Electric Dipole Moments and Molecular Solute Conformations of Some *trans*-2-Styryl-furans and -thiophens

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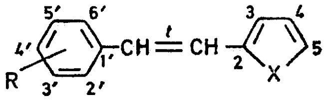
Electric dipole moments have been measured for *trans*-2-styryl-furansand-thiophens with 2'-,3'- and 4'-chloro- and -nitro-substituents, in benzene solution at 25°. The data obtained have been interpreted in terms of preferred conformations for these molecules.

THE preferred molecular conformations of isomeric *trans*-1,2-dipyridylethylenes have been recently investigated by study of their dipole moments[1] and ^{1}H n.m.r. spectra.[2] Experimental data and conformational studies for *trans*-1,2-diarylethylene systems in which the two aryl groups are different, however, have not yet been reported. We have therefore determined the preferred conformations for a series *trans*-2-styryl-furans and -thiophens by analysis of data from dipole moment measurements in benzene solution (25°).



(1) R = H (8)
(2) R = 2'-Cl (9)
(3) R = 3'-Cl (10)
X = O (4) R = 4'-Cl (11) X = S
(5) R = 2'-NO$_2$ (12)
(6) R = 3'-NO$_2$ (13)
(7) R = 4'-NO$_2$ (14)

EXPERIMENTAL

Materials.—The styryl compounds were usually prepared from a Wittig reaction between the appropriate benzyltriphenylphosphonium chloride and furancarbaldehyde or thiophen-2-carbaldehyde.[3-5] In all cases the reaction product (a mixture of *cis*- and *trans*-isomers) was chromatographed on alumina with benzene–light petroleum (1 : 1) as eluant. The *trans*-isomer fraction was concentrated and then crystallized, or distilled under reduced pressure when liquid, to constant m.p. or b.p. and $\varepsilon_{max.}$. Each sample was $\geqslant 99\%$ pure *trans*-isomer, as determined by g.l.c. just before the determination of dipole moment.

Physical Measurements.—Dielectric constants of benzene solutions were measured at 25° ± 0·01 using a Dipolmeter WTW type DMO1 apparatus. Specific volumes and refractive indices of solutions were determined as described elsewhere.[6]

The total solute polarization $P_{2\infty}$ was obtained by extrapolation with the Halverstadt–Kumler method.[7] The distortion polarization $P_E + P_A$ was assumed to be $1{\cdot}05R_D$, where R_D is the experimental molar refraction. The R_D values obtained compare well with those computed by the sum of Vogel's additive increments.[8] The small difference observed in some cases does not significantly affect the final dipole moment values.

The probable error in μ was estimated not to exceed $\pm 0{\cdot}02$ D for each compound examined.

Experimental results are collected in Table 1.

RESULTS AND DISCUSSION

U.v. spectroscopic studies[9] have shown that the *trans*-stilbene molecule and its derivatives with no substituents on the α or 2,6 carbon atoms are essentially planar in solution, as there is no steric hindrance between atoms or groups attached at these positions. Large

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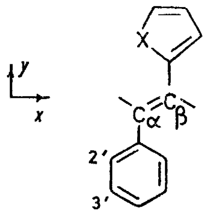
conjugative effects due to delocalization in the extended π-electron system thus appear to determine conformational preferences in these molecules. From this we deduce that the analogous *trans*-2-styryl-furan and -thiophen systems also exist in a resonance-stabilized planar conformation. Two kinds of planar conformations, *i.e. cisoid* (*c*) and *transoid* (*t*), are therefore to be considered for the unsubstituted and 4′-substituted molecules of both series, according to the relative position of the vinyl group and the heteroatom X. It thus follows that for each of the 2′- and 3′-substituted molecules [(2), (3), (5), (6), (9), (10), (12), and (13)] four non-identical planar conformations, (I*c*), I*t*), (II*c*), and (II*t*), are possible.

TABLE 1

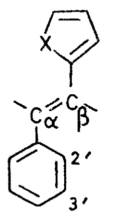
Polarization data and dipole moments of *trans*-2-styryl-furans (1)—(7) and -thiophens (8)—(14) in benzene at 25°

Compound	Concentration range $100w_2$	α [a]	ε_{10} [b]	β [c]	v_{10} [d]	$P_{2\infty}$/cm³	R_D/cm³	μ/D
(1)	0·2291—0·9456	1·21	2·2723	−0·403	1·14337	76·23	48·0	1·12
(2)	0·1269—0·7873	2·44	2·2720	−0·319	1·14305	144·05	60·0	1·99
(3)	0·1755—0·5511	2·51	2·2726	−0·318	1·14331	146·83	60·0	2·02
(4)	0·1904—0·8002	2·69	2·2720	−0·402	1·14320	148·63	60·8	2·03
(5)	0·0578—0·1571	8·38	2·2727	−1·760	1·14387	299·50	61·1	3·39
(6)	0·0608—0·1644	8·89	2·2724	−0·736	1·14330	385·61	61·0	3·96
(7)	0·0548—0·2985	12·65	2·2722	−0·508	1·14311	552·22	61·4	4·88
(8)	0·3218—0·8235	0·69	2·2729	−0·448	1·14280	62·49	54·1	0·53
(9)	0·1429—0·6612	1·84	2·2725	−0·412	1·14296	124·34	66·3	1·63
(10)	0·1755—0·5511	2·04	2·2723	−0·427	1·14298	131·65	66·9	1·73
(11)	0·1637—0·4126	1·89	2·2728	−0·444	1·14285	124·29	66·9	1·62
(12)	0·0793—0·1514	6·71	2·2735	−0·418	1·14289	341·31	67·0	3·64
(13)	0·0703—0·2742	9·32	2·2719	−0·441	1·14281	453·28	67·5	4·32
(14)	0·1149—0·2983	11·57	2·2722	−0·519	1·14289	545·65	68·4	4·81

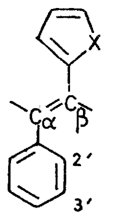
[a] $\alpha = d\varepsilon_{12}/dw_2$. [b] $\varepsilon_{10} = \lim_{w_2\to 0}\varepsilon_{12}$. [c] $\beta = dv_{12}/dw_2$. [d] $v_{10} = \lim_{w_2\to 0}v_{12}$.



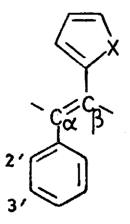
(I*c*)



(II*c*)



(I*t*)



(II*t*)

It should be noted, however, that these molecules contain a maximum of two polar groups (*i.e.* the heterocyclic nucleus and the substituted Ph ring) the relative orientation of which changes only in the different conformations (I) and (II). Therefore the dipole moment method prevents us from determining the conformational preference about the C(2)–C(β) linkage, since the *c* and *t* forms will not differ in the magnitude of the expected moment.

We thus analyse the dipole moment data in terms of conformational possibilities (I) and (II) only, which correspond to the possible orientations of the five-membered and the Ph rings in the 2′- and 3′-substituted derivatives.

Theoretical dipole moments for the possible planar conformers (I) and (II) of these molecules have been represented as the sum of the vectors of the moments of the whole unsubstituted molecule (1) or (8) and the suitable group moments μ_S of the substituents. For this purpose, the molecular model was oriented relative to an arbitrary system of cartesian co-ordinates which are defined such that the y axis is parallel to the C(2)–C(β) and C(1′)–C(α) bonds. Denoting the rotation angle of the Ph ring out of the molecular plane by θ, we assume the conformers (I) and (II) as corresponding to angle values $\theta = 0$ and 180°, respectively.

Information concerning the precise direction of the resultant dipole moment of (1) and (8) was obtained in the following way. By considering the moment of the styrene fragment to be 0·12 D [10] and that the vector of the furan and thiophen moment acts from the five-membered ring to the heteroatom,[11] it can be reasonably assumed that the total molecular moment of *trans*-2-styryl-furan and -thiophen is located near to this direction. On this basis, using as a model the conformer (I*c*), the projections on x, y of the resultant vector for the unsubstituted molecules (1) and (8) are easily calculated from the measured moments of (1) or (8), and of its 4′-chloro-derivatives (4) or (11), and from the chloro-group moment by equations (i) and (ii) from

$$x^2 + y^2 = \mu_{(1)}^2 \qquad \text{(i)}$$

$$(x - \mu_{\mathrm{Cl}})^2 + y^2 = \mu_{(4)}^2 \qquad \text{(ii)}$$

which $x = -1{\cdot}115$, $y = -0{\cdot}1064$ and $x = -0{\cdot}5268$, $y = 0{\cdot}0518$ for (1) and (8), respectively.

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[10] A. von Hippel and L. G. Wesson, *Ind. Eng. Chem.*, 1946, **38**, 1121.

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In all the computations we assume the group moment values $\mu_{Cl} = 1\cdot58$, $\mu_{NO_2} = 3\cdot98$ D.[12]

TABLE 2

Calculated dipole moment values for the possible conformations (I) and (II) of *trans*-2-styryl-furans and -thiophens

Compound	$\mu_{calc.}$/D (I)	$\mu_{calc.}$/D (II)	Conformer ratio (I) : (II)
(2)	2·59	0·74	55 : 45
(3)	2·65	0·94	52 : 48
(5)	4·94	3·00	16 : 84
(6)	5·02	3·14	38 : 62
(9)	2·09	1·20	42 : 58
(10)	2·04	1·13	59 : 41
(12)	4·47	3·57	7 : 93
(13)	4·42	3·50	88 : 12

We thus calculate theoretical moments of molecules listed in Table 2 as a function of θ by equation (iii)

$$\mu = [(x - \mu_S \cos\alpha \cos\theta)^2 + (y + \mu_S \cos\beta)^2 + (\mu_S \cos\alpha \sin\theta)^2]^{\frac{1}{2}} \quad \text{(iii)}$$

where $\alpha = 30°$ and $\beta = 90° - \alpha$ (for the 2′-substituted molecules) and $90° + \alpha$ (for the 3′-substituted molecules).

From the experimental and calculated data in Tables 1 and 2 it can be seen that the molecules examined cannot exist in solution in a single (I) or (II) planar conformation. The content of the (I) and (II) forms in the conformational mixture was thus calculated by applying the usual root mean square relationship and is reported in Table 2.

For the 2′-Cl and 2′-NO_2 derivatives a precise choice can be made between the possibilities *c* and *t* for each conformation (I) and (II). Use of scale molecular models suggests that in the derivatives (2), (5), (9), and (12) the sterically allowable planar conformations are undoubtedly the ones in which the β-carbon is as far from the 2′-substituent as possible. On this basis, it is probable that the molecules above participate in the equilibrium essentially as (I*c*) and (II*t*) conformers. Computations show that these conformations are approximately equally probable for the 2′-Cl derivatives (2) and (9), whereas the 2′-NO_2 compounds (5) and (12) exist predominantly as, or close to, the (II*t*) conformer.

We now consider the possibility of a steric interaction between the 2′-substituent and the β-hydrogen atom which could give rise to stable non-planar conformations for these compounds. Analogy with previous ^{1}H n.m.r. results for 2-chlorostyrenes [13,14] and u.v. studies for *trans*-2,2′-dichlorostilbene,[15] however, clearly indicates that planarity or near-planarity of the Ph–CH=CH– fragment is to be expected in the *trans*-2-(2-chlorostyryl)-furan (2) and -thiophen (9) molecules. Nevertheless, in the case of the derivatives (5) and (12) we exclude the occurrence of a rotational equilibrium between the two planar conformations (I*c*) and (II*t*), because of the presence of the bulky NO_2 group in the 2′-position. We therefore calculate the angle of twist θ which corresponds to a single, non-planar, stable conformation of (5) and (12). Computation showed that the observed moment for *trans*-2-(2-nitrostyryl)-furan (5) and -thiophen (12) is compatible with a twisted conformation (II*t*) in which the Ph ring is forced out of the molecular plane by *ca.* 57 and 31°, respectively.

These resulting conformations seem to be controlled by two factors: (i) non-bonded repulsions between the heteroatom X and the oxygens of the NO_2 group, leading to a preference for a form (II) with these atoms arranged on opposite sides of the *y* axis; (ii) inhibition of the mesomerism responsible for a planar conformation, by steric repulsion between the α-hydrogen atom and the large NO_2 group.

The results obtained for the 3′-Cl derivatives of both series indicate that (I) and (II) forms * are populated with nearly equal probabilities. By considering the size and position of the substituent group, it can be assumed that the same steric and electronic effects operate in these molecules which determine the preferred conformation of the unsubstituted systems (1) and (8). We would therefore predict that conformations (I) and (II) will not substantially differ in energy and thus that both structures are equally likely. On these bases, the results obtained for molecules (3) and (10) appear to be quite acceptable.

The same kind of reasoning also applies to the 3′-NO_2 derivative (6) which was found to exist with approximately the same probability in conformations (I*c*) and (II*c*). As can be seen from Table 2, the more stable conformation for the corresponding derivative (13) was (I*c*). Such a difference in the conformational preferences of corresponding compounds of the two series, however, cannot be rationalized at the present time.

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* By using Dreiding models it is possible to decide in favour of the *c* arrangement about the C(β)–C(2) bond, since steric contact is observable between the van der Waals radii of the β- and 3-hydrogen atoms in the *t* conformation.

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