Theoretical Studies of Transannular Interactions. III. The Absorption and Emission Spectra of a Multilayered Paracyclophane

Ian H. Hillier, Leon Glass,[1] and Stuart A. Rice

Contribution from the Department of Chemistry, Institute for the Study of Metals, The University of Chicago, Chicago, Illinois 60637. *Received June 13, 1966*

Abstract: An interpretation of the absorption and emission spectra of a multilayered paracyclophane, consisting of four stacked benzene rings, is described. The formalism previously applied to the singlet and triplet states of the paracyclophanes is extended to this compound. The interaction of charge-transfer and neutral excitation states leads to a set of energy levels which tally with experiment (emission spectra reported in this paper) within the framework of the semiquantitative computations reported herein.

The effect on the $\pi \rightarrow \pi^*$ transitions of molecular benzene of a second benzene ring in close proximity is manifest in the absorption and emission spectra of the paracyclophanes.[2a] In these compounds the separation of the aromatic rings, which is as small as 3 A in [2.2]paracyclophane, is ensured by the methylene bridges between the rings. The ground-state repulsion between the π-electron clouds of the two monomers is effective in preventing a similar anomalous absorption in benzene solutions, although eximer emission is observed.[2b,3] The interpretation of such transannular interactions has been the subject of a number of studies.[3-5] It is the general conclusion that the interaction of neutral monomer excited states is far too small to account for the large energy shifts observed (for example, the lowest absorption band in [2.2]paracyclophane occurs at ~30,000 cm^{-1} compared to 38,000 cm^{-1} in molecular benzene), while the introduction of electron delocalization has been found to result in energy shifts of the required magnitude.[3,5] The formalism can take account of such delocalization in two possible ways. Molecular orbitals for the two (or four) benzene "supermolecule" may be constructed by the LCAO method, and limited configuration interaction used in the calculation of the excited states.[4] This is a natural extension of the Pariser–Parr–Pople semiempirical theory, which has been used with considerable success in studying the excited states of simple aromatic hydrocarbons. In an alternative description, the exciton formalism is extended to include charge-transfer states which result when an electron from the highest bonding molecular orbital of one benzene monomer is promoted to the lowest antibonding molecular orbital of another. This treatment has been found to be adequate for the interpretation of the absorption and emission spectra of the paracyclophanes.[5] In this paper we shall consider the multilayered paracyclophane (henceforth referred to as MLP) consisting of four-stacked benzene rings, recently synthesized by Longone and Chow[6] (Figure 1). We shall use the extended exciton treatment to describe the transannular interactions in this compound, because such an analysis provides a clearer picture of the interactions included than does the Pariser–Parr–Pople treatment in which molecular orbitals would have to be constructed using all 24 carbon $2p\pi$ atomic orbitals.

Experimental Details

The low-temperature emission spectrum of the MLP dissolved in EPA (ethyl ether, isopentane, ethyl alcohol, volume ratio 5:5:2, respectively) was obtained using an apparatus which has previously been described.[7] Briefly, the radiation from a high-intensity xenon lamp was passed through a filter train, resulting in a continuous band of exciting light extending from about 2100 to 2800 A. The sample was contained in a Suprasil (nonfluorescent fused quartz) tube which was mounted in a cylindrical dewar having Suprasil windows. Light coming from the sample cell entered a Cary 14 spectrophotometer which had been modified to operate as a scanning monochrometer. The signal coming from a photomultiplier tube mounted on the exit slit was amplified and displayed on a strip chart recorder.

The MLP was provided by Dr. D. T. Longone and used without further purification. A concentration of about 5×10^{-4} M was used. The EPA was obtained from the Scientific Supply Co. and used without purification. Before cooling the sample was saturated with high-purity, dry nitrogen so as to purge the sample of oxygen which might quench the emission.

The total emission spectrum of the MLP at liquid nitrogen temperature is displayed in Figure 2. The fluorescence spectrum has a maximum at 4050 A, while the phosphorescence spectrum has a maximum at 5350 A. Phosphorescence is not found in the room temperature emission spectrum.

Stationary-State Wave Functions

The formalism used herein follows closely that developed in the interpretation of the paracyclophane spectra,[5] and to avoid unnecessary repetition we shall emphasize only those points peculiar to the MLP discussed here. The computation is performed for the model consisting of four stacked planar benzene rings equally spaced and directly above one another (Figure 1). Neglecting the bonds between rings, which are not considered in our approximation, we take the symmetry of this arrangement to be D_{6h}. If the methylene bridges and the methyl groups are included in the molecule, the MLP is of C_{2h} symmetry. In the [2.2]- and [3.3]-

---

[1] U. S. Public Health Service Predoctoral Fellow.

[2] (a) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954); (b) T. V. Ivanova, G. Mokeeva, and B. Sveshnikov, *Opt. i Spektroskopiya*, **12**, 325 (1962).

[3] (a) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3131 (1964); (b) *ibid.*, **42**, 1675 (1965).

[4] J. Koutecky and J. Paldus, *Collection Czech. Chem. Commun.*, **27**, 599 (1962).

[5] (a) M. T. Vala, I. H. Hillier, S. A. Rice, and J. Jortner, *J. Chem. Phys.*, **44**, 23 (1966); (b) I. H. Hillier, L. Glass, and S. A. Rice, *ibid.*, in press.

[6] D. T. Longone and H. S. Chow, *J. Am. Chem. Soc.*, **86**, 3898 (1964).

[7] M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).

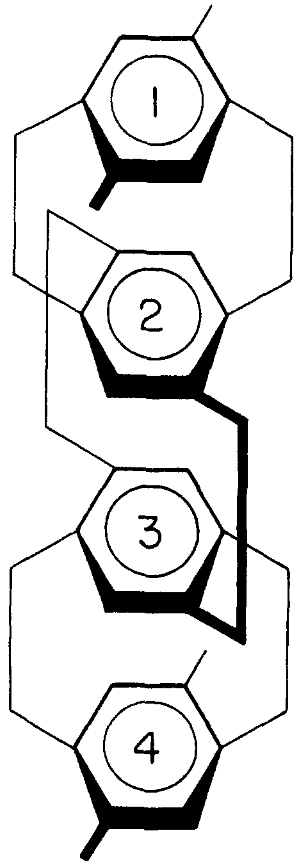

Figure 1. Schematic representation of multilayered paracyclophane (MLP).

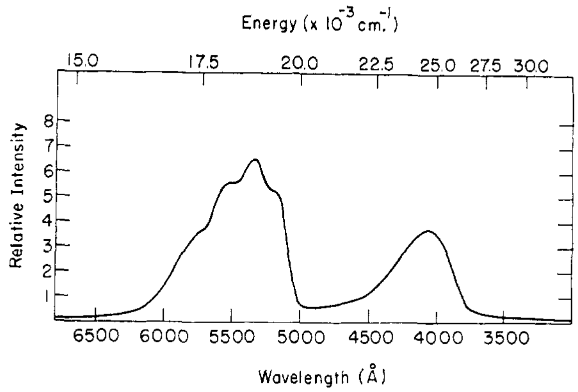

Figure 2. Emission spectrum of multilayered paracyclophane in EPA solvent at 77°K.

paracyclophanes there is crystallographic evidence of distortions from this ideal dimer symmetry.[8,9] Previous studies have shown that these slight deviations have little effect on the computed energy levels, but may introduce changes in the selection rules, and probably make any detailed calculation of transition intensities very suspect.[5] Until a crystallographic structure analysis of the MLP is available, there is little to be gained by considering arrangements other than the ideal D_{6h} structure. In a zero-order approximation, the ground state and one of the four locally excited states of the MLP may be represented in the form

$$\Phi^0 = \mathcal{A}_N\phi_1{}^0\phi_2{}^0\phi_3{}^0\phi_4{}^0 \tag{1}$$

and

$$R_2{}^f = \mathcal{A}_N\phi_1{}^0\phi_2{}^f\phi_3{}^0\phi_4{}^0 \tag{2}$$

where $\mathcal{A}_N$ is the antisymmetrization operator, the superscript 0 refers to the ground state, and $\phi_2{}^f$ represents the neutral excited state f of molecule 2. We shall also consider charge-transfer states, wherein an electron is exchanged between adjacent rings. The transfer of an electron from the rth bonding molecular orbital of ring i to the tth antibonding orbital of ring j leads to a wave function $\mathcal{A}R_i{}^{+(r)}R_j{}^{-(t)}$, it being understood that the two remaining benzene units are in their ground state. Equation 2 and the other three locally excited states do not represent stationary states of the MLP. The symmetry adapted neutral and ionic stationary states of the MLP (Table I) may be derived from those of the dimer (which have already been given: part I,[5a] Table I) by the application of group theory. We use Pople's[10] wave functions for the three $\pi \rightarrow \pi^*$ transi-

Table I. MLP Stationary-State Wave Functions

	Symmetry
$\frac{1}{2}(R_1{}^P \pm R_2{}^P \pm R_3{}^P + R_4{}^P)$ $\frac{1}{2\sqrt{2}}(\phi_1 \pm \phi_2 \pm \phi_3 + \phi_4)$ $\frac{1}{2}(\phi_5 + \phi_6)$	B_{1u}
$\frac{1}{2}(R_1{}^P \pm R_2{}^P \mp R_3{}^P - R_4{}^P)$ $\frac{1}{2\sqrt{2}}(\phi_1 \pm \phi_2 \mp \phi_3 - \phi_4)$ $\frac{1}{2}(\phi_5 - \phi_6)$	B_{2g}
$\frac{1}{2}(R_1{}^\alpha \pm R_2{}^\alpha \pm R_3{}^\alpha + R_4{}^\alpha)$ $\frac{1}{2\sqrt{2}}(\phi_7 \pm \phi_8 \pm \phi_9 + \phi_{10})$ $\frac{1}{2}(\phi_{11} + \phi_{12})$	B_{2u}
$\frac{1}{2}(R_1{}^\alpha \pm R_2{}^\alpha \mp R_3{}^\alpha - R_4{}^\alpha)$ $\frac{1}{2\sqrt{2}}(\phi_1 \pm \phi_2 \mp \phi_3 - \phi_4)$ $\frac{1}{2}(\phi_{11} - \phi_{12})$	B_{1g}

Definitions

$\phi_1 = R_1{}^{+3}R_2{}^{-4} + R_1{}^{+2}R_2{}^{-5}$
$\phi_2 = R_1{}^{-4}R_2{}^{+3} + R_1{}^{-5}R_2{}^{+2}$
$\phi_3 = R_4{}^{-4}R_3{}^{+3} + R_4{}^{-5}R_2{}^{+2}$
$\phi_4 = R_4{}^{+3}R_3{}^{-4} + R_4{}^{+2}R_3{}^{-5}$
$\phi_5 = R_2{}^{+3}R_3{}^{-4} + R_2{}^{+2}R_3{}^{-5}$
$\phi_6 = R_3{}^{+3}R_2{}^{-4} + R_3{}^{+2}R_2{}^{-5}$
$\phi_7 = R_1{}^{+2}R_2{}^{-4} - R_1{}^{+3}R_2{}^{-5}$
$\phi_8 = R_1{}^{-4}R_2{}^{+2} - R_1{}^{-5}R_2{}^{+3}$
$\phi_9 = R_4{}^{-4}R_3{}^{+2} - R_4{}^{-5}R_3{}^{+3}$
$\phi_{10} = R_4{}^{+2}R_3{}^{-4} - R_4{}^{+3}R_3{}^{-5}$
$\phi_{11} = R_2{}^{+2}R_3{}^{-4} - R_2{}^{+3}R_3{}^{-5}$
$\phi_{12} = R_2{}^{-4}R_3{}^{+2} - R_2{}^{-5}R_3{}^{+3}$

---

(8) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.* (London), **A255**, 82 (1960).

(9) P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965).

Table II. Spectrum of Benzene

Band	Wave function	Symmetry	Frequency, cm^{-1}	Ref
α	$\frac{1}{\sqrt{2}}(\chi^{2-4} - \chi^{3-5})$	$^1B_{2u}$	38,000	10
p	$\frac{1}{\sqrt{2}}(\chi^{3-4} + \chi^{2-5})$	$^1B_{1u}$	48,000	
β,β'	$\frac{1}{\sqrt{2}}\left\{\begin{matrix}\chi^{2-4} + \chi^{3-5}\\ \chi^{3-4} - \chi^{2-5}\end{matrix}\right\}$	$^1E_{1u}$	54,500	
^3p	$\frac{1}{\sqrt{2}}(^3\chi^{3-4} + {^3\chi^{2-5}})$	$^3B_{1u}$	29,700	11
$^3\beta,{^3\beta'}$	$\frac{1}{\sqrt{2}}\left\{\begin{matrix}^3\chi^{2-4} + {^3\chi^{3-5}}\\ ^3\chi^{3-4} - {^3\chi^{2-5}}\end{matrix}\right\}$	$^3E_{1u}$	36,600	
$^3\alpha$	$\frac{1}{\sqrt{2}}(^3\chi^{2-4} - {^3\chi^{3-5}})$	$^3B_{2u}$	37,900	12

tions of molecular benzene here considered, and these, together with the transition energies, are shown in Table II. All the transition energies have been determined experimentally[11] with the exception of that of the $^3B_{2u}$ state. The estimated value, from Pariser,[12] is here used for this quantity.

Calculation of Transition Energies

It is now necessary to diagonalize the energy matrices for the various representations of the D_{6h} group (Table I). As we are here concerned only with transition energies, the diagonal elements are determined with reference to the repulsive ground state of the MLP. The diagonal matrix elements may be obtained from those used in the calculation of the transition energies of the benzene dimer. We now illustrate this by considering the ground state of the MLP. The Hamiltonian of the MLP is written

$$\mathcal{H} = \sum_{i=1}^{4}\mathcal{H}_i + \sum_{i>j} V_{ij} \tag{3}$$

where $\mathcal{H}_i$ is the Hamiltonian of monomer i, and V_{ij} contains all the interactions not included in $\mathcal{H}_i$ and $\mathcal{H}_j$. We consider only those interactions between adjacent monomers (*i.e.*, $V_{i,i+1}$). Next nearest neighbors are assumed to be separated by about 6 A, at which distances the interactions we consider are negligible. The ground-state energy now becomes

$$E_0^{\mathrm{MLP}} = E_0^1 + E_0^2 + E_0^3 + E_0^4 + \frac{\langle \mathcal{A}\phi_1^0\phi_2^0\phi_3^0\phi_4^0 | \sum_{i=1,3} V_{i,i+1} | \phi_1^0\phi_2^0\phi_3^0\phi_4^0\rangle}{\langle \mathcal{A}\phi_1^0\phi_2^0\phi_3^0\phi_4 | \phi_1^0\phi_2^0\phi_3^0\phi_4^0\rangle} \tag{4}$$

This expression may be derived by taking ϕ_i^0 to be an eigenfunction of $\mathcal{H}_i$ with eigenvalue E_0^i. We now take the repulsive ground-state energy of the MLP (the final term in eq 4) to be equal to three times that of the dimer. The calculation of the dimer ground-state energy has been outlined in part II[5b] of this work. Note that in making this assignment of the repulsive ground-state energy we have assumed the additivity of intermonomer forces. Further refinement to include the effect of nonadditivity is not considered of value in the semiquantitative computations reported here. The excited-state energies of the MLP may be similarly estimated. For example, we take

$$\frac{\langle \mathcal{A}\phi_1^0\phi_2^f\phi_3^0\phi_4^0 | \mathcal{H} | \phi_1^0\phi_2^f\phi_3^0\phi_4^0\rangle}{\langle \mathcal{A}\phi_1^0\phi_2^f\phi_3^0\phi_4^0 | \phi_1^0\phi_2^f\phi_3^0\phi_4^0\rangle} = E_0^1 + E_f^2 + E_0^3 + 2E_f^{\mathrm{D}} + E_0^{\mathrm{D}} + E_0^4 \tag{5}$$

where E_f^{D} is the interaction energy of a dimer when one monomer is in excited state f, and E_0^{D} is the dimer ground-state interaction energy. The energy of the ionic states may be similarly estimated, *e.g.*

$$\frac{\langle \mathcal{A}R_2^+R_3^- | \mathcal{H} | R_2^+R_3^-\rangle}{\langle \mathcal{A}R_2^+R_3^- | R_2^+R_3^-\rangle} = E_0^1 + \mathrm{IP} - \mathrm{EA} + E_0^4 + E_{+,-}^{\mathrm{D}} + E_{+,0}^{\mathrm{D}} + E_{-,0}^{\mathrm{D}} + E_0^2 + E_0^3 \tag{6}$$

where IP and EA are, respectively, the ionization potential and electron affinity of benzene, $E_{+,0}^{\mathrm{D}}$ and $E_{-,0}^{\mathrm{D}}$ are the interaction energy between a benzene ion and a neutral benzene molecule, and $E_{+,-}^{\mathrm{D}}$ is the interaction energy between two benzene ions.

We consider only those charge-transfer states where the positive and negative ions are adjacent to each other, as states where they are separated by 6 A yield small configuration interaction matrix elements with the neutral states. The off-diagonal matrix elements represent the interaction between neutral and ionic states. If we retain only those terms of order S (overlap), and consider only overlap between adjacent monomers (valid for small overlap), we may make the approximations

$$\langle \mathcal{A}\phi_1^0\phi_2^f\phi_3^0\phi_4^0 | \mathcal{H} | R_2^+R_3^-\rangle \simeq \langle \mathcal{A}\phi_2^f\phi_3^0 | \mathcal{H} | R_2^+R_3^-\rangle \tag{7}$$

and

$$\langle \mathcal{A}\phi_1^f\phi_2^0\phi_3^0\phi_4^0 | \mathcal{H} | R_2^+R_3^-\rangle \simeq 0 \tag{8}$$

These off-diagonal terms may be obtained from the corresponding dimer-neutral ion-pair interaction matrix elements. The evaluation of the matrix elements is straightforward, but somewhat lengthy. Their determination for both singlet and triplet dimer states has already been described in detail in parts I and II[5] of this investigation, and readers are referred to these publications where the relevant formulas are described. The orbital approximation is used to represent the monomer wave functions; *e.g.*

$$\phi_2^0 = |u_2(1)\bar{u}_2(2)u_3(3)\bar{u}_3(4)| \tag{9}$$

where u_i is the ith benzene molecular orbital, given in the LCAO approximation as

$$u_i = \sum_j C_{ji}\psi_j \tag{10}$$

Here ψ_j is a carbon $2p\pi$ atomic orbital and is taken in these calculations as the SCF 2p atomic orbital of the ^3P state of carbon. The intermolecular overlap of the π-electron clouds is included in a way consistent with the use of a core potential in the Goeppert–Mayer–Sklar representation. As the electrons in the lowest bonding molecular orbital of benzene are not involved in the excitations considered here, they are included in the specification of the core. This approximation is expected to affect the ground and excited states simi-

---

[10] J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 591 (1965).

[11] S. D. Colson and E. R. Bernstein, *J. Chem. Phys.*, **43**, 2661 (1965).

[12] R. Pariser, *ibid.*, **24**, 250 (1956).

Table III. Calculated Transition Energies of MLP and Benzene Dimer (cm^{-1})

	3.0 A		3.5 A	
Symmetry	MLP	Dimer	MLP	Dimer
$^1B_{1g}$	27,800	26,200	34,700	34,400
	21,000		32,300	
$^1B_{2u}$	22,600	29,500	32,800	36,000
	27,900		34,700	
$^1B_{2g}$	30,900	30,600	42,500	42,400
	22,600		38,500	
$^1B_{1u}$	23,500	31,900	38,700	42,600
	31,000		42,500	
$^1E_{1g}$	42,400	35,800	51,000	46,900
	28,800		44,200	
$^1E_{1u}$	35,600	46,200	47,800	53,400
	44,800		51,800	
$^3B_{2g}$	22,800	25,500	27,800	28,700

Table IV. Comparison of Absorption Spectra of [2.2]Paracyclophane and the Multilayered Paracyclophane[6]

Compound	Position of λ_{max}, cm^{-1} (log ϵ)			
[2.2]Paracyclophane	33,300 (2.31)	34,800 (2.38)	40,300 (3.53)	44,300 (4.2)
Multilayered paracyclophane	30,300 (2.65)	34,000 (3.45)	38,800 (3.84)	43,900 (4.3)

larly, and will thus tend to cancel when transition energies are calculated.

Results and Comparison with Experiment

Computations have been performed for the MLP of D_{6h} symmetry, the separation of all adjacent rings being taken as equal. The ring-to-ring distance in [2.2]paracyclophane is very close to 3 A, and, although the corresponding distance is unknown for the MLP, we will focus our attention on the results for separations of 3.0 and 3.5 A. As was found for the benzene dimer, the lowest triplet state is the $^3B_{2g}$ state of benzene ^{3}p parentage. In Table III are displayed the lowest triplet and singlet states of the MLP, for the irreducible representations of Table I. The corresponding values for the benzene dimer of D_{6h} symmetry are also shown for purposes of comparison. We first discuss the emission spectrum (Figure 2) of the MLP in relation to our calculations. The onset of the fluorescence and phosphorescence occurs at approximately 27,000 and 20,400 cm^{-1}, with maxima at 24,700 and 18,600 cm^{-1}. The first pair of values, corresponding approximately to the 0–0 transitions, are to be compared with the calculated values of Table III. In case of [2.2]paracyclophane, the onset of fluorescence and phosphorescence is at ~30,000 and ~25,000 cm^{-1}, with maxima at 27,700 and 21,200 cm^{-1}.[5,7] The emission of the MLP thus shows a further shift to the red from that exhibited by [2.2]paracyclophane. This is a reflection of the increased transannular interaction in the MLP, which may be regarded as a dimer of [2.2]-paracyclophane. In the case of the phosphorescence, the increased displacement to the red correlates well with the results of our calculations. For a separation of 3 A we predict the phosphorescence to occur at 22,800 cm^{-1}, a shift of 2700 cm^{-1} from the corresponding value calculated for the benzene dimer. These figures are to compared to the experimental values of 20,400 and 4600 cm^{-1}. Comparison of the predicted fluorescence with the observed fluorescence is not as good. We predict, compared with the fluorescence of [2.2]paracyclophane, a further shift to the red of 5200 cm^{-1}. The observed shift is 3000 cm^{-1}. As we noted in our study of [2.2]paracyclophane, the lowest singlet transition energy we calculate is lower than the observed fluorescence (21,000 cm^{-1} compared to an experimental value of 27,000 cm^{-1}). However, the results displayed in Table III show that the lowest singlet transition energy is more sensitive to interring separation than is the lowest triplet transition energy. Hence, our interpretation of the fluorescence will be more sensitive than that of the phosphorescence to the uncertainty in the interring separation of the MLP. The interpretation of the absorption spectra is rendered difficult for a number of reasons. The structureless solution spectra does not allow the position of the 0–0 transition to be located unambiguously, and furthermore, provide no information as to the polarization of the transitions. The singlet transition energies are seen to be very sensitive to interring separation, the values changing by 10,000 cm^{-1} when this separation is varied between 3.0 and 3.5 A. Hence, an uncertainty of only ±0.1 A in this value will prevent the prediction of transition energy to better than ±2000 cm^{-1}. For this reason, in the discussion of the absorption spectra of the MLP (details given in Table IV, taken from ref 6), we shall be primarily concerned with correlation between experimental and theoretical transition energies, and with the differences between the MLP and dimer. Table IV shows that all absorption bands of the MLP exhibit a shift to the red when compared to those of [2.2]paracyclophane, a qualitative feature also shown by our calculations (Table III), but the predicted shift at 3.0 A is greater than that found experimentally. Assignment of the bands is difficult owing to the greater number of predicted excited states in the MLP than in the dimer. The four lowest calculated states are separated by only 2500 cm^{-1}, and the MLP transition with ν_{max} 30,300 cm^{-1} may result from a superposition of these states. The second transition of the MLP, which shows a marked hyperchromic effect when compared to the corresponding dimer transition, may be interpreted in terms of the next four states (Table IV) separated by only 3000 cm^{-1}. The greater intensity of this transition is probably due to the B_{1u} member of this set, of benzene p-state parentage. The corresponding transition in [2.2]paracyclophane was assigned to the B_{2u} dimer state of benzene α-state parentage. The remaining two transitions, which are the most intense, may be assigned to the E_{1u} and E_{1g} states of benzene β,β' parentage.

Discussion

The increased transannular interaction in the MLP is reflected in the shift to the red of its emission and absorption spectra, when compared to those of [2.2]paracyclophane. Our calculations, based on the configuration interaction of neutral excited and charge-transfer states, predict this trend and, furthermore, provide an interpretation of the origin of the observed transitions. We have used a carbon SCF 2p atomic wave function which avoids the parameterization introduced by using a Slater orbital with arbitrary exponent. However, in the absence of SCF functions for aromatic molecules, the use of this atomic SCF function introduces an unavoidable approximation, the quantitative effect of which we are unable to assess.

Acknowledgments. We wish to thank Dr. D. T. Longone of the University of Michigan for a gift of MLP. We are indebted to Professor Joshua Jortner for helpful discussions. This research was supported by the Directorate of Chemical Sciences AFOSR and the U. S. Public Health Service. We have also benefited from the use of facilities provided by ARPA for materials research at the University of Chicago.

Nuclear Magnetic Resonance Study of the Rotational Equilibrium in Acryloyl Fluoride

D. F. Koster

Contribution from the Mellon Institute, Pittsburgh, Pennsylvania 15213.
Received June 29, 1966

Abstract: Solvent and temperature effects (+80 to −95°) on the nmr spectrum of acryloyl fluoride have been used to study the rotational equilibrium in this molecule. ΔH for an assumed *s-trans* to *s-cis* equilibrium is calculated to be 800 ± 250 cal/mole. The large uncertainty in ΔH arises mainly from the indeterminable value of ΔS. The data cannot exclude the possibility of a threefold barrier.

The rotation about the carbon–carbon single bond between sp^2–sp^2 hybridized carbon atoms gives rise to rotational isomers of varying stability. A variety of techniques, such as infrared,[1–3] Raman,[4] microwave,[5] and ultraviolet[6,7] spectroscopy have been used to study conformations in butadiene and substituted butadienes, while ultrasonic relaxation techniques[8] have been applied to the study of acrolein and several substituted acroleins. Nmr techniques, however, which have been extremely valuable in elucidating conformational equilibria in cyclohexane[9,10] and substituted ethanes,[11] have been only recently applied to problems of this type. Anet and Ahmad[12] have investigated benzaldehyde and several *para*-substituted benzaldehydes, and Dahlqvist and Forsén[13] have reported results for 2-furanaldehyde. We wish to report here the results for a similar study on the molecule acryloyl fluoride.

The equilibrium process in acryloyl fluoride is assumed to be between an *s-trans* and an *s-cis* form, although the data do not rule out a skew form in place of the *s-cis* one. The rotational barrier is evidently lower here than it is in the case of benzaldehyde[12] and 2-furanaldehyde,[13] and an averaged spectrum is observed over the temperature range +37 to −95°. Changes in the three-bond HF coupling constant (^3J_s), however, can be used to follow the equilibrium. A method similar to that used to study the internal rotation in substituted ethanes[11,14] allows one to deduce a value for ΔH, although inclusion of a ΔS term in the analysis introduces considerable uncertainty in the calculation of ΔH by this method. The chemical shifts are quite temperature and solvent dependent, an effect which is probably due to intermolecular attraction in the liquid.

I II

Experimental Section

Materials. The sample of acryloyl fluoride was prepared as described by Brügel.[15] The absence of stray nmr peaks and agreement with its reported boiling point (34.5° at 760 mm) was taken as a criterion of its purity.

Sample Preparation. The samples were vacuum degassed and sealed in 5-mm o.d. nmr tubes. Variable temperature studies were made on a sample containing approximately 50% fluorotrichloromethane as a solvent. Room temperature spectra were also analyzed for the pure compound and 5% solutions of the compound in the respective solvents fluorotrichloromethane, carbon disulfide, and acetonitrile. A trace of TMS was added to each sample as an internal reference.

Spectra. The proton spectra taken above −60° were recorded at 60 MHz on a Varian A-60 equipped with the V-6040 variable-temperature accessory. The temperature was calibrated against the methanol peaks separation before and after recording the spectrum. The spectra were sidebanded with a General Radio 1161-A frequency synthesizer, and the average of four separate spectra at each temperature was used in the calculations. A Varian DP-60, equipped with a variable-temperature probe, was used to record the 60-MHz proton spectrum at −95°. Temperature calibration

---

(1) J. G. Aston, G. J. Szasz, H. W. Woolley, and F. G. Breckwedde, *J. Chem. Phys.*, **14**, 67 (1946).

(2) G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953).

(3) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1964).

(4) K. W. F. Kohlrausch and H. Wittek, *Ber.*, **75**, 227 (1942).

(5) D. Lide, Jr., *J. Chem. Phys.*, 37, 2074 (1962).

(6) A. Roedig and R. Kloss, *Ann.*, **612**, 1 (1958).

(7) M. I. Batuev and A. D. Matveeva, *Zh. Obshch. Khim.*, **28**, 2903 (1958).

(8) M. S. de Groot and J. Lamb, *Proc. Roy. Soc.* (London), **A242**, 36 (1957).

(9) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964).

(10) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964).

(11) H. S. Gutowsky, *Pure Appl. Chem.*, 793 (1963).

(12) F. A. L. Anet and M. U. Ahmad, *J. Am. Chem. Soc.*, **86**, 119 (1964).

(13) K. Dahlqvist and S. Forsén, *J. Phys. Chem.*, **69**, 4062 (1965).

(14) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **37**, 1466 (1962).

(15) W. Brügel, *Z. Elektrochem.*, **64**, 1149 (1960).