The Dipole Moments of Bromothiophenes

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The molecular structures of bromothiophene derivatives were determined by dipole moment measurements. On the basis the results of these values, the bond nature of C-Br bonds can be discussed. The bond moment of the C-Br bond in the α-position of the thiophene is 1.08 D., while that of the bond in the β-position is 1.53 D. The ortho-effect causes the C-Br moment to decrease by about 12%. The bond angle of C-Br bonds in tetrabromothiophene may be increased by steric hindrance.

A number of bromine derivatives of thiophene synthesized by Professor Eiji Imoto of Osaka Prefectural University[1] were used for dipole moment measurements without further purification.

The dipole moments were observed by the solution method at 25.0°C, using benzene as a solvent. The method has been reported previously in detail.[2] The observed and the calculated dipole moments are listed in Table I.

The values listed in column A of Table I were calculated by making the following assumptions: 1) the C-Br bond moment is 1.20 D.; 2) the dipole moment of the thiophene ring is 0.53 D.[3] and has its negative end at the sulfur atom, and 3) the bond angles are the same as in the thiophene ring[4] (Fig. 1). The agreement between the observed and calculated values is fairly good, so that the molecular structures of these molecules may be obtained by the dipole moment measurement. However, it can be expected that the bond moments of the C-Br bonds will change

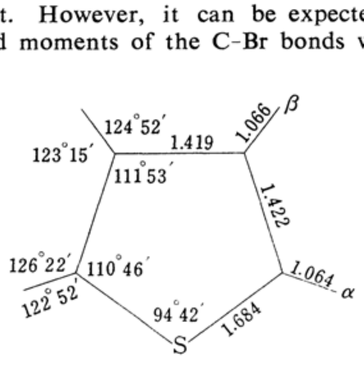

Fig. 1. The molecular structure of thiophene. (Cumper et al., Ref. 4)

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[1] E. Imoto et al., *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 779 950 (1957).

[2] T. Shimozawa, Y. Morino and R. Riemschneider, This Bulletin, **58**, 222 (1954).

[3] H. de V. Robles, *Rec. Trav. chim.*, **58**, 111 (1939).

[4] C. W. N. Cumper et al., *Trans. Faraday Soc.*, **54**, 1266 (1958).

TABLE I. THE DIPOLE MOMENTS OF BROMOTHIOPHENES (BENZENE SOLUTION, 25.0°C)

Molecules			Obs. (D).	Calcd. (D.)		
				A	B	C
α-Bromothiophene	(I)	b. p. 74—75°C/55 mm Hg	1.33	1.44		
β-Bromothiophene	(II)	b. p. 66—68°C/31 mm Hg	1.13	0.82		
3, 4-Dibromothiophene	(III)	b. p. 221—222°C	1.59	1.42	1.95	1.59
2, 3-Dibromothiophene	(IV)	b. p. 212—213°C	1.74	1.85	1.96	1.74
2, 3, 4, 5-Tetrabromothiophene	(V)	m. p. 115—116°C	0.12	0.80		0.71

their values according to their positions. In fact, the observed values of dipole moments are different for the two kinds of monobromothiophenes. These two C–Br bond moments were calculated from the observed values using the second assumption above. The C–Br bond moment of the α-position is 1.08 D., while that of the β-position is 1.53 D. The latter is nearly the same as that of the C–Br bond moment of about 1.5 D. in benzene derivatives. On the other hand, the C–Br bond moment at the α-position is smaller than the usual value. It has been reported[6] that the electron charge density of a carbon atom in the α-position of the thiophene ring is larger than that in the β-position; this would make the bond moment of the C–Br bond at the α-position smaller than that at the β-position.

The values calculated for molecules III and IV by the use of moments described above are listed in Table I (column B). They do not agree with the observed values. As is well known, the value of the dipole moment of ortho di-substituted benzenes is smaller than the values calculated by the vector addition of the dipole moment of mono-substituted compounds; i. e., in the case of ortho-dibromobenzene, for example, the C–Br bond moment calculated from the observed value is 12% smaller than the value for bromobenzene (the so-called the "ortho effect"). It may be assumed that the "ortho-effect" affects the dipole moments of compounds III and IV, too. The dipole moments of these molecules were recalculated using the smaller C–Br bond moments for each pair. These results are also listed in Table I (column C). These values agree with the observed values quite well, except for compound V.

In the case of 2, 3, 4, 5-tetrabromothiophene (V), the observed value of the dipole moment is 0.12 D., which differs greatly from the calculated value. As the experimental error involved in this value of the dipole moment is about ±0.2 D., the difference between the observed and the calculated values is worth further consideration.

If the C–Br bond is assumed to be 1.89 Å, and the valence angles, to be the same as in thiophene, the Br···Br distance is found to be 3.59 Å, which is much smaller than the sum of the van der Waals' radii of two bromine atoms (3.80 Å[7]). Therefore, the steric hindrance between Br···Br atoms would be exerted rather strongly. Thus, in order to avoid this steric hindrance, the C–Br bonds must be bent mutually in-plane or out-of-plane with respect to the thiophene ring. It can easily be shown that the in-plane bending of C–Br bonds strongly affects the value of the dipole moment; on the other hand, the out-of-plane bending does not appreciably change the dipole moment. The bending angles were obtained by a comparison of the observed and the calculated (column C) dipole moments. The results are shown in Fig. 2, where θ is calculated to be about 5°. This value of θ seems to be unusually large. However, the Br···Br distance was calculated as 3.83 Å by using this new angle. Since this value is practically the same as the van der Waals value, the steric hindrance mentioned above does not seem to exist under this deformation. Therefore, the discrepancy between the observed and the calculated values (column C) might be due to the deformation. In order to determine the molecular structure of compound V, it is, of course, desirable to investigate its crystal structure by X-ray

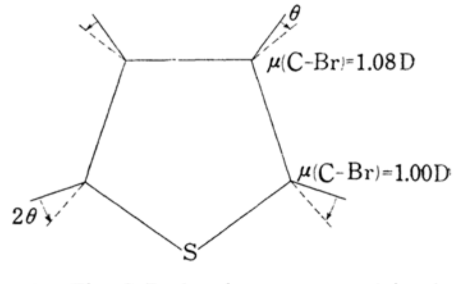

Fig. 2. The C–Br bond moments and in-plane deformations of 2, 3, 4, 5-Tetrabromothiophene.

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[5] See McClellan, "Tables of Experimental Dipole Moment," W. H. Freeman and Co., San Francisco and London (1963).

[6] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

[7] L. Pauing, "The Nature of Chemical Bonds," p. 189.

diffraction and/or by the Zeeman effect of nuclear quadrupole resonance, because these are direct methods for the determination of the bond angles.

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