ESR studies of the triplet state of [n,n] paracyclophanes

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ESR experiments were performed on the triplet state of randomly oriented paracyclophanes in a variety of rigid glasses at temperatures ranging from 103 to 15°K. Spectra were recorded for [2.2]; [3.3]; (4,7,12,15)-tetramethyl [2.2]-paracyclophane and stagger-ring paracyclophane. For all the samples except stagger ring, a four-ringed paracyclophane, only the H_{min} feature was observed from which D*, the root-mean-square zero-field splitting, was calculated. For stagger ring the triplet spectrum has two features in the $\Delta m_s = 1$ region in addition to the H_{min} feature. From these, the zero-field splittings, D and E, were calculated. The triplet spectra for the paracyclophanes show that there is strong transannular interaction with electron delocalization over all benzene rings. There is evidence for strongly coupled intramolecular exciton effects. The effect of increasing the inter-ring separation from [2.2] paracyclophane to [3.3] paracyclophane is to decrease the transannular interaction. The effect of methyl substitution is to increase transannular effects relative to the parent compound. Transannular interactions in stagger ring are greater than in [2.2] paracyclophane despite the increased electron delocalization possible through the introduction of more than two rings. The large value of E for stagger ring represents a significant deviation from axial symmetry for the zero-field-splitting tensor and indicates that the methylene bridges, the methyl substituents, or the ring distortion, may make important contributions to the electronic distribution of the triplet state.

INTRODUCTION

The investigation of the symmetry and intramolecular dynamics of excited states in aromatic and partially aromatic hydrocarbons through electron spin resonance has been of considerable interest in the last few years. Temperature-dependent spectra observed for the lowest triplet state in corannulene[1] and in benzene[2] suggest a conversion between distorted molecular configurations of less than threefold symmetry. For molecules such as trypt'cene and tribenzotrypticene, which are characterized as having aromatic subsystems linked by a σ-bonded carbon frame, such spectra have been interpreted in terms of an intramolecular exciton, transferring spin polarization among subsystems.[2]

The series of [n.n] paracyclophanes appears to be a suitable choice to examine for similar evidences of intramolecular exciton transfer. Two warped benzenoid rings connected at the *para* positions by methylene bridges n carbons in length (n≤2), represent the basic structure of the symmetric paracyclophane molecule. When n≤3, the crystal structure forces the molecular conformation of the rings to be closer than the van der Waals radius of 3.4 Å and introduces the possibility of transannular interactions.[3] In order to clarify the nature of these interactions and the conformational dynamics of the triplet state, experiments were conducted on [2.2]; [3.3]; (4, 7, 12, 15) tetramethyl, and stagger-ring paracyclophane.

The x-ray structure of [2.2] paracyclophane indicates that it is a highly strained symmetric cycle.[4-6] The rings are coaxial and warped in a dish-shaped

fashion such that the inter-ring separation varies from 2.79 to 3.10 Å. Evidence for the transannular effects was found through ESR studies of the radical anion[7] and the NMR spectrum of the neutral molecule in CCl_4.[8]

Theoretical[9,10] and experimental[11,12] investigations of the excited states of the neutral molecule indicate that there are no significant conformational changes on excitation.

[3.3] Paracyclophane is the largest symmetrical paracyclophane that exhibits transannular electronic effects and ring warping. X-ray structure[3,6] determinations indicate that in contrast to [2.2] paracyclophane the rings are not coaxial and are much less warped.

Experiments on tetramethyl [2.2] paracyclophane[13] were performed to gain information about substituent effects upon transannular interactions. Although the x-ray crystal structure is not known, information inferred from molecular models implies that the methyl groups may assume a staggered conformation, without steric hindrance, in the framework of [2.2] paracyclophane, the parent compound.

15, 31, 33, 35 - Tetramethylheptacyclo[28 . 2 . 2 . 2 .[14,17]0 . [4,25]0 . [6,27]0 . [9,20]0 . [11,22]] hexatriaconta - 1(32) , 4 , 6(27) , 9 , 11(22) , 14 , 16 , 20 , 25 , 30 , 33 , 35 - dodecanene, stagger ring, may be regarded as a multilayered paracyclophane, consisting of four stacked benzenoid rings separated by methylene bridges in a face-to-face arrangement, lying at separations less than the normal van der Waals radii.[14] Evidence for transannular interactions is shown in both its absorption and emission spectrum in EPA glasses.[15]

Although the x-ray crystal structure is unknown, molecular models indicate that the greatest distortion and strain should exist between the inner two rings and that inter-ring separations are not uniform. The investigation of this compound was begun in the hopes of obtaining information about intramolecular exciton transfer and the electronic structure of its triplet state.

EXPERIMENTAL TECHNIQUES

The experimental apparatus and techniques are basically the same as reported earlier.[1] However, to minimize photodecomposition of the paracyclophanes,[16] a Dow Corning 7–54 filter, which prevents the transmission of wavelengths shorter than 2700 Å, was inserted into the optical train. The 1000-W Osram HBO lamp was replaced by a 1200-W Xe–Hg Hanovia lamp. Linewidths were estimated by measuring half the peakwidth at half the signal height.

Preparation and Purification of Compounds

[2.2] Paracyclophane, obtained from Hi Laboratories, Whitmore Lake, Michigan, was vacuum sublimed twice producing white crystals whose melting point in unsealed capillaries was 277–279°C. Decomposition of the molecule occurred above these temperatures.

[3.3] Paracyclophane was used as received from S. Wong and D. J. Cram of U.C.L.A.

(4,7,12,15)-Tetramethyl [2.2] paracyclophane was recrystallized from ethanol and then vacuum sublimed twice. Snowy, white crystals whose melting point in unsealed capillaries was 105.5–106°C were obtained.

Stagger-ring paracyclophane and biduryl were used as received from D. T. Longone of the University of Michigan.

Matrix Preparation

Samples were thoroughly degassed under high vacuum. They were prepared in high-quality (Suprasil) quartz tubing, 2- and 3-mm i.d., in a variety of solvent mixtures which formed rigid glass matrices near liquid-nitrogen temperatures.

There are several properties a solvent or solvent mixture should possess to form suitable glasses for low-temperature ESR triplet studies: (1) optical transparency; (2) rigidity and noncracking; (3) the ability to dissolve a reasonable quantity of solute; (4) not readily photolyzed or easily capable of producing free radicals. The following were judged suitable for use: (1) dimethylformamide and ethanol (DMF:EtOH, 1:4 by volume); (2) cyclohexane and decalin (CD, 1:3 by volume); (3) ethanol, pentane, and ether (EPA, 5:5:2 by volume); (4) ether and tetrahydrofuran (ETHF, 1:1 by volume); (5) 2-methyltetrahydrofuran (2THF).

Reagent-grade Baker tetrahydrofuran was doubly distilled under nitrogen from calcium hydride and degassed under vacuum from lithium aluminum hydride. The sample was then stored under vacuum over a sodium mirror.

Spectroquality Matheson, Coleman, and Bell diethyl ether, 1,2-dimethoxyethane, and 2-methyltetrahydrofuran were prepared as above. The samples were stored over LiAlH$_4$ under vacuum.

Reagent-grade U.S. Industrial Chemical Corporation absolute ethanol; Matheson, Coleman, and Bell spectroquality pentane and cyclohexane, and Eastman Organic Chemicals decalin were used as received.

Spectroquality Matheson, Coleman, and Bell (n.n) dimethyl formamide was passed over an activated alumina column under nitrogen until an odorless solvent was produced. The solvent was then stored over molecular sieves under nitrogen and away from light and heat.

Spectrum Analysis

Since the triplet features are light dependent, they were identified by observing whether or not the feature remained or decayed within a few seconds after the uv excitation was removed. The spectra, which were analyzed with the aid of the computer programs described earlier,[1] were interpreted in terms of a spin Hamiltonian which considers only Zeeman and dipolar couplings, other effects being orders of magnitude smaller[17] and is given by

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_D = g\beta H_0 \cdot S - X S_x^2 - Y S_y^2 - Z S_z^2, \quad (1)$$

$$X + Y + Z = 0, \quad (2)$$

$$D = \tfrac{1}{2}(X + Y) - Z, \quad (3)$$

$$E = -\tfrac{1}{2}(X - Y). \quad (4)$$

X, Y, Z, are the principal values of the traceless zero-field-splitting tensor and can be represented in terms of two parameters, D and E, the zero field energies. g, β, H_0, and S have their usual meanings. In the $\Delta m = 1$ region, two stationary resonance fields are associated with each of the three magnetic axes of the molecule (x, y, or z). The magnetic field values of these six features are denoted $Hx2$, $Hx3$, $Hy2$, $\cdots$, and are determined by the values of X, Y, Z (or D and E) according to[18]:

$$Hx2 = (2g\beta)^{-1}[(2\delta - 3\mid X \mid)^2 - (Y - Z)^2]^{1/2}, \quad (5)$$

$$Hx3 = (2g\beta)^{-1}[(2\delta + 3\mid X \mid)^2 - (Y - Z)^2]^{1/2}. \quad (6)$$

The stationary resonance fields for the Y and Z directions are obtained through cyclic permutations of Eqs. (5) and (6).

In addition, there is another feature at low fields labeled H_{min}, whose value is given by the following

TABLE I. Zero-field splittings and experimental conditions for randomly ordered paracyclophane triplets.

Compound	Matrix[a]	H_{min} Line-width (G)	Temp (°K)	D^{*b} (cm^{-1})
[2.2] Paracyclophane	2THF	9	15	0.1074±0.0008
	EPA	9	15	0.1059±0.0008
[3.3] Paracyclophane	EPA	18	32	0.0802±0.0008[c]
				0.0959±0.0008[d]
	CD	16	69	0.0819±0.0008[c]
				0.0982±0.0008[d]
	CD	21	33	0.0854±0.0008[c]
				0.1013±0.0008[d]
Tetramethyl paracyclophane	DMF:EtOH	11	15	0.1183±0.0008
	EPA	10	15	0.1193±0.0008
	ETHF	9	103	0.1188±0.0008
	CD	11	44	0.1170±0.0008
	2THF[e]	10	15	0.1183±0.0012
Stagger-ring paracyclophane	DMF:EtOH	10	15	0.1164±0.0008

[a] For matrix designations see text.
[b] Calculated from Eq. (9) using the H_{min} resonance.
[c] Calculated from Eq. (9) using the low-field H_{min} resonance.
[d] Calculated from Eq. (9) using the high-field H_{min} resonance.
[e] Impurities in the matrix increase the uncertainty of this measurement.

equation:

$$H_{min} = (2g\beta)^{-1}[\delta^2 + 4(XY + XZ + YZ)]^{1/2}. \quad (7)$$

δ is defined as the microwave energy. This resonance field has special significance in that it is related to the root-mean-square zero-field splitting, D^*, which represents the net interaction from the contribution of D and E to the triplet state,

$$D^* = (D^2 + 3E^2)^{1/2} \quad (8)$$

$$= [\tfrac{3}{4}\delta^2 - 3(g\beta H_{min})^2]^{1/2}. \quad (9)$$

Stationary resonance field values were determined from the experimental spectra in the same manner as reported by Lhoste et al.[19] Since the signs of the zero-field splittings cannot be determined by these methods except through extensive studies at liquid-He temperature,[20] Z was arbitrarily chosen less than zero. In addition, the convention $|Z| > |Y| > |X|$ was adopted. Phosphorescent lifetimes were estimated by shuttering the uv excitation and recording the decay of the resonance signal.

RESULTS

The results of the triplet studies are listed in Table I. With the exception of stagger-ring paracyclophane, only the H_{min} feature and a free-radical absorption were obtained.

A combination of energy transfer to solvent molecules, small molar absorptivity, and low solubility are factors which resulted in weak signal intensities and prevented the detection of other features of the triplet spectra.

In CD, DMF:EtOH, and 2THF matrices, no triplet signal decay or matrix color change on continued irradiation was observed. The signal-to-noise ratio of about 15:1 for all samples except stagger ring ($\simeq$30:1) could not be improved upon by attempting to concentrate the solutions. For [2.2] and [3.3] paracyclophane maximum solubility was reached at about $10^{-3}M$.

Rapid decay of the H_{min} signal accompanied by the generation of a yellow color in the matrix and a rapid increase in the free-radical signal was observed, however, in EPA and ETHF glasses. Less than a minute was required for the signal-to-noise ratio of the H_{min} absorption to decrease from an initial value of about 80:1 to about 5:1. Further decay occurred
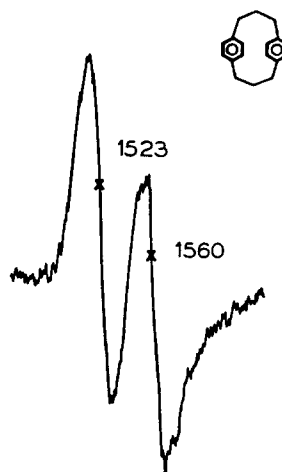

FIG. 1. H_{min} feature for [3.3] paracyclophane. [3.3] paraacyclophane in CD matrix at 33°K. $\delta = 0.3079$ cm^{-1}.

more slowly, but it was possible to completely obliterate the signal after 6–8-min irradiation. The yellow color disappeared upon warming the sample. After irradiation, examination of the sample by thin layer chromatography, vapor-phase chromatography, and uv absorption spectroscopy did not reveal any new molecular species. After the yellow color had been removed by warming the sample, it was possible to regenerate the signal with about the same initial intensity. This indicates that the decrease in signal intensity on irradiation is due primarily to quenching by solvent radicals rather than by permanent radiation damage. Solvent radicals are predicted to be created by a transfer of energy from aromatic molecules already in the triplet state causing the decomposition of the host and quenching of the guest phosphorescence.[21,22] Further guest phosphorescence or triplet-state behavior is quenched through spin exchange to the neighboring free radical.

The molar absorptivity, ϵ, values for the absorption bands of the paracyclophanes which were irradiated during the experiments are quite small.[15] Because of these small values of ϵ, it is therefore difficult to obtain large steady-state triplet populations.

Assignment of the spectra to the paracyclophane molecules and not to a photodecomposition product was made for the following reasons: (1) in some of the matrices used (2THF, CD, and DMF:EtOH) no signal decay or signal change on irradiation was observed; (2) in the EPA and ETHF glasses where signal decay occurred, the signal could be regenerated as previously described and there was little variation of the position and shape of the H_{min} resonance with change of the matrix; (3) biduryl is similar to the reported photodecomposition products of paracyclophane,[16] and no triplet spectrum from biduryl could be observed in either an EPA or DMF:EtOH matrix.

For all the molecules except [3.3] paracyclophane in the CD matrix, no change in line shape or line position between 15 and 77°K was observed.

The small amount of [3.3] paracyclophane available made detailed investigations difficult. The molecule proved soluble in CD and EPA solvent mixtures. In both matrices the H_{min} absorption consisted of a doublet with unusually broad widths (see Fig. 1). The D^* values associated with each peak were calculated from the observed resonance positions.

In the CD matrix, the spectrum was slightly temperature dependent, shifting 7 G to lower fields as the temperature decreased from 66 to 33°K. The lifetime of the triplet, as measured by the decay of the ESR signal, varied with temperature. At 77°K the doublet decayed in 15±1 sec. At 33°K, the lifetime of the low-field peak was 20±1 sec, the high-field peak was 17±1 sec.

In the EPA matrix, no spectral temperature dependence was observed from 77 to 16°K. Although the line shape and relative intensity were initially similar
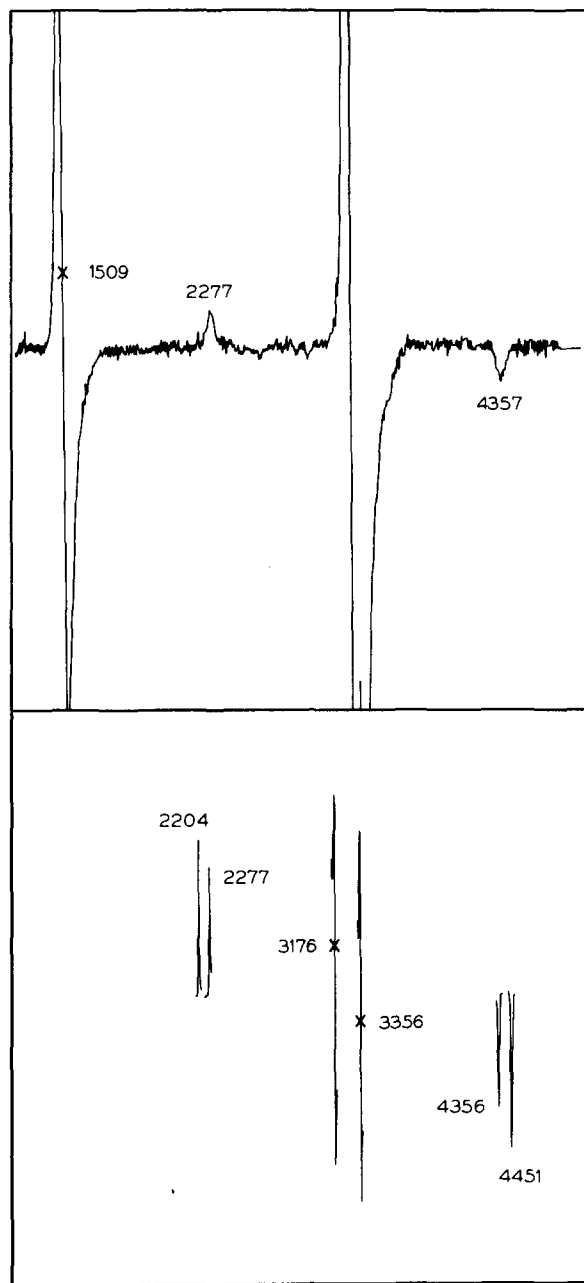

FIG. 2. Experimental and computed stagger-ring triplet spectra at 15°K. Top: experimental spectrum. (Composite of observed spectrum, see text.) The large signal near 3300 G is due to a photolytically produced free radical. $\delta = 0.3126$ cm^{-1}. Bottom: computer-simulated spectrum for the $\Delta m_s = 1$ region. $X = 0.0055$ cm^{-1}, $Y = 0.0643$ cm^{-1}, $Z = -0.0697$ cm^{-1}, $g = 2.0023$.

to those observed in the CD matrix, spectrum degradation of the type previously mentioned did not allow accurate lifetime measurements to be made. An approximate value would be 15±5 sec.

For [3.3] paracyclophane, D^* for either peak varied with the matrix to a much greater extent than for the other molecules. The difference in D^* for the two peaks, however, was the same within experimental error in both

CD and EPA. In addition, the line shape and relative amplitudes of the two peaks were the same in both matrices and both peaks were simultaneously affected by degradation in the EPA matrix. These observations indicate that the processes for triplet population and for host–guest interaction are the same for both peaks, and hence, that both peaks originate from [3.3] paracyclophane.

The limited supply of stagger-ring paracyclophane allowed experiments to be performed in only the DMF:EtOH matrix. The spectrum was not temperature dependent between 77 and 15°K. Two features of the $\Delta m_s = 1$ transitions and an H_{min} resonance were observed permitting a calculation of the zero-field parameters.

The experimental conditions allowed accurate measurement of the features of the triplet spectrum, but did not permit the entire spectrum to be recorded at one time. A composite of the computer analysis and the observed spectrum are shown in Fig. 2. The central and dominating feature of the spectrum is the free-radical signal. Its size is such that it prevented observation of the weaker triplet transitions at nearby resonance fields.

There is excellent agreement between the computed and observed stationary resonance fields (see Fig. 2). The computed value of H_{min} is 1509 G. In this manner the three features of the spectrum determined two parameters: $D = 0.1046 \pm 0.0003$ cm^{-1}; $E = 0.0294 \pm 0.0003$ cm^{-1}. There is also excellent agreement between the value of D^* calculated not only from the H_{min} resonances but also from the $\Delta m_s = 1$ transitions using Eq. (8). The values obtained were

$$D_{H_{min}}{}^* = 0.1164 \text{ cm}^{-1},$$

$$D_{\Delta m_s = 1}{}^* = 0.1166 \text{ cm}^{-1}.$$

Two independent calculations determined one parameter, D^*.

There is, however, some discrepancy between the calculated intensities and the intensities which were observed. The computed spectrum predicts that those features associated with the Z canonical resonance field should be more intense than those associated with the Y canonical resonance field. However, the most intense features observed in the region were assigned to the Y canonical resonance fields.

If the ad hoc assumption is made that there are small matrix interactions which more strongly perturb the value of D about the observed average D, but which leave E nearly constant, then the difference between the calculated and observed spectra is a consequence for the following reason. The effect on stationary resonance field positions of a variation in D while keeping E constant is to vary the field positions for the Z features about twice as much as those for the Y features. For example, on variation of D by ± 0.0012 cm^{-1}, the Z features varied over 26 G while

the Y features varied only over 11 G. Thus, the linewidth of the Z features would be broadened to a greater extent than that of the Y features, and, given the small intensity of the observed Y features, the broadened Z features would not be detected.

It is important to note that the linewidth of the H_{min} feature is relatively insensitive to this variation of D.

DISCUSSION

The ESR results are interpreted in terms of the exciton formalism first proposed by Smith et al.[23] to describe excimer fluorescence in concentrated naphthalene solutions, and later developed by Vala et al.[9] and by Hiller et al.[15] to describe the absorption, fluorescence, and phosphorescence spectra of the paracyclophanes. The exciton formalism has been applied to the paracyclophanes by considering them to consist of unwarped benzene rings constrained to a fixed internuclear distance by methylene bridges. The effect of either of these bridges or of ring warping on electronic transitions is not included in this model.

The benzene rings, interacting via transannular mechanisms, are described as being either weakly or strongly coupled, depending on the extent of interaction. For strong couplings the molecular energy levels are greatly displaced from those of benzene and excitations are delocalized over the entire molecule. For weak couplings the converse is true, excitation is trapped on individual benzene rings, and the observed ESR or uv spectrum would be similar to that of benzene. Thus in the case of weakly coupled benzene rings, D^* should be close to the value for benzene itself (0.158 cm^{-1}), while for strongly coupled rings D^* would be substantially less since the unpaired electrons are distributed over a larger region and therefore further apart on the average than in benzene.

Experimental evidence for weak coupling has been observed for the triplet of tribenzotrypticene[2] at 20°K randomly oriented in a glass. At this temperature the excitation is trapped on a monomeric naphthalene subunit, and the observed triplet spectrum is almost identical to that of naphthalene. In the presence of an applied magnetic field, the orientation of each monomeric subunit is different. As the temperature is raised, the rate of intramolecular exciton transfer among magnetically inequivalent monomeric subunits increases, and the ESR spectrum is broadened.

[2.2] Paracyclophane

Within the exciton formalism, transannular interactions produce changes in the ground and excited states of paracyclophane relative to benzene. The ground state of [2.2] paracyclophane, Ψ^0, is represented as the antisymmetrized product of the individual benzene molecular orbitals, $\Phi_i{}^0$, such that

$$\Psi^0 = \alpha \prod_{i=1} \Phi_i{}^0,$$

where α is the antisymmetrization operator. The Hamiltonian describing the system consists of the ground-state Hamiltonian for each benzene ring plus the interaction potential. The effect of the interaction potential is to destabilize the ground state of paracyclophane relative to benzene by introducing internuclear repulsions.[9]

The excited electronic states of [2.2] paracyclophane are described by antisymmetrized products of charge transfer and excimer states of the benzene molecular orbitals which are mixed through configuration interaction. The charge-transfer configuration is represented by the transfer of an electron from the bonding orbital of one benzene ring to the antibonding orbital of the other ring. The result may be pictured as an interaction between a benzene anion and a benzene cation.

The excimer configuration is represented by the interaction of a benzene ring in an excited state with the neutral ring adjacent to it. The importance of configuration interaction in mixing charge-transfer and excimer states is underlined by these calculations. The effect of excimer and charge-transfer interactions is to split each electronic transition of benzene into two transitions.

Further, there is a low-frequency shift of the electronic spectrum of the paracyclophanes relative to that of benzene. This is ascribed to the ground-state destabilization introduced by internuclear repulsions.

The ESR experiment indicates that [2.2] paracyclophane appears to have electron delocalization over both benzene rings and thus gives evidence for strong transannular interaction in the triplet state. If there were no coupling or weak coupling among the benzene rings then the triplet excitation would be localized on one ring and an rms zero-field splitting, D^*, similar to that of benzene or a substituted benzene[2] ($\simeq 0.158$ cm^{-1}), would be expected. However, the inter-ring interaction and strong coupling are evidenced by the low value of D^* ($\simeq 0.106$ cm^{-1}) relative to benzene or a substituted benzene.

Molecular motion is not observed under the experimental conditions in the triplet state and may be evidence against the torsional twist mechanism proposed by Andrews and Westrum for the molecular crystal.[24] The Andrews–Westrum model postulates that an anomaly noted in the heat-capacity curve of [2.2] paracyclophane at about 50°K may be ascribed to the population of a vibrational or vibronic state in which the two benzenoid rings oscillate in opposite directions about the out-of-plane axis. At temperatures above the transition temperature, 50°K, if there is considerable molecular motion, a temperature-dependent ESR triplet spectrum should be observed. It should be characterized by broad linewidths which narrow as the temperature is lowered and the molecular conformation becomes rigid. The lack of a change in either linewidth or in line position of the $H_{\min}$ feature over temperatures ranging from 80 to 15°K

is difficult to rationalize within the framework of the Andrews–Westrum model.

[3.3] Paracyclophane

Vala, Haebig, and Rice have applied the exciton model to [3.3] paracyclophane.[9] As a first approximation, the form of the interaction potential is assumed to be the same as for [2.2] paracyclophanes, making the inter-ring separation the only variable parameter. The effect of this variation is to decrease the π-electron overlap of the benzene rings and thus to decrease the transannular interaction potential and the effect of charge-transfer and excimer interactions. However, the possibility of strong coupling as described earlier, still exists. The ground-state destabilization and the energy splittings of the excited states are predicted, therefore, to be smaller than those in [2.2] paracyclophane. The observed electronic spectrum is not as shifted to low frequencies, reflecting a decrease in transannular interaction.

Transannular interaction is evident in the triplet ESR spectrum of [3.3] paracyclophane. In an analogous argument to that proposed for [2.2] paracyclophane, the fact that D^* is much less than D^* for benzene, implies that the benzenoid rings are strongly coupled and that electron delocalization occurs over the entire molecule.

For [3.3] paracyclophane, D^* calculated from either peak of the doublet was substantially lower than D^* for [2.2] paracyclophane. This indicates that the unpaired electrons are distributed over a larger molecular volume in [3.3] paracyclophane than in [2.2] paracyclophane. This would imply that transannular interactions are smaller in [3.3] paracyclophane in the triplet state than for [2.2] paracyclophane. The two peaks in the [3.3] paracyclophane spectrum both arise from the [3.3] paracyclophane molecule (see Results), and we suggest that they are due to triplet [3.3] paracyclophane in two molecular conformations. In the molecular crystal the rings in [3.3] paracyclophane are not coaxial, but on the basis of chemical evidence Sheehan and Cram[25] suggest that in salts formed by reaction with tetracyanoethylene (TCNE), the rings are eclipsed. Also, the NMR spectrum[26] in CDCl$_3$ is consistent with a molecular structure with eclipsed rings as indicated by the equivalence of the aromatic protons. In solution, therefore, a different conformation may exist than in the crystal. There is no similar evidence of different conformations for [2.2] paracyclophane.

Hence, it is not unreasonable that in a glass matrix, triplet [3.3] paracyclophane exists in two conformations and that each peak in the ESR spectrum is associated with a different conformation. The unusually large width of each peak could be attributed to a distribution of matrix perturbations causing a range of structural variation about each of the two basic conformations.

(4,7,12,15)-Tetramethyl [2.2] Paracyclophane

The ESR triplet experiment again indicates that for tetramethyl [2.2] paracyclophane there is a strong coupling in which there is electron delocalization over both rings. In a variety of hosts and over a wide range of temperatures (15–103°K), the H_{min} feature remained sharp, and the value of D^* varied less than ±2.5%. D^* for the tetramethyl-substituted [2.2] paracyclophane ($\approx$0.118 cm^{-1}) is significantly larger than D^* for the parent compound ($\approx$0.106 cm^{-1}). Methyl substitution generally produces a very small decrease in D^* for aromatic compounds.[2]

Theoretical calculations by Godfrey et al.[27] of substituent effects on the zero-field splittings of aromatic compounds indicate the difficulty in describing the effects of methyl substitution. Their calculations indicate that the influence of methyl substitution on the zero-field splitting is not predictable, although it may be rationalized a posteriori in terms of inductive and weakly mesomeric effects.

Experiments by Smaller et al.[28] on the emission and ESR triplet spectra of substituted aromatics fail to yield correlations among methyl-substituted compounds and the change in zero-field splittings. They found that the zero-field splittings as measured by ESR were much more sensitive to substituent effects than the phosphorescence spectra. The unusually large increase in D^* for tetramethyl paracyclophane could be due to an increase in transannular interaction and a concomitant increase in unpaired electron density in the inter-ring region upon methyl substitution.

Stagger-Ring Paracyclophane

Hiller et al.[15] extended the exciton formalism to four stacked benzene rings to interpret the uv spectra of stagger-ring paracyclophane. The ground- and excited-state wavefunctions are represented in an analogous manner to those of [2.2] paracyclophane. Inter-ring interactions are represented by charge transfer and excimer resonances between adjacent benzene rings, the other rings being too far separated to make a substantial contribution.

The exciton interaction shifts to lower frequency the fluorescence and phosphorescence spectra relative not only to benzene but also to [2.2] paracyclophane. From the semiquantitative calculations it is concluded that the observed shift is indicative of greater transannular interaction than in [2.2] paracyclophane. The upfield shift of the aromatic protons in the proton NMR and the π-base strength of TCNE and (1,3,5)-trinitrobenzene complexes[14] indicate that interactions among the four rings are enhanced relative to [2.2] paracyclophane in accord with the conclusions of the exciton treatment.

The ESR results indicate that transannular interactions involving electron delocalization characteristic of strong coupling occur over all four rings in the triplet state of stagger ring. Neither localization of charge to form a weakly coupled intramolecular exciton nor motional processes are indicated because the line positions are stationary, the line widths are narrow and, except for a Boltzmann enhancement of intensity, temperature independent from 80 to 15°K.

The increase in D^* upon going from [2.2] paracyclophane to stagger-ring paracyclophane and the near equality of D^* for tetramethyl paracyclophane and the stagger ring are evidence for increased transannular interaction in the four-ring compound. If transannular interactions were the same among all three compounds, then the larger delocalization possible through interactions involving four rings would imply that D^* for stagger ring should be considerably less than that for [2.2] or tetramethyl paracyclophane. In comparing a four-ring system to a two-ring system, D^* is not directly proportional to transannular interaction. In this case, the increased internuclear bonding is offset somewhat by the larger delocalization possible through interaction involving the four rings.

To determine the orientation of the zero-field-splitting axes with respect to the molecular axes, experiments on mixed crystals of stagger-ring doped into an inert host are required. However, from randomly oriented triplets the absolute values of the zero-field splittings are obtained. The nonzero E value ($E = 0.0294 \pm 0.0003$ cm^{-1}) indicates that the spin distribution in the triplet is not axially symmetric, having less than threefold symmetry. The magnitude of E indicates that the distortion from threefold symmetry is large. For example, in naphthalene,[29] $E = 0.01536$ cm^{-1}, which is about half of the value observed for stagger ring.

There is, therefore, experimental evidence that either the methylene bridges, the methyl substituents, the ring distortion, or more probably a combination of all of these are important in determining the spin distribution in stagger-ring paracyclophane. It is impossible to determine from the available data, the extent to which each group affects the triplet spin distribution. However, a model which assumes a stagger ring to consist of four stacked benzene rings with a sixfold symmetry axis must be refined to account for the observed E value.

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