

IV. ELECTRON MAGNETIC RESONANCE*

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A. TRIPLET-TRIPLET ABSORPTION OF BIPHENYL-LIKE MOLECULES

The magnetic energy levels at zero external field of the $S = 1$ excited state of a series of hydrocarbons consisting of two phenyl (benzene) rings with the angles $\theta_d \approx 20^\circ$, 52° , 81° , 90° in between were examined in a previous report.¹ The result indicated that the zero-field splittings, ZFS, behave as functions of θ_d , and hence the trend of such behavior is predictable from an approximate theory.² In the present report we present the results of measurement by the flash spectroscopic method of the electronic-vibrational (vibronic) energy separation between the lowest and the next lowest triplet states, $\left| E_{|T_{kr}^{II}\rangle} - E_{|T_{kr}^I\rangle} \right|$, for the same series of molecules. The results are compared with the expectation values obtained by using the Pariser-Parr approximation.³ The computed θ_d dependence of vibronic energy separation is in good agreement with experiment. The measurements were done in both liquid and semirigid (glass) phases. The molecules that were studied and the schematic representation of the energy levels are indicated in Fig. IV-1.

1. Computation of Triplet \leftarrow Triplet Transition Energies

a. Zero-Differential Overlap Assumption

For the computation of the triplet \leftarrow triplet transition energies the Pariser-Parr modifications⁴ of Goeppert-Mayer-Sklar⁵ ASMO-CI (antisymmetrized molecular orbitals with configuration interactions) are used.

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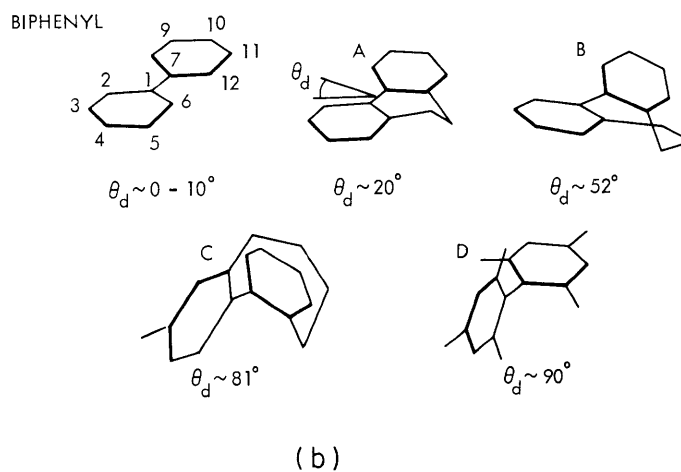
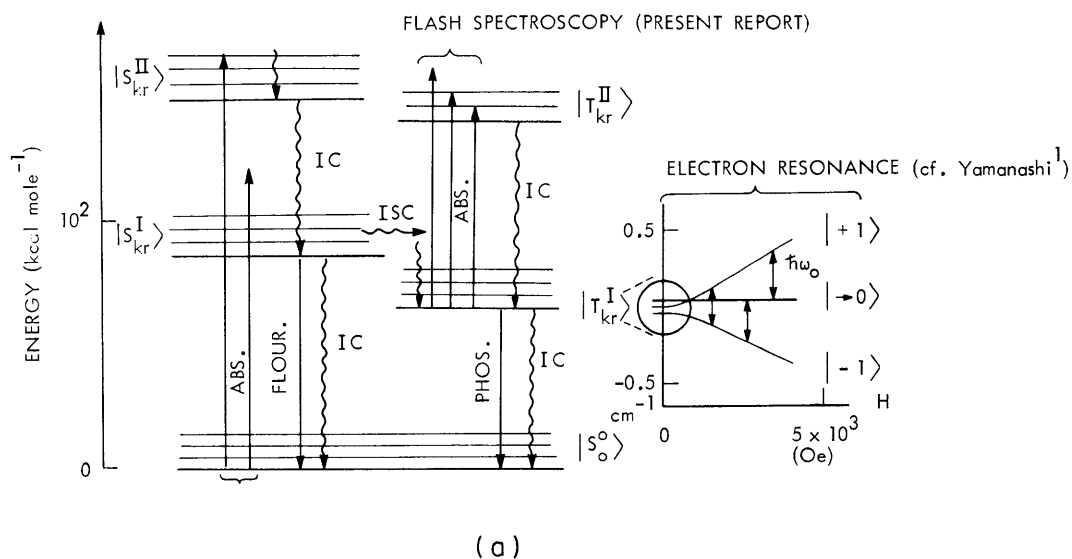


Fig. IV-1. (a) Schematic diagram of the vibronic (left) and the magnetic energy levels of biphenyl.

Abs. = absorption of photon(s)

Fluor. = fluorescence

Phos. = phosphorescence

IC = internal conversion

ISC = intersystem crossing

$|T_{kr}^I\rangle$ = first triplet electronic manifold resulting from electron promotion of the type $k \rightarrow r$

$|S_{kr}^I\rangle$ = first singlet electronic manifold resulting from electron promotion of the type $k \rightarrow r$

$|S_0^O\rangle$ = ground state

$|+1\rangle, |0\rangle, |-1\rangle$ = electronic spin eigenstate in an external magnetic field.

(b) Molecules with twist angle θ_d for which $|T_{kr}^{II}\rangle \leftarrow |T_{kr}^I\rangle$ transitions are examined.

Let LCAO-MO (linear combination of atomic orbitals) be represented as

$$|\psi_k\rangle = \sum_p C_{kp} \chi_p, \quad (1)$$

where subscript k labels the MO, and p runs over the AO. The triplet electrons i and j are "viewed" as "sitting" on the core consisting of the paired electrons and nuclei. Thus the Hamiltonian takes the form

$$\mathcal{H} = \sum_i \mathcal{H}_i^{\text{core}} + 2^{-1} \sum_i \sum_{j \neq i} \frac{e^2}{r_{ij}}, \quad (2)$$

where r_{ij} is the separation between electrons i and j . For the interactions between these two electrons matrix elements of the following general form must be considered. In the short notation, they are

$$[kr|df] = \langle \psi_f(i) \psi_k(j) | \sum_i \sum_{j \neq i} \frac{e^2}{r_{ij}} | \psi_r(i) \psi_d(j) \rangle, \quad (3)$$

where k, r, d, f label the MO.

Substitution of (1) in (3) yields

$$[kr|df] = \sum_p \sum_m \sum_q \sum_n C_{kp} C_{rm} C_{dq} C_{fm} (pm|qn), \quad (4)$$

where

$$(pm|qn) = \langle \chi_p(i) \chi_n(j) | \frac{e^2}{r_{ij}} | \chi_m(i) \chi_q(j) \rangle, \quad (5)$$

and p, m, q, n are different AO. Here we may consider the matrix element (5) as the energy of interaction between two charge distributions $e\chi_p^* \chi_m$ and $e\chi_q \chi_n^*$. The Pariser-Parr assumption is

$$\chi_p^* \chi_m = 0 \quad \text{if } p \neq m, \quad (6)$$

where the star indicates the complex conjugates in an alternant hydrocarbon. Equation 6 is equivalent to saying that repulsions between electrons are described by the properties of just two of the atomic centers and that differences caused by small changes in the bondings of the atoms can be neglected. With this assumption (5) transforms to

$$(pm|qn) = \delta_{pm} \delta_{qn} (pp|qq) \equiv \delta_{pm} \delta_{qn} X_{pq} \quad (7)$$

(see Fig. IV-3).

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Substitution of (7) in (4) gives

$$[kr|df] = \sum_p \sum_q C_{kp} C_{rq} C_{dq} C_{fq} X_{pq}. \quad (8)$$

Specific types used in the evaluation of triplet-triplet energy level separation are the Coulomb repulsion integral J_{kr} and the exchange integral K_{kr} . Using (8), we may define these integrals as

$$\left. \begin{aligned} J_{kr} &\equiv [kk|rr] = \sum_p \sum_q C_{kp} C_{kq} C_{rq} C_{rq} X_{pq} \\ K_{kr} &\equiv [kr|kr] = \sum_p \sum_q C_{kp} C_{rq} C_{kq} C_{rq} X_{pq} \end{aligned} \right\}. \quad (9)$$

X_{pq} has been determined for the carbon atom as a function of internuclear separation R_{pq} . For R_{pq} greater than 2.8 Å,

$$X_{pq} = (7.1975/R_{pq}) \left[1 + \left(1 + 2.0007/R_{pq}^2 \right)^{-1/2} \right] \text{ eV}. \quad (10)$$

For R_{pq} less than 2.8 Å

$$X_{pq} = 10.53 - 2.625R_{pq} + 0.2157R_{pq}^2 \text{ eV}, \quad (11)$$

where in the specific case of biphenyl-like molecules⁶ with the twist angle θ_d , when p and q atoms are on different phenyl rings, R_{pq} is a function of θ_d with the relations

$$R_{pq}(\theta_d) = \left[\left\{ R_{pq}(\theta_d=0^\circ) \pm 5.8 \sin^2(\theta_d/2) \right\}^{1/2} \right],$$

with "+" for p = 2 or 3 and q = 8 or 9, and "-" for p = 2 or 3 and q = 11 or 12.

$$R_{pq}(\theta_d) = R_{pq}(\theta_d=0^\circ)$$

for p, q with any other assignment than those above. (See Fig. IV-1b for the numerical assignment of p and q for each atomic position.)

The resonance terms β_{pq} for carbon have been given as a function of R_{pq} as follows

$$\beta_{pq} = -6442 \exp(-5.6864R_{pq}) \text{ eV}. \quad (12)$$

Reasonably accurate values of C_{ij} can be readily obtained by simple HMO calculations. If more accuracy is desired, other methods such as extended HMO-SCF (Hückel molecular orbital with self-consistent field) could be employed.

b. Triplet Transition Energies in Alternant Hydrocarbons

By the use of pairing theorems and some algebra it can be shown⁷ that

$$E_{T_{kr}^N} - E_{S_o^O} = E_{T_{rk}^N} - E_{S_o^O} = \mathcal{H}_r + \mathcal{H}_k - J_{kr}, \quad (13)$$

where

$$\mathcal{H}_k \equiv W_{-k}(-\beta) + \sum_f K_{f,k}^{(d)} \quad (14)$$

and

$$\sum_f K_{f,k}^{(d)} = 2^{-1} \sum_p \sum_q P_{pq} C_{kp} C_{rq} X_{pq}^{(d)}. \quad (15)$$

Here, $E_{T_{kr}^N}$ is the energy of the $|T_{kr}^N\rangle$ state (N, M refer to different electronic manifolds) resulting from the promotion of an electron from the orbital k to the orbital r . $E_{S_o^O}$ is the energy of the ground state, $W_{-k}(-\beta)$ refers to the eigenvalues of the Hückel approximation, P_{pq} is the bond order for the p - q bond defined as

$$P_{pq} \equiv \sum_m n_m C_{mp} C_{mq}. \quad (16)$$

When m is summed over all occupied orbitals and n_m is the number of electrons in the m^{th} orbital (16) is simply

$$P_{pq} = \delta_{pq}. \quad (17)$$

In (14) and (15) "(d)" means that summations are taken only over those combinations of p and q such that atoms p and q belong to different pairing sets. Then it follows from the perturbation argument that

$$E_{T_{kr}^{M-}} - E_{T_{kr}^{N+}} = 2K_{kr}. \quad (18)$$

Table IV-1. Triplet transition energies in $\left\{ \begin{array}{l} \text{eV and} \\ (\text{cm}^{-1}) \end{array} \right\}$.

θ_d	$\Delta^2 = \Delta^3$	Δ^4	$K_{12} = K_{13}$	K_{14}	$\Delta E'$
10°	0.5004 (4030)	3.2295 (26,800)	0.2327* (1877)	0.6619 (5335)	3.1535 (25,400)
30°	0.6180 (4980)	3.5784 (28,800)	0.1653* (1333)	0.1654 (13,030)	3.3168 (26,700)
50°	†	3.4397 (27,700)	0.1476* (1190)	1.7066 (13,740)	4.3585 (35,200)
60°	†	3.3818 (27,300)	0.1371* (1106)	2.4387 (19,630)	4.7430 (38,200)
70°	†	3.3996 (27,400)	0.1266* (1040)	2.8013 (22,630)	5.2888 (42,600)
80°	0.0389 (312)	3.4409 (27,700)	0.1175* (947)	3.1788 (25,400)	3.5596 (28,700)
85°	†	3.2886 (26,500)	0.1140 (918)	3.3615 (27,100)	6.6647 (53,700)
symbol	●	▲	×	□	○

$$\begin{aligned} \Delta^r &\equiv E_{T_{1r}^{II}} - E_{T_{1r}^I} = K_{1r} - \beta(W_{-r} - W_{-1}) + (J_{11} - J_{1r}) + \left(\sum_f K_{fr} - \sum_f K_{f1} \right) \\ &= K_{1r} - \beta \Delta W_{r \rightarrow 1} + \Delta J_{r \rightarrow 1} + \Delta \sum_f K_{fr \rightarrow 1}. \end{aligned}$$

$$K_{kr} \equiv [kr|kr] = \sum_p \sum_q C_{kp} C_{rq} C_{kq} X_{pq} \text{ (cf. (10) and (11)).}$$

$$\Delta E' \equiv E_{T_{14}^{II}} - E_{T_{14}^I} = \Delta^4 - \Delta^2 + 2K_{12}.$$

† = No possible transitions, since the transition has negative energy.

* = Average of the K_{ij} .

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Equation 18 allows one to calculate the energy levels of all of the triplet states $|T_{kR}^{M\pm}\rangle$, and hence the energies of triplet-triplet transitions. Selection rules for electronic transitions are the following.

- (i) Only transitions of the type $|T^{M+}\rangle \longleftrightarrow |T^{N-}\rangle$ are allowed.
- (ii) The ground state $|S_0^O\rangle$ acts as a minus state; $|T_{kk}^N\rangle$ acts as a plus state.
- (iii) No configuration interaction occurs between plus and minus states.

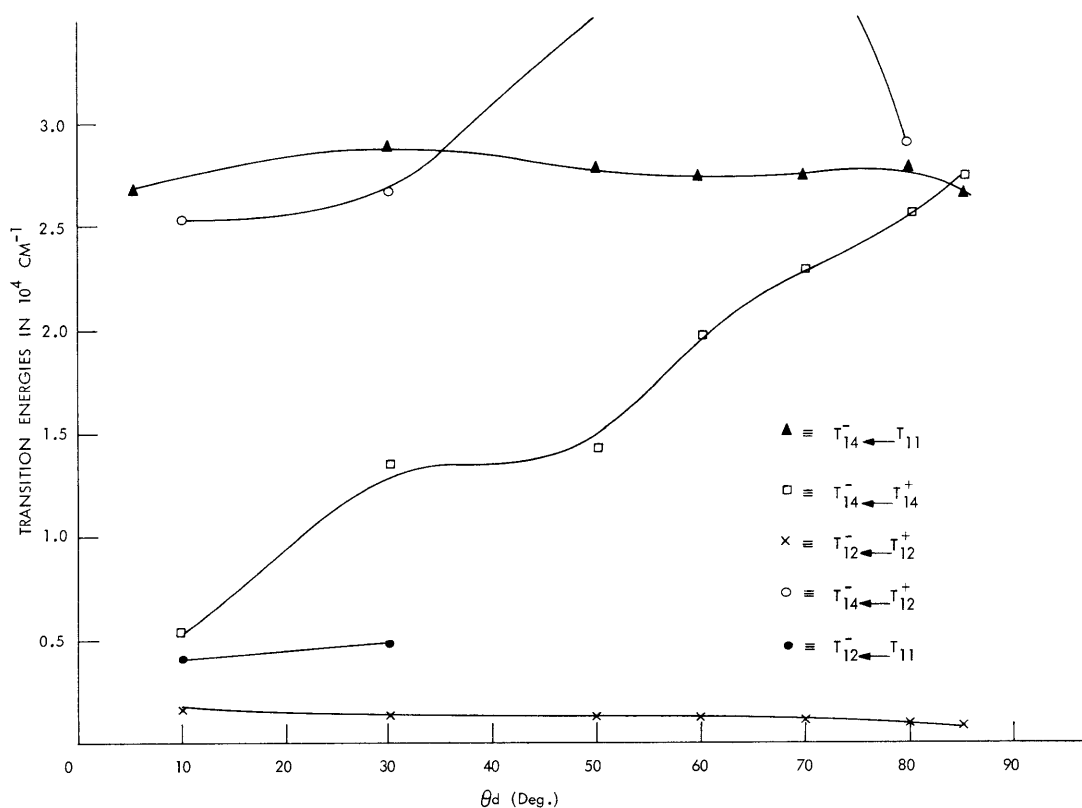


Fig. IV-2. Comparison of possible transition energies as functions of the twist angle θ_d . Note that the ▲'s ($T_{14}^- \leftarrow T_{11}$ transition) correspond well with Δ 's and \diamond 's in the experimental plots of Fig. IV-5.

The result of the computations for biphenyl, compounds A, B, C, D are indicated in Table IV-1, and Fig. IV-2. A plot of the Pariser-Parr ($pp|qq$) against R_{pq} is shown in Fig. IV-3.

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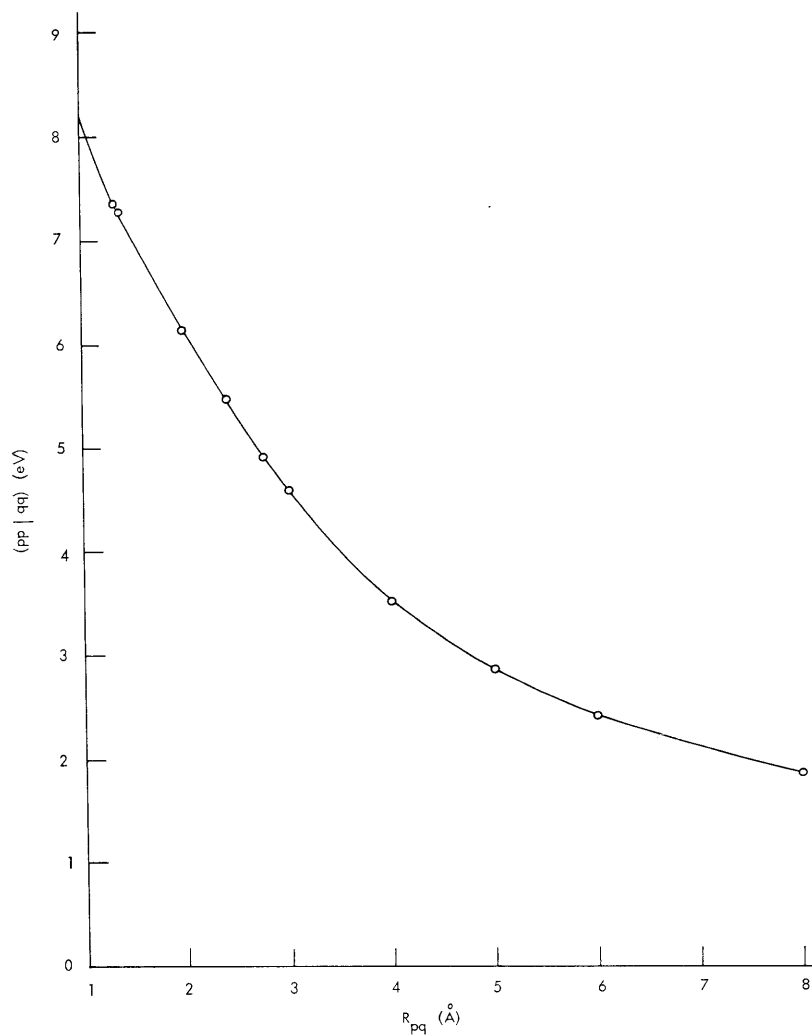


Fig. IV-3. Pariser-Parr values for $(pp|qq)$.

2. Experiment

a. Apparatus

The apparatus is diagrammatically indicated in Fig. IV-4. The special feature of this apparatus is that it allows the sample to form a glass in the reaction cell so that we can take spectra of the sample both in solution and in glass. All other parts are similar to those of Porter et al.

b. Settings

The photoflash was typically charged to 5 kV at 75 μ F; the spectroscopic flash was used at 2.5 kV at 4 μ F. Kodak XXX film was used in segments of appropriate length for

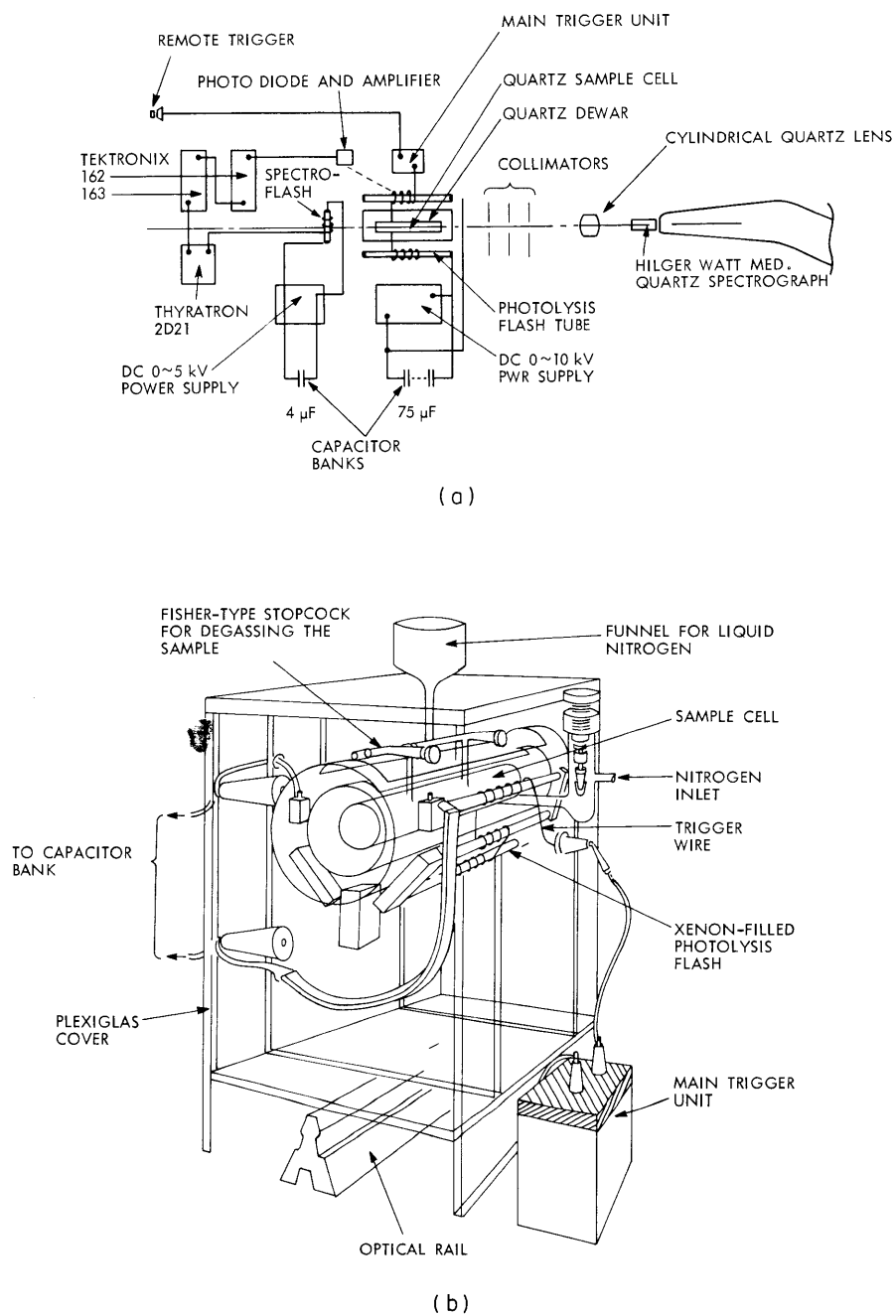


Fig. IV-4. (a) Diagram of the flash spectrographic apparatus for studying vibronically excited molecules. (b) Detail of the photolysis cell unit.

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the Hilger and Watts medium quartz spectrograph. Each film strip was utilized for 5 spectra made by three to five exposures. The spectrographic flash was set to delay the photolysis flash by 10^{-6} sec. D-76 developer and standard fixer were used.

c. Samples

The samples were biphenyl, A \equiv 9,10-dihydrophenanthrene, B \equiv 1,2,3,4-dibenz-1,3-cycloheptadiene-6-one, C \equiv 1,2,3,4-dibenz-1,3-cyclo-octadiene-6-one, D \equiv bimesityl. All but one (methyl cyclohexane is used for B in the liquid phase) of the samples were flashed in EPA in both liquid and glass phases. The concentrations of all samples were 0.001 M, except for the compound C which was diluted to 5×10^{-5} M because of its scarcity.

d. Recording of Spectra

The spectra on film, developed and fixed, were read by precalibrated microdensitometer. Xenon emission lines were subtracted from the spectra. The correlation of specific lines for different samples were made by combined criteria of (i) wavelength region, (ii) intensity and (iii) comparison of liquid and glass phase spectra. The experimental results are exhibited in Table IV-2 and Fig. IV-5.

3. Discussion of Results

Comparing the computational results, in Table IV-1 and Fig. IV-2, with the experimental results in Table IV-2 and Fig. IV-5, we first notice the marked resemblance of the computational Δ^4 (with symbol \blacktriangle) as a function of θ_d and the experimental absorption peaks occurring in the 4200 ~ 4300 Å region (marked by Δ) recorded for compounds with different θ_d (biphenyl, A, B, C, and D). The agreement in both the general trend and the energy values implies that for this particular transition the assumption $\chi_p^* \chi_m = 0$ for $p \neq m$ is not unreasonable, and we can tentatively assign the transition to the type $|T_{14}^{II-} - T_{11}^I\rangle$.

The change in the general behavior of the transition occurring in the 4800 ~ 5100 Å region (marked by \square) with respect to θ_d , when the temperature of the liquid samples was lowered to 77°K to form a glassy solution, is indicative of dissimilar vibronic eigenstates in the same electronic manifold arising from the change in the mode of vibration in the two different phases.

In this experiment the absorption reported by Porter and Windsor at $27,130 \text{ cm}^{-1}$ was not observed. This is probably due to the weakness of intensity of the particular flash tubes that were used.

Table IV-2a. Comparison of triplet' ← triplet absorption peaks in liquid.

Compound	Biphenyl	A	B	C	D
θ_d	0 ~ 10°	20°	52°	81°	90°
	~7200 (1.39)	~7300 (1.37)	~7450 (1.34)	~7850 (1.27)	—
	5590 (1.79)	5670 (1.76)	—	—	5790 (1.73)
□	4800 (2.08)	4800 (2.08)	4690 (2.14)	5030 (1.91)	—
	4340 (2.30)	4540 (2.20)	—	—	4570 (2.19)
△	4230 (2.36)	4200 (2.38)	4250 (2.36)	4300 (2.32)	4280 (2.34)
◇	4030 (2.48)	4120 (2.43)	4070 (2.46)	4170 (2.40)	4120 (2.43)

Top values in Å; values in parentheses in 10^4 cm^{-1} . □, △, ◇ are peaks plotted against θ_d in Fig. IV-5a; other peaks are not plotted.

Table IV-2b. Comparison of triplet' ← triplet absorption peaks in EPA glass.

Compound	Biphenyl	A	B	C	D
θ_d	0 ~ 10°	20°	52°	81°	90°
	~3500 (1.36)	—	~7200 (1.39)	~7350 (1.36)	—
	5700 (1.75)	5750 (1.74)	—	—	5790 (1.73)
□	5130 (1.95)	4910 (2.04)	4910 (2.04)	4990 (2.00)	—
	4510 (2.22)	4750 (2.10)	—	—	4580 (2.18)
△	4360 (2.30)	4250 (2.35)	4310 (2.32)	4400 (2.28)	4330 (2.31)
◇	4150 (2.41)	4160 (2.40)	4140 (2.42)	4190 (2.38)	4090 (2.44)

Top values in eV; values in parentheses in 10^4 cm^{-1} . □, △, ◇ are peaks plotted against θ_d in Fig. IV-5b; other peaks are not plotted.

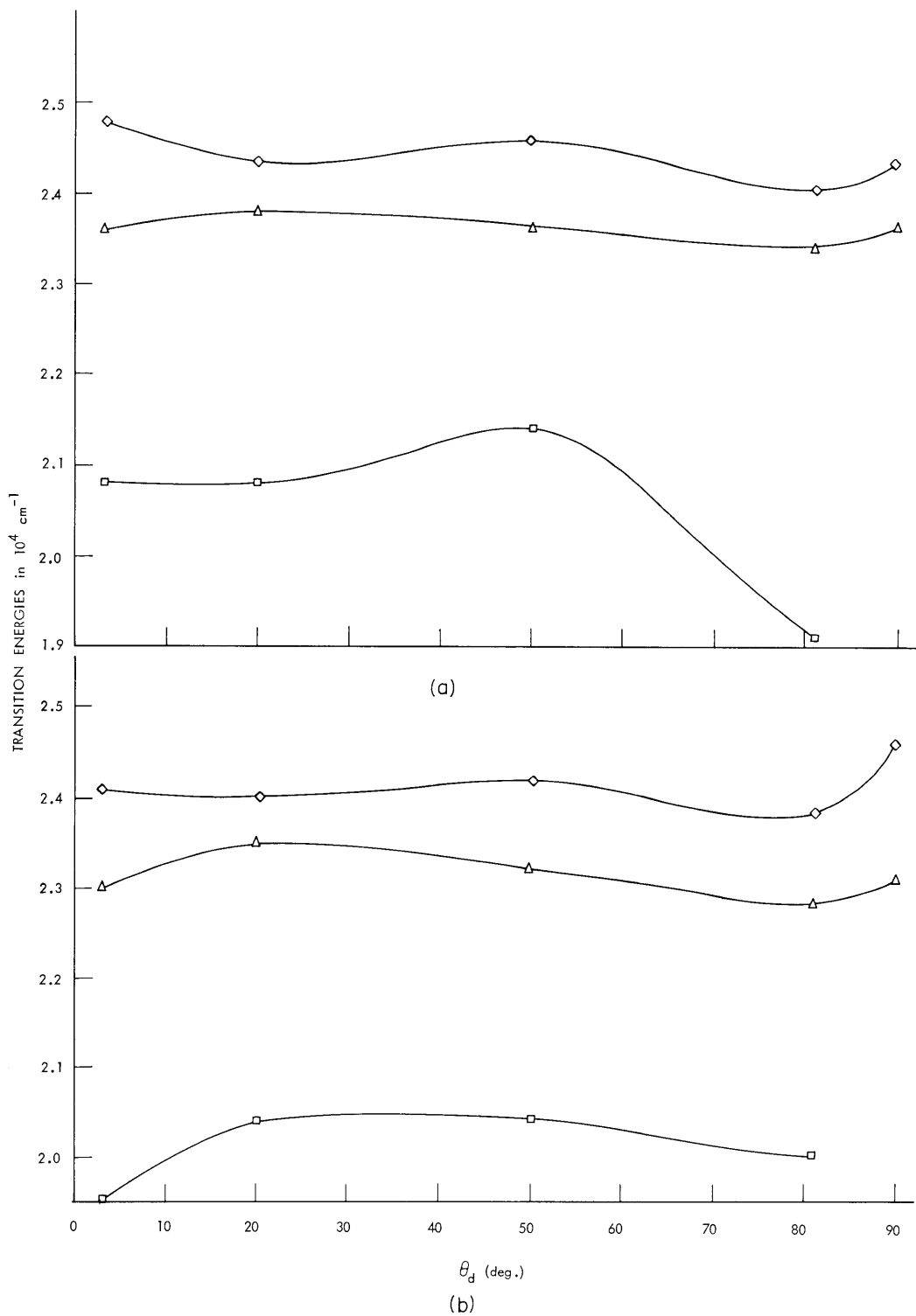


Fig. IV-5. (a) Triplet \leftrightarrow triplet transition energies obtained from flash absorption spectra of biphenyl-like molecules in liquid solution (at room temperature). (b) The same in EPA glass (at 77°K). In both (a) and (b), the trend of ◇'s and ▲'s corresponds closely with the ▲'s in the computed transition $T_{14}^- \leftrightarrow T_{11}$; the values of the ◇'s are within 16% of the ▲'s.

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The disagreement in the trend of the computational " \blacktriangle " curve and the last experimental " Δ " point obtained from compound D, ($\theta_d = 90$), is quite reasonable, since the exact analogy does not hold with D and 90° twisted biphenyl, because of the six-methyl substituent in the former. Since the shift (the difference of energy between " Δ " and " \blacktriangle " at $\theta_d \geq 85$) is toward the blue, the hyperconjugative effect of the methyl group may be considered negligible, and it may be attributed to the inductive effect caused by the methyl substituents.

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