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Triplet-State Zero-Field Splittings. III.[1] Effect of the Two-Center Coulomb Repulsion Integrals

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We here report that a Pariser-Parr-type approximation[2] for the two-center Coulomb repulsion integrals yields much better triplet-state zero-field splitting (ZFS) parameters for aromatic hydrocarbons and nitrogen heterocycles than the Nishimoto-Mataga-type approximation.[3] Compounds studied are shwon in Fig. 1 with a coordinate system adopted.

In our previous paper,[1] it was shown that the SCF-AO's expanded by Löwdin are useful for the calculation of the electron spin dipolar interactions in the triplet-state ZFS's of aromatic molecules, and particularly for the ZFS calculation the SCF-AO's have formally replaced the Slater AO's used in the wavefunction calculation. In other words, the SCF-AO's have been used for the evaluation of the electron spin dipolar interactions in combination with a set of approximations consisting of (1) the π-electron approximation (Pariser-Parr-Pople method),[2,4] (2) the use of configurations which are only singly excited with respect to the lowest-energy singlet configuration for the triplet-state wavefunctions, and (3) the two-center integral approximation for the electron spin dipolar interactions.

Thus, in Part I[1] we have obtained excellent agreement with experiments for benzene and naphthalene, and also some promising results for aromatic nitrogen heterocycles such as quinoline and isoquinoline, as shown in Table 1 under the heading of Eq. (1), employing the following Nishimoto-Mataga-type formula of the two-center Coublomb repulsion integrals for all interatomic distances R_{pq},

$$(pp|qq) = 6.588/(Z_p^{-1}+Z_q^{-1}+0.457529\,R_{pq})\ \text{eV}, \tag{1}$$

where R_{pq} is given in angstroms, and Z_p stands for the effective nuclear charge of the p-th $2p\pi$AO and was given 3.25 and 3.90 for carbon and nitrogen, respectively. Eq. (1) was obtained by combining the approximations proposed by Paoloni[5]

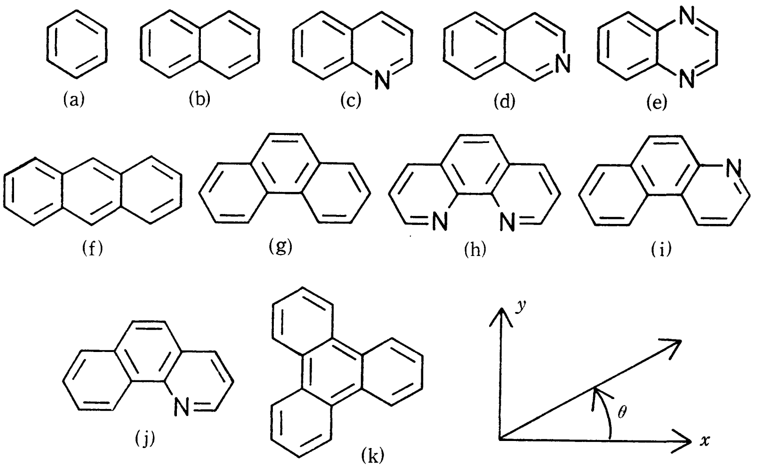

Fig. 1 Compounds studied in this work, with coordinate axes: (a) benzene, (b) naphthalene, (c) quinoline, (d) isoquinoline, (e) quinoxaline, (f) anthracene, (g) phenanthrene, (h) 1,10-phenanthroline, (i) 5,6-benzoquinoline, (j) 7,8-benzoquinoline, (k) triphenylene.

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[2] R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

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TABLE 1. CALCULATED AND OBSERVED ZFS PARAMETERS FOR THE LOWEST EXCITED TRIPLET STATES OF SOME AROMATIC HYDROCARBONS AND NITROGEN HETEROCYCLES[a] (cm^{-1})

Compound	Calculated						Observed			
	Formulas for $(pp\|qq)$ integrals									
	Eq. (1)[b]			Eq. (2)[c]						
	D	E	θ[d]	D	E	θ[d]	D	E	θ[d]	Ref.
Benzene	0.1598			0.1565			0.1581	0.0064		8
Naphthalene	0.1142	−0.0281		0.1027	−0.0243		0.10119	−0.01411		9
Quinoline	0.1180	−0.0352	5.1°	0.1054	−0.0293	3.8°	±0.1030	∓0.0162	±13°	10
Isoquinoline	0.1191	−0.0301	14.8°	0.1033	−0.0249	14.7°	±0.1004	∓0.0117	±25°	10
Quinoxaline	0.1225	−0.0406		0.1101	−0.0347		±0.1007	∓0.0182		10
Anthracene	0.0836	−0.0161		0.0747	−0.0117		0.072	−0.007		11
Phenanthrene	0.1197	−0.0475		0.1102	−0.0537		0.10044	−0.04658		9
1,10-Phenanthroline	0.1277	−0.0493		0.1158	−0.0564		±0.1038	∓0.0485		12
5,6-Benzoquinoline	0.1219	−0.0461	−5.0°	0.1105	−0.0544	−17.6°	±0.1023	∓0.0477		12
7,8-Benzoquinoline	0.1233	−0.0495	−3.2°	0.1113	−0.0565	−12.0°	±0.1011	∓0.0468		12
Triphenylene	0.1374			0.1316			±0.134			13

a) For the coordinate axes, see Fig. 1.
b) Ref. 1 and this work.
c) For $R_{pq} > 2.8$ Å, the multipole expansion formula has been used. See text.
d) Principal axis direction of the ZFS tensor as defined in Fig. 1.

and by Nishimoto and Mataga.[3]

In this note the following quadratic Pariser-Parr-type expression,[6]

$$(pp|qq) = 3.294\,Z + (3.836 - 1.993Z)R_{pq} - (0.7661 - 0.3004Z)R_{pq}{}^2 \text{ eV}, \qquad (2)$$

where $Z = 1/2(Z_p + Z_q)$, is employed for $R_{pq} \leq 2.8$ Å, and for $R_{pq} > 2.8$ Å a multipole expansion formula.[7] Eq. (2) is derived through the Paoloni approximation[5] and the application of the multipole expansion formula for $R_{pq} = 2.8$ and 3.7 Å.[2] The ZFS parameters calculated with this approximation are shown in the columns under the heading Eq. (2), of Table 1. The whole computational scheme is the same as Method 1 of Part I, namely the SCF-AO's are used for all interatomic distances in evaluating the electron spin dipolar interactions.

Comapring the data calculated with the observed ZFS parameters given in Table 1, it can be concluded that the Pariser-Parr-type formula is much better than the Nishimoto-Mataga-type formula at least for the triplet-state ZFS calculation. For quinoxaline, phenanthrene and azaphenanthrenes, agreement with experiments is not so good as that for the other compounds listed in Table 1, although considerably improved. The reason for this is not clear at present.

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