metals and organic molecules.[15] The null effect of TMP on the nontransition metal indium ($\Delta T_c = 0$) may indicate that the enhancements seen on vanadium ($\Delta T_c = +0.09$ °K) are related to π–d bonding between the unfilled d orbitals of the metal and the π molecular orbitals of the molecule.[16]

Conclusion

We feel that the possibility of correlating molecular properties with molecular effects on superconductivity in what is yet a preliminary investigation of a new phenomenon augurs well for an eventual understanding of the microscopic mechanisms involved and for the profitable extension of these studies to other systems.

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(15) D. O. Hayward and B. M. Trapnell, "Chemisorption," Butterworth, Inc., Washington, D. C., 1964, Chapter VII.

(16) NOTE ADDED IN PROOF. In a private communication, R. E. Glover has kindly pointed out to us that electron withdrawal in *unannealed* indium thin films *decreases* the transition temperature. Further discussion of this point and additional experimental results are presented elsewhere (H. M. McConnell, F. R. Gamble, and B. M. Hoffman, *Proc. Natl. Acad. Sci. U. S.*, to be published).

Some Generalizations Concerning the Magnetic Circular Dichroism of Substituted Benzenes[1]

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Abstract: The magnetic circular dichroism (MCD) of a series of substituted benzenes has been measured. It was found that there is a correlation between the magnitude and sign of the MCD and the substituent's Hammett σ_{para} value for both the mono- and disubstituted benzenes. The MCD also appears to be quite sensitive to the symmetry of the derivative being smaller in molecules with higher symmetry.

Recently the authors published a note[2] in which it was suggested that the magnetic circular dichroism (MCD) observed in aromatics originated in the magnetically induced mixing of their B_{1u} and B_{2u} states. The object of this communication is to: (1) extend the results presented earlier to a series of benzene derivatives; (2) point out some generalizations which can be made concerning these data; and (3) provide additional evidence for the mixing of the B_{1u} and B_{2u} states.

At this time the authors feel that there is little reason for publishing extensive MCD spectra. Instead, apart from Figure 1, the experimental results will be summarized by indicating whether the B_{2u} bands have a positive or negative[3] MCD. Since the assignment of the B_{2u} band is not always certain, the approximate wavenumber (in kilokaisers) used is indicated in parentheses after the name of the compound.

Experimental Section

The MCD was measured on a JOUAN dichrograph with very extensive modifications which included (1) the use of a 500-w xenon arc light[4] source; (2) the replacement of the original monochromator with one of the type used in a Cary Model 15 spectrophotometer; (3) changing the crystal modulation to 82 cps; (4) addition of an electromagnet capable of providing fields up to 13.1 kgauss in a 5-mm gap. Unless otherwise specified, all of the measurements to be reported were made in ethanol at concentrations sufficient to give an absorbance of 1 or 2. The molar MCD is defined as the experimental MCD per 10 kgauss divided by the product of the molarity and path length (in cm) of the sample. All of the comparisons made in the text are among the maximum molar MCD values observed in the B_{2u} bands. (Theoretically it would be more desirable to use the MCD integrated over the band. However the B_{2u} band widths and shapes are similar in all of the compounds studied so the ratio of the maximum MCD to the integrated MCD will be approximately constant.) While the precision of the MCD measurements was generally good to a few per cent, the absolute values given in Figure 1 are probably not accurate to better than 10% since literature molar absorptivities were used in calculating the molar MCD values.

For convenience in discussing the results, the compounds will be divided into four major classes and several subdivisions. The first three classes will include mono-, di-, and polysubstituted benzenes having a well-characterized MCD. The fourth class will include miscellaneous compounds which have a very small or ambiguous MCD.

Class Ia. Positive MCD. N,N-Dimethylamino (40.0 kK), amino (35.8), hydroxy (37.1, in aqueous 0.1 *N* HCl), methoxy (37.3), methyl (38.5), ethyl (37.0), chloro (38.0), bromo (38.5), and iodo (38.9).

Class Ib. Negative MCD. Carboxy (36.5), carboxylate (37.4, in aqueous 0.1 *N* NaOH), carbonyl (35.4), cyano (36.9), sulfonic (38.7), sulfonamide (37.8), and sulfonyl chloride (37.4).

Class IIa. Positive MCD. *o*-Aminohydroxy (35.1), *m*-aminochloro (34.3), *m*-aminobromo (34.1), *m*-hydroxymethyl (36.3), *p*-hydroxymethyl (35.7), and *o*-, *p*-, and *m*-dimethyl (all *ca.* 37.0).

Class IIb. Negative MCD. *p*-Nitrocarbonyl (33.3).

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(1) This work was supported under a grant from the U. S. Public Health Service, Contract No. GM-11043.

(2) J. G. Foss and M. E. McCarville, *J. Chem. Phys.*, **44**, 4350 (1966).

(3) Since the sign of the MCD will be of some importance in this discussion, it should be pointed out that the sign convention used here is in agreement with that used for conventional Faraday measurements. This leads, for example, to a positive MCD near 20 kK for an aqueous cobalt chloride solution. Unfortunately, some workers, *e.g.*, P. N. Schatz, P. J. Stephens, and co-workers, have chosen to use the opposite convention; see, for example, P. J. Stephens, W. Suëtaak, and P. N. Schatz, *J. Chem. Phys.*, **44**, 4592 (1966).

(4) J. G. Foss, *Anal. Chem.*, **35**, 1329 (1963).

Class IIc. Negative MCD. *p*-Chlorosulfonic (39.3) and *p*-methylacetyl (35.7).

Class III. Positive MCD. Pentamethyl (36.4). Negative MCD. Hexachloro (35.3).

Class IV. Small or Ambiguous. Benzene, anilinium (in water, pH 0), fluoro-, *o*- and *m*-methyliodo-, *m*-bromofluoro-, *o*-carboxyhydroxy-, 1,3,5 trimethyl-, hexaethyl-, and *p*-carboxyaminobenzene.

Discussion

The first generalization is that the MCD of the $A_{1g} \rightarrow B_{2u}$ band of monosubstituted benzene is positive if the substituent is *ortho–para* directing and negative if *meta* directing. Thus far the only exception found has been N,N-dimethylaniline (unless one also considers the very small MCD of nitrobenzene and fluorobenzene as exceptions). However, the MCD of this substituted aniline is complicated by the presence of an additional band at 33.0 kK whose positive MCD is probably the result of mixing with the B_{2u} state approximately 7 kK higher in energy. Since the directing ability of various substituents may be quantitatively characterized by Hammett σ values,[5] attempts were made to relate these to the observed MCD. A surprisingly good linear correlation was found between σ_{para} and either MCD (B_{2u}) or log $|\text{MCD}\ (B_{2u})|$. Figure 1 shows the linear plot which includes all of the experimental MCD values for which Ferguson has σ_{para} values listed except two very poorly fitting points for nitrobenzene and dimethylaniline. (For reasons mentioned below negative σ_{para} values were used for the halogens.) While many correlations of spectral properties to Hammett σ values have been made, it is not clear to the authors that such a relationship would follow from the theory of the origin of MCD.[6,7] (A note is in preparation by the authors, together with Dr. William Simpson, in which it is suggested that the sign of the MCD may be related to the sign of the charge carrier in the benzene ring.)

As a corollary of this relationship between the MCD and the Hammett σ values, it might be expected that (1) in the disubstituted benzenes, if both substituents are of the same type (*i.e.*, either *ortho–para* or *meta* directing), the sign of the MCD would be the same as in the monosubstituted case; and (2) in disubstituted benzenes with different classes of directing groups the sign would be determined by the group with the larger σ_{para}. While the data at present are quite limited, both of these predictions seem to be correct. Thus, all the compounds of class IIa have two *ortho–para* directing groups and all have the expected positive MCD, while in class IIb, in which both groups are *meta* directing, the MCD is negative. Class IIc contains only two compounds with mixed directing groups and as expected both show a negative MCD since the *meta*-directing group is dominant. It appears that a simple addition of the σ_{para} values even gives a quantitatively correct fit to the line of Figure 1. Four examples are shown in the figure; but to obtain a satisfactory fit for *p*-chlorohydroxy- and *p*-chlorobromobenzene, it was necessary to use negative σ_{para} values suggesting the resonance component of the constant is of greater importance. For this reason, negative values were used for all of the halogens. (This does not affect the rather poor fit of the monosubstituted halogens.)

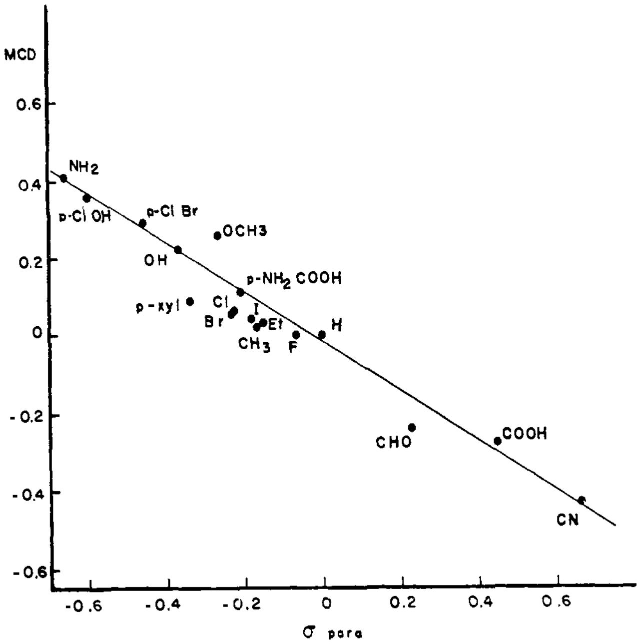

Figure 1. The maximum molar MCD in the B_{2u} band of a number of mono- and disubstituted benzenes *vs.* the Hammett σ_{para} constant. As mentioned in the text negative σ_{para} values have been used for the halogens.

Another compound with mixed directing groups is *p*-carboxyaminobenzene which should give a positive MCD since the carboxy has a large σ_{para} value. However, this compound gave an ambiguous but interesting result. The ordinary absorption spectrum has what appears to be a single peak at 34.5 kK, but the MCD has a positive peak near 33.3 kK, goes to zero near 34.7 kK, and has a negative peak near 36.8 kK. From these results, it is clear that the peak at 34.5 kK must really contain two strongly overlapping bands, probably the $A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow B_{2u}$ transitions.[8] If the second occurs, as usual, at the lower energy, then the prediction about the sign of the MCD is correct. Conversely, if in the future some confidence is gained in the sign predictions, one could use this type of MCD measurement as a means of determining the relative energies of the B_{1u} and B_{2u} states.

(If one grants that the transitions to the B_{2u} and B_{1u} states occur near 33.3 and 36.8 kK, respectively, then the equal and opposite MCD of these bands also constitutes additional evidence that the magnetic mixing of these levels is responsible for the observed MCD. Unfortunately, this does not constitute an unequivocal proof since each of the levels might independently be interacting with a third level and only accidentally have equal and opposite MCD's.)

The second generalization is that the symmetry of the molecule seems to play a very important role in determining the magnitude of the MCD. Consider, for example, that toluene, *o*-, *m*-, and *p*-xylene, and

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(5) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963.

(6) P. J. Stephens, *Inorg. Chem.*, **4**, 1690 (1965).

(7) I. Tinoco and C. A. Bush, *Biopolymers Symp.*, **1**, 235 (1964).

(8) Consistent with this interpretation is the observation that in an aqueous acid solution (pH 1), the MCD is similar to that observed for benzoic acid, *i.e.*, a negative MCD near 36.5 kK. Just as with ordinary absorption spectra, the anilinium ion appears to have little effect on the MCD of the benzene ring. Thus, in an acid solution aniline has a very small MCD and for this reason it was included, somewhat arbitrarily, in class IV.

pentamethylbenzene all show a substantial (positive) MCD while the very closely related, but more symmetrical benzene, *sym*-mesitylene and hexaethylbenzene have a very much smaller MCD. A possible partial explanation of this finding comes from an examination of the C_{2v}, D_{2h}, D_{3h}, and D_{6h} point groups. In the first two groups, to which the compounds showing MCD belong, the electric dipole transition moments to the B_{1u} and B_{2u} states are not symmetry forbidden and their vector cross products are parallel to the symmetry-permitted magnetic dipole transition moment between these states. Thus, the theoretical requirements for the existence of a "B term" MCD[6] are not symmetry forbidden. On the other hand, in the D_{6h} and D_{3h} groups the electric dipole transitions are all symmetry forbidden, and therefore the MCD should be symmetry forbidden. While this argument is suggestive, it is quite clear that the difference in the MCD of these two groups of compounds is more than just the result of their having either symmetry-permitted or symmetry-forbidden MCD's since the molar absorptivities of both the symmetry-permitted and -forbidden transitions are similar in magnitude. Furthermore, there is at least one exception known: hexachlorobenzene (negative MCD). This molecule is in point group D_{3d}[9] and, therefore, has one permitted magnetic and one permitted electric transition moment perpendicular to the ring; *i.e.*, the MCD is symmetry forbidden.

(9) O. Schepp and R. Kopelman, *J. Chem. Phys.*, 30, 868 (1959).

Electron Paramagnetic Resonance Studies of Ion Pairs. Metal Ketyls[1]

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Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received June 22, 1966

Abstract: The temperature dependence of the alkali metal and C^{13} hyperfine splittings of the epr spectra of fluorenone monomer ketyls is reported. The mechanism to produce such temperature dependence is discussed in terms of rapid ion-pair equilibria among structurally different ion pairs. Rigid media and low-temperature epr spectra of various aliphatic and aromatic ketyls are presented. The observed spectra are explained by the presence of contact and solvent-shared ion quadruplets. The zero-field parameters in aliphatic ketyls are estimated from the contact ion quadruplet structures and compared with the observed values. The equilibrium processes involving ketyl radicals are modified including the possibility of the presence of contact and solvent-shared structures. The factors which affect such equilibria are also discussed.

In the previous epr and optical studies,[2] the presence of the monomer–dimer[3] equilibrium in the ion pairs of ketyls was demonstrated. The detailed natures of the structures of these ion pairs, however, remained to be investigated more thoroughly. In the present paper we report the epr evidences for the presence of structurally different ion pairs[4] in monomer and dimer ketyls, respectively, and discuss their structures.

Temperature dependence of the alkali metal splittings in ketyls is now well known.[5] The mechanism of the temperature dependence, however, is not fully established. We have investigated temperature dependence of both C^{13} and metal splittings in monomer ketyls in the hope of clarifying the mechanism of the temperature dependence. A decrease in the magnitude of both C^{13} and metal splittings at lower temperatures seems to indicate that the average separation between positive and negative ions increase at lower temperatures. This is explained in terms of rapid equilibrium among different ion pairs.

Rigid media epr spectra of many ketyl ion quadruplets were previously found[2] to be characterized by a spin Hamiltonian.

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + DS_z^2 + E(S_x^2 - S_y^2)$$

The magnitude of D, however, varies very much from one system to another (D/hc varies from 0.01 cm^{-1} to less than 0.001 cm^{-1}). Such a large difference seems to indicate that they may have quite different structures. Although the ion quadruplets with large dipole interaction can only show broad solution spectra, some ion quadruplets showed very narrow solution spectra at room temperature. Such narrow spectra are compatible only with the species of small dipole interaction. From these observations it is speculated that in many ion quadruplets two negative ions may be separated from each other by solvent molecules giving small magnitude of dipole interaction.

Accordingly, we have investigated epr spectra of various ketyls from 77 to 300°K in order to answer the question of the structures of ion quadruplets. Our results show the presence of both contact and solvent-shared species and the equilibria among them in most systems.

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(1) This research is partially supported by a grant from the National Science Foundation (GP-5040).

(2) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, 86, 2538 (1964).

(3) Throughout the present paper the word "ion quadruplet" is used to describe the paramagnetic species which was designated as paramagnetic dimer in the previous paper. This species should be clearly distinguished from the diamagnetic dimer, such as pinacolate.

(4) Evidences for the presence of structurally different ion pairs in hydrocarbon negative ions by optical spectra and conductivity measurements were given recently by T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).

(5) (a) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2537 (1964); (b) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963).