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The Absorption Spectra of Diphenyl

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A LCAO—MO—SCF calculation including configuration interaction(CI) of all singly excited states was performed for diphenyl. The singlet and triplet electronic levels are given as a function of the angle of twist of the two benzene rings and the singlet and triplet (T—T) absorption spectra are discussed.

The electronic structure of diphenyl has been the subject of a large number of theoretical studies. Most of them attemped to correlate the electronic absorption spectrum with the angle between the planes of the two benzene rings[1]. On the other hand some authors[2] were concerned with the nature of the forces causing the observed nonplanarity of the molecule in the vapour phase (42^0) and in the liquid phase (18^0—23^0). These calculations, especially the recent ones showed excellent agreement with the vapour phase absorption spectrum, the T—T spectrum[3] and between the calculated and experimentally observed angle of twist in diphenyl. In view of these results a new calculation would not bring much improvement. We performed it for the following reasons: a) in the previous papers the best description of a single property was sought, so that either the singlet absorption spectrum, the T—T spectrum or the geometry of the molecule had been considered in detail; b) although most recent calculations were based on the SCF—MO—CI formalism to describe the absorption spectra, different authors used various approximations and modifications which make the direct comparison of their results rather difficult; and c) only limited sets of configurations have so far been used for the CI.

OUTLINE OF THE CALCULATION

As already said we used the SCF—MO—CI formalism of the Pariser — Paar and Pople method[4,5]. The semiempirical π-electron parameters in this calculation were

$$\beta_{CC} = -2.39 \text{ eV} \qquad W_C = -11.16 \text{ eV} \qquad \gamma_{CC} = 10.60 \text{ eV}$$

The electronic repulsion integrals have been calculated by the Nishimoto-Mataga approximation[6]. The non-coplanarity of the phenyl rings in the twisted diphenyl molecule has been taken into consideration by changing the resonance, β_{CC}, and repulsion, γ_{CC}, integrals for carbon atoms joining the rings. The procedure proposed by Streitwieser[7] in which these integrals are calculated using the following expressions

$$\beta_{CC} = \beta^{o}_{CC} \cos \vartheta \qquad \gamma_{CC} = \gamma^{o}_{CC} \cos^2 \vartheta$$

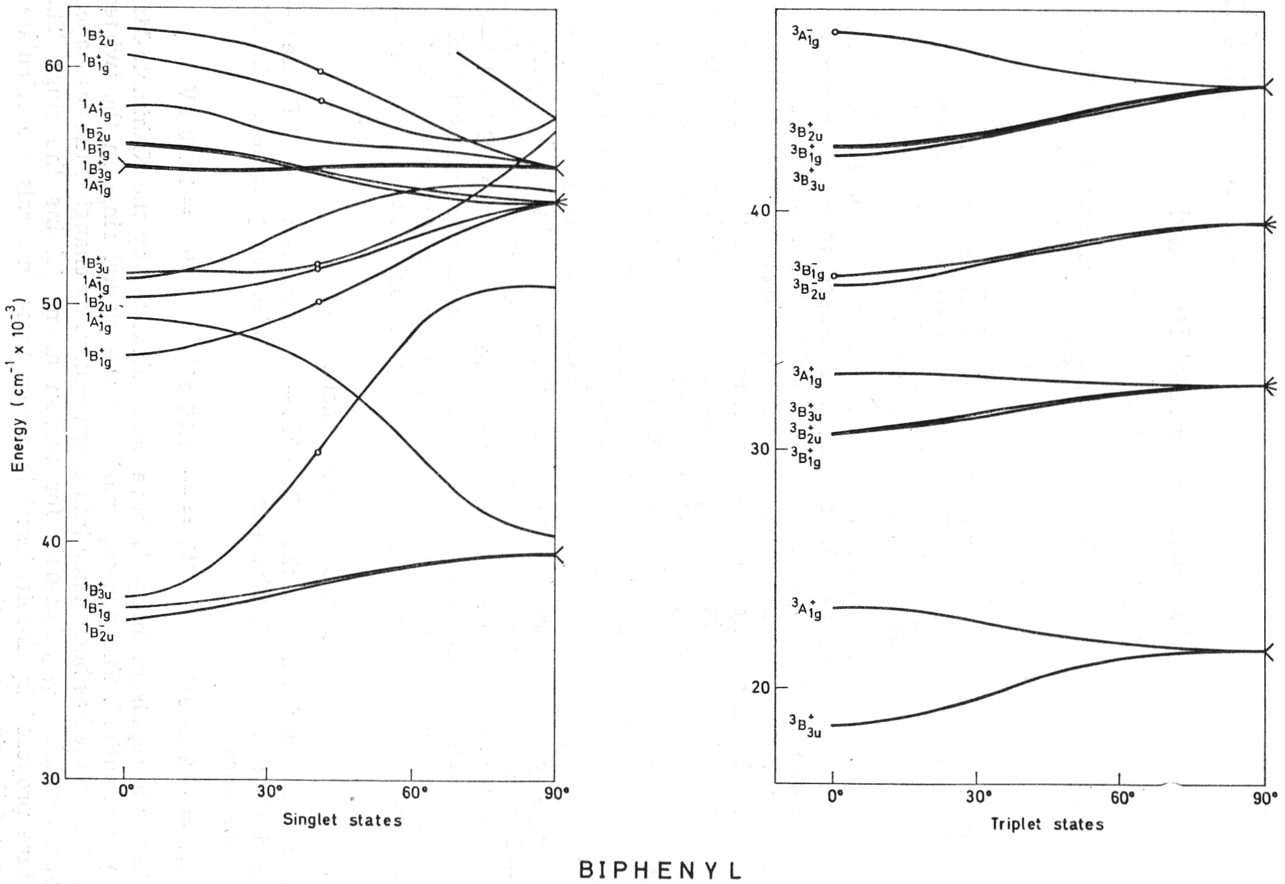

Fig. 1. CI energies of the electronically excited singlet and triplet states of diphenyl shown as a function of ϑ, the angle of twist. The state symmetries correspond to the planar molecule ($\vartheta = 0^0$). The circles indicate allowed transitions from the ground state and from the first triplet state at experimental angles of twist.

has been applied. Here β^{o}_{CC} and γ^{o}_{CC} are the values of the integrals for the planar molecule and ϑ the angle of twist. A complete calculation was performed for the following values of the angle $\vartheta = 0^0, 15^0, 30^0, 40^0, 42^0, 45^0, 55^0, 70^0, 85^0$ and 89.9^0. The iterative procedure in SCF calculations was maintained at a tolerance of 10^{-5}. Subsequently the CI calculations including *all* monoexcited configurations with respect to S_0 (*i. e.* 36 configurations) were carried out for the singlet and triplet states. The reported oscillator strengths for all transitions were evaluated from[8]

$$f_{mn} = 0.0875\,(E_m - E_n)\,|\,M_{mn}\,|^2$$

and the usual method was employed to obtain transition moments.

RESULTS AND DISCUSSION

The singlet and triplet excited state energies for various angles of twist are shown in Fig. 1. The assignment of the symmetry of the states given on the left of each diagram corresponds to the planar case ($\vartheta = 0^0$, point group D_{2h}). The circles indicate the allowed singlet transitions (from the ground state) and T—T transitions (from the lowest triplet state $^3B^+_{3u}$) for experimental angles of twist. As known from experimental facts the singlet spectrum in the gas phase must be assigned to the absorption of diphenyl twisted by 42^0, whereas the T—T spectrum of diphenyl measured in cooled solutions and glasses seems to be generated by the planar molecule. Fig. 1. shows that by rotation around the central bond great changes in the position of the excited singlet states *i. e.* in the singlet absorption spectrum occur, whereas the energy of the triplet states and consequently the T—T spectrum is not much influenced by the rotation. A comparison between the vapour phase absorption spectrum and the calculated transition energies and oscillator strengths for 42^0 of twist is shown in Fig. 2. In the singlet spectrum especially the longest wavelength transition $B^+_{3u} \leftarrow A^-_g$ is highly sensitive to changes in the geometry.

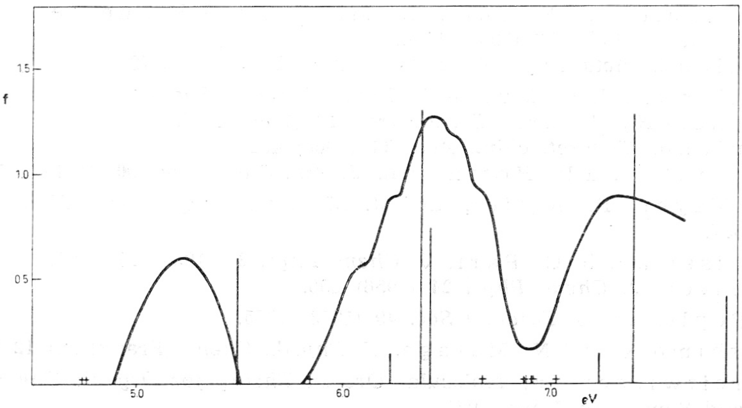

Fig. 2. Comparison of the observed (gas phase) and calculated (42^0 of twist) singlet absorption spectrum of diphenyl.
Abscissa: Energy in electron-volts
Ordinate: Oscillator strength f. Forbidden transitions are indicated as crosses. The observed spectrum is given arbitrary (log ε > 3)

From 30^0 to 60^0 the change in the energy of these transitions is nearly 1 eV and the adjustement of this band to the »*correct*« position can be achieved by a slight change in the parameters β_{CC} and γ_{CC} used in the calculation. Once the parameters are established the correlation between the energy of this band and the angle of twist makes possible prediction of ϑ in different diphenyl derivatives by comparing the calculated and observed absorption spectra[9].

The recently published T—T spectrum of diphenyl[3] indicated the presence of the sign-forbidden transitions to the $^3A_g^+$ states.Namely, in cooled alcoholic media a very weak structured absorption was observed in the region corresponding to a transition to the higher of the two $^3A_g^+$ levels in Fig. 1. Based on very extensive calculations including all monoexcited configurations with respect to the lowest triplet state in the CI these authors have concluded that a transition to $^3A_g^+$ is more probable than to the $^3B_g^+$ state since the corresponding alloved $^3B_g^-$ transition is already wery weak. Consequently, a weak transition to the lower $^3A_g^+$ state in Fig. 1. should be found in the infrared region.

Note added in proof:

We thank to one of the referees for drawing our attention to the recent paper on hindered rotation in diphenyl by Golebiewski and Parcewski, Z. *Naturforsch.* **25a** (1970) 1710., which contains an extensive literature survey on this subject. Our results concerning the singlet absorption spectrum agree with theirs.

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REFERENCES

1. J. N. Murrell, *J. Chem. Soc.* **1956** 3779.
   Y. Gondo, *J. Chem. Phys.* **41** (1964) 3928.
   R. Grinter, *Mol. Phys.* **11** (1966) 7.
   A. Golebiewski and A. Parcewski, *Theoret. chim. Acta* **7** (1967) 171.
   G. Hohlneicher, F. Dörr, N. Mika, and S. Schneider, *Ber. Bunsenges. physik. Chem.* **72** (1968) 1144.
   B. Tinland, *Acta Phys. Acad. Sci. Hung.* **25** (1968) 5379.
2. K. Miller and J. N. Murrell, *Trans. Faraday Soc.* **63** (1967) 806.
   I. Fischer-Hjalmars, *Tetrahedron* **19** (1963) 1805.
   B. Tinland, *Theoret. chim. Acta* **11** (1968) 452.
   A. Imamura and R. Hoffmann, *J. Am. Chem. Soc.* **90** (1968) 5379.
3. Y. H. Meyer, R. Astier, and J. M. Leclerq, *Chem. Phys. Letters* **4** (1970) 587.
4. R. Pariser and R. G. Parr, *J. Chem. Phys.* **21** (1953) 466, 767.
   R. Pariser, *J. Chem. Phys.* **24** (1956) 250.
5. J. A. Pople, *Trans. Faraday Soc.* **49** (1953) 1375.
6. K. Nishimoto and N. Mataga, *Z. Physik. Chem.* (Frankfurt) **12** (1957) 335.
7. A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists,* John Wiley and Sons, New York, 1961.
8. R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.* **8** (1941) 231.
9. B. Tinland, *J. Mol. Structure* **2** (1968) 391; **3** (1969) 516.
   B. Tinland, *Theoret. chim. Acta* **11** (1968) 385.

IZVOD

Apsorpcijski spektri difenila

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LCAO—MO—SCF računi uz konfiguracijsku interakciju svih monoekscitiranih stanja s obzirom na osnovno S_0 stanje difenila vršeni su u zavisnosti o međusobnom kutu benzenskih prstena u difenilu. Na osnovu dobivenih rezultata diskutiraju se apsorpcijski singlet i triplet-triplet spektri difenila.

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