# VI. ELECTRON MAGNETIC RESONANCE[*]

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## RESEARCH OBJECTIVES

Various problems, all of which are related to the question of energy transfer, are being attacked by our group. Specifically, some of them are the following.

1. <u>Excited States</u>. We are studying excited triplet states of large and simple molecules by the combined technique of flash irradiation and electron spin resonance spectroscopy. We now have in our laboratory a spectrometer capable of scanning 350 Gauss, or more, in 25 msec, which with flash discharge (100-10,000 J into a Xenon-filled tube) of comparable duration provides the most powerful method extant for the study of excited electronic states.

2. <u>Collisional Effects</u>. Gas phase relaxation studies of hydrogen atoms with hydrogen molecules (ortho and para separately and together) and other species are being undertaken to learn more about intermolecular interactions. Other atoms in the gas phase are being studied similarly. We are also looking at collisional cross sections of excited alkali atoms (e.g., $^2P_{1/2}$ and/or $^2P_{3/2}$ states) with their ground states. Part of the instrumentation for data handling is described in Section VI-A.

3. <u>Charge Transfer</u>. We are studying, via ESR, fluorescence and phosphorescence, charge and energy transfer in semiconductorlike materials in solution and the solid state, to determine the nature of the donor-acceptor complex.

4. <u>Photoionization</u>. Work is being done on the mechanism of photoionization in large molecules in the vacuum ultraviolet.

5. <u>Radicals in the Gas Phase</u>. Work is proceeding in the study of the electronic, vibrational, and rotational structure of alkyl radicals (methyl, ethyl, and so forth) in the gas phase from work with gaseous discharges, flash photolysis, and thermal dissociation processes at high temperatures.

6. <u>Processes Related to Combustion.</u>

K. W. Bowers

## A. EXCITED STATES

### 1. Introduction

The immense importance of the lowest triplet state in molecular systems is due to the fact that, because of the spin "forbiddenness" of the transition to the singlet ground state, the lifetime of this state is several orders of magnitude greater than any singlet

excited state or higher triplet state. Thus the usefulness of the structural elucidation of this excited metastable state, which plays the role of an intermediate for photochemical reactions, cannot be overemphasized.

A recent review, "Electron Spin Resonance Studies of the Triplet State," by Thomson[1] indicates that most of the experimental and theoretical work in this particular field, up to the present time, dealt with planar aromatic systems. The geometrical generalization of molecules in the triplet state demands an extensive inclusion of nonplanar systems, both in experimental and interpretative studies.

This report, as well as two previous reports,[2,3] are parts of a series of studies on excited molecules directed toward the generalization stated above. In previous reports,[2,3] the zero-field splittings (ZFS) of biphenyl-like twisted molecules were presented. A simple mathematical model consisting of "1/2 electron" double-delta function weighted with Hückel coefficients to examine the trend of the spin-dipolar interaction between triplet electrons in a biphenyl with respect to the dihedral angle was offered.

In this report the physical significance of the method of employing an intramolecular interaction as a means of obtaining geometrical information is briefly discussed. The application of the double-delta 1/2 electron model[3] is extended to some molecules with more than one "twist site" with angles $\theta_n$. The experimental ZFS of polyphenyls, $(Ph)_n$, $n = 1, 2, \ldots, 5$ are presented and compared with the model computations.

2. General Discussion

a. Variation in Geometry

In the structural study of excited molecules the statements concerning the geometry must be made with reference to two essential questions: What is the difference in geometry between the ground electronic state and the excited state? and How does the geometry change in different molecular environments? For example, the ground state of biphenyl is known to assume a planar configuration in the crystalline phase[4] (dihedral angle = 0°), whereas in the gaseous phase it is approximately 42°.[5] Recently, Orloff and Brinen[6] studied biphenyl (the lowest triplet state) in a glassy matrix at 77°K and reported their conclusion, $\theta_d = 0°$, by comparing the ZFS observed and those computed by use of SCF-MO-CI-LCAO.

b. Determination of Geometry by Use of an Intramolecular
   Interaction Present in the Excited State

First, the type of the intramolecular interaction must be characterized so that agreement between the expectation computed from the assumed geometry, $g_a(r)$, and the ensemble average from the experiment may be analyzed; this means that the system has an equilibrium geometry $g_a(r)$, and that one can deduce a particular value of $g(r)$ if there
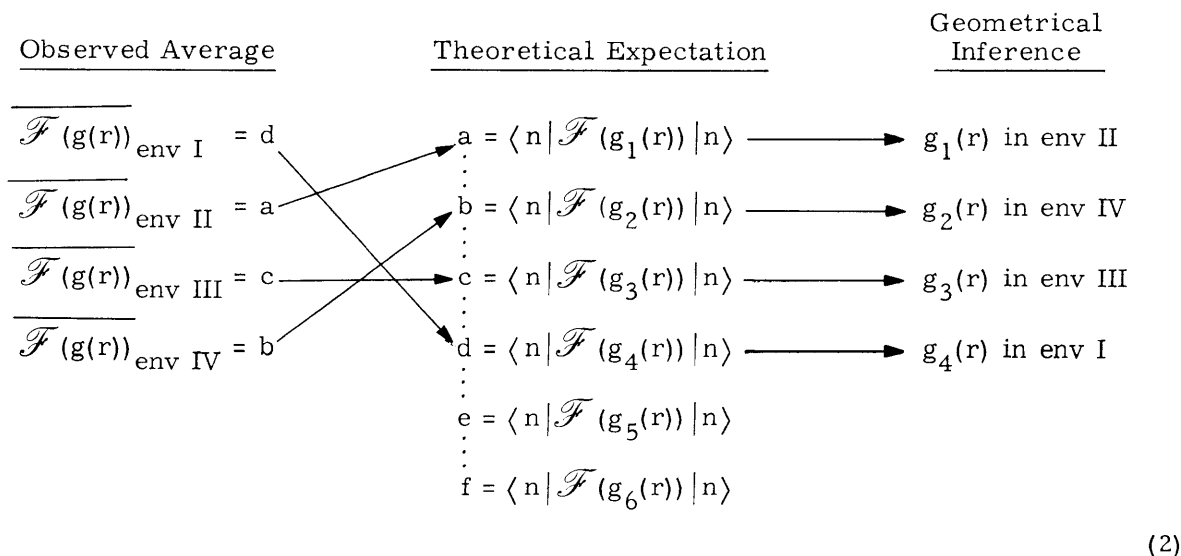
is a sufficient number of mappings (one-to-one) between the expectation values and their assumed geometries.

Let $\mathscr{F}$ represent an intramolecular interaction operator, then $\mathscr{F}$ is characterized as follows. $\mathscr{F}$ must be a function having an explicit dependence on a geometrical parameter $g(r)$, where $g$ is a function defined in a molecular fixed coordinate system $r$, and continuous at $r_0$ in the domain of $g$, $\mathscr{D}_g$, and continuous at any $g_0(r)$ in the domain of $\mathscr{F}$, $\mathscr{D}_{\mathscr{F}}$. Thus, from the definition of continuity,[7] for each $\epsilon > 0$ there exists $\delta > 0$ such that

$$\left| \mathscr{F}(g(r)) - \mathscr{F}(g_0(r)) \right| < \epsilon, \tag{1}$$

whenever $g(r) \in \mathscr{D}_{\mathscr{F}}$ and $\left| g(r) - g_0(r) \right| < \delta$. Then it follows that the expectation value(s) of $\mathscr{F}$ over the characteristic vectors of a given excited state $n$, $\langle n | \mathscr{F} | n \rangle$, is a function that is continuous at any $g_0(r)$ in the domain of $\langle n | \mathscr{F} | n \rangle$, $\mathscr{D}_{\langle n | \mathscr{F} | n \rangle}$.

The manner by which the inference concerning the geometry of a system in the state $n$ at a given molecular environment (simple cases!) is a mapping between a set of observed ensemble averages under different molecular environments and that of generated expectation values over possible values of $g(r)$. A typical example is shown below.

| Observed Average | Theoretical Expectation | Geometrical Inference |
|---|---|---|
| $\overline{\mathscr{F}(g(r))}_{\text{env I}} = d$ | $a = \langle n | \mathscr{F}(g_1(r)) | n \rangle$ | $g_1(r)$ in env II |
| $\overline{\mathscr{F}(g(r))}_{\text{env II}} = a$ | $b = \langle n | \mathscr{F}(g_2(r)) | n \rangle$ | $g_2(r)$ in env IV |
| $\overline{\mathscr{F}(g(r))}_{\text{env III}} = c$ | $c = \langle n | \mathscr{F}(g_3(r)) | n \rangle$ | $g_3(r)$ in env III |
| $\overline{\mathscr{F}(g(r))}_{\text{env IV}} = b$ | $d = \langle n | \mathscr{F}(g_4(r)) | n \rangle$ | $g_4(r)$ in env I |
| | $e = \langle n | \mathscr{F}(g_5(r)) | n \rangle$ | |
| | $f = \langle n | \mathscr{F}(g_6(r)) | n \rangle$ | |

$$\tag{2}$$

where env I, etc. denote particular molecular environments in which the measurement is made. The dotted line connecting the theoretical values indicates the continuous nature of $\langle \mathscr{F} \rangle$. Therefore if $\overline{g(r)}$ of a molecule in a given state $n$ is known to be $\overline{g_0(r)}$, and the measurement and the expectation agree, that is,

$$\overline{\mathscr{F}(g_0(r))}_{\text{env 0}} = s = \langle n | \mathscr{F}(g_0(r)) | n \rangle, \tag{3}$$

then the desired geometrical inferences in a given molecular environment are obtained.

Furthermore, if the distribution of the observed $\mathscr{F}(g(r))$ can be distinguished from the known sources of line broadening by controlled experiments, then it follows that the mapping becomes

$$\mathscr{L}(\mathscr{F}(g(r)) \rightarrow \mathscr{L}(\langle n | \mathscr{F}(g(r)) | n \rangle) \rightarrow \mathscr{L}(g(r)), \tag{4}$$

where $\mathscr{L}$ is a Gaussian or Lorentzian function. Parentheses are used here only for functions. Braces and brackets are reserved for multiplicative factorization.

3. Application of the Methods: Polyphenyls

a. Intramolecular Repulsion and Resonance Energy

Polyphenyls are molecules in which phenyl (benzene) rings are "hooked" together by $\sigma$ bonding in the ground electronic state. They are classified by the manner in which these rings are connected to each other (see Fig. VI-1). In all



para - n - phenyl          ortho - n - phenyl          meta - n - phenyl
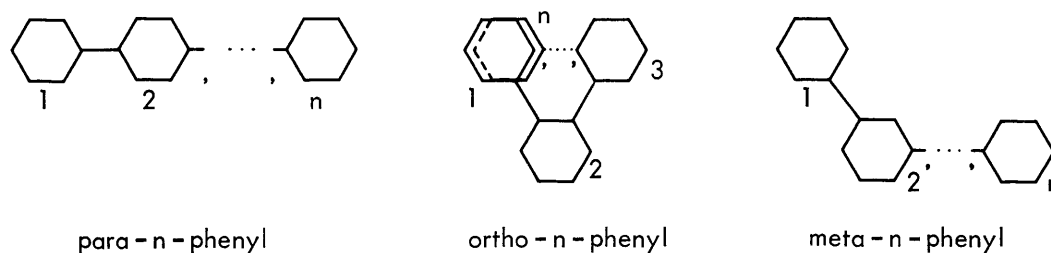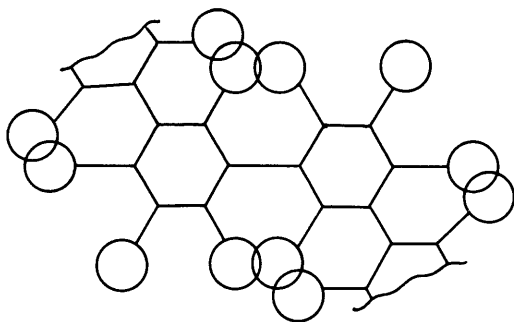
Fig. VI-1. Polyphenyl nomenclature.



Fig. VI-2. Repulsion among the van der Waal's radii of nonbonded hydrogen.

of these molecules there are van der Waal's radii[8] (see Fig. VI-2) attributable to the hydrogens at nonlinked positions contributing to the steric energy $E_s$ and the delocalization of $\beta$ electrons contributing to the resonance energy $E_R$. Both $E_s$ and $E_R$ fall into the general category of $\mathscr{F}$. Since the nonbonded repulsion is the difference between Coulomb and exchange energy, $E_s$ is dependent on the distance
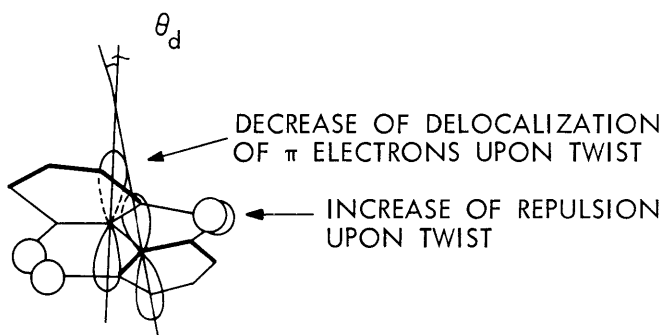
Fig. VI-3. Nonbonded interactions in biphenyl.

between the nonbonded hydrogen atoms and on the distance between hydrogen atoms and carbon atoms, and is treated as a function of the twist angle $\theta_d$; $E_R$ is due to conjugation of the $\pi$ electron across the twist sites, and it also depends on $\theta_d$ (see Figs. VI-3 and VI-4).
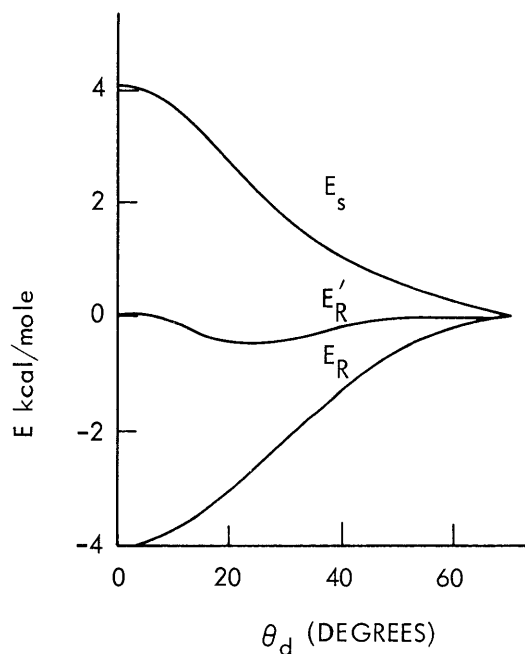


Fig. VI-4. F. J. Adrian's plot[9] of the steric and resonance energies for biphenyl as functions of the twist angle $\theta_d$. $E_R'$ is the effective resonance energy $E_s + E_R$.

In meta- or para-n-phenyl, nonbonded steric interactions are those between hydrogen atoms at ortho positions, whereas in ortho-n-phenyl, n > 2, nonbonded interactions between carbon atoms and hydrogen atoms also add appreciably to $E_s$. Furthermore, as the n increases, the number of possible conformations of meta- and ortho-n-phenyl increases. Thus there may be more than one equilibrium at a given molecular environment.

b.  Electronic Spin Dipolar Interaction in the Triplet State of
    Biphenyl in a Glassy Matrix

The advantages of the selection of the electronic spin dipolar operator as $\mathscr{F}(g(r))$ are (i) it is characteristic of the systems possessing more than one unpaired electron — often an electronically excited state, and (ii) it is several orders of magnitude more sensitive to the geometry of systems than phosphorescence.

Let

$$\mathscr{F}(g(r)) = \mathcal{K}_{dip} = \frac{1}{2}\left[\frac{e}{mc}\right]^2 \sum_i \sum_j \left\{ \frac{\bar{s}_i \cdot \bar{s}_j}{r_{ij}^3} - \frac{3[\bar{s}_i \cdot \bar{s}_j][\bar{r}_i \cdot \bar{s}_i]}{r_{ij}^5} \right\},\tag{5}$$

with

$$g(r) = r_{ij}.$$

If $g'(r) = \theta_{n-1}$ for the twist angle of n-polyphenyl, $g'(r) = f(g(r))$, and $\mathscr{F}(g'(r))$ is continuous at $g_0'(r)$, $0 < g_0'(r) < \pi/2$; hence, $\mathcal{K}_{dip}$ satisfies the general type characterized for $\mathscr{F}$. Referred to the principal axes and expressed in the total spin, (5) becomes

$$\mathscr{F}(g'(r)) = -XS_x^2 - YS_y^2 - ZS_z^2,\tag{6}$$

where X, Y, and Z are the expectation values of $\mathcal{K}_{dip}$ over the spatial part of the triplet function, $^3\psi_0(g'(r))$ such that

$$X(g'(r)) = \langle \mathscr{F}_x(g'(r)) \rangle = \frac{1}{2}\frac{e^2}{m^2c^2} \left\langle {}^3\psi_0(g'(r)) \left| r_{12}^{-5}\left[3x_{12}^2 - r_{12}^2\right] \right| {}^3\psi_0(g'(r)) \right\rangle$$

$$Y(g'(r)) = \langle \mathscr{F}_x(g'(r)) \rangle = \frac{1}{2}\frac{e^2}{m^2c^2} \left\langle {}^3\psi_0(g'(r)) \left| r_{12}^{-5}\left[3y_{12}^2 - r_{12}^2\right] \right| {}^3\psi_0(g'(r)) \right\rangle$$

$$Z(g'(r)) = \langle \mathscr{F}_z(g'(r)) \rangle = \frac{1}{2}\frac{e^2}{m^2c^2} \left\langle {}^3\psi_0(g'(r)) \left| r_{12}^{-5}\left[3z_{12}^2 - r_{12}^2\right] \right| {}^3\psi_0(g'(r)) \right\rangle\tag{7}$$

The evaluation of the integrals in (7) was reported in detail in a previous report.[3] The antisymmetric spatial part of the triplet function was assumed to consist of the configuration of the lowest excitation energy alone. Hückel molecular orbitals were used to approximate the highest bonding and the lowest antibonding orbitals. The simplification in the evaluation of (7) was achieved by replacing the AO by delta functions located above and below the ring plane at the distance from the nucleus corresponding to the expectation value of $2p\pi_z$ electrons so that the "twist effect" may effectively be

incorporated. The result of the simple double-delta model is

$$X_{AV}(g'(r)) = \frac{1}{2}\frac{e^2}{m^2c^2}\sum_i\sum_{i\neq k} b_i(\theta_d)\, b'_k(\theta_d)\, \{b_i(\theta_d)b'_k(\theta_d)-b_k(\theta_d)b'(\theta_d)\}$$

$$\times\left[\left\{r_{12}^{-5}\left[3x_{12}^2-r_{12}^2\right]\right\}_{i_1^+k_2^+} + \left\{r_{12}^{-5}\left[3x_{12}^2-r_{12}^2\right]\right\}_{i_1^+k_2^-}\right.$$

$$\left. +\left\{r_{12}^{-5}\left[3x_{12}^2-r_{12}^2\right]\right\}_{i_1^-k_2^+} + \left\{r_{12}^{-5}\left[3x_{12}^2-r_{12}^2\right]\right\}_{i_1^-k_2^-}\right], \tag{8}$$

where $\left\{r_{12}^{-5}\left[3x_{12}^2-r_{12}^2\right]\right\}_{i_1^+k_2^-}$ means, for example, the operator within braces evaluated

with electron 1 at nuclear site i, "+" position (above the phenyl plane), and electron 2 at nuclear site k, "-" position (below the phenyl ring). (See Fig. VI-5.) The spin
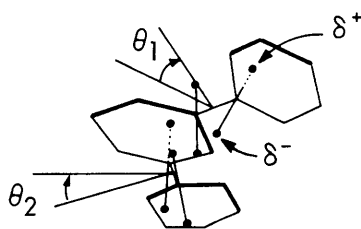


Fig. VI-5. "Double-delta" model of m-terphenyl. (Only those at the twist site are shown.)

Hamiltonian, basis kets, and the stationary resonance fields for the canonical orientations of molecules in an external magnetic field are discussed in detail in a previous report on methylnaphthalenes.[2]

## c. New Method for Determination of Excited Isomers

We shall give an example of the canonical orientations in m-quater-phenyl, and present a method in which the stationary resonance fields specific to one canonical orientation are used as the probe to detect (i) the existence of isomeric forms, and (ii) the type of isomeric geometry (see Fig. VI-6). In particular, if the "$\sigma$ skeletal" structure of the compound is known, this method enables one to determine along which axes the isomeric forms are occurring. A mathematical proof of the validity of this method follows.

Proof. If geometrical isomers in a triplet state exist and differ only in one canonical orientation with respect to the external field, $\overline{H}$, then their Zeeman levels for that canonical orientation $\overline{H} \mathbin{/\mkern-4mu/} u_1$ are
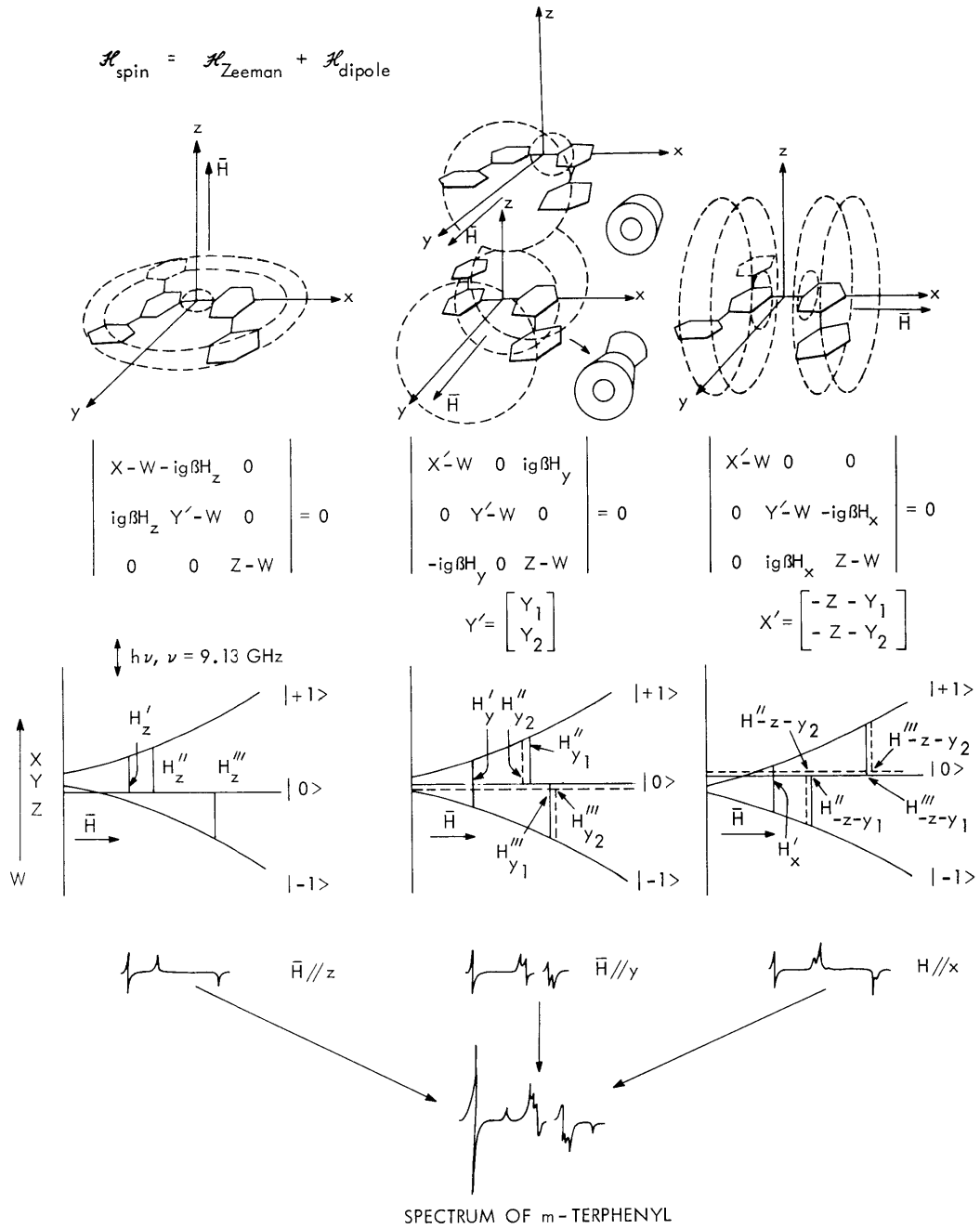
$$\mathcal{H}_{spin} = \mathcal{H}_{Zeeman} + \mathcal{H}_{dipole}$$

$$\begin{vmatrix} X - W - ig\beta H_z & 0 & \\ ig\beta H_z & Y' - W & 0 \\ 0 & 0 & Z - W \end{vmatrix} = 0$$

$$\begin{vmatrix} X' - W & 0 & ig\beta H_y \\ 0 & Y' - W & 0 \\ -ig\beta H_y & 0 & Z - W \end{vmatrix} = 0$$

$$Y' = \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}$$

$$\begin{vmatrix} X' - W & 0 & 0 \\ 0 & Y' - W & -ig\beta H_x \\ 0 & ig\beta H_x & Z - W \end{vmatrix} = 0$$

$$X' = \begin{bmatrix} -Z - Y_1 \\ -Z - Y_2 \end{bmatrix}$$

$h\nu, \ \nu = 9.13 \ GHz$

$|+1\rangle$

$H_z'$  $H_z''$  $H_z'''$  $|0\rangle$

$\bar{H}$

$X$
$Y$
$Z$

$W$

$|-1\rangle$

$H_y'$  $H_{y_2}''$  $H_{y_1}''$  $|+1\rangle$

$|0\rangle$

$\bar{H}$  $H_{y_1}'''$  $H_{y_2}'''$

$|-1\rangle$

$H''_{-z-y_2}$  $H'''_{-z-y_2}$  $|+1\rangle$

$|0\rangle$

$\bar{H}$  $H''_{-z-y_1}$  $H'''_{-z-y_1}$

$H_x'$  $|-1\rangle$

$\bar{H} // z$

$\bar{H} // y$

$H // x$

SPECTRUM OF m - TERPHENYL

Fig. VI-6. Detection method of excited geometrical isomers via ESR.

$$\left\{ \begin{array}{l} W_1 = \begin{bmatrix} U_{1a} \\ U_{1b} \end{bmatrix} \\ \\ W_{2,3} = 2^{-1}\left\{ \begin{bmatrix} -[U_3+U_{1a}] \\ -[U_3+U_{1b}] \end{bmatrix} + U_3 \right\} \pm \left\{ 4^{-1}[U_2-U_3]^2 + g\beta H_{U_1} \right\}^{1/2} , \end{array} \right. \tag{10}$$

where $U_1$, $U_2$, $U_3$ are principal values of the zero-field splitting tensor, and

$$U_1 = \begin{bmatrix} U_{1a} \\ U_{1b} \end{bmatrix}$$

for isomeric forms "a" and "b", and the tracelessness of the tensor causing

$$U_2 = \begin{bmatrix} -U_3 - U_{1a} \\ -U_3 - U_{1b} \end{bmatrix}.$$

For the orientation $\overline{H} \ // \ u_3$ these levels become

$$\left\{ \begin{array}{l} W_{1,2} = 2^{-1}\left\{ \begin{bmatrix} U_{1a} \\ U_{1b} \end{bmatrix} + \begin{bmatrix} -U_3 - U_{1a} \\ -U_3 - U_{1b} \end{bmatrix} \right\} \pm \left\{ 4^{-1}\left\{ \begin{bmatrix} U_{1a} \\ U_{1b} \end{bmatrix} - \begin{bmatrix} -U_3 - U_{1a} \\ -U_3 - U_{1b} \end{bmatrix} \right\} + g\beta H_{U_3} \right\}^{+1/2} \\ \\ W_3 = U_3 \end{array} \right. \tag{11}$$

Thus the isomeric doubling of the Zeeman level (linear) corresponding to the $\overline{H} \ // \ u_1$ orientation has a gap $|U_{1a}-U_{1b}| = |W_{1a}-W_{1b}|$, whereas the gap corresponding to $\overline{H} \ // \ u_3$ is

$$\left\{ 2^{-1}|U_{1a}-U_{1b}| \right\}^{1/2} = |W_{1a,2a}-W_{1b,2b}|.$$

Clearly,

$$|U_{1a}-U_{1b}| > \left\{ 2^{-1}|U_{1a}-U_{1b}| \right\}^{1/2}. \tag{12}$$

Thus, provided a sufficient population of both excited isomers exists and $|U_{1a}-U_{1b}| > 10^{-4}$ cm$^{-1}$, the lower instrumentation resolution limit, the axis dependence of the isomeric forms are distinguishable.
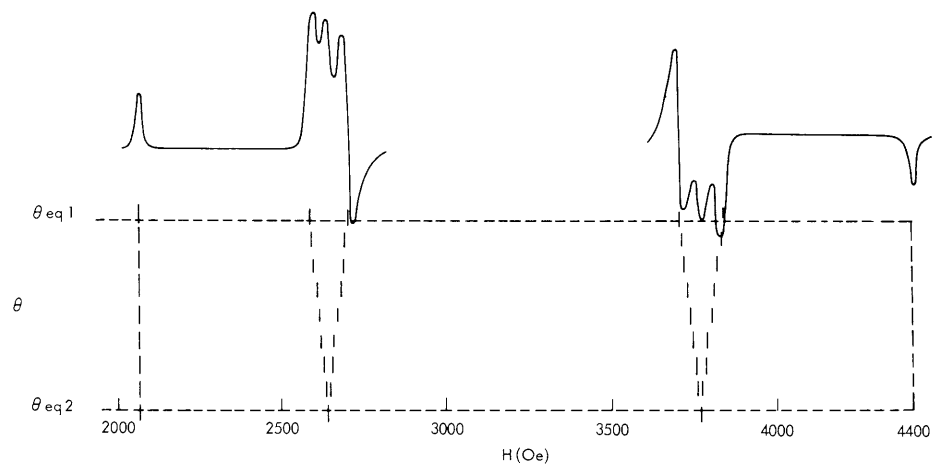
Fig. VI-7. Assimilation of the stationary resonance fields ($\Delta M_S = \pm 1$) of m-quaterphenyl, with $Z = -0.0712$, $X + Y = 0.0712$.


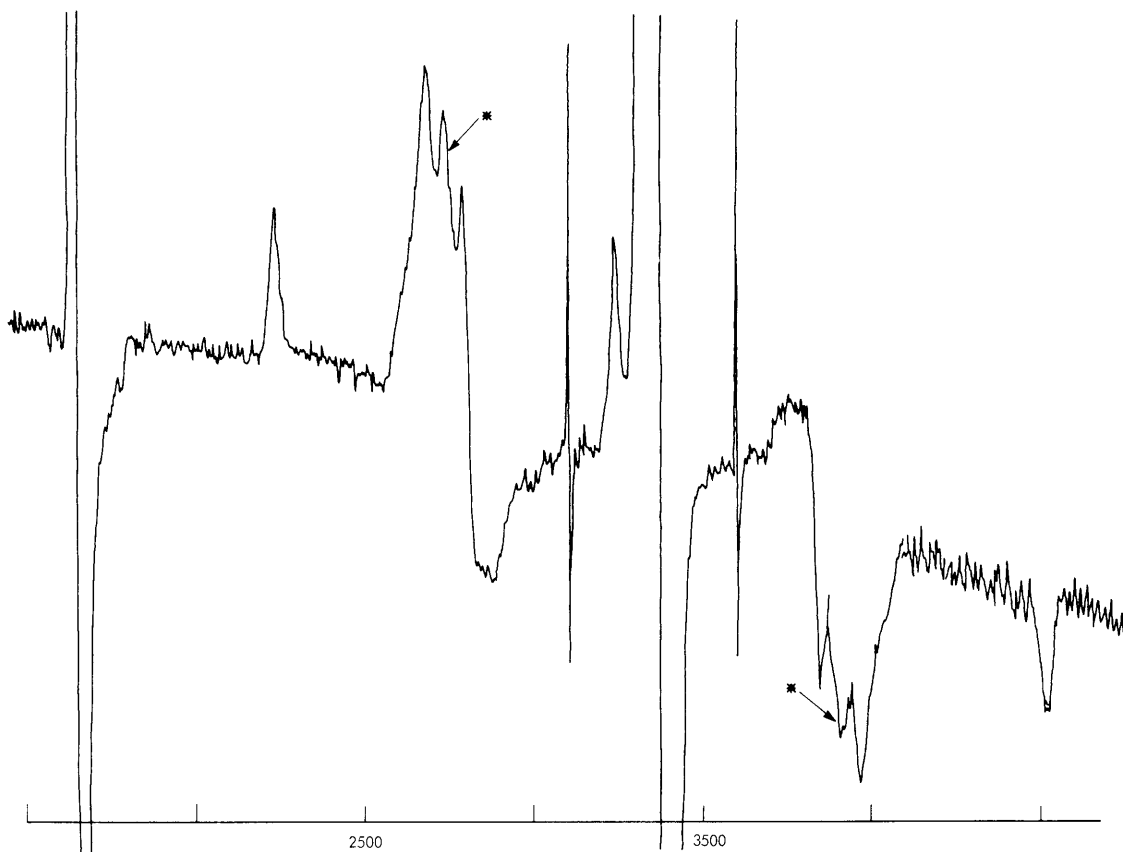
Fig. VI-8. ESR spectrum of m-quaterphenyl in the lowest triplet state. * Indicates the isomeric form whose SRF differs in the orientation H // y.

In the specific case of m-quaterphenyl, the ESR spectrum indicates that there are two isomeric equilibrium configurations, and when rotation is along the y axis the distinction arises.  Since the sample is in a semirigid randomly oriented glassy matrix, the isomeric forms have distribution differing in the central twist angle and having maxima at two stable configurations.  Figure VI-7 indicates the assimilation of the stationary resonance fields by use of the Kottis-Lefèbvre expression[2] and the traceless condition of the tensor Z = -0.0712, X + Y = 0.0712.  Figure VI-8 shows the actual ESR spectrum of m-quaterphenyl.

d.  Experiments

The preparation of samples and the instrumental arrangement have been given in detail in a previous report.[3]  Table VI-1 gives the observed value of the zero-field

Table VI-1.  Experimental values of zero-field splittings in polyphenyls.

| Compound | X | Y | Z | D | E |
|---|---|---|---|---|---|
| biphenyl | .0390 | .0322 | § - .0712 | .1069 | § - .0034 |
| m-terphenyl | .0401 | .0311 | - .0712 | .1069 | - .0045 |
| p-terphenyl | .0336 | .0170 | - .0506 | .0758 | .0083 |
| o-terphenyl | .0436 | .0124 | - .0560 | .0840 | .- .0156 |
| m-quaterphenyl | * | * | - .0708 | .1062 | * |
| o-quaterphenyl | .0393 | .0135 | - .0528 | .0793 | - .0129 |
| m-quinquephenyl | * | * | - .0708 | .1062 | * |

*Cf. section 3c.

§The sign of ZFS cannot be determined absolutely from experiment alone.

splittings.  (Values for X, Y and E of m-quaterphenyl and m-quinquephenyl have been given.)

e.  Computational Results

The ZFS approximated by Eq. 8 and the Kottis-Lefèbvre resonance field equation[2] were computed on the IMB 360 computer for m-, p-, and o-terphenyls.  The values of approximate ZFS, $X_{AV}$, $Z_{AV}$, and $D_{AV}$, $E_{AV}$ are adjusted with proportionality factors $\xi_d$ and $\xi_e$ in the following manner (see Table VI-2) for each compound.
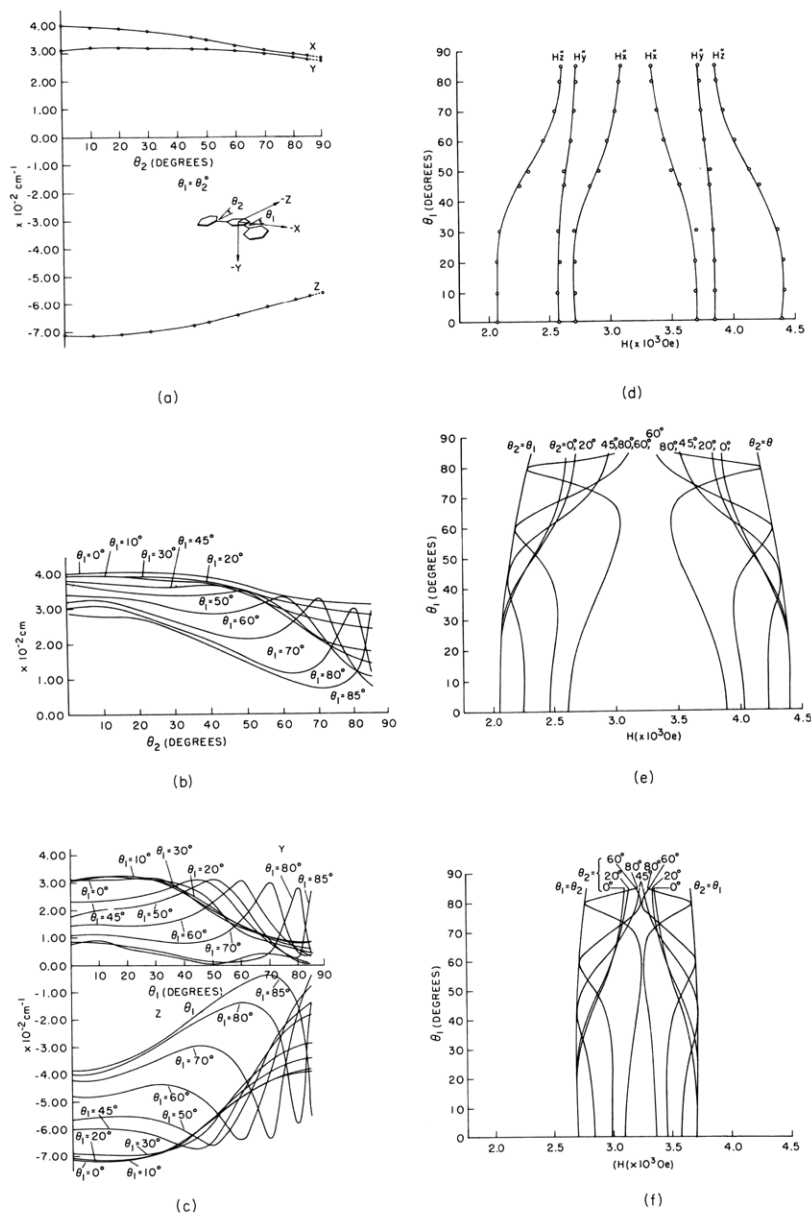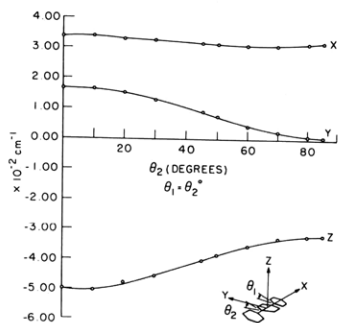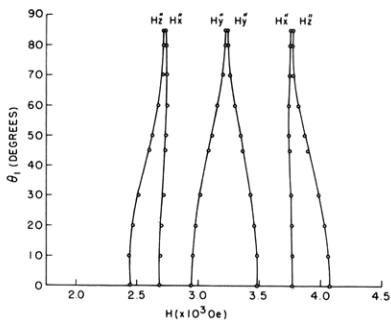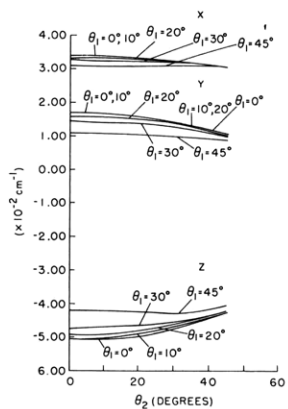
(a)



(d)



(b)



(e)



(c)



(f)

Fig. VI-9.

(a) Computed ZFS of m-terphenyl as functions of twist angles, $\theta_1 = \theta_2$.

(b) Computed ZFS of m-terphenyl as a function of twist angle $\theta_2$ ($\theta_1 = $ const.); X, principal value.

(c) Computed ZFS of m-terphenyl as a function of twist angle $\theta_2$ ($\theta_1 = $ const.); Y and Z, principal values.

(d) Computed stationary resonance fields, SRF, of m-terphenyl as functions of twist angles, $\theta_1 = \theta_2$.

(e) Computed stationary resonance fields, SRF, of m-terphenyl as a function of twist angle $\theta_1$ ($\theta_2 = $ const.).

(f) Computed stationary resonance fields, SRF, of m-terphenyl as a function of twist angle $\theta_2$ ($\theta_2 = $ const.).
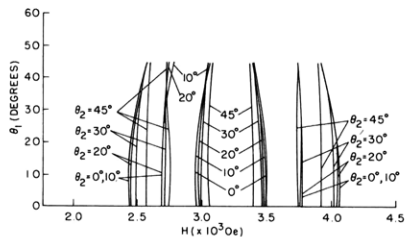
Fig. VI-10.

(a) Computed ZFS of p-terphenyl as functions of twist angles $\theta_1 = \theta_2$.

(b) Computed ZFS of p-terphenyl as functions of twist angle $\theta_2$, $\theta_1$ = const.

(c) Computed stationary resonance fields, SRF, of p-terphenyl as functions of twist angles $\theta_1 = \theta_2$.

(d) Computed stationary resonance fields, SRF, of p-terphenyl as functions of twist angle $\theta_1$, $\theta_2$ = const.
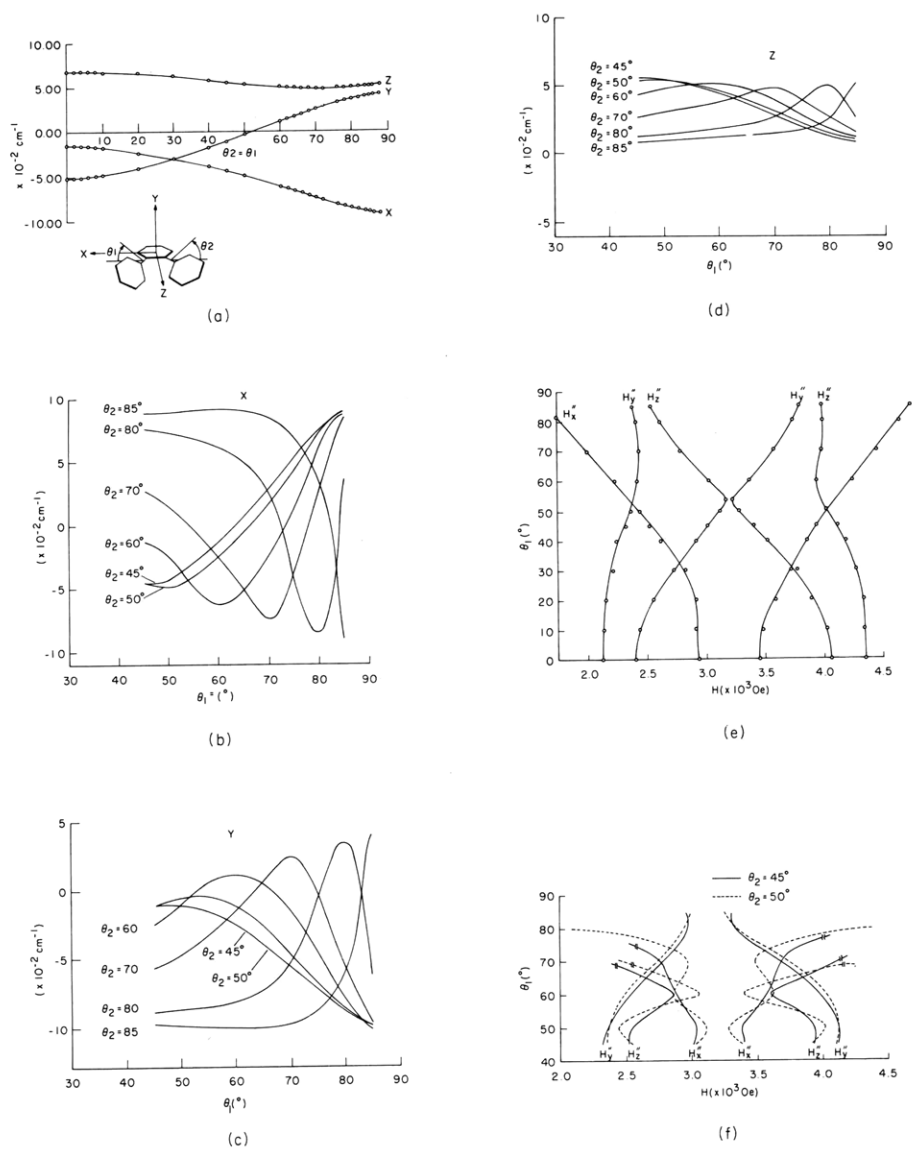
Fig. VI-11.  (a) Computed ZFS of o-terphenyl as functions of twist angles, $\theta_1 = \theta_2$.

(b) Computed ZFS of o-terphenyl as a function of twist angle $\theta_1$, $\theta_2$ = const.; X, principal value.

(c) Computed ZFS of o-terphenyl as a function of twist angle $\theta_1$, $\theta_2$ = const.; Y, principal value.

(d) Computed ZFS of o-terphenyl as a function of twist angle $\theta_1$, $\theta_2$ = const.; Z, principal value.

(e) Computed SRF of o-terphenyl as functions of twist angles, $\theta_1 = \theta_2$.

(f) Computed SFR of o-terphenyl as a function of twist angle $\theta_1$, $\theta_2$ = const.

$$\xi_d = D/D_{AV}(g'(r))_{dp}$$

$$\xi_e = E/E_{AV}(g'(r))_{dp},$$

(13)

where D and E are the experimental values obtained from $\Delta M_s = \pm 1$ canonical fields, and $(g'(r))_{dp} = \theta_{dp}$ is the most stable angle assumed, in which $\theta_1 = \theta_2$. The results are shown in Figs. VI-9 through VI-11. For each compound the cases $\theta_d = \theta_1 = \theta_2$ and $\theta_d = \theta_1$, $\theta_2 = $ const. are treated separately. In the latter case both ZFS and SRF have extrema (maxima or minima) at $\theta_1 = \theta_2$; in the former case there are no extrema.

Table VI-2. Proportionality factors $\xi_d$ and $\xi_e$ for polyphenyls.

| Compound | $\xi_d$, $\xi_e$ | $D_{av}(\theta_{dp}), E_{Av}(\theta_{dp})$ | D, E | $\theta_{dp}$ |
|---|---|---|---|---|
| m-terphenyl | $\xi_d = -.2699$ | $D_{av}(\theta_{dp}) = -.3960$ | D = .1069 | $0°$ |
| | $\xi_e = .0456$ | $E_{av}(\theta_{dp}) = -.0987$ | E = .0045 | |
| p-terphenyl | $\xi_d = .2021$ | $D_{av}(\theta_{dp}) = .3750$ | D = .0753 | $0°$ |
| | $\xi_e = .1313$ | $E_{av}(\theta_{cp}) = -.0632$ | E = -.0033 | |
| o-terphenyl | $\xi_d = -.3889$ | $D_{av}(\theta_{dp}) = -.2160$ | D = .0540 | $45°$ |
| | $\xi_e = -.5932$ | $E_{av}(\theta_{dp}) = .0263$ | E = -.0156 | |

## 4. Conclusions

1. In the randomly oriented glassy matrix, the ZFS of some polyphenyls reflect the existence of geometrical isomers differing in twist angles in the manner $\theta_d = \theta_{eg} \pm \Delta\theta$, where $\theta_{eg}$ is the twist angle associated with the stable conformation(s), and $\pm\Delta\theta$ is some deviation from $\theta_{eg}$.

2. The sensitivity of ZFS and of SRF vary widely with (a) the value of $\theta_d$, (b) the relative magnitude of the $\theta_d$. The sensitivity is greater for $\{\theta_d = \theta_1, \theta_2 = $ const.$\}$ or $\{\theta_d = \theta_2, \theta_1 = $ const.$\}$ than for $\{\theta_d = \theta_1 = \theta_2\}$.

The appearance of "extraneous" SRF of the $\Delta M_s = \pm 1$ fields in the manner described

in this report can be utilized to detect the existence of isomeric forms in the excited triplet state. The principal axes about which the isomeric distinction arises can be identified. This can be separated from trivial impurity cases, since the isomeric doubling (tripling, etc.) of the canonical fields is related to the nondoubled fields through the tracelessness of the spin-dipolar tensor.

The broadening of SRF in the cases of o-terphenyl and o-quaterphenyl can be explained in terms of the great sensitivity of ZFS within small range of $\theta_d$ (relative to other polyphenyls), and of level crossings of eigenvalues when $\theta_d = \theta_1$, $\theta_2$ varying (see Fig. VI-11). An approximation for the range of $\theta_d$ from SRF vs $\theta_d$ is $35° < \theta_d < 47°$.

5. A possible explanation of the broadening of the inner $\Delta M_s = \pm 1$ SRF of m-polyphenyls may be the existence of geometrical isomers having different $\theta_d$ (and/or different combinations of $\theta_d$) within the limit, so that one of the zero-field energy levels remains virtually the same, while two others vary appreciably. From the superposition of the plots of SRF against $\theta_d$, for example, $0° < \theta_d < 25°$ for m-terphenyl is obtained.

6. A possible reason for the "extraneous" $\Delta M_s = \pm 1$ peaks in the case of m-quaterphenyl (see Fig. VI-8) is that the assembly of the sample may be considered as a species having two comparably stable twist angles, $\theta_{eq1}$ and $\theta_{eq2}$. Thus the geometrical isomers exist in such a manner that

$$\left. \begin{aligned} \theta_{d1} &= \theta_{eq1} \pm \theta_1 \\ \theta_{d2} &= \theta_{eq2} \pm \theta_2 \end{aligned} \right\}. \tag{27}$$

A semiempirical computation can be made for SRF, using ZFS biphenyl and satisfying the condition (see Fig. VI-7).

7. The sharpness and uniformity of p-terphenyl SRF may be related to the near planarity. From the plotted results of SRF ($\theta_d$) (see Fig. VI-10), the range of $\theta_d$ is approximated as $0° < \theta_d < 10°$.

8. The simple approximation used here, D-DELTA, predicts the trend of ZFS in terms of relative magnitude with respect to $\theta_d$. Hence if the assumed most stable angle, $\theta_{dp}$, is correct, then the approximate predicted range of $\theta_d$ describes the distribution range of twisted isomeric forms.

9. If an intramolecular interaction is a continuous function having an explicit dependence on a geometrical parameter, and if an ensemble average at a particular point of the geometrical parameter is measurable at a given molecular environment and agrees reasonably well with the computed expectation value, under the assumption of the same geometry, then it can be made a probe to determine the geometry at other molecular environments.

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