large $\Delta E^{\pm}$. The large reduction in the reactivity of CH_2Br_2 relative to that of CF_2Br_2, however, cannot be convicingly attributed to polarizability effects. Since the polarizability of CH_2Br_2 (9.3 Å³) is roughly the same[19] as that of CF_2Br_2 (9.0 Å³), the species R = CH_2Br and CF_2Br might also be expected to have similar polarizabilities. Therefore, some additional factor appears to be responsible for the very low reactivity of CH_2Br_2 relative to that of CF_2Br_2.

The greater reactivity of CF_2Br_2 relative to that of CH_2Br_2 may reflect the importance of preferred orientations of these molecules in their ion complexes $(A^-·RX)^*$ and their CADET transition states. CF_2Br_2 has a dipole moment of 0.66 D,[20] with the positive end located near the two bromine atoms. As the ion complex $(A^-·CF_2Br_2)^*$ becomes tighter and moves toward its transition state, the ion–dipole force will tend to preferentially align the CF_2Br_2 molecule so that the bromine atoms point to the direction of A^-. A preference for this orientation with facilitate the forward conversion of $(A^-·CF_2Br_2)^*$ to $(A·Br^-·CF_2Br)^*$. The dipole moment of CH_2Br_2 is larger (1.43 D) and has a polarity that is reversed relative to that of CF_2Br_2, so that its positive end is near its two hydrogen atoms. Therefore, the ion–dipole force in $(A^-·CH_2Br_2)^*$ will tend to align the CH_2Br_2 molecule so that the bromine atoms point away from A^-. An increased preference for this orientation as $(A^-·CH_2Br_2)^*$ moves toward its transition state will tend to inhibit its conversion to $(A·Br^-·CH_2Br)^*$. This factor would tend to lower the reactivity of CH_2Br_2 relative to that of CF_2Br_2, and would also lower the reactivities of $CHCl_3$ and CH_3I, since the dipole moments of these molecules (1.01 and 1.63 D, respectively) would also tend to align these molecules unfavorably within their CADET transition states.

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Symmetry-Breaking Solvent Effects on the Electronic Structure and Spectra of a Series of Triphenylmethane Dyes

Horst B. Lueck, Jeanne L. McHale,* and W. D. Edwards

Contribution from the Department of Chemistry, University of Idaho, Moscow, Idaho 83843. Received August 26, 1991

Abstract: Solvent effects on the electronic structure of a series of para-substituted triphenylmethane dyes have been investigated using polarized Raman scattering and fluorescence spectroscopy, with interpretation aided by the results of intermediate neglect of differential overlap (INDO) molecular orbital calculations. While the evidence points to D_3 symmetry for the triphenylmethane cation in solution, resonance Raman and fluorescence data indicate that the symmetry of the substituted dyes is lowered by an interaction with the solvent. Semiempirical molecular orbital calculations support the idea that interaction of a charge or dipole with one of the amino groups could be responsible for breaking the symmetry of the crystal violet and parafuchsin ion, thus lifting the degeneracy of the excited electronic state which gives rise to absorption of visible light. The splitting of the excited electronic state shows up in the polarization dependence of both the resonance Raman spectra and the fluorescence emission. INDO calculations as well as fluorescence measurements argue against the existence of two ground-state conformations, such as a symmetric and an unsymmetric propeller form, as has been previously suggested.

Introduction

Para-substituted triphenylmethanes form a class of dyes for which there are a number of interesting structural questions concerning their solution-phase properties. In this work we examine the series shown in Figure 1: triphenylmethane (TPM), parafuchsin (PF), crystal violet (CV), ethylviolet (EV), malachite green (MG), and Victoria Pure Blue (VPB). One reason for interest in these compounds is the possible existence of twisted intramolecular charge-transfer (TICT) excited states,[1,2] for example, in CV. These have been investigated by a variety of time-resolved spectroscopic methods, such as two-photon fluorescence emission[3] and picosecond absorption spectroscopy.[4,5]

Quantum mechanical calculations have been applied to the study of the torsional potential of TPM derivatives[1,6] and other molecules having TICT excited states.[7] Aggregation in solution, of certain of the dye derivatives (those with three amino groups), has been investigated spectroscopically.[8]

On the basis of X-ray crystallographic study of triphenylmethyl perchlorate,[9] and an older diffraction study of CV,[10] the expected geometry of the triply substituted dyes is a D_3 symmetric propeller form. Various investigations, however, have pointed to evidence that the symmetry of the solution-phase triply substituted dyes may be lower than D_3. For example, a magnetic circular dichroism (MCD) spectroscopic study suggested that TPM maintains its D_3 symmetry in solution, but that CV, although probably still in

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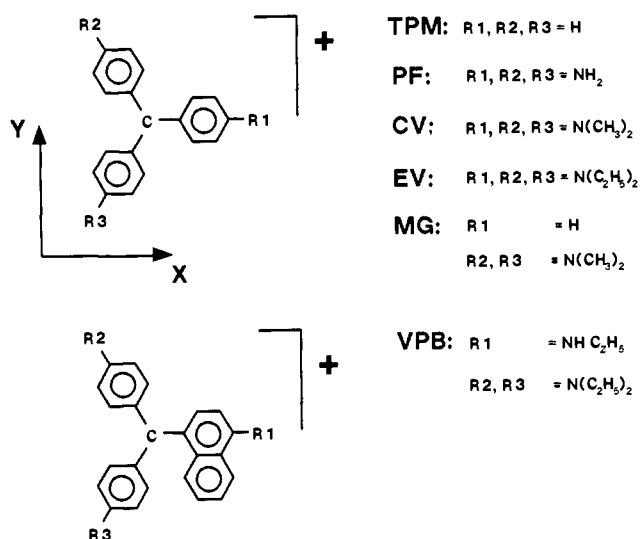(8) (a) Stork, W. H. J.; Lippitis, G. J. M.; Mandel, M. *J. Phys. Chem.* **1972**, *76*, 1772. (b) Sheppard, S. E.; Geddes, A. L. *J. Am. Chem. Soc.* **1944**, *66*, 1995. (c) Michaelis, L.; Granick, S. *J. Am. Chem. Soc.* **1945**, *67*, 1212.
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Table I. Calculated Spectral Transition Energies and Oscillator Strengths of D_3 Symmetry TPM, PF, CV, and MG Cations, Compared to Experimental Spectra

compound	TPM	PF	CV	MG
ring torsion, deg	30, 30, 30	30, 30, 30	30, 30, 30	30, 30, 30
amino group				
rotation		0, 0, 0	0, 0, 0	0, 0, 0
pyramidal, planar		pyramidal	pyramidal	pyramidal
energy (cm⁻¹), oscil strength	26 904, 0.327 xy	23 910, 0.7345 xy	23 766, 0.763 xy	22 912, 0.7943 y
	26 904, 0.327 xy	23 910, 0.7345 xy	23 766, 0.763 xy	26 672, 0.5771 x
	29 205, 0.2622 xy	30 264, 0.0012 xy	29 740, 0.0013 xy	29 247, 0.0302 x
	29 205, 0.2622 xy	30 264, 0.0012 xy	29 740, 0.0013 xy	29 364, 0.0054 x
	30 138, 0.031 z	32 329, 0.0106 z	31 788, 0.0103 z	31 429, 0.0209 z
experiment				
solvent	ACN/H⁺	H₂O	H₂O	H₂O
energy (cm⁻¹), absorptivity (1000 cm⁻¹ M⁻¹)	23 200, 28	18 600, 84	16 900, 102	16 200, 80
	24 800, 29	20 500, 42	18 150, 70	23 500, 17
		32 000, 7	33 000, 24	31 600, 16
		35 300, 24		

Figure 1. Structures of triphenylmethane dyes of interest in this study.

a propeller geometry, has lower symmetry in solution.[6] In an early paper, G. N. Lewis and co-workers[11] suggested that the CV ion exists in solution as two rotational isomers in equilibrium: a symmetric (D_3) propeller and an unsymmetric (C_2) propeller in which one of the three phenyl rings is rotated counter to the other two. More recently, Korppi-Tommola and Yip[12] proposed that the D_3 symmetry of CV ion, and thus the degeneracy of the electronic transition in the visible, is lifted by interaction with the solvent, in polar solvents, or with the counterion, in nonpolar solvents. This would explain why the visible spectrum of CV in polar solvents consists of two overlapped bands, whereas in nonpolar solvents the two visible transitions are well resolved. Resonance Raman data,[13] however, were presented as evidence in favor of D_3 symmetry for the crystal violet ion in methanol. The observed biexponential decay of the fluorescence of CV has been presented as evidence of two nearby electronic transitions.[14] As will be shown below, the D_3 ion would be expected to have a single doubly degenerate transition in the visible region of the spectrum. In spite of the array of physical methods that has been brought to bear on the problem, the question of the existence of conformational isomers or solvent effects in the ground electronic state of triply substituted triphenylmethane dyes remains unsettled.

Do crystal violet, ethyl violet, and parafuchsin exist as two rotational isomers, or does an interaction with the solvent break the symmetry and cause splitting of the otherwise degenerate excited electronic state? In this paper, we address this question using the results of polarized resonance Raman and fluorescence emission data, which support the idea that there is a solvent-induced symmetry breaking of the triply substituted dyes, and consequently lifting of the degeneracy of the excited electronic states expected for the D_3 ion. Spectroscopic intermediate neglect of differential overlap (INDO/S) calculations are presented which model a symmetry-breaking solvent perturbation, due to interaction of a charge or dipole with one of the amino groups. INDO calculations of the ground-state energy as a function of torsional angle also indicate that the energy difference as well as the barrier separating different torsional isomers is large compared to kT, making it unlikely that the symmetry breaking is due to a rotation of one of the phenyl groups away from the D_3 geometry. In a separate paper, we discuss the association equilibria of CV, EV, and VPB in aqueous solution.[15]

Experimental Methods

All dyes were purchased as chloride salts, except MG which was obtained as the oxalate. Solvents were HPLC grade and were used without further purification. Nonpolar impurities were extracted from aqueous solutions of the dyes, which were then recrystallized from ethanol/hexane mixtures. To obtain dyes soluble in nonpolar solvents, chloride salts were converted to acetates via the carbinols, which were obtained from aqueous solution by addition of 1 M NaOH followed by cyclohexane extraction and recrystallization from hexane/cyclohexane. The resulting colorless carbinol was then converted to the dye acetate by addition of acetic acid. Due to the tendency of the dyes to adsorb on the glass surface, all glassware was preexposed to dye solutions of the same concentration. TPM solutions had to be acidified in order to measure stable spectra. Still, the absorption of TPM did decrease slowly with time.

Absorption spectra were recorded on a Perkin-Elmer Lambda 4B spectrophotometer, using quartz cells of 0.1–10.0-mm path length, and samples having maximum optical density between 0.5 and 2.5, a range where the response of the spectrometer was determined to be linear. Raman spectra were recorded with previously described instrumentation,[16] using 500-μm slits and a rotating quartz cell in either 90° or back-scattering geometry. The weak fluorescence spectra were collected with the same instrumentation as the Raman spectra. Excitation of Raman and fluorescence spectra was provided by an argon laser or by a dye laser using coumarin 6 or rhodamine 6G as the dye.

The INDO programs used for the calculation of the torsional potential energy employed geometry parameters,[17] and for the transition strengths and energies of the excited states, spectroscopic parameters.[18] The initial input geometry of crystal violet was determined from an MM2 molecular mechanics calculation, which resulted in a D_3 propeller structure with a 30° torsional angle of the phenyl groups. Bond lengths and angles for

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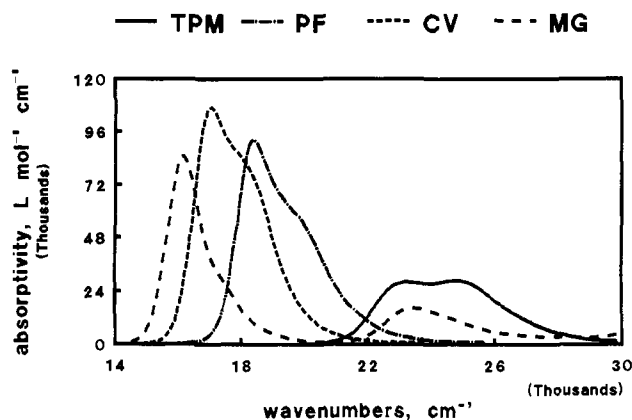
— TPM —·— PF ······ CV — — MG

Figure 2. Visible absorption spectra of MG, CV, PF, all in methanol, and TPM in acidified acetonitrile.
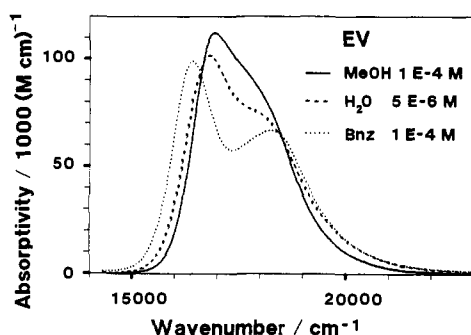

Figure 3. Absorption spectra of EV in methanol, water, and benzene.

the other substituted dyes were taken from a handbook,[19] and were not significantly different from those resulting from the MM2 calculation.

Visible Absorption Spectra

Absorption spectra of PF, CV, and MG in alcohol and TPM in acetonitrile are shown in Figure 2. The molar absorptivities in these solutions are independent of concentration, and thus the dyes are believed to exist as monomers. The molar absorptivity of TPM is inaccurate due to its instability. The spectrum of TPM shows two nearly equal intensity bands which are assigned to transitions from the ground state to the S_1 and S_2 states, each of which is doubly degenerate.[6] The spectra of the substituted dyes, however, show a more intense band in the red and a less intense shoulder in the blue. We will refer to these two transitions as the R and B bands, respectively. (A somewhat weaker transition in the UV spectra of CV, MG, and PF is not shown in the figures, but is listed in Table I.) In the spectrum of MG, the B band should would appear to be missing, and we argue below that the asymmetry of the spectrum is inherent in the Franck–Condon profile; i.e., there is only one visible transition of MG in this region of the spectrum. Another visible transition of MG, shown in Figure 2, is found in the violet.

The wide range of solvent behavior possible for these dyes is illustrated by the spectra of EV in Figure 3 and VPB shown in Figure 4. In dilute aqueous solution, the overlapped R and B bands are observed, the latter being less intense. In concentrated aqueous solutions of CV, EV, and VPB, to be discussed in another paper,[15] dimerization leads to an increase in intensity of the B band at the expense of that of the R band. In nonpolar solvents, the R and B bands are clearly resolved and nearly equal in intensity. Whereas the R and B bands of CV, EV, and VPB are well resolved in nonpolar solvent compared to polar solvent, the effect of polarity on the spectrum of MG is much less dramatic. On going from methanol to benzene, the main visible transition of MG is merely red shifted by 240 cm^{-1}, with no apparent change in line shape, and the weaker violet band is not perturbed at all.

(19) *CRC Handbook of Chemistry and Physics*, 52nd ed.; Weast, R. C., Ed.; The Chemical Rubber Co.: Cleveland, 1971.
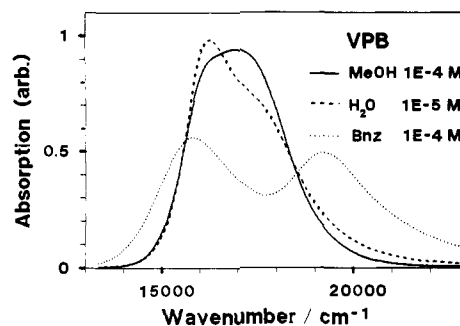

Figure 4. As in Figure 3, but for VPB.

As will be discussed below, these differences stem from the fact that the R and B bands of the symmetrically substituted dyes PF, CV and EV result from solvent-induced symmetry breaking of an otherwise degenerate excited electronic state. MG, on the other hand, has no degenerate states to be separated, so the visible absorption spectra consists of two transitions which are already well resolved in the absence of solvent perturbations. The lower inherent symmetry breaking in VPB versus MG points out the importance of the presence of three versus two amino group substituents, as will become clear in the following discussions.

In ref 11 it was suggested that the more intense band in the triply substituted dye monomers was due to a symmetric propeller geometry (D_3 symmetry), and that the weaker B band was due to a distorted (C_2 symmetry) propeller having one phenyl group rotated in an opposite direction to the other two. Also in that work, it was suggested that only the symmetric structure results for MG, giving one absorption band which is analogous to the R band in the triply substituted dyes. In ref 12, however, it was proposed that interactions with the solvent or counterion, the latter being a stronger perturbation and giving rise to widely separated R and B bands in nonpolar solvent, are responsible for lifting the degeneracy of the excited state. We explored these hypotheses using INDO calculations discussed in the next section.

Semiempirical Molecular Orbital Calculations

INDO spectroscopic calculations (Table I) were performed on TPM, PF, CV, and MG. Initial calculations of the electronic transition strengths and energies of TPM, PF, and CV were performed at a D_3 symmetric geometry determined from an empirical force field (MM2) calculation. The symmetry of MG was of course C_2 rather than D_3, but the three phenyl rings were nevertheless synchronously rotated as in the other dyes. In the initial calculations, the torsional angles of all the phenyl groups were kept fixed at angles of 30° with respect to the plane containing the central carbon atom and the three σ bonds attached to it. The geometry about each nitrogen was constrained to be pyramidal, with the lone pair oriented most favorably for conjugation with the benzene rings. This is indicated in Table I as a rotational angle of zero. The results for these calculations are summarized in Table I, where the transition energies and oscillator strengths of the first five excited states are listed. The results for TPM are in good qualitative agreement with experiment, considering that solvent effects are not accounted for in the calculation, and concur with previous reports that assign the two observed bands, of comparable intensity and separated by about 1600 cm^{-1}, to two doubly degenerate transitions. The two observed transitions are red shifted from the calculated ones by about 4000 cm^{-1}, and while both the calculated and observed intensities of the two bands are nearly equal, the observed intensity ratio is opposite to that predicted. This level of agreement between theory and experiment is to be expected for the computational approach we have used.

The results for symmetric CV and PF, however, do not agree well with experiment. Here, a strong lower energy visible transition $S_0 \rightarrow S_1$ is predicted ($f \approx 0.7$–0.8), followed by a much weaker UV transition $S_0 \rightarrow S_2$ ($f \approx 0.001$) about 6000 cm^{-1} higher in energy. As in TPM, each of these transitions is to a doubly degenerate excited state and is polarized in the xy plane. In TPM, CV, and PF, the S_1 excited state is dominated by a configuration

Table II. Calculated Spectral Transition Energies and Oscillator Strengths of PF for Various Torsion Angles of the Phenyl Rings and Amino Groups

compound	PF	PF	PF	PF	PF
ring torsion, deg	30, 30, 30	30, 30, −30	20, 30, 40	30, 30, 30	30, 30, 30
amino group rotation	0, 0, 0	0, 0, 0	0, 0, 0	90, 90, 90	0, 0, 0
pyramidal, planar	pyramidal	pyramidal	pyramidal	pyramidal	planar (*x*), pyramidal, pyramidal
energy (cm^{-1}), oscil strength	23 910, 0.7345 *xy*	21 334, 0.5729 *xy*	23 583, 0.6495 *xy*	26 472, 0.6221 *xy*	23 147, 0.7635 *x*
	23 910, 0.7345 *xy*	23 241, 0.6791 *xy*	23 911, 0.7653 *xy*	26 472, 0.6221 *xy*	24 099, 0.7241 *y*
	30 264, 0.0012 *xy*	29 500, 0.0318 *xy*	30 187, 0.0016 *xy*	29 263, 0.0317 *xy*	30 403, 0.0004 *x*
	30 264, 0.0012 *xy*	29 529, 0.0279 *xy*	30 237, 0.004 *xz*	29 263, 0.0317 *xy*	30 459, 0.0026 *y*
	32 329, 0.0106 *z*	31 506, 0.0105 *xz*	32 192, 0.0133 *zx*	31 247, 0.0241 *z*	32 471, 0.0084 *z(y)*

in which an electron from the doubly degenerate HOMO has been promoted to the singly degenerate LUMO. The S_2 excited state is well described by a configuration in which an electron has been promoted from the doubly degenerate HOMO-1 to the LUMO. The LUMO contains a large contribution from the central carbon atoms p_z orbital, having a coefficient of about 0.7.

The calculated spectra of D_3 PF and CV can be derived from that of TPM by considering the effect of the amino group: in the substituted dyes, the nitrogen p_z orbital contributes to the HOMO but not to the HOMO-1. The result is that the $S_0 \rightarrow S_1$ band is red shifted and the $S_0 \rightarrow S_2$, while only slightly perturbed in energy, is greatly decreased in intensity. By rotating the amino group, it was learned that the energy shift of the S_1 state relative to that of TPM depends on conjugation of the nitrogen lone pair with the π system of the phenyl ring; however, the small S_2 intensity is unaffected by this rotation. The predicted spectra of the symmetric substituted dyes are in disagreement with the observed spectra of CV and PF, where two comparable intensity bands are observed in the visible. These two bands do not appear to result from a Franck–Condon progression, as evidenced by the temperature dependence of the spectral shape in some solvents,[12] so it is assumed that these are two overlapped electronic transitions. The band that is observed in the UV, for example, at about 33 000 cm^{-1} for CV, is much too intense ($\epsilon \cong 24\,000$ M^{-1} cm^{-1}) to be assigned to the transition calculated to have $f = 0.0013$ at about 29 740 cm^{-1} for the D_3 ion. The calculated spectrum of MG, however, is in good qualitative agreement with experiment: a strong band in the visible ($f \approx 0.8$ at 22 900 cm^{-1}) is predicted along with a slightly less intense transition almost 4000 cm^{-1} to the blue, having $f \approx 0.6$. The observed spectrum of MG has two visible absorption bands: one at 16 200 cm^{-1} having $\epsilon \cong 80\,000$ M^{-1} cm^{-1} and one at 23 500 cm^{-1} having $\epsilon \cong 17\,000$ M^{-1} cm^{-1}. Allowing for solvent effects on the transition strengths and energies as in TPM, the better agreement between theory and experiment for the lower symmetry dye is striking, and suggests that a symmetry-breaking perturbation may be responsible for the discrepancy in the case of PF and CV.

We first explored the model proposed by Lewis et al.[11] to see if rotational isomers could explain the observed spectra. In Table II, the results of spectroscopic INDO calculations on PF are reported for a number of different geometries other than the D_3 propeller. Rotations of an individual phenyl group in a direction opposite to the other two was found to lead to significant splitting (about 2000 cm^{-1}) of the first transition into an R band and a slightly stronger B band. An order of magnitude weaker UV transition, only slightly split, is calculated for the asymmetric propeller. A distorted propeller geometry having the same sense of rotation for all three rings (20°, 30°, and 40°) did not result in much splitting of the visible or UV transition.

The possible existence of rotational isomers was further explored by calculating the ground-state energy as a function of torsional motion of the phenyl groups. The calculated torsional potential of PF is shown in Figure 5, where the positive angles indicate data for the symmetric propeller and the negative angles represent the energy of the distorted propeller (e.g., −30 represents angles of 30°, 30°, and −30° with respect to a geometry having all phenyl groups coplanar). The minimum in the symmetric torsional well is about 5000 cm^{-1} higher than that of the unsymmetric torsional well. The energy difference is large compared to kT at room temperature, so we expect little equilibrium population of the
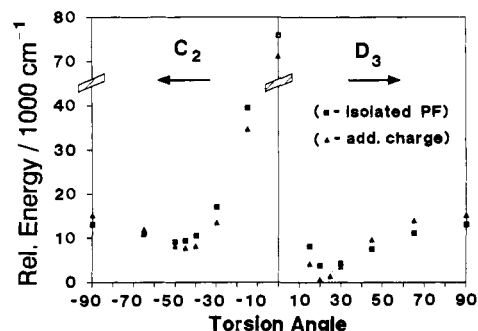
Figure 5. Ground-state energy as a function of torsional angle of the phenyl rings of PF, for the isolated cation and in the presence of a counterion.

unsymmetric propeller form. Furthermore, the lower barrier to interconversion of the symmetric and unsymmetric forms, going through the 90° intermediate, is 10 000 cm^{-1} (in good agreement with the PPP calculation presented in ref 1). Even considering the approximate nature of this calculation and the uncertain consequence of solvent effects, the large barrier and the large energy difference separating the two rotational isomers argue against the existence of a distorted propeller form in the ground electronic state. Thus, the symmetry breaking manifest in the visible absorption spectra of CV, EV, and PF is unlikely to be due to a torsional distortion of the D_3 propeller molecule. Further evidence against the idea of torsional isomers is provided by the results of temperature studies reported in ref 12a: The relative intensities of the R and B bands of CV in acetone and toluene were found to be independent of temperature. (In alcoholic solution, the temperature dependence of solvent association was believed to be responsible for the spectral changes in the R and B band positions.[12b])

Another way of lifting the degeneracy was explored by forcing one amino group to be planar and retaining the tetrahedral configuration of the other two. These results are shown in the last column of Table II. In terms of a simple resonance structural model, this geometry would correspond to localizing the positive charge on the planar amino group, compared to being located at the central carbon in the symmetric D_3 geometry. A resonance structure which puts the positive charge on one amino group could be stabilized by an interaction with the solvent or counterion. This geometry gives reasonable agreement with the experimental visible band, but fails to account for the fairly strong UV band and its shoulder. However, we expect the agreement between theory and experiment to be poorer at higher excitation energies.

We next explored the effect of an external symmetry-breaking perturbation due to an interaction with a solvent molecule or counterion. This type of interaction was investigated by calculating the spectrum of the PF cation in the presence of a negative charge or dipole oriented near one of the three amino groups. Except for the presence of the external charge or dipole, the D_3 symmetry of the ion was preserved in this calculation. This picture is envisioned to be a reasonable model for the interaction with the solvent in polar solution, and for ion pair formation in nonpolar solution, and might be related as well to the tendency of the triply substituted dyes to aggregate in aqueous solution.[15] In Table III are shown the results of spectroscopic calculations of PF in the

Table III. Effect of an External Charge or Dipole on the Calculated Spectrum of PF

compound	PF	PF	PF	PF	PF
ring torsion, deg	30, 30, 30	30, 30, 30	30, 30, 30	30, 30, 30	30, 30, 30
amino group					
rotation	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0
pyramidal, planar	pyramidal	pyramidal	pyramidal	pyramidal	pyramidal
additional charge, distance	-0.2 e, 1.5 Å	-0.3 e, 1.5 Å	-0.3 e, 3.0 Å	dipol, 0.2 e, 1.5-Å sep	-0.2 e, 1.5 Å
charge location	amino group (x axis)	amino group (x axis)	amino group (x axis)	C–N bond (x axis)	center carbon
energy (cm^{-1}), oscil strength	22692, 0.7777 x	22177, 0.8082 x	23080, 0.766 x	23683, 0.7315 x	25524, 0.7114 xy
	25074, 0.6907 y	25117, 0.6396 y	24888, 0.7021 y	24406, 0.7211 y	25524, 0.7114 xy
	28973, 0.0119 yz	28228, 0.0423 yz	29220, 0.0076 yz	29541, 0.0036 yz	31607, 0.0046 xy
	31160, 0.0004 x	31589, 0.0005 x	30942, 0.0007 xz	30663, 0.0009 x	31607, 0.0046 xy
	32729, 0.008 yz	33009, 0.0077 yz	32608, 0.0089 z	32402, 0.0103 yz	33367, 0.0055 z

presence of a charge or dipole of variable strength and distance from the nitrogen. The effect of a charge or dipole near the amino group of one ring, which is arbitrarily assigned to the x direction, is that the $S_0 \rightarrow S_1$ transition splits into a lower energy x-polarized R band, and a y-polarized B band. The resulting splitting and intensity change of the visible transition is clearly in good qualitative agreement with experimental observation.

For example, in aqueous solution the more intense R band of PF appears at 18600 cm^{-1}, and the B band appears as a shoulder at 20500 cm^{-1}. As shown in Table III, placing either a negative charge of 0.30 e at a distance of 3 Å or a dipole of 1.4 D at a distance of 1.5 Å above the para position of one of the phenyl rings leads to qualitative agreement with the observed spectra. In agreement with physical intuition and the interpretation of ref 12a, the charge perturbation leads to a much larger splitting than is caused by a nearby dipole. Obviously, the larger or closer the charge or dipole, the greater the effect on the calculated spectrum, so one can only draw qualitative conclusions from this analysis. Nevertheless, the calculations illustrate how the degeneracy of the electronic transition can be broken without actually perturbing the D_3 symmetry of the ion itself. Similarly, the S_2 state is also predicted to be split by the perturbation. The small shoulder in the UV band of PF (Table I) agrees well with the calculation. Placing a negative charge at the central carbon preserves the degeneracy, but leads to an increase in the energy of the S_1 and S_2 states. Interestingly, the X-ray study of ref 9 concluded that the chloride ion was situated near one of the dimethylamino groups rather than at the central carbon. Comparison of experimental spectra with the INDO calculations shown in Table III indicates that a similar structure might result for the solution-phase dyes as well.

It seemed reasonable to ask whether solvent or counterion perturbation and rotational isomerization might occur simultaneously, perhaps in a cooperative fashion. We therefore repeated the calculation of the symmetric and asymmetric torsional potential in the presence of a symmetry-breaking external negative charge. As shown in Figure 5, the addition of an external negative charge does not change the qualitative features of the torsional potential. In other words, the calculation does not support the idea that the solvent or counterion might enhance the formation of the C_2 propeller form.

Fluorescence Spectra

The fluorescence anisotropy is determined by the fluorescence lifetime, the rotational diffusion time, and the angle between the transition moments for absorption and emission.[20] When the symmetry of the D_3 ion is lowered to C_2, each formerly degenerate excited state splits into x- and y-polarized states. Following Kasha's rule,[21] excitation within the R or B band should lead to emitted light which is polarized parallel or perpendicular, respectively, to the incident light polarization.

Fluorescence anisotropy, r, was determined by measuring the polarized, $I_\parallel$, and depolarized, $I_\perp$, intensities of emitted radiation as a function of several excitation wavelengths:

$$r = (I_\parallel - I_\perp)/(I_\parallel + 2I_\perp) \qquad (1)$$

(20) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983.
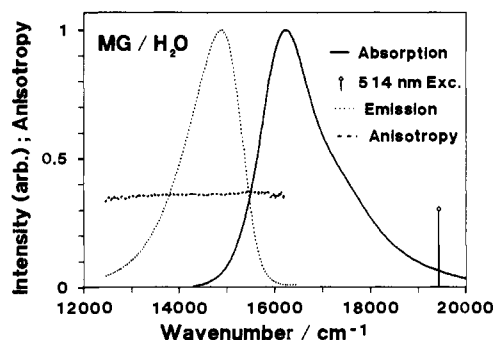(21) Kasha, M. *Chem. Rev.* **1947**, *41*, 401.

Figure 6. Absorption and emission spectra, and fluorescence anisotropy, of MG.

In a randomly oriented collection of fluorophores, the maximum possible anisotropy r_0 is determined by the angle α between the absorption and emission transition dipoles:

$$r_0 = \tfrac{2}{5}[\tfrac{3}{2} \cos^2 \alpha - \tfrac{1}{2}] \qquad (2)$$

For parallel absorption and emission transitions dipoles, r_0 is expected to be 0.40, and for perpendicular transition moments r_0 should be -0.20. The observed anisotropy is reduced by the rotational motion of the chromophore during the lifetime of the excited state, by an amount that depends on the ratio of the fluorescence lifetime τ to the rotational diffusion time ϕ:

$$r = r_0/(1 + \tau/\phi) \qquad (3)$$

The lifetime τ of the weak fluorescence of CV and MG in low viscosity solvents has been determined to be on the order of 5 ps.[3] A reasonable estimate of the rotational relaxation time in water is 200 ps, from $\phi = \eta V/kT$, so that one can expect nearly the maximum anisotropy to be observed for these dyes, in the absence of other depolarization mechanisms. In the case of these dyes, which are capable of forming TICT states, torsional motion on the excited-state surface can also depolarize the fluorescence.

As shown in Figure 6, the emission spectrum of MG excited at 514.5 nm is very nearly the mirror image of the absorption spectrum. The anisotropy r was found to be 0.35, at wavelengths across the emission band shown in the figure. This is slightly less than the value of 0.40 expected when the transition moments for absorption and emission are parallel, as we expect them to be on the basis of INDO calculations. This confirms the idea that there is one excited state in the region of the major visible absorption band of MG, and that the fluorescence lifetime is much shorter than the rotational relaxation time. When the fluorescence is excited at 458 nm, within the $S_0 \rightarrow S_2$ band of MG, the emission still resembles the mirror image of the $S_0 \rightarrow S_1$ absorption, but r is found to be -0.07. This indicates that when excited to the S_2 state, fluorescence takes place from the S_1 level, and the anisotropy is nearly that expected for perpendicular absorption and emission transition dipoles.

The fluorescence spectra of CV, EV, and PF, however, are mirror images of only the R absorption band (the spectra of PF are shown in Figure 7), indicating that the B band corresponds to a separate transition and not just an absorption of a second ground-state isomer. In the case of PF, it was possible to measure the fluorescence anisotropy as a function of excitation wavelength:
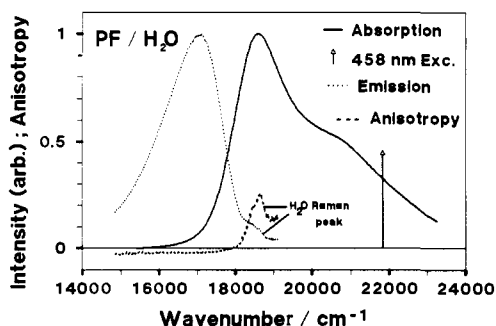
Solvent Effects on a Series of Triphenylmethane Dyes

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Figure 7. Absorption and emission spectra, and fluorescence anisotropy, of PF.
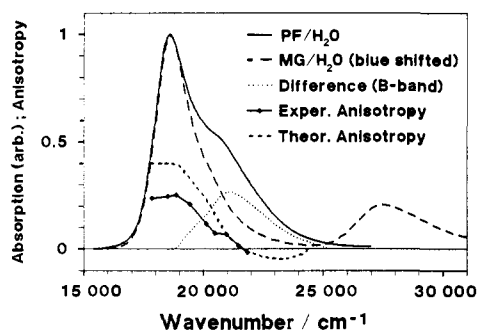

Figure 8. Decomposition of absorption spectrum of PF into R and B bands, theoretical and observed fluorescence anisotropy.

the results are shown in Figure 8. In this figure, a spectral subtraction was done to attempt to resolve the R and B bands by subtracting the shifted and scaled spectrum of MG from the spectrum of PF. In the case of overlapping electronic transitions, the maximum anisotropy is expected to be an absorption weighted average of the values expected for the excitation within the two separate states:[20]

$$r_o = 0.4S_R - 0.2S_B \qquad S_R + S_B = 1 \qquad (4)$$

Here, S_R (S_B) is the fraction of the absorbance due to the red (blue) band. In Figure 8, the above theoretical anisotropy is compared to the measured value, as a function of excitation wavelength. The observed anisotropies are less than expected, due possibly to polarization scrambling involving torsional motion on the excited-state potential. However, the shape of the calculated dispersion in r agrees well with that observed, lending support for the spectral decomposition we have employed. A spectral deconvolution of the observed band using symmetric gaussians, as in refs 12b and 22, would be inconsistent with the experimental anisotropy.

Raman Spectra

Polarized resonance Raman (RR) experiments provide information about the symmetries of the normal modes and the resonant excited state. As shown in ref 23, the invariants of the molecular polarizability tensor are the following:

$$\Sigma^0 = \tfrac{1}{3}|\alpha_{xx} + \alpha_{yy} + \alpha_{zz}|^2$$

$$\Sigma^1 = \tfrac{1}{2}\{|\alpha_{xy} - \alpha_{yx}|^2 + |\alpha_{xz} - \alpha_{zx}|^2 + |\alpha_{yz} - \alpha_{zy}|^2\} \qquad (5)$$

$$\Sigma^2 = \tfrac{1}{2}\{|\alpha_{xy} + \alpha_{yx}|^2 + |\alpha_{xz} + \alpha_{zx}|^2 + |\alpha_{yz} + \alpha_{zy}|^2\} +$$
$$\tfrac{1}{3}\{|\alpha_{xx} - \alpha_{yy}|^2 + |\alpha_{xx} - \alpha_{zz}|^2 + |\alpha_{yy} - \alpha_{zz}|^2\}$$

The depolarization ratio ρ is the ratio of the intensity of the scattered light polarized perpendicular to the incident radiation to that polarized parallel:

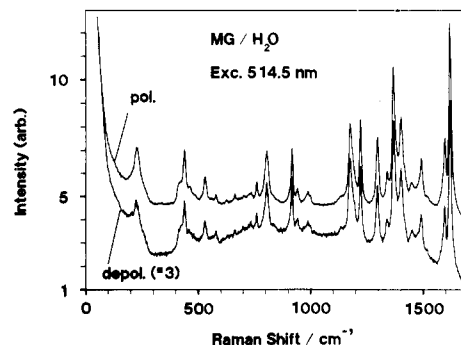$$\rho = I_\perp/I_\parallel = (5\Sigma^1 + 3\Sigma^2)/(10\Sigma^0 + 4\Sigma^2) \qquad (6)$$

(22) Menzel, R.; Kessler, W. *J. Mol. Liq.* **1988**, *39*, 279.
(23) Sonnich Mortensen, O.; Hassing, S. *Adv. Infrared Raman Spectrosc.* **1980**, *6*, 1.
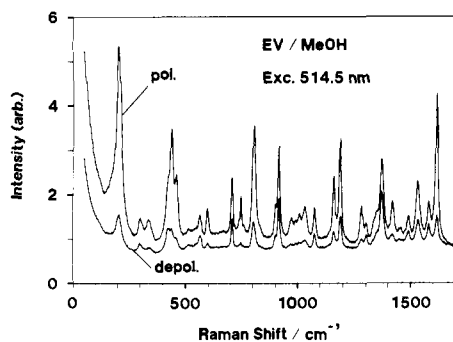

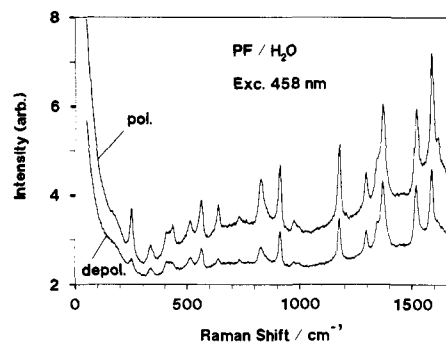**Figure 9.** Polarized and depolarized Raman spectra of MG.

Table IV. Depolarization Ratios of MG Raman Modes

ν (cm^{-1})	MG in water (514 nm)	ν (cm^{-1})	MG in water (514 nm)
226	0.27	1221	0.32
806	0.30	1402	0.29
918	0.32	1596, 1619	0.29

Table V. Depolarization Ratios of EV Raman Modes

ν (cm^{-1})	EV in methanol (514 nm)	EV in methanol (488 nm)	EV in benzene (488 nm)
207	0.16	0.20	0.36
805	0.24	0.33	0.37
918	0.54	0.66	0.50
1161	0.26	0.29	0.44
1191	0.31	0.37	0.45
1585	0.54	0.47	0.54
1620	0.20	0.23	0.33

In the case of a totally symmetric vibration enhanced via resonance with a single, nondegenerate excited state, the expected depolarization ratio $\rho = I_\perp/I_\parallel$ is $^1/_3$. Totally symmetric vibrations enhanced by doubly degenerate excited electronic states, on the other hand, lead to $\rho = ^1/_8$. When resonance with more than one electronic state is possible, as in the case of two nearby electronic states for which a normal mode has simultaneous Franck–Condon activity, dispersion in the depolarization ratio can result.[23]

The Raman spectrum of CV was previously presented in evidence of the D_3 symmetry of the ion in methanol solution. In ref 13a, the D_3 point group was used to assign the coupled benzene-like vibrations of the three equivalent phenyl rings into A and E components. The depolarization ratios of the symmetric A modes were reported to be $^1/_8$; the corresponding ρ values of the E modes were reported to be $^3/_4$. Most of the assignments were corroborated in ref 13b, where the deuterated derivative of CV was also studied. Although we found $\rho = ^1/_8$ for the breathing vibration of TPM at 284 cm^{-1}, our studies of CV as well as those of PF and EV revealed no ρ values close to that expected for D_3 symmetry.

In Figure 9 are shown the polarized and depolarized Raman spectra of MG excited at 514.5 nm, where resonance with the S_1 state is expected. As seen in the figure, and in Table IV, the depolarization ratios of all the strong Raman bands are close to 0.33.

For the symmetrically trisubstituted dyes PF, CV, and EV, we consider a perturbation which lowers the symmetry from D_3 to C_2. This lifts the degeneracy of the S_1 state into A and B components. Vibrational modes which are Franck–Condon active in both of these states can now be resonance enhanced when excited within either the R or B band. If these two states are well separated and the excitation wavelength is well within one absorption band, then depolarization ratios of $^1/_3$ will be observed for the totally symmetric vibrations. If the two states are overlapped, as they are for PF, CV, and EV, especially in polar solution, one can only predict that the totally symmetric vibrations have $\rho \leq ^3/_4$ and may show dispersion; i.e., the depolarization ratio will depend on excitation frequency.

Figure 10. Polarized and depolarized Raman spectra of EV.

Table VI. Depolarization Ratios of PF Raman Modes

ν (cm^{-1})	PF in water (514 nm)	PF in water (458 nm)
249	0.27	0.23
828	0.32	0.35
1177	0.45	0.55
1371	0.41	0.71
1526	0.41	0.68
1589	0.62	0.53
1615	0.22	very small

In principle, vibrations which were originally E symmetry in the D_3 ion break up into A + B components in the C_2 species. Barring a large frequency shift of the B vibrations in the excited electronic state, they are not expected to be Franck–Condon active and would have to derive RR intensity via Herzberg–Teller coupling of two excited electronic states. This would lead to nonzero off-diagonal elements of the polarizability tensor, resulting in $\rho \geq {}^3/_4$ and also a function of frequency. We did not observe any Raman modes having $\rho > {}^3/_4$ in this study.

The above considerations go a long way toward explaining the RR data presented here. For example, the RR spectrum of EV in methanol solution, excited at a wavelength within the B band, is shown in Figure 10. Clearly all the observed ρ values are less than ${}^3/_4$, and none are close to the value of ${}^1/_8$ expected for the D_3 ion. As shown in Table V, some of these vibrations have depolarization ratios which depend on excitation wavelength. In benzene solution where the R and B bands of EV are more well resolved, ρ begins to approach 0.33 for some of the observed bands. Although the reported values are somewhat uncertain (they were determined from peak heights after background subtraction), they clearly argue against the assignment of D_3 symmetry for EV. We do not observe any ρ values indicative of activity of the nontotally symmetric B vibrations. Unfortunately, intrinsic fluorescence prevents the Raman spectrum from being excited at wavelengths within the R band.

The RR spectrum of PF in methanol was excited at two wavelengths, 458 nm, shown in Figure 11, which is in the blue tail of the B band, and 514 nm, which is in a region of the R band which probably contains some contribution from B band absorption. Again, as shown in Table VI, ρ values less than ${}^3/_4$ are obtained, some of which vary with excitation wavelength. None of the observed depolarization ratios are close to ${}^1/_8$, ruling out D_3 symmetry.

It is important to consider whether these results could be explained in terms of the unsymmetrical propeller model for the ground-state geometry of the ions. The depolarization ratios alone

Figure 11. Polarized and depolarized Raman spectra of PF.

are consistent with any picture which invokes a symmetry-breaking perturbation to lift the degeneracy of the excited states. However, as shown in ref 13, the Raman and IR activity, and the assignment of the normal modes into A and E vibrations, is more consistent with D_3 than with C_2 symmetry. The distorted propeller would be expected to have normal mode activities very different from that of the D_3 propeller. The solvent perturbation proposed in this work is unlikely to present much of a mechanical perturbation to the normal modes of the unsolvated molecule. However, as the quantum mechanical calculations show, the solvent (or counterion) effect on the excited electronic states is a large one, and thus can lead to alterations in the RR intensity patterns. Thus, the RR data is consistent with a model where symmetry breaking is caused by the solvent and not by a distortion within the molecule.

Conclusions

The combination of polarized Raman and fluorescence measurements with semiempirical molecular orbital calculations reveals that the symmetry of this series of triply amino-substituted triphenylmethane dyes must be lower than D_3 in solution. Fluorescence spectra reveal that the existence of overlapping visible absorption bands, in parafuchsin, ethyl violet, and crystal violet, is due to symmetry breaking and not to the existence of two isomers in equilibrium. INDO calculations favor the idea that the symmetry breaking is due to the presence of a perturbing polar solvent molecule or counterion near one of the amino group positions, rather than to a torsional distortion of the molecule. Polarized resonance Raman data yield depolarization values greatly different from those expected for D_3 symmetry, although the normal mode activity is well accounted for using the D_3 point group. This suggests that an electronic rather than a mechanical perturbation is responsible for the symmetry breaking. Further support for the idea of a perturbing change or dipole being responsible for the splitting is provided by comparing the visible absorption spectra of PF, CV, and EV. As one goes to increasingly bulky substituents on the amino group, a smaller separation of the R and B bands is observed. This is consistent with increasing separation of the amino group from the perturber in the series PF, CV, and EV. A more complete discussion of the Raman data and the aggregation of the triply substituted dyes will be discussed in separate papers.