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A Study of the Zero Field Splittings of the Lowest Excited Triplet States of Substituted Benzenes and Related Molecules by Optical Detection of Magnetic Resonance, Electron Paramagnetic Resonance, and Molecular Orbital Calculations

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The zero field splittings of a series of substituted benzenes and related molecules have been examined by means of optical detection of magnetic resonance (ODMR), electron paramagnetic resonance (EPR), and molecular orbital (MO) calculations. It is experimentally shown that D and E values vary remarkably depending on the type of molecule despite the similarlity in the molecular size. In particular, E varies from $+0.038\ \mathrm{cm}^{-1}$ for phenylacetylene to $-0.0597\ \mathrm{cm}^{-1}$ for aniline reflecting large differences in the spin distributions. The calculation of the zero field splittings of the molecules studied here on the basis of the Pariser-Parr-Pople-type MO's can give the values reasonably close to those obtained experimentally with a few exceptions. On the basis of the obtained results the natures of the T_1 states of substituted benzenes are characterized from the zero field splittings.

The zero field splittings (ZFS's) of the lowest excited triplet (T_1) states of aromatic molecules have been studied extensively for more than two decades.[1–18] Since in most molecules ZFS's are determined by spin-spin interactions between two unpaired electrons, the ZFS's reflect spin distributions which are directly related to the electronic wave functions of the T_1 states. One would hope to extract useful information about electronic structures of the T_1 states from the analysis of ZFS's. Yet, use of ZFS's in elucidating the electronic structures of the T_1 states of aromatic molecules has been limited so far in spite of numerous experimental data accumulated. This is due partly to the fact that the ZFS's are often not very sensitive to structural changes. In the present work we have attempted to analyze the ZFS's of substituted benzenes and related molecules with a hope of utilizing the ZFS's to characterize the electronic structures of the T_1 states.

Substituted benzenes form an attractive group of molecules for a detailed study of ZFS, because their ZFS's are markedly dependent on the nature of substituent.[2–18] This situation is quite different from the cases of other hydrocarbons such as naphthalene.[19] The triplet states of substituted benzenes are often classified as having quinonoidal (Q) or antiquinonoidal (AQ) structures. The ZFS's are expected to vary depending on whether the T_1 state is of Q type or of AQ one and an examination of the ZFS's may be helpful in characterizing their electronic structures.

The main purposes of the present work are the following. First, we compare the ZFS's of various substituted benzenes in order to find general qualitative trends. For this purpose we have supplemented the existing data by conducting optical detection of magnetic resonance (ODMR) and electron paramagnetic resonance (EPR) experiments on a series of substituted benzonitriles, anilines, and anisoles. On the basis of the obtained results we attempt to characterize the natures of the T_1 states of substituted benzenes from the ZFS's. Second, we calculate the ZFS's of the representative systems by using the semiempirical Pariser-Parr-Pople-type molecular orbitals (MO's) to see whether or not such calculations reproduce the experimentally obtained ZFS's adequately. Substituted benzenes which we examine here are divided into two groups, one having electron-attracting mesomeric groups such as -CCH, -CN, and -CHO, and the other having electron-donating inductive substituents such as $-NH_2$ and $-OCH_3$. The effects of weakly perturbing substituents such as F, Cl, and CH_3 were examined in benzonitrile, aniline, and anisole. We also studied other related molecules such as benzofuran, indole, and indazole as the examples of the molecules with very strongly mesomeric groups.

Experimental

Sample Preparation. 1,4-Dibromobenzene (DBB) was purified by recrystallization from ethanol followed by zone refining. All of the solid guest samples were purified by recrystallization and all the liquid samples were purified by distillation. Mixed crystals containing small amounts of guest molecules were grown using the standard Bridgman method starting from the melts containing approximately 2 wt% of the guest molecules.

ODMR and EPR Measurements. The ZFS's (D's and E's) of benzonitriles, anilines, and anisoles were determined from the microwave frequencies corresponding to the transitions among the zero field (ZF) spin sublevels observed by the zero field optical detection of magnetic resonance (ZFODMR)

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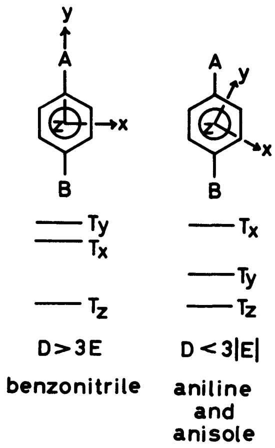


Fig. 1. Direction of axes and ZFS's of the molecules investigated in this work.

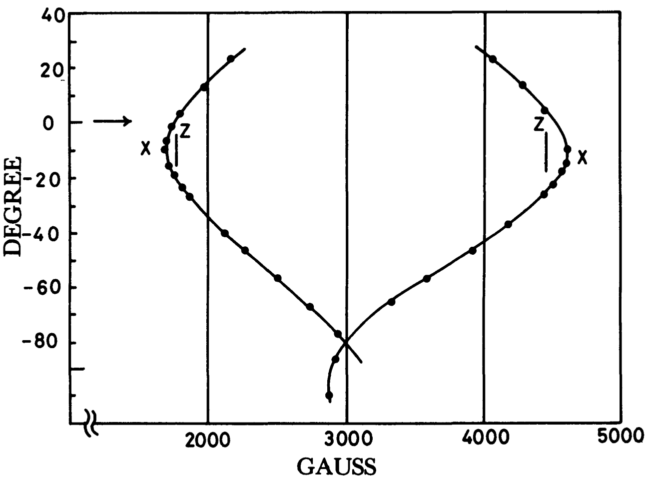


Fig. 2. Angular dependence of the EPR signals of 4-methylanisole in DBB. Magnetic field was rotated in the x-y plane of the molecule.

experiments at about 1.8 K. The experimental setup and procedures are essentially the same as those described in a previous paper.[20] The ODMR experiments were normally made under steady state illumination using the fast passage technique. The lifetimes of the substituted benzenes in DBB host range from 5 to 100 ms and we swept the frequency region of 0.1—0.5 GHz within 0.1—2 s. Normally three ODMR transitions were detected with good S/N ratios. In order to determine the sublevel schemes we also performed the EPR experiments of single crystal on a few anilines and anisoles at 4.2 K. The experimental setup and the method are similar to those described previously.[6]

Experimental Results and Qualitative Interpretation

Experimental Results. The ZFS's, D's and E's, of the molecules studied here are determined from the ZF transition energies using the spin Hamiltonian,

$$H_s = D\left(S_z^2-\frac{1}{3}S^2\right)+E(S_x^2-S_y^2). \qquad (1)$$

When the z axis is taken perpendicular to the molecular plane, the bottom sublevel is the z sublevel. In the cases of benzonitriles and phenylacetylene with the C_{2v} symmetry we take the x and y axes as shown in Fig. 1. Then the order of the sublevels becomes y, x, and z from the top. In these molecules it is known that $T_y-T_x<T_x-T_z$ and $D>3E$.[5] In the ortho- and meta-substituted benzonitriles the y directions are not exactly parallel to the C–CN direction. However, the above sublevel scheme is considered to be correct in all the benzonitriles studied here.

On the other hand, whether D is larger than $3|E|$ is not certain in anisoles and anilines. In most aromatic molecules D is usually larger than $3|E|$. $D>3|E|$ was found in the case of 4-chloroaniline in xylene (X),[3,8] but the same molecule gives $D<3|E|$ in the 1,4-dichlorobenzene (DCB) host.[8,14] Kothandaraman and Tinti also concluded $D<3|E|$ for 4-chloroanisole.[3] One cannot make an a priori assumption about the relative magnitudes of D and $3|E|$. Here we have examined the EPR spectra of 4-methylanisole in the DBB host (Fig. 2). We have obtained the values for the field strengths of the Z stationary points, 4465 and 1755 G (1 G=10^{-4} T). These values are in good agreements with the values calculated from the D and E determined by the ODMR experiments on the assumption of $D<3|E|$. This assignment is also confirmed by the observation that the field separation between the two in-plane stationary peaks is larger than that for the Z stationary peaks. These observations definitely show $D<3|E|$ for 4-methylanisole. $D<3|E|$ was also found for 4-chloroanisole[3] 4-chloroaniline, and 2-fluoroaniline in DBB.[14] Here we calculated D's and E's of other anilines and anisoles by assuming $D<3|E|$.

Another remarkable point about the T_1 states of anilines and anisoles is the spin axis rotation whose occurrence has been confirmed in the cases of aniline in X,[11] 4-fluoroaniline in DBB,[14] and 4-chloroaniline in DCB.[14] It is quite probable that the spin axis rotation is also taking place in anilines and anisoles studied here. If this is the case, the x and y axes deviate from the molecular symmetry axes as shown in Fig. 1. The order of the sublevels determined for aniline is x, y, and z from the top and this is assumed for all anilines and anisoles studied here. The ZFS's determined in this work are tabulated in Table 1 together with those of other related systems.

The values of the ZFS's determined by the present ODMR experiments agree reasonably well with those determined by EPR at 4.2 K. However, the ZFS's determined by the ODMR experiments do not necessarily agree with the values determined by the EPR experiments at 77 K. For instance, EPR at 77 K gives D=0.1371 cm^{-1} for benzonitrile in DBB,[5] while ODMR at about 1.8 K gives D=0.1430 cm^{-1} for the same system. The ZFS's of the substituted benzenes also depend on the nature of the matrix. D and E values of aniline in DBB are considerably different from those obtained in X.[11]

General Trend of ZFS. We first discuss some notable observations about the ZFS's of substituted benzenes. Despite the similarities of the molecular size the ZFS's vary remarkably depending on the substituent. D observed here ranges from 0.1472 cm^{-1} in 4-fluorobenzonitrile to 0.1040 cm^{-1} in 4-fluoroaniline. E ranges from +0.0380 cm^{-1} in phenylacetylene to −0.0597 cm^{-1} in aniline. However, the variations of D and E in the same type of molecules are much smaller. From the results given in Table 1 we conclude the following.

1) Even weakly perturbing substituents such as F, Cl, and CH_3 affect D considerably, but their effect on E is relatively small.

Table 1. Experimental Results of E_T's, D's, and E's

Number	Guest	Host[a]	E_T cm^{-1}	D cm^{-1}	E cm^{-1}	Reference
1	Aniline	DBB	27601	0.1160	(−)0.0597[b]	Present work
2		X	27659	0.1229	(−)0.0352[b]	11
3	2-Fluoroaniline	DBB	27285	0.1126	−0.0435[c]	Present work
4	4-Fluoroaniline	DBB	26838	0.1040	−0.0533[c]	Present work[d]
5	4-Chloroaniline	DCB	26938	0.1220	−0.0500[c]	14
6		X	26514	0.1171	±0.0338[e]	3
7	4-Toluidine	DBB	26795	0.1119	(−)0.0533[b]	Present work
8	4-Fluoroanisole	X	27563	0.1220	(−)0.0562[b]	3
9	4-Chloroanisole	X	27377	0.1323	(−)0.0569[b]	3
10	4-Methylanisole	DBB	27278	0.1236	(−)0.0537[b]	Present work
11	Benzonitrile	DBB	26882	0.1430	0.0106	Present work[f]
12	2-Fluorobenzonitrile	DBB	26788	0.1405	0.0117	Present work
13	3-Fluorobenzonitrile	DBB	26553	0.1370	0.0191	Present work
14	4-Fluorobenzonitrile	DBB	27229	0.1472	0.0073	Present work
15	4-Chlorobenzonitrile	DBB	25840[g]	0.1319	0.0045	15
16	2-Tolunitrile	DBB	26246	0.1325	0.0206	Present work
17	3-Tolunitrile	DBB	26143	0.1231	0.0050	Present work
18	4-Tolunitrile	DBB	26702	0.1344	0.0070	Present work
19	Phenylacetylene	DBB	25120	0.1339	0.0380	5
20	Benzaldehyde	BAC	25456	0.1381	0.0089	9, 10, 13, 17
21	Benzofuran	DBB	24570	0.1076	0.0530	6
22	Indole	DBB	24155	0.0978	0.0453	6
23	Benzimidazole	BAC	26539	0.1123	0.0270	18
24	1*H*-Indazole	BAC	23590	0.1077	0.0293	18
25	2*H*-Indazole	BAC	20903	0.0983	0.0120	16
26	Purine	BAC	26409	0.1042	0.0608	18

a) DBB, X, DCB, and BAC denote 1,4-dibromobenzene, xylene, 1,4-dichlorobenzene, and benzoic acid, respectively. b) The sign of the E parameter seems to be negative by analogy. c) The sign of the E parameter was determined by means of single crystal EPR. d) EPR at 4.2 K gives $D=0.102\,\mathrm{cm}^{-1}$ and $E=-0.0535\,\mathrm{cm}^{-1}$ for 4-fluoroaniline in DBB.[14] The value of the ZFS of 4-fluoroaniline in this table is determined by the ODMR experiment, and agrees well with the value determined by EPR. e) The sign of the E parameter was not determined. f) EPR at 77 K gives $D=0.1371\,\mathrm{cm}^{-1}$ and $E=0.0072\,\mathrm{cm}^{-1}$ for benzonitrile in DBB.[5] The value of the ZFS of benzonitrile in this table is determined by the ODMR experiment. As mentioned in the text, the ZFS's determined by the ODMR experiments do not necessarily agree with the values determined by the EPR experiments at 77 K. g) Present work.

2) D's of benzonitriles are relatively large compared with those of anilines and anisoles.

3) $|E|$'s of anilines and anisoles are similar and quite large, while $|E|$'s of benzonitriles are rather small.

In Fig. 3 we plot D vs. S_0—T_1 transition energy (E_T) for a series of benzonitriles, anilines and anisoles. Brinen and Orloff noted that there is a linear relation between D and E_T for a large number of polyacenes.[21] We have extrapolated their plot to the region of large E_T which is shown by a dotted line in Fig. 3. It is seen that the points for benzonitriles are located above the extrapolated Brinen Orloff line, but D's for anilines and anisoles are located below. For a series of benzonitriles D vs. E_T plot gives an approximately linear relation, but the slope is much steeper than that for the Brinen Orloff plot. It is interesting to note that the D values of benzonitriles with mesomeric substituents, polyacences (extrapolated Brinen Orloff line), and aniline and anisoles with mainly inductive substituents decrease in that order.

A detailed analysis of the ZFS's of benzene and benzene derivatives by Godfrey, Kern, and Karplus showed that the main factors determining the magnitude of D are the extent of configurational mixing and the extent of delocalization of unpaired electrons.[22] The former tends to increase D, whereas the latter to decrease D. It was shown that D calculated for the benzene triplet state with a single configuration can be very small, being $0.1\,\mathrm{cm}^{-1}$, but a small amount of configurational mixing can increase the D drastically. In the present systems benzonitriles and phenylacetylene with more delocalization of unpaired electrons into the substituents have larger D values than anilines and anisoles with less delocalization. Therefore the main factor determining the variation of D in the present systems appears to be the extent of the configurational mixing.

In the aromatic hydrocarbons such as naphthalene, substitution by weakly perturbing substituents hardly affects D.[19] In the molecules studied here D is rather sensitive to the substitution by them. Even fluorine substitution causes a significantly large change in D. Furthermore the change in D caused by the mono fluoro substitution depends on the location of the substitution: D (para)$>D$ (ortho)$>D$ (meta) in benzonitrile, while D (ortho)$>D$ (para) in aniline. It was also found that fluorine substitution at the para position produces a blue shift of E_T in benzonitrile, but a red shift in aniline. Thus the effect of fluorine substitution is opposite in these two types of molecules. These observations seem to indicate that substitution by weakly perturbing substituents changes the extent of configurational mixing considerably in the present systems.

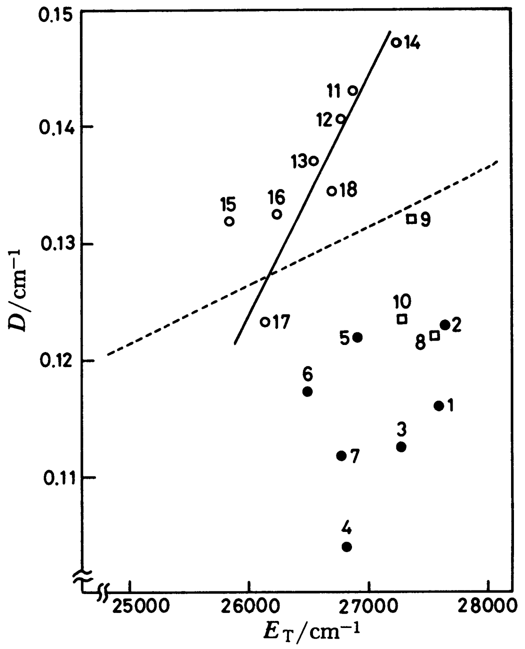


Fig. 3. Plots of D vs. E_T for a series of benzonitriles (○), anilines (●), and anisoles (□). The numbers near the data points correspond to those in Table 1. The dotted line shows the extrapolated Brinen Orloff plot.[21]

The previous investigations have shown that benzonitrile and phenylacetylene have Q structures,[5] while anilines and anisoles have AQ ones.[11,14] Anilines and anisoles studied here all have large $|E|$ values. It seems that substituted benzenes with AQ structures have large $|E|$ values.

Calculation of ZFS

The ZFS's in the lowest excited triplet states of the representative benzene derivatives have been calculated using the semiempirical Pariser-Parr-Pople-type LCAO-MO's.[23,24] The ZFS's of benzofuran, indole, 1*H*- and 2*H*-indazoles, benzimidazole, and purine were also calculated for comparison. Many calculations on the ZFS's of several molecules in their triplet states have been made successfully with various degrees of approximations.[25–34] One of the present authors (J. H.) also obtained good agreements between the observed ZFS's and the calculated ones for aromatic hydrocarbons.[25] We have used a similar procedure in the present calculation.

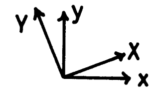
Method and Procedure. The ZFS's were evaluated from the electron spin-spin interactions, using the standard and simple approximation with only Coulomb-type integrals.[35–38] The spin-orbit interactions were ignored. The ZFS parameters, D and E, can be expressed as,

$$D = \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right\rangle, \tag{2}$$

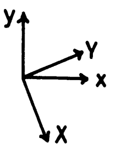
$$E = \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle \frac{x_{12}^2 - y_{12}^2}{r_{12}^5} \right\rangle, \tag{3}$$

where r_{12} is the distance between two unpaired electrons. The wave functions were constructed by including configurations arising from all the single excitations relative to the ground state. For all of the molecules studied here, the overlap integrals and the electron spin-spin interactions were calculated by using double-zeta atomic orbitals by Clementi.[39]

The information obtained from the present calculation for the directions of the principal axes of the ZF tensors is not complete.[40] In fact, we cannot determine whether the direction of the principal axis of the ZF tensor corresponds to, for example,



or



where (x, y) and (X, Y) denote sets of the in-plane axes for the coordinate system of the molecule and for the principal axis system of the ZF tensor, respectively. This means that the absolute sign of E cannot be determined from the calculation. We therefore deduced the directions of the principal axes of the ZF tensors and the signs of E's from the experimental results.

For benzaldehyde, benzonitrile, and phenylacetylene, two-center electron repulsion integrals were estimated by the method suggested by Nishimoto.[41–43] Since the detailed knowledge of the molecular geometry is not required, two-center core integrals (β) were calculated by the method of variable β approximation[43] using the following parameters reported previously.[5,13]

Benzaldehyde:

($-0.51P-2.12$) eV for C–C(ring),
($-0.55P-2.80$) eV for C=O,
($-0.51P-1.70$) eV for C(ring)–C(formyl group).

Benzonitrile:

($-0.51P-2.12$) eV for C–C(ring),
($-0.53P-2.60$) eV for C≡N,
($-0.51P-1.72$) eV for C(ring)–C(cyano group).

Phenylacetylene:

($-0.51P-2.12$) eV for C–C(ring),
($-0.51P-2.40$) eV for C≡C,
($-0.51P-1.72$) eV for C(ring)–C(ethynyl group),

where P is the bond order. In the calculations of these molecules, the ionization potentials (I's) and electron affinities (A's) for C, O, and N were taken as 86% of the values for free atoms[44] following Nishimoto (C trtrtrπ: I=9.60 eV, A=0.00 eV, N tr^{2}trtrπ: I=12.14 eV, A=1.53 eV, O tr^{2}tr^{2}trπ: I=15.22 eV, A=2.12 eV).[5,42] The UHF calculations using these parameters have been made previously for benzaldehyde,[13] benzonitrile,[5] and phenylacetylene[5] with satisfactory results for spin distributions. We checked our program and procedure with naphthalene. The result of the calculation (D=0.101 cm^{-1} and E=-0.010 cm^{-1}) agreed well with the experimental result for naphthalene (D=0.1006 cm^{-1} and E=−0.0138 cm^{-1}).[45]

The above method is not applicable to the molecules with odd π orbitals. Therefore, in the calculations of aniline, anisole, benzofuran, indole, 1*H*- and 2*H*-indazoles, benzimidazole, and purine, two-center electron repulsion integrals and β's were evaluated by using Ohno-Klopman-type[46] and Wolfsberg-Helmholtz-type[47] approximations, respectively. β for benzene was assumed to be −2.39 eV.

In the calculations of the molecules with odd π orbitals, we adopted either of the following two kinds of parameters (parameter A and B). In parameter A, we used the values given by Hinze and Jaffe[44] (C trtrtrπ: I=11.16 eV, A=0.03 eV, N tr^{2}trtrπ: I=14.12 eV, A=1.78 eV, O tr^{2}tr^{2}trπ: I=17.70 eV, A=2.47 eV) and by Dewar and Morita[48] (N trtrtrπ: I=28.59 eV, A=11.96 eV, O tr^{2}trtrπ: I=33.90 eV, A=15.30 eV).

As described later, parameter A does not satisfactorily reproduce the observed trend of ZFS in the calculations of *N*-heterocyclic molecules with N trtrtrπ. The reason for this may be explained by the following fact. N tr^{2}trtrπ and N trtrtrπ provide one and two π electrons to π molecular orbitals, respectively. However, since in a conjugated system the π electron density on N trtrtrπ decreases substantially from 2 owing to the π electron delocalization, while the σ electron density on N trtrtrπ is estimated to increase largely from 3.[49] Thus, the value of semiempirical parameters, such as the one-center repulsion integral ($I-A$), for N trtrtrπ are considered to become close to those for N tr^{2}trtrπ. As a result, the observed trend of ZFS may not be reproduced with parameter A. Accordingly, in parameter B the value of $I-A$ for N trtrtrπ is tentatively assumed to be equal to that for N tr^{2}trtrπ given by Hinze and Jaffe ($I-A$=12.34 eV).[44] On the other hand, since N tr^{2}trtrπ and N trtrtrπ provide one and two π electrons to π molecular orbitals, the electric fields for electrons on N tr^{2}trtrπ and N trtrtrπ approximate to those of N$^+$ and N^{2+}, respectively. The value of A for N^{2+} is considered to be equal to that of I for N$^+$. It may not be unreasonable, thus, to assume that the value of A for N trtrtrπ is nearly the same as that of I for N tr^{2}trtrπ given by Hinze and Jaffe.[44] In parameter B, for N trtrtrπ we used the value thus determined (I=26.45 eV, A=14.11 eV) and for C trtrtrπ and N tr^{2}trtrπ we used the same values as those in parameter A.

The ZFS of aniline was calculated for the conformation in which the benzene ring is hexagonal (H), Q, AQ, or skewed-antiquinonoidal (SAQ) form. The geometries of the benzene rings for the H, Q, and AQ conformations were taken from the results by Fujimura et al.[50] The geometry of the SAQ conformation was assumed to be the same as that of 4-fluoroaniline which had been predicted from the EPR study.[14] The effect of the methyl group in anisole was not taken into account in the present calculation. The ZFS of anisole was calculated with the same geometry as that of the SAQ conformation of aniline.

The geometries of indole, 1*H*-indazole, benzimidazole, and purine were taken from the results of the X-ray diffraction.[51–53] The geometries of the benzene and pyrazole moieties in 2*H*-indazole were assumed to be the same as those of the benzene ring in 1*H*-indazole and of pyrazole ring given in the reference,[51] respectively. The ZFS of benzofuran was calculated with the same geometry as that of indole.

Results and Discussion. The results of the calculations for E_T's, the D's and E's, and the directions of the in-plane principal axes of the ZF tensors (θ) are summarized in Table 2. Here θ denotes the angle between the short axis of the molecule and the principal axis of the top sublevel. It is seen

Table 2. Calculated E_T's, ZFS's, and Directions of Principal Axes of ZF Tensors

					Parameter A				Parameter B			
	E_T 10^4 cm^{-1}	D cm^{-1}	E cm^{-1}	θ	E_T 10^4 cm^{-1}	D cm^{-1}	E cm^{-1}	θ	E_T 10^4 cm^{-1}	D cm^{-1}	E cm^{-1}	θ
Benzaldehyde	2.50	0.129	0.011	31[a]								
Benzonitrile	2.45	0.124	0.010	90								
Phenylacetylene	2.40	0.122	0.029	90								
Aniline H					2.41	0.124	0.004	90	2.49	0.131	0.003	90
Q					2.27	0.110	0.020	90	2.37	0.118	0.026	90
AQ					2.42	0.128	−0.027	0	2.46	0.130	−0.032	0
SAQ					2.50	0.116	−0.011	−52	2.61	0.126	−0.010	−47
Anisole SAQ					2.62	0.129	−0.009	−51				
Benzofuran					2.31	0.109	−0.047	−36				
Indole					2.26	0.102	0.030	−19	2.32	0.107	0.041	−35
1*H*-Indazole					2.48	0.107	0.029	−13	2.60	0.116	0.038	−25
2*H*-Indazole					2.36	0.104	0.025	−10	2.13	0.099	0.018	−13
Benzimidazole					2.49	0.111	0.027	3	2.57	0.117	0.029	13
Purine					2.59	0.097	0.064	43	2.58	0.100	0.080	45

a) In benzaldehyde the principal axis of the top sublevel is nearly parallel to the C=O direction.

that the main characteristics of the observed results (Table 1) are reproduced reasonably well by these calculations with a few exceptions.

The calculated ZFS of benzaldehyde is consistent with the observed value in benzoic acid (BAC) host,[9,10,13,17] although it is very different from those obtained in many other hosts.[4,7] In the present calculation the second order effect of the spin-orbit interaction was ignored, though this effect is known to make a large contribution to the ZFS of benzaldehyde in many hosts.[4,7] In the BAC host, however, the contribution of the spin-orbit interaction is very small owing to the effect of the hydrogen bonding formation between benzaldehyde and BAC.[9,10,13,17]

The calculated D values of benzonitrile and phenylacetylene are considerably smaller than that of benzene.[25] As described in the preceding section, the smaller value of D is related to the situation that one of the singly-excited configurations relative to the ground state dominates over the other configurations in the wave function of the lowest excited triplet state. In fact, the main configuration was calculated to be dominant in benzonitrile and phenylacetylene. However, the calculated D's are somewhat smaller than the observed values. This may indicate that the present calculation underestimates the configurational mixing. The calculated E values of benzonitrile and phenylacetylene are in good agreement with the observed values. The D values calculated for aniline and anisole are in reasonable agreement with the observed values.

Although the observed absolute value of E of aniline is rather large,[11] the calculated one for the H conformation is very small. We examined the influence of distortion from H symmetry upon the ZFS of aniline for the Q, AQ, and SAQ conformations. For the Q conformation the calculated sign of the E parameter is the same as those of benzonitrile and phenylacetylene and contradicts the observation. For the AQ conformation the sign does not contradict the observation, but the calculated $|E|$ is somewhat small. From the angular dependence of the EPR signals of aniline and anisole derivatives, it was indicated that the geometries of these molecules in the lowest excited triplet states are distorted to the SAQ conformations.[11,14] The experimental results show that $|E|$'s of these molecules are relatively large. However, the calculated $|E|$ values of the SAQ conformations are still rather small. Thus the present calculation does not reproduce correctly E's of aniline and anisole.

The ZFS's of indole, indazole, and benzimidazole are reproduced well by the present calculation with parameter B. As to the observed values of E, benzofuran, indole, 1H- and 2H-indazoles, benzimidazole, and purine are divided into two groups.[6,16,18] In benzofuran, indole, and purine, $D<3|E|$,[6,18] while in 1H- and 2H-indazole and benzimidazole, $D>3|E|$.[6,16,18] This trend of the ZFS parameters is well reproduced in the present calculation with parameter B, whereas with parameter A, $D>3|E|$ was obtained for indole. The observed values of D and E of 1H-indazole are considerably larger than those of 2H-indazole.[16] This trend is also reproduced in the calculation with parameter B more clearly than with parameter A.

Summary and Conclusions

We have examined the ZFS's of a series of substituted benzenes. It is experimentally shown that D and E values vary remarkably depending on the type of molecule despite the similarity in the molecular size. In particular, E varies from $+0.038\,\mathrm{cm}^{-1}$ for phenylacetylene to $-0.0597\,\mathrm{cm}^{-1}$ for aniline reflecting large differences in the spin distributions. Generally speaking, the calculation of the ZFS's of substituted benzenes based on the Pariser-Parr-Pople-type MO's can give the values reasonably close to those obtained experimentally, but some more subtle points such as the difference in D between benzonitrile and aniline and large $|E|$'s of aniline and anisole are not reproduced in the present calculation. In the case of molecules with odd π orbitals we have examined two sets of parameters A and B. It was found that parameter B satisfactorily explains the observed trend of ZFS.

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