II. ELECTRON MAGNETIC RESONANCE[*]

Academic and Research Staff

Prof. K. W. Bowers

Graduate Students

Nancy H. Kolodny
C. Mazza
A. C. Nelson
R. S. Sheinson
N. S. Suchard
Y.-M. Wong
B. S. Yamanashi

A. ON GEOMETRY OF EXCITED MOLECULES

One of the major problems of working with excited molecules is that their geometries are not well known. This report presents a reasonably successful approach toward this end.

The spin Hamiltonian of molecules in a triplet state is conventionally expressed in terms of the phenomenological spin operator $\overline{S}$ and its Cartesian components.[1] For aromatic hydrocarbons possessing a long-lived triplet state (of the order of seconds), the spin-orbit interactions are negligible (10^{-4} or less) and thus the g tensor in the Zeeman expression can be replaced by the g_e for the free electron. The Fermi contact interaction of the type $\alpha\overline{S}\cdot\overline{I}$ is highly anisotropic; thus, for randomly oriented samples it does not cause observable hyperfine splitting[2]: Furthermore, the contribution to the zero-field energy is to first approximation, for the systems concerned here, negligible. Thus the spin energy in the present consideration only contains electron Zeeman and electron spin-spin interaction terms. The two most commonly used forms[3] of the spin Hamiltonian are

$$\mathcal{H}_{\text{spin}} = g_e\beta\overline{H}\cdot\overline{S} - \left(XS_x^2+YS_y^2+ZS_z^2\right) \tag{1}$$

$$\mathcal{H}_{\text{spin}} = g_e\beta\overline{H}\cdot\overline{S} + D\left(S_z-\frac{1}{3}\overline{S}^2\right) + E\left(S_x^2-S_y^2\right), \tag{2}$$

where X, Y, and Z are the principal values, and D and E are the zero-field splitting parameters. The matrix elements of (1) are calculated by the use of spin functions $|T_x\rangle$, $|T_y\rangle$, and $|T_z\rangle$, which are linear combinations of Zeeman spin states +1 >, 0 >, and -1 >:

$$\begin{array}{c|ccc|} \langle T_x| & X & -ig\beta H_z & ig\beta H_y \\ \langle T_y| & ig\beta H_z & Y & -ig\beta H_x \\ \langle T_z| & -ig\beta H_y & ig\beta H_x & Z \end{array} \tag{3}$$

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The energy levels of the Wn's are obtained from the secular determinant corresponding to (3), thereby yielding the resulting secular equation

$$W^3 + (XY+YZ+XZ)W + g^2\beta^2\left[H_x^2(X-W)+H_y^2(Y-W)+H_z^2(Z-w)\right] + X\ Y\ Z = 0. \tag{4}$$

The orientation of molecules with respect to the magnetic field $\overline{H}$ can be represented by Euler angles θ and ϕ as shown in Fig. II-1 and, since

$$H_x = H \sin\theta \cos\phi, \quad H_y = H \sin\theta \sin\phi, \quad H_z = H \cos\theta, \tag{5}$$

$\overline{H}^2 = H_x^2 + H_y^2 + H_z^2$. Furthermore, since the dipolar tensor is traceless $\left(X = \frac{D}{3} - E,\ Y = \frac{D}{3} + E,\ Z = -\frac{2}{3}D \text{ so that } X + Y + Z = 0\right)$, Eq. 4 can be rewritten

$$W^2 - [(g\beta H)^2-(XY+XZ+YZ)]W + (g\beta H)^2[X\sin^2\theta\cos\phi + Y\sin\theta\cos^2\theta + Z\cos^2\theta] - XYZ = 0. \tag{6}$$

The energy difference between two of the three roots of (6) can be made equal to a quantum of the microwave energy $h\nu = \delta$, and the relation thus obtained can be separated into the angular-dependent part $f(\theta,\phi)$ and the field-dependent part $F(\delta, H)$ (see P. Kottis and R. Lefebvre[4]).

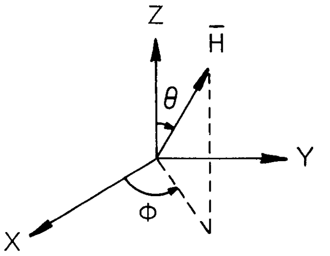

Fig. II-1. X, Y, and Z are molecular coordinates.

This resonance condition is explicity written

$$[X\sin^2\theta\cos^2\phi + Y\sin^2\theta\sin^2\phi + Z\cos^2\theta] = XYZ(g\beta H)^{-2} + 3^{-3/2}[(g\beta H)^{-2}(\delta+XY+XZ+YZ)-1] \times [4(g\beta H)^2-\delta^2-4(XY+XZ+YZ)]^{1/2}. \tag{7}$$

Because of the random orientation of the molecules, stationarity of resonance occurs, when $f(\theta,\phi) = X, Y, Z$ and when $F'(\delta, H) = 0$ (F' is the derivative w.r.t. H). The former corresponds to the physical situation in which molecules are oriented so that one of their axes is parallel to $\overline{H}$; the latter occurs only for the microwave wavelength near 3 cm (X-band). Figure II-2 shows a typical Kottis-Lefebvre plot $F(H, \delta = h(9.130\ GH_z))$ 1-methyl naphthalene. For the experimental determination of ZFS, the conventional

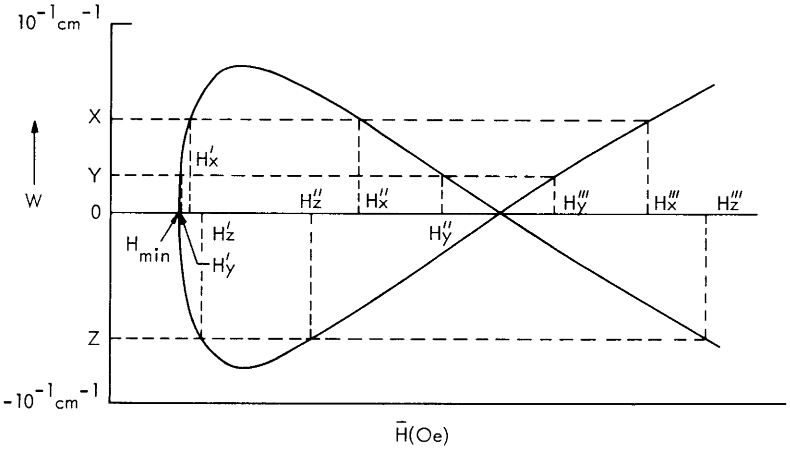

Fig. II-2. Kottis-Lefebvre plot for 1-methyl naphthalene, ν = 9.130 GH_z
H_{min} = 1506 H'_x = 1559 Oe H'_y = 1512 Oe H'_z = 1663 Oe
H''_x = 2482 Oe H''_y = 2917 Oe H''_z = 2912 Oe
H'''_x = 3967 Oe H'''_y = 3480 Oe H'''_z = 4287 Oe,
with X = 0.0469, Y = 0.0183, and Z = -0.0652.

approximation[5] $H_z - H_z \sim 2D/g\beta$ and $\frac{1}{2}[(H'''_x-H'''_y)+(H''_x-H''_y)] \sim 3E/g\beta$ is used. In the former relation the term, $-\frac{1}{2}(E/g\beta)^2(1/H'''_z-H''_z)$, which is of the order of 3×10^{-4} cm^{-1}, is neglected, and in the latter the term, $\frac{1}{2}(D+E) \tan ⓗ_1 - \frac{1}{2}(D-E) \tan ⓗ_2$, where $\tan ⓗ_n = E\left[\sqrt{(g\beta H_n)^2+E^2}+g\beta H_n\right]^{-1}$, which is of similar magnitude and thus neglected.

The experimental X, Y, and Z were substituted in F(δ, H), ($\delta = h\nu$, ν = 9.130 k MH_z) and ZFS, obtained from the resultant stationary resonance fields (SRF), H''_z, H''_x, H''_y, H'''_y, H'''_x, and H'''_z, were compared with the experimental values. This semiempirical method does <u>not</u> prove the correctness of experimental ZFS but merely confirms the appropriateness of the spin Hamiltonian and the spin eigenfunction that were used.

1. Methyl Substituted Naphthalenes

The experimental ZFS parameters D, E, and D* and the principal values X, Y, and Z are compared with the corresponding values obtained from F(δ, H) = F(θ, ϕ) in Table II-1.

Since the expectation value of X, Y, and Z involves integrals of the type[6]

$$\left\langle\begin{pmatrix} X \\ Y \\ Z \end{pmatrix}\right\rangle = \left\langle \phi(1)\,\phi'(2) - \phi(2)\,\phi'(1) \,\middle|\, \begin{matrix} x \\ y \\ z \end{matrix} \,\middle|\, \phi(1)\,\phi'(2) - \phi(2)\,\phi'(1) \right\rangle, \tag{8}$$

Table II-1a. Comparison of ZFS methyl naphthalenes (a) and the values calculated from $F(\delta, H) = f(\theta, \phi)$ (b).

Name		X	Y	Z	D	E
Naphthalene	(a)	.0479	.0179	- .0658	.0987	- .0150
	(b)	.0484	.0184	- .0668	.1003	- .0150
1 Me Naph.	(a)	.0464	.0178	- .0642	.0963	- .0143
	(b)	.0469	.0183	- .0652	.0978	- .0143
2 Me Naph.	(a)	.0456	.0182	- .0638	.0958	- .0137
	(b)	.0461	.0187	- .0648	.0971	- .0137
1,2 dime-	(a)	.0451	.0181	- .0632	.0947	- .0135
	(b)	.0457	.0185	- .0642	.0962	- .0136
1,3 dime-	(a)	.0459	.0169	- .0628	.0941	- .0145
	(b)	.0463	.0173	- .0636	.0954	- .0145
1,4 dime-	(a)	.0445	.0179	- .0624	.0935	- .0133
	(b)	.0449	.0183	- .0632	.0947	- .0133
1,5 dime-	(a)	.0456	.0172	- .0628	.0941	- .0142
	(b)	.0461	.0177	- .0638	.0956	- .0142
1,7 dime-	(a)	.0456	.0172	- .0628	.0941	- .0142
	(b)	.0461	.0177	- .0638	.0956	- .0142
1,8 dime-	(a)	.0443	.0179	- .0632	.0948	- .0137
	(b)	.0462	.0180	- .0642	.0962	- .0141
2,3 dime-	(a)	.0478	.0178	- .0656	.0983	- .0150
	(b)	.0484	.0182	- .0666	.1000	- .0150
2,6 dime-	(a)	.0459	.0173	- .0632	.0949	- .0143
	(b)	.0463	.0177	- .0640	.0961	- .0143

Table II-1b. ZFS of methyl naphthalenes (unit, cm^{-1}).

Name	dif. in D	dif.D/expl.D	dif. in E	dif.E/expl.E	D^*
Naphthalene	.0016	.0162	.0000	.0000	(a) .1020 (b) .1039
1 Me Naph.	.0015	.0156	.0000	.0000	(a) .0995 (b) .1010
2 Me. Naph.	.0013	.0136	.0000	.0000	(a) .0990 (b) .1000
1,2 dime-	.0015	.0158	.0001	.0074	(a) .0975 (b) .0994
1,3 dime-	.0013	.0138	.0000	.0000	(a) .0975 (b) .0985
1,4 dime-	.0012	.0128	.0000	.0000	(a) .0959 (b) .0975
1,5 dime-	.0015	.0159	.0000	.0000	(a) .0975 (b) .0985
1,7 dime-.	.0015	.0159	.0000	.0000	(a) .0975 (b) .0985
1,8 dime-	.0014	.0147	.0004	.0297	(a) .0978 (b) .0995
2,3 dime-.	.0017	.0172	.0001	.0066	(a) .1020 (b) .1034
2,6 dime-.	.0014	.0148	.0000	.0000	(a) .0980 (b) .0990

dif. in D = difference between experimental D and D from $F(\delta,H) = f(\theta,\phi)$

expl. D = experimental D.

$D^* = [D^2 + 3E^2]^{\frac{1}{2}}$ (a) experimental (b) from $F(\delta,H) = f(\theta,\phi)$.

Table II-1d. ZFS calculated from $D = h\nu - g\beta H_1 - H_2\left(\frac{2h\nu}{H_1 + H_2} - g\beta\right)$,

$$E = -\left[2g\beta H_1 H_2\left\{\frac{2h\nu}{H_1 + H_2} - g\beta\right\}\right]^{1/2}.$$

Name	D		ν corrected	E	ν corrected
Naphthalene	(1)	.0999	.0989	- .0099	- .0150
	(2)	.0987	.0987	- .0150	- .0150
1 Me Naph.	(1)	.0974	.0964	- .0096	- .0145
	(2)	.0963	.0963	- .0143	- .0143
2 Me Naph.	(1)	.0967	.0957	- .0096	- .0145
	(2)	.0958	.0958	- .0137	- .0137
1,2 dime.-	(1)	.0953	.0943	- .0093	- .0141
	(2)	.0947	.0947	- .0135	- .0135
1,3 dime.-	(1)	.0949	.0939	- .0095	- .0144
	(2)	.0941	.0941	- .0145	- .0145
1,4 dime.-	(1)	.0944	.0934	- .0092	- .0139
	(2)	.0935	.0935	- .0133	- .0133
1,5 dime.-	(1)	.0951	.0941	- .0093	- .0141
	(2)	.0941	.0941	- .0142	- .0142
1,7 dime.-	(1)	.0951	.0941	- .0093	- .0141
	(2)	.0941	.0941	- .0142	- .0142
1,8 dime.-	(1)	.0958	.0948	- .0093	- .0141
	(2)	.0948	.0948	- .0137	- .0137
2,3 dime.-	(1)	.0996	.0986	- .0098	- .0148
	(2)	.0983	.0983	- .0150	- .0150
2,6 dime.-	(1)	.0958	.0948	- .0094	- .0142
	(2)	.0949	.0949	- .0143	- .0143

Table II-1e. Stationary resonance field of methyl naphthalene (unit, Oe).

	H_{min}	H'_y	H'_x	H'_z	H''_z	H''_x	H''_y	H'''_y	H'''_x	H'''_z
Naphthalene	1499	1506	1555	1634	2163	2458	2912	3478	3989	4313
1 Me Naph.	1506	1512	1559	1633	2192	2482	2917	3480	3967	4287
2 Me Naph.	1507	1513	1560	1632	2199	2483	2923	3474	3969	4280
1,2 dime. nap.	1510	1517	1560	1633	2210	2503	2914	3487	3946	4271
1,3 dime. nap.	1511	1517	1563	1631	2218	2941	2932	3468	3460	4262
1,4 dime. nap.	1514	1520	1562	1632	2226	2523	2918	3485	3937	4256
1,5 dime.nap.	1511	1517	1562	1632	2217	2496	2928	3472	3955	4264
1,7 dime.nap.	1511	1517	1562	1632	2217	2496	2928	3472	3935	4264
1,8 dime.nap.	1510	1516	1561	1633	2210	2500	2928	3472	3949	4271
2,3 dime.nap.	1500	1506	1556	1634	2167	2459	2914	3477	3988	4310
2,6 dime.nap.	1509	1514	1563	1631	2210	2478	2938	3460	3973	4270

where ϕ and ϕ' denote normalized singly occupied molecular orbitals from which the major contribution of the orbital energy is assumed to arise, 1 and 2 label the spatial coordinates of the two triplet electrons, and the operators x, y, and z are defined in terms of the principal axes x, y, and z, and the distance between two electrons,

$$r_{12} = \frac{1}{2} (g\beta)^2 r_{12}^{-5} \left[r_{12}^2 - 3 \begin{pmatrix} x_{12}^2 \\ y_{12}^2 \\ z_{12}^2 \end{pmatrix} \right]. \tag{9}$$

Furthermore, ϕ and ϕ' can be expressed as linear combinations of AO's by various π electron approximations; it may be meaningful to examine the relative magnitude of X, Y, and Z of 1, n-dimethylnaphthalenes in terms of n, the substitution site number, which takes the value $n = 2, 3, \ldots, 8$. The result of such an attempt is indicated in Fig. II-3. The circle indicates the predicted neighborhood of the value for the nonavailable 1,6 dimethyl naphthalene. The periodic behavior of X and Y with respect to n, and the prediction for $n = 6$ can readily be visualized by looking at the highest filled and the lowest unfilled MO's, $\phi = \phi_6$ and $\phi' = \phi_7$, respectively. Some of the Hückel MO's are presented in Fig. II-4.

Since the greatest AO coefficient occurs invariably at the methyl carbons, and the electron density is the square of the coefficients, it is not unreasonable to assume that the major contribution to the expectation values of X and Y in Eq. 8 comes from the magnetic dipolar interactions (last term in Eq. 1) between these methyl substituent centers. This enables one to qualitatively justify the relative magnitude of X and Y for some given dimethyl naphthalenes just by knowing the methyl substituent positions. For instance, given 1,4 and 1,5 dimethyl naphthalene, by comparing the projection of ℓ_{12} (the distance between the two methyl carbons) on the x and y axes, $X_{n=4} \ll X_{n=5}$ can readily be seen. The similar comparison between $n = 2$ and $n = 3$, $n = 3$ and $n = 4$, $n = 3$ and $n = 7$ agrees qualitatively with Fig. II-2. This is, however, a very drastic oversimplification that assumes only the one two-centered interaction, and thus for justification of Fig. II-3, the integrals (8) must be evaluated with all appreciable contributions of AO's included. Figure II-3c is a plot of Z values with respect to n. For the mono-substituted methyl naphthalenes the approximation of ZFS must involve both ϕ_5 and ϕ_6, and since the coefficients of ϕ_5 are not equal in magnitude to ϕ_7, the evaluation of ZFS's are slightly more involved. Thus looking at both ϕ_5 and ϕ_6 of Hückel MO's, one may apply the similar

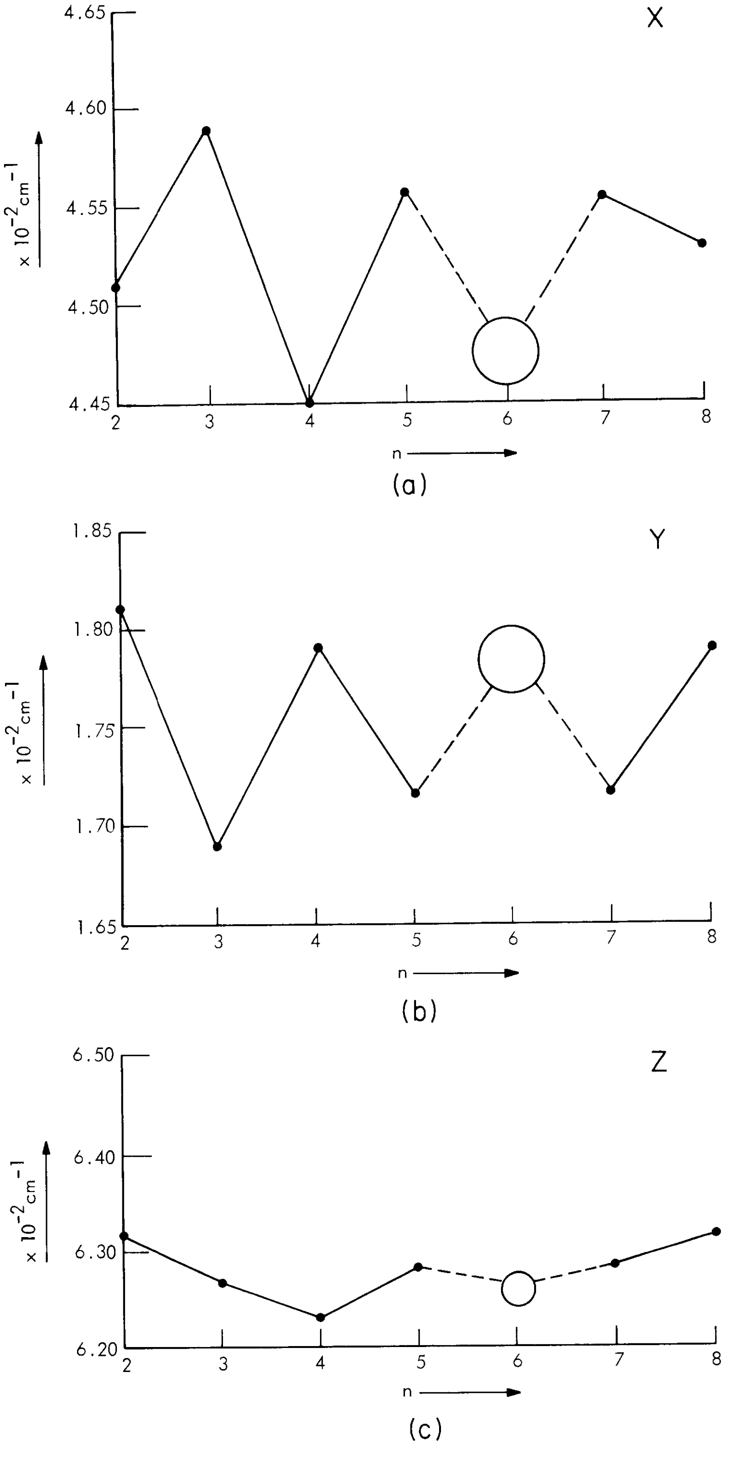

Fig. II-3. (a) X values of 1, n dimethyl naphthalene, n = 2, 3, . . . , 8.

(b) Y values of 1, n dimethyl naphthalene, n = 2, 3, . . . , 8. n = 6 compound is not synthetically available.

(c) Z values of 1, n dimethyl naphthalene, n = 2, 3, . . . , 8. n = 6 compound is not synthetically available.

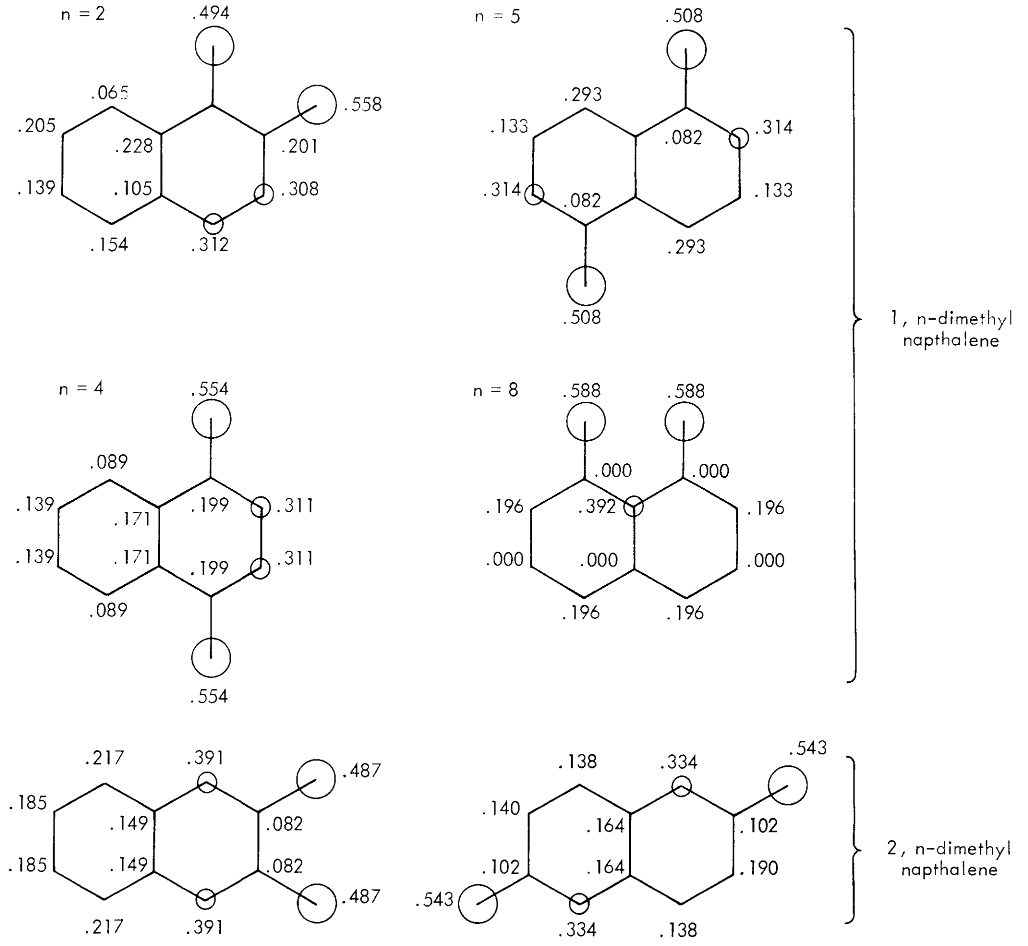

Fig. II-4. Hückel MO coefficients of some dimethylnaphthalenes for ϕ_6 and ϕ_7.

qualitative rationalization for mono-methyl naphthalenes.

What is assumed in Fig. II-5b is that the special function in Eq. 8 has the major contribution from ϕ_5 and ϕ_6 HMO's; thus, we have the proportionality relation

$$\left|\phi(1)\phi'(2)-\phi(1)\phi'(2)\right\rangle \propto {}^3\Phi_o(\phi_5,\phi_6), \tag{10}$$

and the linear combination is radically simplified just by superimposing ϕ_5 and ϕ_6, and ℓ_x and ℓ_y are assumed to be proportional to the result of the operation on $\left|{}^3\Phi_o\right\rangle$ by the x and y operators in (9). As Fig. II-5 indicates, this simple treatment properly predicts the relative magnitude of X and Y in those two compounds; that is, $X_{n=1} > X_{n=2}$, and $Y_{n=1} < Y_{n=2}$. The equation (Fig. II-5a) can be expressed as the simple qualitative rule. "The shorter the $\ell_{(x \text{ or } y)}$ between two major centers of AO's, the greater the ZFS, X or Y." A similar simple scheme applies also for 2, n dimethyl naphthalenes.

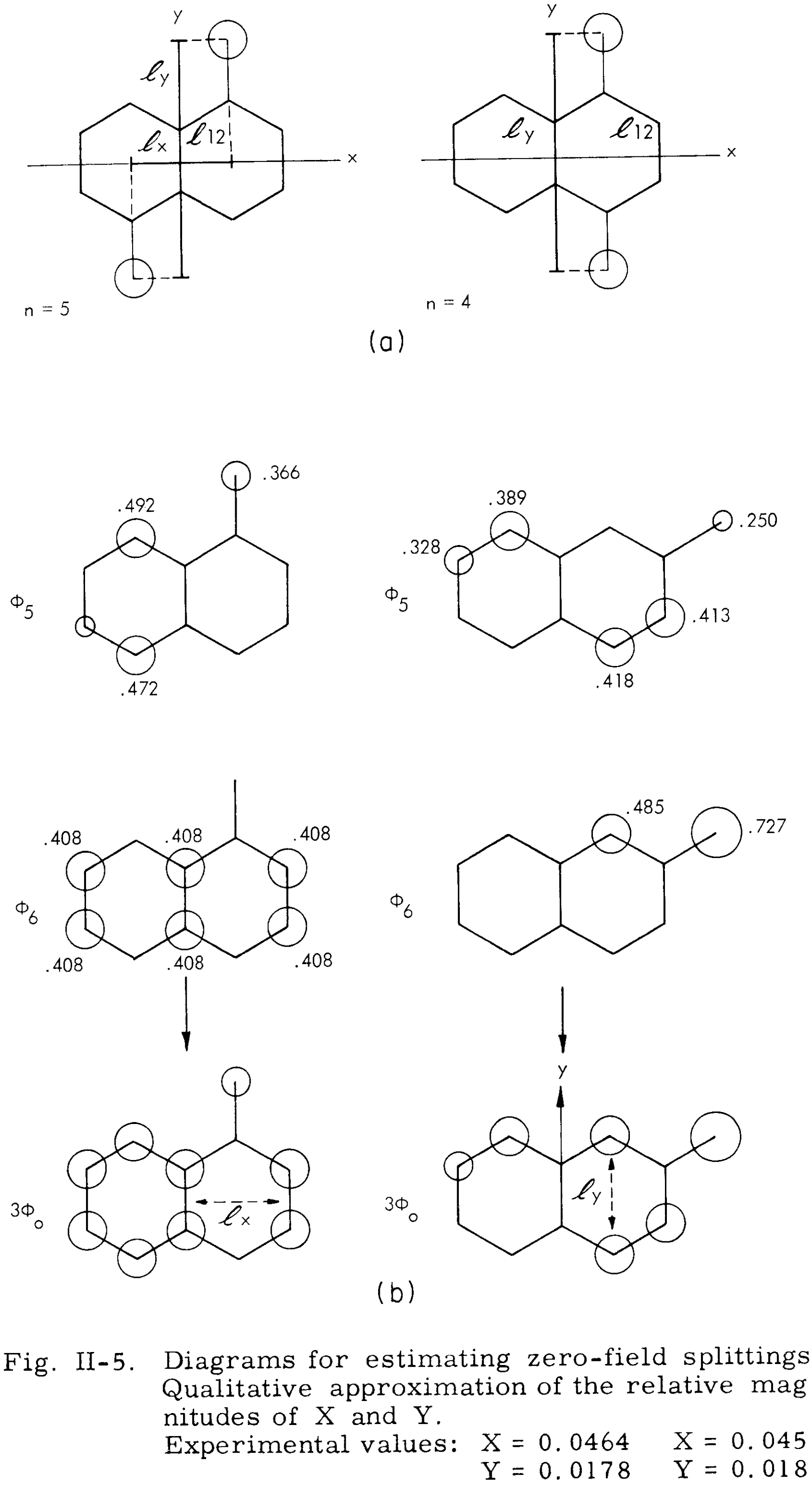

Fig. II-5. Diagrams for estimating zero-field splittings. Qualitative approximation of the relative magnitudes of X and Y.
Experimental values: X = 0.0464 X = 0.0456
Y = 0.0178 Y = 0.0182

In terms of the deviation of ZFS from that of naphthalene,

1,8 dimethyl naphthalene shows greatest $\Delta X = -0.0036$

1,3 dimethyl naphthalene shows greatest $\Delta Y = -0.0010$

1,3 and 1,5 dimethyl naphthalene shows greatest $\Delta Z = -0.0030$.

The parameters ΔX, ΔY, ΔZ are of some interest, since they represent the deviation of zero-field energies of these systems from the D_{2h} symmetry to which naphthalene belongs.

K. W. Bowers

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