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π-Electron Structures of Aromatic Hydrocarbons in Their Low-lying Triplet States

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Since Lewis *et al.*[1] found absorption bands due to transitions between the lowest and higher triplet states, many studies have been made in this field.[2] In addition to strong triplet-triplet transition bands measured at the initial stage of the study, weak low-energy bands were observed by Kellogg[3] and by other authors.[4] Polarization of these bands were investigated by El-Sayed and Pavlopoulos[5] and by others.[6] Thus, a considerable amount of T-T absorption data are now available for theoretical consideration.[7–10]

Theoretical studies of T-T transitions have been made by the composite method,[11] by the Pariser-Parr-Pople method,[12–14] and also by the open-shell SCF MO CI procedure.[15] The transition energies and oscillator strengths calculated so far agree less satisfactorily for the T-T transitions than for the singlet-singlet transitions. Furthermore, most of these theoretical studies are concerned with only a few strong absorption bands for each molecule.

In this paper, the SCF MO CI calculations based on the Pariser-Parr-Pople procedure[16] were applied to the T-T transitions of aromatic hydrocarbons by taking the stable geometrical structure of the lowest triplet state for each molecule and by considering weak T-T transition bands in addition to strong bands.

Method of Calculation

We employed the Pariser-Parr-Pople SCF MO CI procedure,[16] taking all the singly excited configurations for benzene and naphthalene and taking the lower 40 singly excited configurations for each symmetry for anthracene, pyrene, chrysene, and coronene. The penetration integrals were disregarded. The core resonance integral (β) was taken to be proportional to the overlap integral, the value at the equilibrium C-C bond distance of benzene, $\beta_0 = -2.39$ eV, being taken as the standard. Two-center Coulomb repulsion integrals were estimated by the Nishimoto-Mataga approximation.[17] One-center Coulomb integrals and orbital exponents were determined by using the method described by Iwata and Shida.[18]

The results of X-ray crystal analysis experiments[19] of naphthalene, anthracene, pyrene, chrysene, and coronene were used at the first stage of the calculation, and thereafter the geometrical configurations of the lowest triplet states were estimated by using the standdar bond order-bond length relation.[20] The bond lengths used for the final calculation are shown in Fig. 1.[2] The calculations were performed with a FACOM 270-30 computer. Weaker bands ($\varepsilon_{\max} \sim 10^2$) in the longer wavelength region can be assigned to symmetry forbidden or parity forbidden transitions. The calculated transitions forbidden from both symmetry and parity are disregarded.

All the calculated transition energies were found to be larger by $\sim 2000\ \text{cm}^{-1}$ than the corresponding observed values. Therefore, we reduced all the calculated T-T transition energies by $2000\ \text{cm}^{-1}$. A similar correction was made by Orloff.[12]

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1) G. N. Lewis, D. Lipkin, and T. J. Magel, *J. Amer. Chem. Soc.*, **63**, 3005 (1941).

2) D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951); D. P. Craig and I. G. Ross, *J. Chem. Soc.*, **1954**, 1589; G, Porter and M. W. Windsor, *Proc. Roy. Soc.* (London), **A 245**, 238 (1958).

3) R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

4) M. W. Windsor and J. R. Novak, "The Triplet State," ed. by A. B. Zahlan, Cambridge University Press, London (1967), p. 229; R. Astier and Y. H. Meyer, *ibid.*, p. 447; R. Astier, A. Bokobza, and Y. H. Meyer, *J. Chem. Phys.*, **51**, 5174 (1969).

5) M. A. El-Sayed and T. Pavlopoulos, *ibid.*, **39**, 834 (1963).

6) J. B. Gallivan and J. S. Brinen, *ibid.*, **50**, 1590 (1969); T. G. Pavlopoulos, *ibid.*, **52**, 3307 (1970); J. Langelaar, J. Wegdam-Van Beck, J. D. W. Van Voorst, and D. Lavalette, *Chem. Phys., Lett.*, **6**, 460 (1970).

7) J. S. Brinen, *J. Chem. Phys.*, **49**, 586 (1968).

8) W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969).

9) T. M. Naumova and V. I. Glyadkovskii, *Opt. Spectrosk.*, **27**, 228 (1969).

10) T. Takemura, K. Hara, and H. Baba, This Bulletin, **44**, 977 (1971).

11) K. Kimura, *Mol. Phys.*, **15**, 109 (1968).

12) M. K. Orloff, *J. Chem. Phys.*, **47**, 235 (1967).

13) P. L. DeGroot and G. J. Hoytink, *ibdi.*, **46**, 4523 (1967).

14) J. Pancir and R. Zahradnik, *Theoret. Chim. Acta*, **14**, 426 (1969); D. Lavalette, C. Tetreau, and J. Langelaar, *Chem. Phys. Lett.*, **9**, 319 (1971).

15) L. Goodman and J. R. Hoyland, *J. Chem. Phys.*, **39**, 1068 (1963).

16) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953); J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 81 (1955).

17) K. Nishimoto and N. Mataga, *Z. Phis. Chem.* (*N.F.*), **12**, 335 (1957).

18) S. Iwata and T. Shida, to be published. According to this method, the valence state ionization energy for the carbon 2pπ orbital electron was evaluated to be 11.18 eV.

19) "Interatomic Distances," Sp. Pub. No. 11, ed. by L. E. Sutton, The Chem. Soc., London, (1958); *ibid.*, No. 18 (1965).

20) M. J. S. Dewar, H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959). The spectroscopic study made by Nieman and Tinti (G. C. Nieman and D. S. Tinti, *J. Chem. Phys.*, **46**, 1432 (1967)) with benzene in a C_6D_6 host crystal at 4.2 K shows a small distortion from a hexagonal shape arised either from extrinsic or intrinsic perturbations. This small distortion is disregarded in the present study.

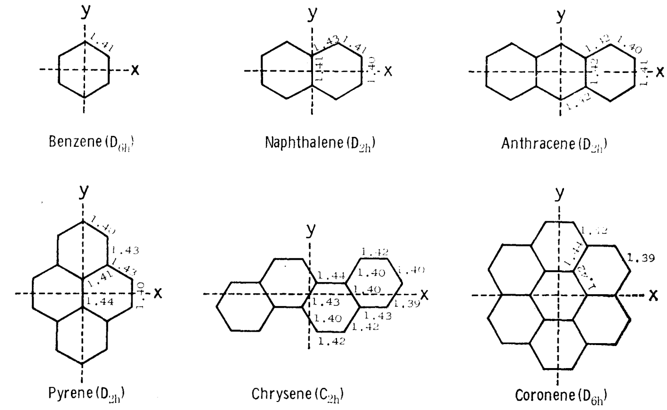

Fig. 1. The geometrical structures used for the present calculation.

Results and Discussion

The $^3E_{2g}^- \leftarrow {}^3B_{1u}^+$ transition energy, 41000 cm^{-1}, calculated for benzene agrees well with the observed band position, 40800 cm^{-1}.[9] The T-T transition energies of naphthalene were calculated to be 20600, 25200, 31100, 39100, and 47000 cm^{-1} for the transitions from the lowest triplet ($^3B_{2u}^+$) state to the $^3A_g^-$, $^3B_{1g}^-$, $^3A_g^-$, $^3B_{1g}^-$, and $^3B_{1g}^-$ states, respectively, the oscillator strengths and the directions of transition moments (in parentheses) being 0.063 (y), 0.48 (x), 0.39 (y), 0.007 (x), and 0.92 (x), respectively. Four bands were observed for naphthalene at ~20000 cm^{-1}, ~25000 cm^{-1}, 29300 cm^{-1}, and 38500 cm^{-1}.[2,4] The calculated values agree well with the observed transition energies for the four longer wavelength bands. Furthermore, the oscillator strength and the direction of the transition moment calculated for the second longest wavelength band agree well with the observed results (f=0.32, x-polarized).[5]

The four T-T absorption bands were observed for anthracene at ~12000 (f=0.0017), ~20000 (f=0.038), ~24000 (f=0.68, x-polarized[5]), and 35700 cm^{-1}.[2,4] The calculated transition energies are 11900, 21000, 23600, and 35700 cm^{-1} for the transitions from the lowest triplet ($^3B_{2u}^+$) state to the $^3A_g^+$, $^3A_g^-$, $^3B_{1g}^-$, and $^3A_g^-$ states, respectively, the oscillator strengths and the directions of transition moments (in parentheses) being calculated to be 0.00, 0.061 (y), 0.80 (x), and 0.37 (y), respectively. The calculated results agree well with the observed ones obtained so far.

The transition energies and oscillator strengths observed and calculated for pyrene are shown in Table 1, together with the band assignment.

The T-T absorption bands were observed for chrysene at ~12000 (f=0.003), 17200 (f=0.40), 24900 (f=0.016), 35200 (f=0.32), and 39500 (f=0.65) cm^{-1}.[4,9] The calculated transition energies are 11900, 17400, 25600, 35400, and 37900 cm^{-1} with the calculated oscillator strengths of 0.007, 0.76, 0.021, 0.26, and 0.37, respectively. The second longest wavelength band was found experimentally to be polarized almost parallel with the L_a band,[6] in good agreement with the theoretical prediction. The five observed bands can be assigned to the $^3A_g^- \leftarrow {}^3B_u^+$ transitions.

Table 1. The observed and calculated transition energies, ΔE's (in the units of 10^3 cm^{-1}), oscillator strengths, f's, directions of polarization, and the assignments of the T–T absorption spectrum of pyrene

Observed			Calculated			
ΔE	f	Polarization[6]	ΔE	f	Polarization	Assignments
11[4]	0.0005		12.5	0		$^3B_{3u}^- \leftarrow {}^3B_{2u}^+$
13.2[4]	0.002		14.0	0		$^3B_{3u}^- \leftarrow {}^3B_{2u}^+$
16.7[4]	0.008		18.3	0		$^3B_{1g}^+ \leftarrow {}^3B_{2u}^+$
~20[4]	0.022	x	21.6	0.051	x	$^3B_{1g}^- \leftarrow {}^3B_{2u}^+$
22.2[6]			23.1	0		$^3A_g^+ \leftarrow {}^3B_{2u}^+$
			24.6	0		$^3B_{3u}^- \leftarrow {}^3B_{2u}^+$
~25[4]	0.48	y	26.7	0.84	y	$^3A_g^- \leftarrow {}^3B_{2u}^+$
27.8[8]	0.03		28.6	0		$^3B_{1g}^+ \leftarrow {}^3B_{2u}^+$
~31[8]	0.08		33.1	0.044	x	$^3B_{1g}^- \leftarrow {}^3B_{2n}^+$
34.4[8]	0.16		35.9	0.24	y	$^3A_g^- \leftarrow {}^3B_{2u}^+$
38.6[8]	0.13		40.1	0.30	x	$^3B_{1g}^- \leftarrow {}^3B_{2u}^+$

Four bands were observed for coronene at ~10000, ~16000, 20800, and ~25000 cm^{-1} with the oscillator strengths of 0.0005, 0.08, 0.16, and 0.12, respectively.[7,21] The longest wavelength band is assigned to the parity forbidden transition (ΔE=7900 cm^{-1}, $^3E_{2g}^+ \leftarrow {}^3B_{1u}^+$). The higher transition energies were calculated to be 12600, 20800, and 25900 cm^{-1} with the oscillator strengths of 0.06, 0.41, and 0.22, respectively. These three bands can be assigned to the $^3E_{2g}^- \leftarrow {}^3B_{1u}^+$ transitions.

One of the characteristics of our calculation is to adopt the stable geometrical configuration of the lowest triplet state in which the bonds are generally elongated compared with those of the structure in the ground state. This reduces the $|\beta|$ values to some extent and brings about a narrowing of the energy separation between the higher and lower transition energies for each of the aromatic hydrocarbon molecules.[22] This is a reason why the present calculation can explain quantitatively the observed peak positions over wide wavelength region. Our assignments are different from those by Orloff[12] in some points; for example, we assigned the 38500 cm^{-1} band of naphthalene to the $^3B_{1g}^- \leftarrow {}^3B_{2u}^+$ transition and the 35700 cm^{-1} band of anthracene to the $^3A_g^- \leftarrow {}^3B_{2u}^+$ transition, while Orloff assigned both bands to the $^3B_{3g}^+ \leftarrow {}^3B_{2u}^+$ transition. Our assignmens give better agreements between the observed and theoretical results concerning both transition energies and absorption intensities. Furthermore, in view of the fact that we are concerned with greater number of observed bands (including weak ones) for each molecule, our assignments are more reasonable than those by Orloff.[12]

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[21] Unpublished results by Windsor and Novak; private communication to one of the authors (S.N.) from Dr. Windsor, to whom the authors' thanks are due.

[22] For example, the transition energies calculated for naphthalene by the use of the ground state geometry are 19400, 26200, 31900, 40700, and 50100 cm^{-1}; the corresponding value obtained by the use of the excited state geometry being 20600, 25200, 31100, 39100, and 47000 cm^{-1}.