DIPOLE MOMENTS OF THIOPHENE ANALOGS OF CHALCONES AND THEIR VINYLOGS

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The dipole moments of 25 α, β unsaturated ketones of the thiophene series are measured in benzene at 25°, and their most probable coplanar conformations established. For the systems studied it is shown that, in the static state, the 2-thienyl group exhibits an electron-donating effect, greater than those of 2-furyl and phenyl. Introduction of electron-donating and electron-accepting substituents into the molecule of 1-(thienyl-2)-3-phenylpropenones as well as shift of the carbonyl group away from the aryl one towards the heterocyclic ring, leads in general to an increase in dipole moment. A linear relationship is found for the changes in dipole moment of isomeric thiophene ketones due to electron-donating substituents. Dipole moments of propen-3-ones correlate satisfactorily with Hammett σ parameters for substituents, and intermolecular distances.

Continuing work on the study of dipole moments of heterocyclic analogs of chalcones and their vinylogs [1, 2], we decided to determine the electric moments of the corresponding thiophene derivatives. Very little has been done on the dipole moments of carbonyl compounds of the thiophene series; μ values are known only for thiophene-2-aldehyde, [3], 2-acetylthiophene [3, 4], thiophene-2-carboxylic acid [4, 5] and the ethyl ester of the latter [3, 5].

Using Debye's dilute solutions method, we measured, in benzene solution at 25°, the dipole moments of 1, 3-di(thienyl-2)propen-1-one (I), isomeric 1-(thienyl-2)-3-arylpropenones, where the aryl group is phenyl (II, III), 4-tolyl (IV, V), 4-anisyl (VI, VII), 2, 4-dimethoxyphenyl (VIII, IX), 2, 4, 6-trimethoxyphenyl (X, XI), 4-dimethylaminophenyl (XII, XIII), 4-chlorophenyl (XIV, XV), 4-nitrophenyl (XVI), 4-xenyl (XVII, XVIII), and 1, 5-di(thienyl-2)pentadienones (XIX, XX), 1-(thienyl-2)-5-phenylpentadienones (XXI–XXIII) with the carbonyl group in the conjugated chain in different positions, and for comparison purposes (thienyl-2)phenylketone (XXIV) and (thienyl-2)-vinylketone (XXV) (see Table 2).

Dipole moments for possible coplanar configurations were calculated by the vector method for most of the compounds. In the calculations, the moment of the thiophene ring was taken as 0.54 D [6], and it was taken as subtending an angle of 79° with the C_2 bond of the thienyl with the side-chain C [7]. The moments of the carbonyl, methyl, methoxyl, dimethylamino, nitro, and chlorine groups were taken as, respectively 2.70; 0.40; 1.25; 1.55; 3.98; 1.58 D [6, 8]. The angle between a double bond and a single one was taken as 120°.

Furthermore, for qualitative evaluation of possible steric effects in compounds II, III, XXIV, plans of possible plane conformations were drawn, taking into account van der Waals' and covalent radii, and in the case of the thiophene ring, the following internuclear distances and bond angles were used: C═C 1.35 Å, C—C 1.44 A, C—S 1.74 Å, <CSC 91°, < C—C—C 113° and <SCC 112° [9]. These latter data differ but little from those recently obtained from microwave spectra [10].

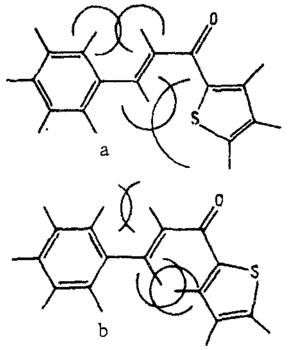

Fig. 1. 1-(Thienyl-2)-3-phenylpropen-1-one (II). a) Anti-s-cis form; b) syn-s-cis-form.

EXPERIMENTAL

The thiophene analogs of chalcone and their vinylogs (I-XXIV) were prepared by crotonoid condensation, using methods which we have previously described [11, 12]. (Thienyl-2)phenylketone was synthesized as described in [13], while (thienyl-2)vinylketone was synthesized as described in [14].

The method of measuring the dipole moments was that previously described by us. The measurements were accurate to ±0.02 D, and it was calculated from the formula given in [15]. The results of the measurements are given in Table 2.

DISCUSSION

From research on the Kerr constant and dipole moments of chalcone and its vinylogs, Le Fevre concluded that in these compounds the carbonyl group is cis to the adjacent double bond, and that the double bonds are cis to one another. In research on furan [1] and quinoline [2] analogs of chalcones two of the present authors also showed that the carbonyl group and the vinylene group conjugated with it have a s-cis configuration. There is no doubt that thiophene derivatives I-XXIII also exist in similar conformations.

For the s-cis isomers of ketones II–XVIII there are two possible coplanar conformations differing in that the sulfur of the heterocyclic ring and the oxygen

Table 1

Dipole moments of Carbonyl Compounds of the Thiophene Series

	Compound	μ_{found}, D	μ_{calc}, D	
			syn-s-cis-form	anti-s-cis-form
I	$C_4H_3S{-}CO{-}CH{=}CH{-}C_4H_3S$*	3.37	2.85	2.10
II	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_5$	3.43	3,15	2,30
III	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_5$	3.11	3,15	2,30
IV	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_4{-}CH_3$	3.75	3,32	2,45
V	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_4{-}CH_3$	3.32	3.32	2,45
VI	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_4{-}OCH_3$	3.94	3,95	2,95
VII	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_4{-}OCH_3$	3.39	3,95	2,95
VIII	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_3{-}(OCH_3)_2$	4.64	—	—
IX	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_3{-}(OCH_3)_2$	3,91	—	—
X	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_2{-}(OCH_3)_3$	5.43	—	—
XI	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_2{-}(OCH_3)_3$	4,64	—	—
XII	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_4{-}N(CH_3)_2$	5.59	4,20	3.15
XIII	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_4{-}N(CH_3)_2$	4.56	4,20	3,15
XIV	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_4{-}Cl$	3.11	2,60	2,30
XV	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_4{-}Cl$	3.31	2,60	2,30
XVI	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_4{-}NO_2$	5,03	3,40	3,85
XVII	$C_4H_3S{-}CO{-}CH{=}CH{-}C_6H_4{-}C_6H_5$	3.67	3,15	2,30
XVIII	$C_4H_3S{-}CH{=}CH{-}CO{-}C_6H_4{-}C_6H_5$	3.33	3.15	2.30
XIX	$C_4H_3S{-}CO{-}(CH{=}CH)_2{-}C_4H_3S$	3.44	—	—
XX	$C_4H_3S{-}CH{=}CH{-}CO{-}CH{=}CH{-}C_4H_3S$	3.19	—	—
XXI	$C_4H_3S{-}CO{-}(CH{=}CH)_2{-}C_6H_5$	3.50	—	—
XXII	$C_4H_3S{-}CH{=}CH{-}CO{-}CH{=}CH{-}C_6H_5$	3.21	—	—
XXIII	$C_4H_3S{-}(CH{=}CH)_2{-}CO{-}C_6H_5$	3.25	—	—
XXIV	$C_4H_3S{-}CO{-}C_6H_5$	3.45	3,15	2.30
XXV	$C_4H_3S{-}CO{-}CH{=}CH_2$	3.28	—	—

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*C_4H_3S = 2-thienyl

Table 2

Dipole Measurement Results

Compound number	α	β	P_∞, cm^2	MR_D, cm^2	Compound number	α	β	P_∞, cm^2	MR_D, cm^2
I	16.28	0.85	288.18	60.79	XIV	14.10	0.90	264.51	67.17
II	17.30	0.69	306.32	62.30	XV	15.95	0.92	291.08	67.17
III	13.15	0.67	245.66	62.30	XVI	36.10	1.09	585.50	67.91
IV	20.27	0.57	355.22	66.92	XVII	19.95	1.00	361.60	86.41
V	16.01	0.67	292.64	66.92	XVIII	16.51	0.94	312.89	86.41
VI	22.36	0.82	386.78	69.49	XIX	17.42	0.94	311.24	69.56
VII	16.66	0.78	304.12	69.49	XX	14.94	0.92	279.45	69.56
VIII	29.95	0.97	503.94	74.19	XXI	18.15	0.75	325.55	71.07
IX	20.99	0.82	376.89	74.19	XXII	15.32	0.73	285.05	71.07
X	42.01	1.18	684.94	82.46	XXIII	15.57	0.75	287.67	71.07
XI	30.84	1.11	522.99	82.46	XXIV	17.39	0.64	300 04	53.53
XII	44.43	0.80	716.05	75.47	XXV	15.53	0.41	262.63	38.20
XIII	29.82	0 80	501.43	75.47					

$^*\varepsilon_0 = 2.2725$; $d_0 = 0.87368$; T = 298°. ε_0—solvent dielectric constant; P_∞—total polarization extrapolated to infinite dilution; MR_D—molecular refraction.

of the carbonyl group are on the same or different sides of the bond joining thienyl to carbonyl, which we have provisionally named syn-s-cis and anti-s-cis forms (see Fig. 1).

Comparison of dipole moments calculated for two possible s-cis forms both for propen-1-ones and propen-3-ones with μ found experimentally (see Table 1), as well as qualitative evaluation of steric hindrance (see Fig. 1), shows that generally syn and anti forms are equally probable, though in some cases it is possible to ascribe preference to the syn form. Some excess of μ as found experimentally over the half sum of those calculated for syn and anti forms is to be ascribed to conjugation. In the cases of compounds I, XIX, XX, with two heterocyclic rings in the molecule, 4 conformations can exist: syn-syn, syn-anti, anti-syn, and anti-anti. However it is then impossible to ascribe preference to either of them.

Because of considerable steric hindrance, ketone XXIV cannot occur in the coplanar state. Deviation from coplanarity in the case of XXIV takes place because of rotation of the phenyl, just as it occurs in the analogously constructed molecule of benzophenone, where the angle between the carbonyl group and the aromatic ring is 45° [16].

Lowering of the conjugation of phenyl with a carbonyl group should affect the value of μ but little, while turning of the thiophene ring, due to its great polarizability [17, 18] and nucleophilicity [19] would, as compared with phenyl cause appreciable lowering of the dipole moment, which is not actually observed. Regarding syn and anti forms of XXIV, the data of Table 1 show that it is not possible to prefer one of the possible configurations, so evidently what is concerned is an equally probable mixture of both.

The dipole moment of chalcone is 2.97 D [1]. Replacement of its aromatic ring next to the carbonyl group by a thiophene ring, results in an appreciable increase of μ (by 0.46 D). At the same time replacement of the phenyl by 2-thienyl remote from the carbonyl group affects the dipole moment of the compound rather less (by 0.14 D, see II and III). This is also found in the pentadienone series (XIX-XXIII), the dipole moments of 1, 5-diphenylpentadien-1 and -3-one being respectively 3.05 and 3.33 D [1]. Hence the thiophene ring is electron-donating and is well-conjugated with carbonyl when the two are next to one another, but separation of these groups by an aliphatic double bond has little effect on the polarization of the carbonyl group in the static state.

Comparison of the dipole moments of thiophene series ketones I–III, XIX–XXIII with those of the corresponding furan derivatives ketones [1] (occurring with identical conformations) shows that if the carbonyl group is separated from the heterocyclic ring by a vinyl group, their electrical moments differ but little from one another. This confirms the view of Braude and Fawcett [20] that the positive mesomeric effects of 2-furyl and 2-thienyl are approximately equal. It is of interest that study of electronic spectra of the corresponding α, β unsaturated ketones containing the furan and thiophene ring [17], shows that these two heterocyclic groups also exhibit approximately the same bathochromic effects.

In the actual case where the heterocyclic ring is right next to the carbonyl group, the thiophene series ketones always have a dipole moment greater by 0.20–0.25 D than their furan analogs, despite the fact that μ thiophene (0.54 D [6]) is less than μ furan (0.71 D [21]), and a corresponding difference is found in the calculated moments. This latter fact can be explained by there being, in addition to a conjugation effect a negative inductive effect operative the latter must be greater for furyl, than thienyl, since the electronegativity of an oxygen atom is greater than that of a sulfur atom (O – 3.44; S – 2.58 [22]). In consequence of this, the total electron-donating effect of thienyl in these systems is greater in the static state, than is the case for furyl, though the reverse obtains in protonation reactions of α,β unsaturated ketones [23] and in solvolysis of the corresponding 2-chloromethyl derivatives [24], where dynamic effects are operative.

Table 3

Basic Data for Correlating Dipole Moments

Substituent	$d_R - d_H$, Å	σ	Propen-3-ones	
			$\mu_R - \mu_H$	$\frac{\mu_R - \mu_H}{d_R - d_H}$
CH_3	1.07	−0.170	0.21	0.20
CH_3O	0.29	−0.268	0.28	0.97
$N(CH_3)_2$	0.33	−0.830	1.45	4.40
Cl	0.61	+0.228	0.20	0.33
C_6H_5	1.84	−0.01	0.22	0.12
NO_2	0.95	+0.778	1.92	2.02

Introduction of the vinylene group into the molecule of the thiophene analog of chalcone, if, as before, the carbonyl group remains next to thienyl or phenyl, has but little effect on the value of the dipole moment (increase by 0.07–0.14 D, of I–III and XIX–XXIII).

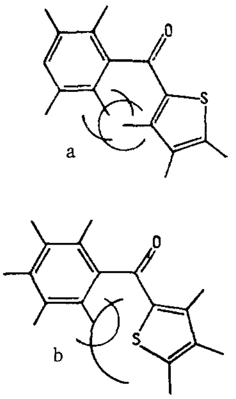

Fig. 2. Conformations of (thienyl-2)-phenylketone (XXIV). a) Syn-s-cis form; b) anti-s-cis form.

Furthermore if, when introducing the vinylene group, the carbonyl is separated from the heterocyclic ring, μ is observed to drop by 0.18–0.22 D (of I and XX, II and XXII). This confirms the statement made above, that conjugation of thienyl with carbonyl is maximal when they are immediately adjacent to one another.

In the compounds studied phenyl possibly also exhibits a small electron-donating effect, somewhat increasing their dipole moments. This follows from comparison of the moments of II and XXV. On the other hand, separation of phenyl from carbonyl by a vinylene bond does not affect the value of μ (cf. II and XXIV).

As expected, introduction of electron-donating substituents into the aromatic ring results in increase in μ of the molecule, this increase being greater for propen-1-ones than for propen-3-ones. The change in dipole moment under the influence of substituents correlates rather satisfactorily with the Hammett σ parameters in connection with our previously suggested empirical formula [2] $(\mu_R - \mu_H)/(d_R - d_H) = \sigma\rho$, where μ_R is the dipole moment of the unsubstituted ketone; d_R is the distance between the center of the aromatic ring and the center of the charge of the substiuent; d_H is the distance between the center of the aromatic ring and hydrogen, 2.28 Å; and σ and ρ are the Hammett equation constants. This is seen from Fig. 3, which shows the correlation for 1-(thienyl-2)-3-arylpropenes (Table 3 gives the corresponding data).

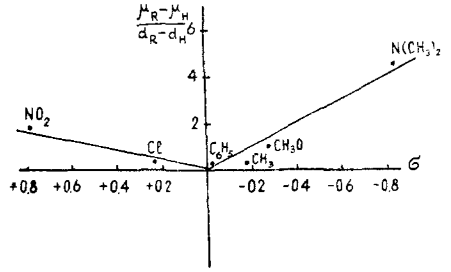

Fig. 3. Relationship between dipole moments of 1-(thienyl-2)-3-arylpropenones and the σ constants of the substituents (from McDaniel and Brown [27]).

The ρ values for electron-donating and electron-accepting substituents differ somewhat. The nitro group and chlorine raise the dipole moments of propen-3-ones, but for the propen-1-ones XIV have μ 0.32 D smaller than for II.

Accumulation of methoxy groups in the ortho position of the aromatic ring (see VI–XI) is found to give an even greater increase in moment than introduction of the first methoxy group in the para position, though it is known that with acetophenones [25] an ortho substituent decreases the value of μ.

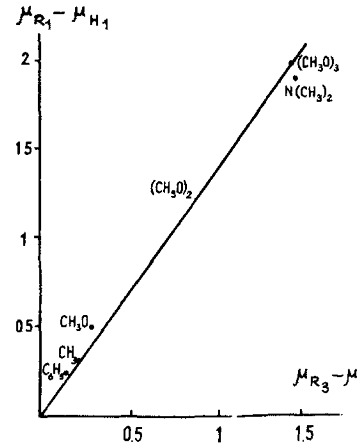

Fig. 4. Relationship between dipole moments of isomeric thiophene chalcones. For propen-1-ones—$\mu_{R_1} - \mu_{H_1}$; for propen-3-ones—$\mu_{R_3} - \mu_{H_3}$.

A similar change in dipole moment due to introduction of methoxy groups has also been previously observed for the corresponding furan analogs of chalcones [1]. The value of the dipole moment increases particularly significantly when the dimethyl amino group is introduced into the molecules of thiophene ketones (see XII, XIII). This can be explained by the good conjugation of the electron-donating dimethylamino group with the electron accepting carbonyl group.

It must also be pointed out that introduction of electron-donating substituents into the aromatic ring of isomeric 1-(thienyl-2)-3-phenylpropenes has the same effect on the change in the dipole moment value. Thus the change in μ for propen-1-ones is laid along one coordinate axis and the same thing for propen-3-ones along another, the corresponding points form a good straight line (see Fig. 4). Hence, it also follows that introducing a substituent does not affect the spatial configuration of α,β unsaturated ketones, of the thiophene derivatives.

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