DIPOLE MOMENTS OF PHENYL, BENZO, AND BENZO[b]THIOPHENO DERIVATIVES OF THIOPHENE; 1,4-DITHIIN, AND THIANTHRENE AND THEIR SULFONES

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The dipole moments of a series of phenyl, benzo-, and benzo[b]thiopheno-derivatives of thiophene, 1,4-dithiin, and thianthrene have been determined. An increase in the dipole moments of the phenyl derivatives of thiophene with an increase in the number of phenyl groups is connected with the existence of conjugation between the thiophene and benzene rings, a quantitative evaluation of the nature of which is given. It is suggested that the structure of the 1,4-dithiin ring is close to coplanar.

We have determined experimentally and calculated the dipole moments (μ) of number of derivatives of thiophene, 1,4-dithiin, and thianthrene (see table). The figures obtained have enabled us to put forward some hypotheses concerning the electronic structures of these compounds.

Because of steric interaction in compounds II–IX, XIII, and XIV, the phenyl groups are not coplanar with the thiophene ring. This interaction exists particularly strongly in compounds V, VII, VIII, XIII, and XIV. However, in spite of the absence of coplanarity, leading to a lower degree of conjugation, the experimental values of the dipole moments of the phenyl derivatives of thiophene show the existence of conjugation between the phenyl groups and the thiophene nucleus. This probably also explains the increase in the dipole moments of the phenyl-substituted thiophenes taking place symbatically with the number of phenyl groups attached in the thiophene nucleus, which is in the following sequence: III $\le$ II $\le$ VII $<$ IV $<$ VI $\le$ V $<$ XIII $\le$ XIV.

In particular, the introduction of one phenyl group into the thiophene nucleus (II and III) causes an increase in its moment by 0.25–0.26 D. The addition of two phenyl groups to the thiophene ring (IV–VII) leads to a rise in μ by 0.32–0.39 D, and the addition of three and four phenyl groups to a rise of 0.50 D (XIII and XIV). A change in the position of the phenyl groups in the monophenyl (II, III) and diphenyl (IV–VII) derivatives of thiophene has almost no effect on their dipole moments. An analogous increase in dipole moments is found for the introduction of phenyl groups into the thiophene ring of benzo[b]thiophene (XV–XVII).

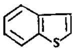
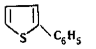
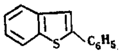
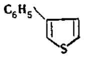
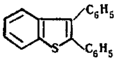
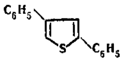
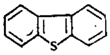
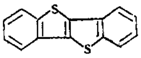
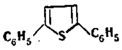
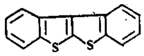
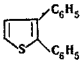
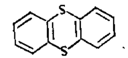
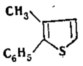
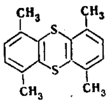
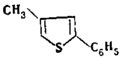
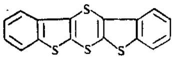
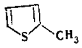
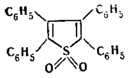
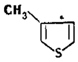
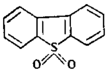
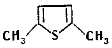
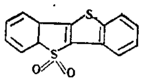
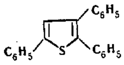
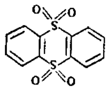
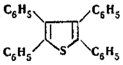
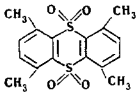
The vectorial calculation of the dipole moments of VIII and IX and also of 3-methylthiophene (XI) leads to the same value (0.73 D), while the observed values are 1.10 D (VIII) and 0.88 D (IX). This discrepancy can be explained by the possibility of hyperconjugation between the methyl group and the thiophene ring. As is well known, such a phenomenon is also characteristic for 2-methyl- and 2,5-dimethylthiophenes (X and VI) [2,3]. In view of the electron-accepting nature of the phenyl group, the smaller increase in the moment of IX can be explained by the breakage of the chain of conjugation between the CH_3 and C_6H_5 groups in the ground state of the molecule which is observed in the 2,3-derivative (VIII).

The difference between the dipole moments of the corresponding methylthiophenes (X, XI) and phenylthiophenes (II, III) $\mu_{CH_3X} - \mu_{C_6H_5X} = \mu_M$ ("Sutton's equation" [4,5]) enables the "mesomeric moment" (μ_M) of the 2- and 3-thienyl groups (X) to be evaluated qualitatively. For the 2-thienyl group $\mu_M = +0.14$ D, and for the 3-thienyl group $\mu_M = -0.03$ D (in the calculation, the values of μ_{CH_3X} and $\mu_{C_6H_5X}$ were taken as negative since the negative ends of the dipoles in the molecules CH_3X and C_6H_5X are located on the thienyl group X, which is more electronegative than the methyl and phenyl groups). These values show that the 2-thienyl group interacts with the benzene ring like a halogen atom or a $C \equiv CH$ (+M, −I effect. At the same time, conjugation of the 3-thienyl and phenyl groups is very weak.

An approximate evaluation of the perturbation in the aromatic ring caused by the addition of a thienyl group to it, which is characterized by the sum of the conjugation moment (μ_π) and the induction moment (μ_i) [5], leads to $\mu_\pi + \mu_i = -0.16$ and -0.33 D for the 2- and 3-thienyl groups, respectively. Thus, the introduction of a phenyl group (like a methyl group) into the thiophene nucleus raises the electron density of the latter.

The zero value of the dipole moment of benzothieno[3,2-b]benzothiophene (XIX) shows its planar

TABLE 1. Dipole Moments of Phenyl, Methyl, and Benzo[b]thiophene Derivatives of Thiophene, 1,4-Dithiin, and Thianthrene and Their Sulfones (in Benzene at 25° C).

Compound	Formula	μ, D	Compound	Formula	μ, D
I		0,54^1	XV		0,82^3
II		0,81	XVI		0,87
III		0,80	XVII		0,95
IV		0,89	XVIII		0,88
V		0,93	XIX		0
VI		0,92	XX		1,11
VII		0,86	XXI		0,37
VIII		1,10	XXII		0,38
IX		0,88	XXIII		1,63
X		0,67^2	XXIV		4,33* 4,50**
XI		0,83^2	XXV		4,99
XII		0,51^3	XXVI		3,99
XIII		1,03	XXVII		0,30
XIV		1,04	XXVIII		0,37

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*In dioxane

**In chloroform.

centrosymmetrical configuration in which the moments of the benzothiophene rings mutually compensate one another. The moment calculated by vectorial scheme for the planar structure of benzothieno[2, 3-b]benzothiophene (XX), isomeric with (XIX), is 1.17 D, i.e., very close to the experimental value (1.11 D). This confirms its planar structure and shows that there is only a slight displacement of the electron density when two molecules of benzo[b]thiophene are condensed in the 2, 3- position.

The low values of the dipole moments of XXI, XXII, XXVII, and XXVIII shows that the 1,4-dithiin ring deviates only slightly from coplanarity. This can be explained by the delocalization of the unshared pairs of electrons of the sulfur atoms in XXI and XXII. In actual fact, the same structure is characteristic for the sulfones XXVII and XXVIII, in which the sulfur atoms have no unshared pairs of electrons. It seems possible that the quasi-planar structure of the 1,4-dithiin ring is due to p → d interaction with the participation of the vacant 3d orbitals of the sulfur atoms. It must be mentioned that the results that we have obtained onthe structure of the 1,4-dithiin ring contradict literature statements [6].

If it is assumed that XXIII, unlike compounds XXI and XXII considered above, has a configuration close to planar, the increase in dipole moment, (as compared with XXI) is explained by a shift of the π-electrons of the thiophene rings into the 3d orbitals of a sulfur atom in the 1,4-dithiin ring, which leads to a separation of the charges and an increase in the moments of each benzo[b]thiophene moiety.

An interesting fact is an increase in the moments of the sulfones on passing from XXIV to XXV (4.33 and 4.99 D), in contrast to the analogous pair of thiophene derivatives XIV (1.04 D) and XVIII (0.88 D). It is probable that the absence of unshared electron pairs on the sulfur atom in the sulfones changes the capacity of the heterocycle for conjugation with the phenyl group. This confirms the hypothesis put forward above concerning the considerable contribution of conjugation to the change in the moments of the phenyl derivatives of thiophene and benzo[b]thiophene.

The methods of synthesis and the properties of the compounds studied have been described previously [7, 8].

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