra. The model that performs most accurately is then used to compute triplet absorption energies of 50 additional chromophores not included in the test calculation, to examine further the reliability of the chosen model.

A. Computational Model. The earliest model proposed for computing triplet−triplet absorption energies was proposed by Pariser and Parr,[41] who employed a π-electron model Hamiltonian, now known as the Pariser−Parr−Pople model,[41,42] and computed the triplet absorption of simple organic molecules such as benzene and pyridine. However, while the PPP model reliably estimates linear and nonlinear optical properties, it is limited to purely π-conjugated molecules. Another model for computing the linear optical properties of organic molecules is the INDO/S model Hamiltonian proposed by Zerner et al.[29−31] This formalism employs a minimal valence shell basis set and has been extensively applied to a wide range of properties and molecules. Reliable triplet absorption energies can be obtained using the INDO/S Hamiltonian with modified parameterization, reduced two-electron integrals, and a CI calculation employing all singles from a ROHF triplet ground-state reference determinant. The parameters used in the INDO/S model can be described by the INDO/S Hamiltonian, written in second quantized notation

$$H = \sum_{ij}\sum_{\mu} t_{ij} a^{\dagger}_{i\mu} a_{j\mu} + \frac{1}{2}\sum_{ij}\sum_{\mu\nu} \gamma_{ij} a^{\dagger}_{i\mu}\, a^{\dagger}_{j\nu} a_{j\nu} a_{i\mu} \qquad (1)$$

$$+ \frac{1}{2}\sum\nolimits'_{il}\, \sum\nolimits'_{jk} \sum_{\mu\nu} \langle ij|kl\rangle a^{\dagger}_{i\mu}\, a^{\dagger}_{k\nu} a_{j\mu} a_{l\nu}$$

where i, j label local valence basis orbitals and μ, ν label spins, the primed summations implying that exchange terms are restricted to one atom, t_{ij} are the transfer or resonance or one-electron integrals, and γ_{ij} and $\langle ij|kl\rangle$ are the two-electron integrals are parametrized by the Mataga−Nishimoto[43] or the Ohno−Klopman approximation,[44] details of which can be found

TABLE 1: Experimental and Computed Triplet−Triplet Absorption Results for 50 Typical Organic Molecules[a]

		λ_{max} (nm)					
number	molecule	expt	Model 1	Model 2	Model 3	Model 4	Model 5
1	acenaphthene	422	554.1	594.5	570.3	552.1	570.1
2	acetone	300	304.6	321.5	326.8	342.3	312.4
3	acetophenone	330	295.1	269.3	274.1	266.3	284.4
4	acridine	440	424.6	410.6	419.6	408.3	430.5
5	aniline	320	459.6	434.6	403.8	393.3	417.1
6	anisole	252	171.3	162.7	437.8	152.3	164.6
7	anthracene	430	451.8	437.6	451.1	438.1	462.8
8	anthraquinone	390	492.8	441.6	439.3	414.4	333.1
9	anthrone	341	476.4	310.3	422.4	411.3	268.1
10	azulene	360					
11	benzene	235	175.6	162.3	167.6	161.3	174.4
12	benzil	480	512.5	520.4	480.6	464.5	497.7
13	benzo[ghi]perylene	465	598.0	588.4	569.3	550.8	581.4
14	benzophenone	525	272.7	247.5	418.6	235.9	257.2
15	benzo[a]pyrene	465	542.9	529.6	520.4	494.6	539.5
16	benzo[e]pyrene	560	595.2	583.4	554.1	536.8	585.8
17	biacetyl	315	476.4	475.5	424.9	406.6	444.4
18	biphenyl	360	567.2	553.8	534.2	487.7	555.5
19	4,4′-bis(dimethylamino)benzophenone	500	568.8	663.4	628.1	638.9	634.0
20	carbazole	418	337.6	347.2	387.0	294.2	316.1
21	chrysene	575	794.1	810.5	768.9	751.0	788.1
22	coronene	480	672.7	697.4	670.0	649.3	682.0
23	4,4′-dimethoxybenzophenone	350	437.2	426.3	420.6	407.1	433.9
24	*N*,*N*-dimethylaniline	460	438.3	443.7	412.7	391.4	428.8
25	1,4-diphenyl-1,3-butadiene	390	483.4	464.3	444.2	428.6	465.3
26	1,6-diphenyl-1,3,5-hexatriene	420	512.9	483.8	472.7	456.5	490.3
27	1,8-diphenyl-1,3,5,7-octatetraene	440	647.4	625.2	655.7	630.0	668.7
28	*N*-ethylcarbazole	420	720.2	724.4	327.8	312.0	346.5
29	fluorene	380	573.1	573.7	545.8	503.2	567.2
30	fluorenone	425	564.6	559.4	482.1	462.6	524.6
31	isoquinoline	418	515.7	502.7	509.8	492.2	528.7
32	phenazine	355	227.7	243.1	315.0	298.2	331.5
33	phenol	250	251.2	243.6	224.8	214.9	235.7
34	phenothiazine	460	504.8	486.2	470.2	452.8	493.1
35	pyrazine	260	304.0	278.6	257.3	244.5	271.9
36	quinoline	425	541.0	501.6	492.4	478.3	546.4
37	styrene	324	514.3	479.9	463.5	442.5	487.2
38	tetracene	465	512.7	536.8	514.6	499.4	530.4
39	*trans*-stilbene	360			260.6		
40	11-*cis*-retinal	450			388.4		
41	13-*cis*-retinal	450			382.0		
42	9-*cis*-retinal	450			382.8		
43	*trans*-retinal	450			384.5		
44	naphthalene	360			480.7		
45	1-nitronaphthalene	360			480.7		
46	*N*,*N*-dimethylaminonitroaniline	390			399.3		
47	1-methoxy-naphthalene	440			419.5		
48	2-methoxy-naphthalene	435			487.5		
49	*s*-triazine	245			156.8		
50	uracil	350			290.9		
correlation coefficient			0.65	0.69	0.75	0.72	0.70
RMS deviation (nm)			130.3	128.8	95.5	100.8	99.29

[a] Singles-only CI using various parametrizations was employed in the calculations. See text for details.

elsewhere.[45] The off-diagonal one-electron integral is approximated by a modified Wolfsberg−Helmholz approximation,[46] given by

$$t_{ij} = (t_{ii} + t_{jj})\bar{S}_{ij}/2 \tag{2}$$

where $\bar{S}_{ij}$ is a weighted orbital overlap integral, with different weighting factors for the σ (f_σ), π (f_π), and δ (f_δ) types of orbital interactions. The suggested weighting factors[29] for computing triplet absorption are 1.267 and 0.68 for the σ- and π-type orbital interactions, respectively. In addition, a Pariser−Parr type approximation[41] was suggested for parametrization of the two-electron integrals. With this parametrization and singles-excitation CI (CIS), Zerner et al. obtained reasonably good agreement with the experimentally observed triplet absorption of benzene, pyridine, and pyrazine.[29] This parametrization has been recently used by Ochsner[26] to compute the triplet absorption of zinc(II) phthalocyanine; he suggested that this parametrization gives good estimates of triplet absorption for porphyrin and phthalocyanine systems. In our initial model, we have used this triplet parametrization to compute the triplet absorption of the 50 organic chromophores listed in Table 1.

A plot of computed versus experimental triplet absorption maxima of the test molecules obtained using the triplet parametrization suggested by Zerner[29] and CIS is shown in Figure 1. It can be seen that while there is clearly some scatter, the triplet absorptions of many molecules are reasonably well reproduced. The correlation coefficient for this plot is 0.75. While extensive deviation from the observed values in some

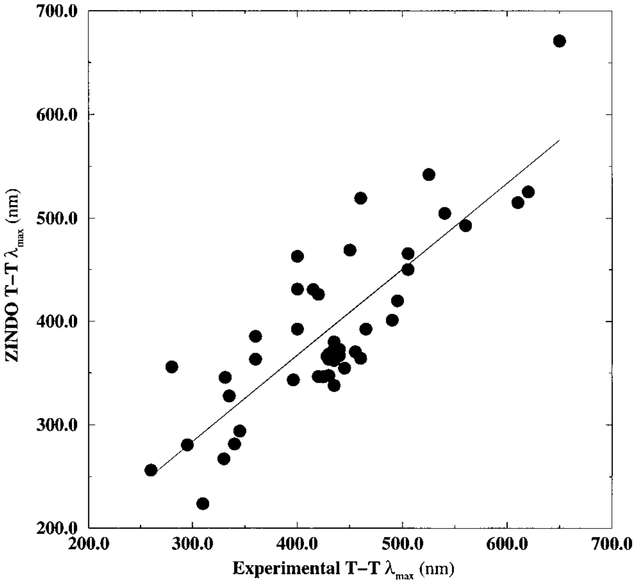

Figure 1. Computed triplet–triplet absorption wavelengths for a series of organic π-conjugated chromophores using parametrization Model 3 plotted versus the experimental triplet–triplet absorption data. Experimental data are taken from ref 50.

cases is discouraging, it is encouraging to note that most of the computed absorption λ_{max} are overestimates of the experimental values. Such systematic overestimation may arise from neglect of electron correlation, the inclusion of which is known to be important in obtaining reliable estimates of organic molecule linear and nonlinear optical properties. Support for this conjecture comes from the substantial experimental and theoretical evidence for strong electron correlation in organic π-conjugated systems,[47,48] and the systematic improvement of computed organic molecule linear and nonlinear response properties using achievable models that systematically enhance the level of correlation included.[38] Note that it is also possible to improve the agreement between theory and experiment by reparametrization. Such a calculation has been carried out by Ochsner on porphyrin and phthalocyanine systems.[26] However, as shown in Section III, simple parameter modification does not lead to significant improvement in the absorption λ_{max} of the test molecules, while improving the level of correlation included in the CI indeed leads to systematic improvement.

III. Results and Discussion

INDO/S-derived triplet absorption λ_{max} for the 50 test molecules computed using Zerner's suggested triplet parametrization are presented in Table 1. Additionally, computed triplet absorption from four different parametrizations are also presented in Table 1. In all the cases, the level of CI was restricted to only singles generated from a ROHF triplet ground reference determinant and using 11 occupied and 11 unoccupied molecular orbitals (MOs). The only parameters that are varied are the π-interaction factor, f_π, and the two-electron integral approximation. The five different parametrizations are as follows:

- Model 1. $f_\pi = 0.585$ and the Ohno–Klopman approximation. This parametrization reproduces the singlet optical absorption spectra of organic π-conjugated polyenes and many unsubstituted systems,[38] and works well with higher excited CI.
- Model 2. $f_\pi = 0.65$ and the Mataga–Nishimoto approximation. This parametrization has been employed to model linear and nonlinear optical properties of donor–acceptor systems and works well with CIS schemes.[38,49]
- Model 3. $f_\pi = 0.68$ and the Pariser–Parr approximation.[41] This is the parametrization recommended by Zerner.[29]
- Model 4. $f_\pi = 0.64$ and the Pariser–Parr approximation.[41]
- Model 5. $f_\pi = 0.72$ and the Pariser–Parr approximation[41] as suggested by Ochsner.[26]

The performance of these five models in estimating the triplet–triplet absorption of the test molecules is summarized in Table 1. The first two models, which employ conventional singlet parametrization, perform very poorly. While the parametrization suggested by Ochsner ($f_\pi = 0.72$) performs more acceptably in terms of scatter, the RMS deviation from the experimentally observed maxima is still quite large. Of the five models examined, Model 3, which uses Zerner triplet parametrization, performs most acceptably in terms of scatter and RMS deviation. The RMS deviation from experimental absorption values is still quite large, however, and as mentioned above, most computed absorption λ_{max} are overestimates of the experimental λ_{max}, and such systematically overestimated absorption energies might in principle be improved by more elaborate treatment of electron correlation.

To include correlation, three additional sets of calculations were performed, where in addition to the configurations used in Model 3, doubles and higher excited configurations are also included. The details of the three models are as follows.

- Model 6. As in Model 3, but including all doubles generated from 5 occupied and 5 unoccupied MOs.
- Model 7. A singlet HF calculation with the same set of parameters used in Model 3, followed by a multi-reference doubles CI(MRDCI). The two reference determinants used in the calculations were HH and HL, where H and L are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. All singles from 11 occupied and 11 unoccupied MOs from each of the reference determinants (HH and HL) and all doubles from 5 occupied and 5 unoccupied MOs from the singlet reference deteminant (HH) are used. The spin state of the generated configurations was restricted to triplets only.
- Model 8. As in Model 7, but all excited configurations (singles to full CI) from 3 occupied and 3 unoccupied MOs are included in the CI.

The results with these three models are presented in Table 2. While the addition of doubles (Model 6) does improve the RMS deviation, the scatter is still quite substantial and yields a poor correlation coefficient. Model 7, by dealing more extensively with correlation effects, provides remarkable improvement over the other models considered. The RMS deviation is about 55 nm and the correlation coefficient is 0.83. In the entire set of 50 molecules considered in this study, there are only two molecules where computed absorption λ_{max} deviate by greater than 100 nm. These are benzil and *N*,*N*-dimethylaniline. While the large deviation of the computed absorption in the case of benzil could be attributed to possible out-of-plane deviations of the dihedral twist angle of the carbonyl groups and phenyl rings used in the computation, the large deviation of the computed absorption of *N,N*-dimethylaniline is quite surprising. In an attempt to relate the large deviation of the above molecules to the possibility of inadequate geometry optimization used in the calculation, the triplet geometries of the aforementioned molecules were optimized with ab initio ROHF calculations using a 6-31G** basis set. We then find significant improvement in the computed absorption maxima of *N*,*N*-dimethylaniline, the triplet–triplet absorption maximum of which shifts from 324.6 to 427.6 nm, in far better agreement with the experimental absorption energy of 465 nm.[50,51] Similarly, a substantial

TABLE 2: Triplet−Triplet Absorption Data for Typical Organic Molecules from Singles and Doubles CI and MRDCI Calculations (see text for details)

		λ_{max} (nm)			
number	molecule	expt	Model 6	Model 7	Model 8
1	acenaphthene	422	571.2	361.9	349.5
2	acetone	300	305.1	304.7	302.7
3	acetopohenone	330	260.6	268.5	260.8
4	acridine	440	402.8	384.5	371.8
5	aniline	320	423.2	264.0	263.2
6	anisole	252	169.9	244.3	238.0
7	anthracene	430	415.2	370.7	359.6
8	anthraquinone	390	410.1	394.1	391.4
9	anthrone	341	373.4	337.7	330.1
10	azulene	360	321.1	388.4	375.3
11	benzene	235	167.9	213.6	208.3
12	benzil	480	440.6	419.0	411.6
13	benzo[ghi]perylene	465	532.1	459.4	454.6
14	benzophenone	525	366.4	459.2	459.2
15	benzo[a]pyrene	465	496.0	405.9	385.1
16	benzo[e]pyrene	560	526.2	645.8	610.5
17	biacetyl	315	443.3	362.3	358.6
18	biphenyl	360	497.1	303.1	287.3
19	4,4′-bis(dimethylamino)benzophenone	500	385.5	546.9	544.3
20	carbazole	418	308.2	386.7	375.8
21	chrysene	575	683.8	522.3	550.1
22	coronene	480	608.9	465.3	516.1
23	4,4′-dimethoxybenzophenone	350	421.2	322.2	318.6
24	*N*,*N*-dimethylaniline	460	412.8	427.6	425.7
25	1,4-diphenyl-1,3-butadiene	390	393.9	330.3	325.0
26	1,6-diphenyl-1,3,5-hexatriene	420	420.5	349.2	342.0
27	1,8-diphenyl-1,3,5,7-octatetraene	440	569.9	408.1	403.0
28	*N*-ethylcarbazole	420	575.1	354.0	341.9
29	fluorene	380	514.2	314.7	300.1
30	fluorenone	425	450.7	342.6	339.3
31	isoquinoline	418	509.6	346.3	342.3
32	phenazine	355	298.5	433.1	429.7
33	phenol	250	298.5	238.2	229.8
34	phenothiazine	460	426.6	476.9	523.1
35	pyrazine	260	299.1	337.2	320.6
36	quinoline	425	337.2	355.0	334.2
37	*trans*-stilbene	360	379.0	312.2	325.0
38	styrene	324	439.0	262.4	253.7
39	tetracene	465	475.8	395.5	385.3
40	11-*cis*-retinal	450		508.0	505.0
41	13-*cis*-retinal	450		509.3	505.8
42	9-*cis*-retinal	450		509.0	506.0
43	*trans*-retinal	450		507.2	504.7
44	naphthalene	415		332.9	321.3
45	1-nitronaphthalene	360		387.3	381.5
46	*N*,*N*-dimethylaminonitroaniline	390		439.4	427.4
47	1-methoxy-naphthalene	440		366.5	354.0
48	2-methoxy-naphthalene	435		376.9	329.2
49	*s*-triazine	245		306.2	304.7
50	uracil	350		307.9	307.0
correlation coefficient			0.68	0.82	0.83
RMS deviation (nm)			86.33	55.34	60.37

improvement is found in the absorption maximum of benzil, which shifts from 355.4 to 419 nm, in more favorable agreement with the experimental value of 480 nm.[50]

In an attempt to improve the correlation treatment, additional configurations, that include all excited configurations generated from a HF singlet ground state and using 3 occupied and 3 unoccupied orbitals (the spin state of the configurations was restricted to triplets only), were included in Model 7 (Model 8). From Table 2 it can be seen that, while this model performs noticeably better than Models 1−6, there is no significant improvement over Model 7. The absorption maxima are generally blue-shifted versus Model 7 by 10−25 nm. However, deviations from the triplet−triplet experimental absorption λ_{max} still exist in the case of *N*,*N*-dimethylaniline and benzil when AM1 geometries are employed. There is again a substantial improvement when the ab initio ROHF/6-31G** geometries are used. The computed absorption λ_{max} of the 50 molecules from Model 7 and Model 8 are presented in Figure 2. The absorption maxima of *N*,*N*-dimethylaniline and benzil shown are those computed using the 6-31G** geometries.

To elucidate the performance of the three models (Models 3, 7, and 8) in estimating triplet−triplet absorption of two important classes of chromophores, namely, series of acenes and α,*ω*-diphenylpolyenes, we plot the computed absorption λ_{max} of the two classes of molecules in Figures 3 and 4 respectively. Figures 3 and 4 demonstrate the favorable agreement of the computed absorption λ_{max} for acenes and α,*ω*-diphenylpolyenes, respectively, with the experimental data. The RMS deviation of the computed absorption λ_{max} of the acenes evidences deviations of 55.70 and 62.68 nm for Models 7 and 8 with correlation coefficients of 0.93 and 0.92, respectively. Similarly, the RMS deviations of the computed absorption λ_{max}

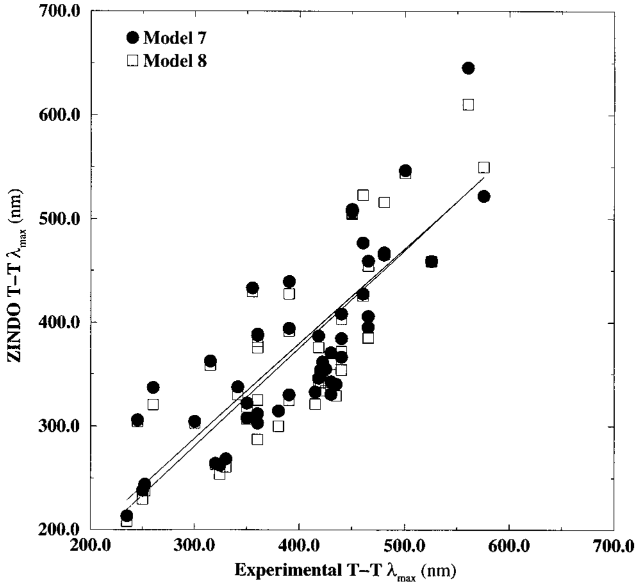

Figure 2. Computed triplet−triplet absorption wavelengths of a series of 50 test molecules using parametrization Models 7 and 8, plotted versus experimental triplet−triplet absorption data.

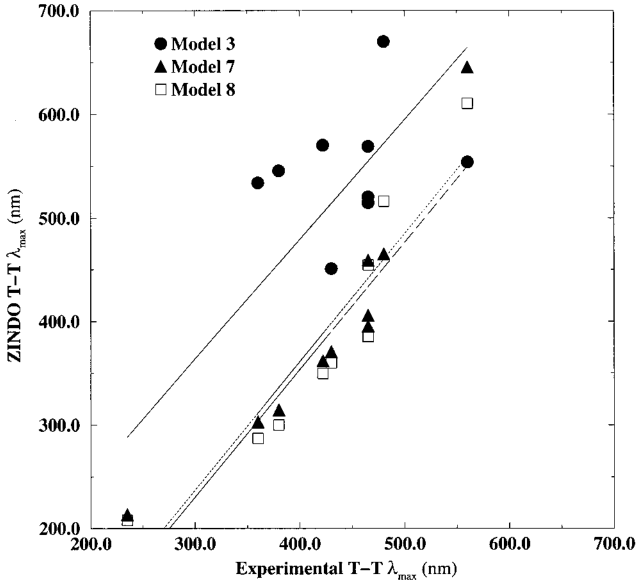

Figure 3. INDO/S-derived triplet−triplet absorption maxima of a series of acenes (fused aromatic ring systems, molecules 1, 7, 11, 13, 15, 16, 23, 29, 39, and 44) plotted versus the experimental wavelengths. Filled circles use parametrization Model 3, filled triangles use Model 7, and open squares use Model 8. For details of parameters and level of CI used in the calculations, see text.

of the α,*ω*-diphenylpolyenes show deviation of 56 and 64 nm with correlation coefficients of 0.96 and 0.97, respectively. The RMS deviations and correlation coefficients of Model 3 for the acenes are 117.22 nm and 0.66, respectively, and those for the α,*ω*-diphenylpolyenes are 124.64 nm and 0.76, respectively. This clearly brings out the importance of electron correlation in these systems as also demonstrated in the case of singlet absorption energies by other computations.[28,38]

Since inclusion of additional configurations does not result in any substantial improvement in computed triplet−triplet absorption, we employed Model 7 to compute absorption of 50 additional molecules, not included in the first set (see Table 3). The geometries of the molecules were optimized at the ROHF/AM1 level as in the previous case. In Figure 5, the computed triplet absorption of all 100 molecules is plotted versus the experimental data. The model performs equally well for the entire set of molecules, the triplet−triplet absorption λ_{max} of which also span a wide range of energies, with a correlation coefficient of 0.83 and a RMS deviation of 60 nm. For the entire set of 100 molecules, the correlation coefficient is 0.83 and the RMS deviation is 58 nm.

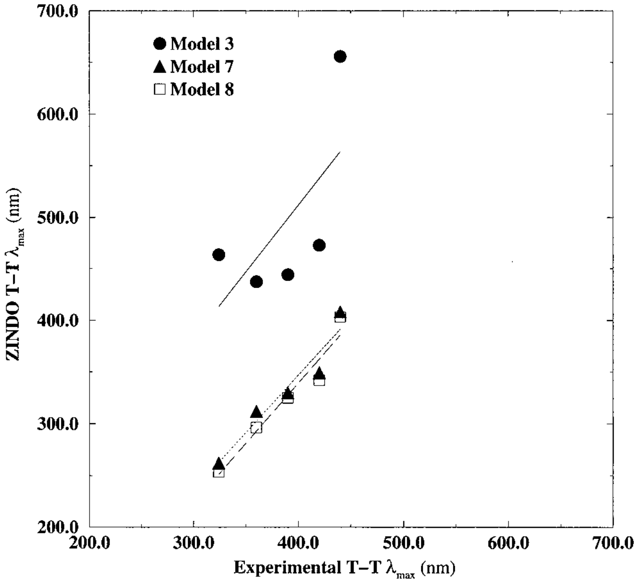

Figure 4. Computed triplet−triplet absorption energies for a series of α,*ω*-diphenylpolyenes (molecules 25, 26, 27, and 39) plotted versus the experimental absorption energies. Filled circles employ parametrization Model 3, filled triangles employ Model 7, and open squares Model 8.

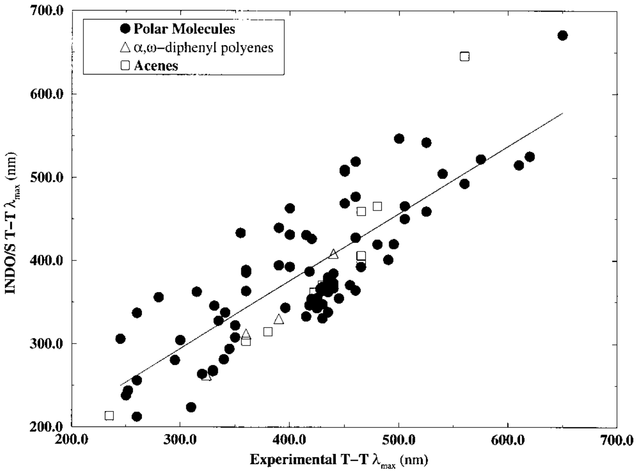

Figure 5. INDO/S-derived vertical triplet−triplet absorption wavelengths of the entire set of 100 test molecules using parametrization Model 7 plotted versus the corresponding experimental values. The 100 molecules are 50 from Table 2 and 50 additional molecules listed in Table 3.

It must be noted that the triplet absorption is expected to be quite sensitive to molecular geometry and solvents. While AM1 geometry optimization might be well suited for ground state geometries, it may perform rather poorly for the triplet state. To the best of our knowledge, there is no information on the performance of the ROHF/AM1 model in predicting the triplet state geometries of organic molecules. The substantial variation of the geometries of benzil and *N*,*N*-dimethylaniline from ROHF/AM1 and ROHF/6-31G** approaches supports the above conjucture. For example, in the case of *N*,*N*-dimethylaniline, while ROHF/AM1 calculation gives a non-planar geometry with the N assuming a pyramidal configuration, the ROHF/6-31G**

TABLE 3: Triplet−Triplet Absorption Data for Additional Organic Molecules Computed Using Model 7 (see Text for Details)

molecule	expt	Model 7
1,10-phenanthroline	440	462.8
phenoxazine	465	462.3
9-phenylanthracene	428	365.8
2-phenylnaphthalene	430	347.6
phthalazine	396	343.3
picene	560	492.6
psoralen	450	468.8
pyrazine	260	256.5
pyrene	415	430.9
rubrene	495	419.8
p-terphenyl	460	364.2
thiobenzophenone	400	431
benz[a]anthracene	490	400.9
4,4′-bis(dimethylamino)thiobenzophenone	335	327.8
2′-acetonaphthone	430	363.6
coumarin	400	392.4
9-cyanoanthracene	435	372.5
1,3-cyclehexadiene	310	224.1
di-*t*-butylthioketone	280	355.7
9,10-dicyanoanthracene	440	372.9
1,4-dicyanonaphthalene	455	370.3
4,4′-dimethoxybenzophenone	295	280.7
9,10-dimethylanthracene	435	362
diphenylamine	540	504.5
9,10-diphenylanthracene	445	354.6
β-ionone	330	267.4
lumiflavin	650	671
4′-methoxyacetophenone	360	363.2
1-methoxynaphthalene	440	366.8
9(10H)-acridone	620	525.4
2-methoxynaphthalene	435	337.8
4′-methylacetophenone	331	345.7
9-methylanthracene	430	368.3
methylene blue	420	470.1
1-methylnaphthalene	425	346.2
2-methylnaphthalene	420	346.6
1-naphthol	430	363.2
2-naphthol	435	380
1-nitronaphthalene	525	542.1
2-nitronaphthalene	360	385.4
pentacene	505	465.7
thioxanthione	505	450.1
thymine	340	281.7
tryptophan	460	519.3
xanthione	345	294.1
xanthone	610	514.9
9-bromoanthracene	430	330.8
phthalazine	396	343.3

calculation gives a planar geometry. The performance of Model 7 with ROHF/6-31G** geometries on benzil and *N*,*N*-dimethylaniline suggests that it is possible to obtain better correlation of triplet absorption λ_{max} by using ab initio geometries. While solvent effects on absorption characteristics of organic π-conjugated systems have been extensively studied both experimentally and theoretically in the singlet ground state, they have been much less characterized in the triplet state. Experimentally, the observation of large solvatochromic shifts in donor−acceptor π-conjugated systems has been reported.[52] It is well known that many aldehydes and ketones have nearly isoenergetic $^3(\pi,\pi^*)$ and $^3(n,\pi^*)$ states. A consequence of the energetic proximity of the two triplet states is that even small perturbations such as substituents or solvents, may produce level inversions or changes in the vibronic coupling between the two states, or large shifts in absorption maxima. The study of the effects of geometry or solvent, however, has not been carried out at this time for the entire set of molecules chosen for this study. The much better description of acenes and polyenes than of donor/acceptor systems here indeed suggests that solvent effects may be the cause of the latter descrepancies.

IV. Comments

The results of this investigation demonstrate, via analysis of a broad variety of organic π-conjugated architectures, that reliable estimates of triplet−triplet absorption λ_{max} can be obtained from the semi-empirical INDO/S model Hamiltonian. The results from eight different models that vary in parameter selection and level of CI used in the computation clearly demonstrate that parametrization distinctly different from that conventionally used in estimating singlet-state properties must be employed. Realistic estimates of triplet−triplet absorption λ_{max} must include computations with sufficient electron correlation, at least at the level of singles and doubles. The model employing Zerner's suggested triplet parametrization and including both singly and doubly excited configurations, generated from a HF singlet ground reference determinant and singly excited configurations generated from the HF triplet ground reference determinant, reproduces experimental absorption maxima of 100 electronically and structurally diverse organic molecules with favorable accuracy. The model performs exceptionally well in the case of acenes (correlation coefficient = 0.93 and RMS deviation = 56 nm) and α,ω-diphenylpolyenes (correlation coefficient = 0.97 and RMS deviation = 56 nm), and we suspect that a good deal of the error results from inappropriate geometries. Indeed, the functionalized chromophores might be expected to show greater geometry variations between the S_0 and T_1 than would the acenes or polyenes. Accordingly (and strikingly), in the entire set of 100 test molecules there were only two molecules the absorption λ_{max} of which varied by more than 100 nm. To understand the origin of these deviations in *N*,*N*-dimethylaniline and benzil, the geometries of the two molecules were reoptimized at 6-31G** level (rather than at the initial ROHF/AM1 level). The computed absorption λ_{max} evidence remarkable improvement when the ab initio geometry is used (correlation coefficient = 0.82 and RMS deviation = 38 nm). Nevertheless, the triplet−triplet absorption spectra are far less accurate than the ground (singlet)-state case. Accurate triplet absorption spectra remain a challenge.

The use of the INDO/S parametrization, with more extensive treatment of electron correlation, clearly produces much better agreement with observed triplet−triplet absorption maxima. An even more accurate model chemistry might possibly be defined by parameter modification, comparing (say) multi-reference doubles CI (our Model 7) with data for a selected set of molecules. Our results show that, even in the absence of such reparametrization, the INDO/S model hamiltonian performs quite well for triplet−triplet absorption maxima, if sufficient electron correlation is included.

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