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The Dipole Moment of Halogenobenzotropones

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The dipole moments of three bromobenzotropones and a chlorobenzotropone were measured in benzene solutions, and the positions of halogen atoms on the tropone ring were determined by comparing the observed and calculated values of their dipole moments. The bond moments of C=O and C–X (X=halogen) bonds were examined through an analysis of their dipole moments. The dipole moment of 4,5-benzotropone was also measured, and the derived bond moment of the corbonyl group suggested that the carbonyl group is affected by the conjugation of the benzene ring through the double bonds of the tropone ring.

Experimental and Results

a) Samples. The synthesis of the samples has been described elsewhere.[1] The samples were used for the observations without any further purification.

b) Dipole Moment Measurements. The dipole moment (μ) was observed by the solution method using benzene as a solvent. The dielectric constant (ε) was measured by the heterodyne beat method, and the density (d) was obtained using a pycnometer. The details of the measurements of the dipole moments were the same as in a previous report of one of the authors (T.S).[2]

The observed values of the total polarization (P), the summation of the electronic and the atomic polarization and the dipole moments are listed in Table 1. The electronic polarizations (P_E) are computed from the table of atomic refraction; and the atomic polarization (P_A) was taken as 5% of the electronic polarization. Each value of the observed dipole moment includes an inaccuracy of ± 0.01 D.

TABLE 1. OBSERVED VALUES OF DIPOLE MOMENTS

Compound	P	P_E+P_A	μ(D)
5-Bromobenzotropone (I)	215.52cc	56.70cc	2.79
5-Chlorobenzotropone (II)	200.91	53.66	2.68
4,7-Dibromobenzotropone (III)	263.04	64.85	3.08
5,7-Dibromobenzotropone (IV)	326.67	64.85	3.53
4,5-Benzotropone (V)	535.44	48.54	4.88

Calculation of Dipole Moments

a) Bond Angles. The bond angles of these compounds were assumed to be such as would result if the tropone ring and the benzene ring are connected with each other holding their skeletal angles. Figure 1 shows the bond angles of the benzotropone ring.

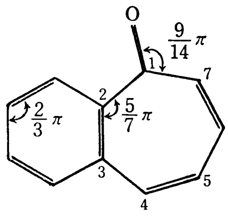

Fig. 1. The bond angle of benzotropone.

b) Bond Moments. The bond moments of C=O and C–X (C–Cl and C–Br), were assumed to be 4.0 and 1.4 D, respectively, which are the values of halogenotropones.[3,4]

c) Monosubstituted Compounds (Compounds I and II). The calculated values of dipole moments for monohalogenobenzotropones are listed in Table 2, where the bond moments of C=O and C–X assumed in (b) are used.

TABLE 2. CALCULATED VALUES OF DIPOLE MOMENTS FOR MONOSUBSTITUTED BENZOTROPONES

Position of halogen atom	4	5	6	7
μ calcd (D)	2.80	2.80	3.93	4.99

d) Disubstituted Compounds (Compounds III and IV). The disubstituted compounds have six possible structures, as listed in Table 3, in which the corresponding values of dipole moments calculated using the bond moments assumed in (b) are shown.

TABLE 3. CALCULATED VALUES OF DIPOLE MOMENTS FOR DISUBSTITUTED BENZOTROPONES

Position of halogen atoms	(4,5)	(4,6)	(4,7)	(5,6)	(5,7)	(6,7)
μ calcd (D)	1.48	2.54	3.64	3.13	3.99	5.18

Discussion

1) Monosubstituted Benzotropones. Compounds I and II (Table 1) have dipole moments of 2.7—2.8 D; therefore, the position of the halogen atom in each of these compounds could be chosen from either the 4 or 5 position by a comparison of the observed (Table 1) and calculated (Table 2) values of their dipole moments. However, the position of the halogen substituent in compound I has been determined to be 5, by NMR study of this compound and its Diels-Alder adduct with maleic anhydride.[5,6] Thus the possibility of substitution

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1) S. Ebine and M. Hoshino, This Bulletin, **41**, 2942 (1968).

2) T. Shimozawa, *ibid.*, **38**, 1046 (1965).

3) Y. Kurita and M. Kubo, *ibid.*, **27**, 364 (1954).

4) D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969).

5) S. Ebine, to be published.

6) W. E. Parham, D. A. Bolon, and E. E. Sweizer, *J. Amer. Chem. Soc.*, **83**, 603 (1961).

at the 4-position is eliminated.

For compound II, two kinds of substitution reactions can be considered, namely, 5 or 7.[6] The dipole moment measurements excluded the possibility of 7-bromobenzotropone for this compound II. Thus, compound II is determined to be 5-chlorobenzotropone by the dipole moment measurement.

2) Disubstituted Compounds (III and IV). The calculated values of dipole moment in Table 3 are thought to be accurate within the range of ±0.7 D, so the comparison of the observed and the calculated values results in three possibilities for compound III: (4,6), (4,7), or (5,6). However, it is not possible that compound III has a halogen atom at the 6-position, considering the chemistry of III.[1] Therefore, compound III is determined to be 4,7-dibromobenzotropone which has no halogen atom at the 6-position.

The possible structures of compound IV are (4,7), (5,6), or (5,7), for which the calculated values of dipole moments are in agreement with the observed within ±0.7 D. It has also been reported that in the case of compound IV, the halogen atom could not be at the 6-position.[1] Therefore, there remain two possibilities, (4,7) or (5,7) for compound IV through a consideration of the dipole moment.

Fortunately, compound III is uniquely determined as the 4,7-disubstituted compound. Since compound III is different from compound IV, the latter should be 5,7-dibromobenzotropone. Although the calculated values for monosubstituted compounds are in agreement with those observed, there are substantial differences between the calculated and observed values of the disubstituted series. These discrepancies can be explained using the so-called ortho effect. Both of these compounds have a halogen atom at the 7-position which is an ortho position to the carbonyl group, and because of negative groups adjacent to each other, the values of the bond moments of both C=O and C–X bonds should decrease.

By bringing the calculated and the observed values of compounds III and IV into agreement through repeated calculations, the bond moments for C=O and C_7–X were finally obtained as 3.6 and 1.2 D, respectively. The decreases in the C=O bond moment of 0.4 D and that in the C–X of 0.2 D are thought to be reasonable, on considering the ortho effect of compounds such as *o*-dichlorobenzene, where 10—20% decreases in C–Cl bond moment from that of chlorobenzene are known.[7]

3) 4,5-Benzotropone (V). The observed value of compound V, 4.88 D, is larger than that of tropone which was used for the estimation of the C=O bond moment (4.0 D) of the benzotropone series. The difference of 0.8 D in those bond moments might be the induction moment resulting from the conjugation between the carbonyl bond and the benzene ring (Fig. 2), provided that the intrinsic bond moment of the C=O group has the same magnitude in both 4,5-benzotropone and 2,3-benzotopone.

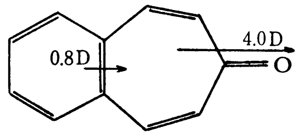

Fig. 2. Dipole moment of 4,5-benzotropone μ(C=O) and μ(induction)

Summary

The dipole moments of 5-bromo-, 5-chloro-, 4,7-dibromo-, and 5,7-dibromobenzotropones and 4,5-benzotropone were reported; and the positions of the substituents were determined and the bond moments of the carbon-halogen bonds and the carbonyl bonds were estimated.

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[7] A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman and Company, San Francisco, Calif. (1963).