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The Dipole Moments and Conformations of *cis*-2-Styrylfurans and *cis*-2-Styrylthiophenes

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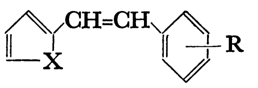
Synopsis. Electric dipole moments at 25 °C in benzene have been measured for *cis*-2-styrylfurans and -styrylthiophenes which are chloro- and nitro-substituted in 2′-, 3′-, 4′-position. Results of dipole moment analyses in conjunction with UV spectroscopic data have been discussed in terms of preferred conformations for these compounds.

Recent studies on 1,2-diarylethylenes have led to the isolation of stable *cis*-isomers of unsymmetrical derivatives bearing two distinct aryl groups.[1—5] In these works the assignment of configuration was made by means of IR, UV, and NMR spectroscopy. Information about the conformational properties of these molecular systems, however, is still lacking in the literature.

We therefore report here the results of dipole moment measurements (benzene, 25 °C) for a number of derivative compounds of the series *cis*-2-styrylfuran (**1**)—(**7**) and -styrylthiophene (**8**)—(**14**). Their preferred molecular solute conformations are discussed on the basis of comparison between the observed and calculated dipole moments.



1—**7** X=O; **8**—**14** X=S;
1, **8** R=H; **2**, **9** R=2′-Cl; **3**, **10** R=3′-Cl;
4, **11** R=4′-Cl; **5**, **12** R=2′-NO$_2$; **6**, **13** R=3′-NO$_2$;
7, **14** R=4′-NO$_2$

Experimental

Materials. The *cis*-2-styrylfurans (**1**)—(**7**) and -styrylthiophenes (**8**)—(**14**) were prepared as previously described.[1—3] Each compound, just before dipole moment determination, was crystallized or distilled under reduced pressure when liquid to constant mp or bp and $\varepsilon_{\max}$. Each sample examined was at least 99% in the pure *cis* isomer, as checked by glc.

Physical Measurements. Dielectric constants of benzene solutions were measured at 25±0.01 °C using a Dipolmeter WTW DM01 apparatus. Specific volumes and refractive indexes of solutions were determined using experimental techniques described in detail elsewhere.[6]

The total solute polarization $P_{2\infty}$ was evaluated using the Halverstadt-Kumler[7] method. The distortion polarization P_e+P_a was assumed to be 1.05 R_D, where R_D is the experimental molar refraction.

The probable error in μ was estimated not to exceed ±0.03 D for each compound examined.

Experimental results are summarized in Table 1.

TABLE 1. POLARIZATION DATA AND DIPOLE MOMENTS OF *cis*-2-STYRYLFURANS (**1**)—(**7**) AND -STYRYLTHIOPHENES (**8**)—(**14**) IN BENZENE AT 25 °C

Compound	Concentration range $100w_2$	α	ε_{10}	β	v_{10}	$P_{2\infty}$ cm^3	R_D cm^3	μ D
(**1**) *cis*-2-Styrylfuran	0.1882—0.8835	0.68	2.2729	−0.349	1.14283	61.99	48.0	0.75
(**2**) *cis*-2-(2′-Chlorostyryl)furan	0.1255—0.9404	2.14	2.2723	−0.325	1.14287	132.12	59.0	1.85
(**3**) *cis*-2-(3′-Chlorostyryl)furan	0.1341—1.6136	1.99	2.2728	−0.343	1.14300	125.27	58.7	1.76
(**4**) *cis*-2-(4′-Chlorostyryl)furan	0.2177—1.3438	1.91	2.2728	−0.317	1.14294	123.77	60.1	1.72
(**5**) *cis*-2-(2′-Nitrostyryl)furan	0.1802—0.4111	8.70	2.2725	−0.358	1.14296	402.01	60.4	4.06
(**6**) *cis*-2-(3′-Nitrostyryl)furan	0.2750—0.7363	9.36	2.2729	−0.599	1.14299	413.19	59.9	4.13
(**7**) *cis*-2-(4′-Nitrostyryl)furan	0.1264—0.4751	10.75	2.2723	−0.430	1.14297	480.34	60.5	4.51
(**8**) *cis*-2-Styrylthiophene	0.1594—1.0556	0.405	2.2724	−0.296	1.14303	60.83	54.0	0.45
(**9**) *cis*-2-(2′-Chlorostyryl)thiophene	0.1094—0.9897	1.60	2.2723	−0.233	1.14292	126.15	66.0	1.67
(**10**) *cis*-2-(3′-Chlorostyryl)thiophene	0.2186—0.9893	1.48	2.2723	−0.325	1.14306	115.14	66.0	1.50
(**11**) *cis*-2-(4′-Chlorostyryl)thiophene	0.1977—0.8937	1.61	2.2727	−0.284	1.14285	123.20	66.0	1.62
(**12**) *cis*-2-(2′-Nitrostyryl)thiophene	0.1681—0.8003	7.50	2.2726	−0.359	1.14301	379.83	66.5	3.89
(**13**) *cis*-2-(3′-Nitrostyryl)thiophene	0.2833—0.6764	8.68	2.2725	−0.404	1.14326	428.11	66.9	4.18
(**14**) *cis*-2-(4′-Nitrostyryl)thiophene	0.1230—0.6807	9.08	2.2727	−0.391	1.14296	446.23	67.0	4.28

Results and Discussion

In order to predict dipole moments for the various conformations of the compounds studied, the first task is estimating the direction of action of the resultant moment μ_X of the unsubstituted molecules (**1**), (**8**). The data in Table 1 show that the experimental dipole moment values for *cis*-2-styrylfuran (**1**) and -styrylthiophene (**8**) are fairly close, at less than ±0.08 D, to those of furan (0.67 D[8]) and thiophene (0.53 D[8]), respectively. On this basis we assume that: (i) the interaction moment between the phenyl and the heterocyclic ring can be neglected; (ii) the resultant μ_X can be taken as equal to the individual moment of furan or thiophene molecule; (iii) μ_X acts from the ring to the hetero-atom along the bisector of the C–X–C angle.[9]

In the calculations the following group moments were used:[10] μ_{NO_2}=3.98 D; μ_{Cl}=1.58 D.

The rotational conformations of the molecules dealt with are defined by the angles θ and ϕ described by the phenyl and furan (or thiophene) rings in clockwise and *anti*-clockwise direction, respectively, starting from the planar structure shown in Fig. 1.

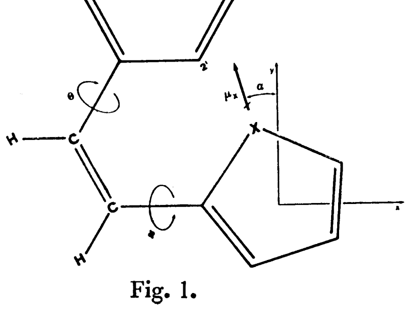


Fig. 1.

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By reference to this model, the total moment was calculated using the relation (1)

$$\mu = (\mu_x^2+\mu_y^2+\mu_z^2)^{1/2}, \tag{1}$$

in which the component moments μ_x, μ_y, and μ_z along the co-ordinate axes are given as a function of θ and ϕ by Eqs. (2)—(4)

$$\mu_x = \pm\mu_R \cos 60° \cos\beta - \mu_R \sin 60° \sin\beta \cos\theta - \mu_X \sin\alpha \tag{2}$$

$$\mu_y = \mp\mu_R \cos 60° \sin\beta - \mu_R \sin 60° \cos\beta \cos\theta + \mu_X \cos\alpha \cos\phi \tag{3}$$

$$\mu_z = \mu_R \sin 60° \sin\theta + \mu_X \cos\alpha \sin\phi \tag{4}$$

In Eqs. (2)—(4) μ_X is the moment of the hetero-ring and μ_R is the group moment of the substituent; the angle α takes the values 18.5° for X=O and 11.8° for X=S, as can be calculated using the given geometries for furan[11] and thiophene.[12] The above equations are in general valid for all compounds examined by substituting $\beta=300°$ and lower signs for 2′-substituted derivatives; $\beta=300°$ and upper signs for 3′-substituted derivatives; $\beta=180°$, $\theta=0°$ and lower signs for 4′-substituted derivatives.

Results of computations show that for each 2′- and 3′-substituted derivative numerous combinations (ϕ,θ) are possible for which the predicted dipole moment agrees with the experimental value. Therefore the most probable conformation within the ranges (ϕ,θ) indicated cannot be decided with certainty. However, the number of possible conformations can be restricted by assuming that the ϕ angles found in the 4′-Cl derivatives **4** and **11** are preserved in all the 2′- and 3′-substituted compounds with slight distortions due to steric factors. Computations produce a value of $\phi=78°$ for **4** and $\phi=89°$ for **11**, thus indicating that non-bonded repulsive interactions, due to crowding, essentially operate to force the hetero-ring out from coplanarity with the ethylenic fragment. On the other hand, it seems highly unlikely that the angles $\phi=0°$ and $\phi=43°$ found for the 4′-NO_2 derivative compounds **7** and **14**, respectively, are retained in *cis*-2-styrylfurans and -styrylthiophenes. The powerful electron withdrawing group in 4′-position is, in fact, a factor determining a coplanarity-favoring conjugative interaction which tends to minimize ϕ in these particular derivatives.

In Table 2 are given the possible conformations (ϕ,θ) obtainable, on the basis of the above assumptions, from our calculations.

Use of scale molecular models shows that the conformations denoted by II are sterically more favorable. The general preference in both series for these conformations can be clearly understood in terms of repulsive steric interactions which determine the arrangement of the phenyl ring with the 2′- or 3′-substituent group as far as possible from the heterocyclic nucleus. A combined mesomeric effect, moreover, is the factor determining the preference for structures in which the phenyl ring is coplanar to the ethylenic fragment, *i.e.* for conformations having a ϕ value near 180°.

Table 2. Preferred conformations of *cis*-2-styrylfuranes and -styrylthiophenes

	Compound	Conformation		
			I	II
		ϕ	θ	θ
2	*cis*-2-(2′-Chlorostyryl)furan	78°	36°	186°
3	*cis*-2-(3′-Chlorostyryl)furan	78°	30°	198°
5	*cis*-2-(2′-Nitrostyryl)furan	78°	26°	200°
6	*cis*-2-(3′-Nitrosrytyl)furan	78°	32°	192°
7	*cis*-2-(4′-Nitrostyryl)furan	0°	—	—
9	*cis*-2-(2′-Chlorostyryl)thiophene	89°	8°	192°
10	*cis*-2-(3′-Chlorostyryl)thiophene	89°	348°	212°
12	*cis*-2-(2′-Nitrostyryl)thiophene	89°	—	210°
13	*cis*-2-(3′-Nitrostyryl)thiophene	89°	35°	168°
14	*cis*-2-(4′-Nitrostyryl)thiophene	43°	—	—

An interesting feature of the UV spectroscopic data available[1–4] is that the conjugation band of each *cis*-2-styrylfuran derivative compound is shifted to shorter wavelengths in the corresponding derivative of thiophene series. This fact suggests that the tendence for aryl rings to be coplanar with the ethylenic group is in general more reduced in *cis*-2-styrylthiophenes. The present dipole moment results are therefore consistent with these deductions in that the twisting angle values found (see Table 2) are correspondingly greater in the derivatives of the thiophene series.

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