STRUCTURE AND PROPERTIES OF FURAN-2-CARBOXYLIC ACID ESTERS.

1. DIPOLE MOMENTS AND IR SPECTRA

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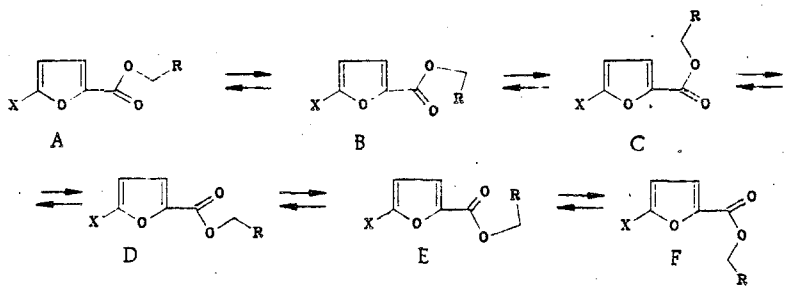
Dipole moment studies have revealed that furan-2-carboxylic acid esters exist in nonpolar solvents predominantly in O,O-cis-conformations. The dipole moment value of a 2-furoate ester depends on the electronic and steric effects of the substituents in the alcohol portion of the ester. The complex nature of the $\nu_{C=O}$ band region in the IR spectra of 2-furoates is due primarily to the appearance of resonance absorption bands.

Many of the results reported [1-6] of studies of the stereochemistry of furanyl α-oxo compounds have been contradictory. The main reason for the discrepancies probably lies in the very small difference in the conformational energies of α-carbonyl-containing furan derivatives* [6]. This factor impinges to an even greater extent on the relatively small number of reports [1, 2, 5, 6] which have appeared concerning the conformations of furan-2-carboxylic acid esters and spectroscopic characterizations of the conformers.

A simple and very informative method of studying the structures of organic compounds involves comparing experimentally determined dipole moment values with theoretically calculated dipole moments for several of the most probably conformations. The following flat conformations are possible for furan-2-carboxylic acid esters:



X=H, CH_3, C_2H_5, Br; R=H, CH_3, C_2H_5, C_3H_7, $CH=CH_2$, $C\equiv CH$, 2-furyl, C_6H_5

Comparison of the theoretically calculated molecular dipole moments of 2-furoate derivatives, which were obtained from vector sums of the group dipole moments for conformations A-F, with the experimentally determined values (Table 1) leads us to the conclusion that under the conditions of these measurements the 2-furoate esters exist predominantly in the O,O-cis conformation, since μ_{calc} values for the type A, B, and C structures are much closer in value to the experimentally determined value than μ_{calc} for the type D, E, and F structures.

Since the conformational equilibrium in this system is determined by coulombic interaction of the heterocyclic oxygen atom with the carbonyl group oxygen atom, this conclusion would seem to be contradictory to the results of earlier papers [4, 7]. However, from one point of view, in the case of esters the I-effect of the ether oxygen atom should to a

*Here and elsewhere the conformers are characterized by a mutual orientation of the oxygen atom in the heterocyclic ring with either the carbonyl oxygen or carboalkoxy oxygen atom:

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TABLE 1. Calculated μ_{calc} Values for Different Planar Conformations of Furan-2-carboxylic Acid Esters (X = H) and the Corresponding μ_{exp} Dipole Moment Values

Conformation	μ_{calc}, D, for R						
	CH_2CH_3	CH_2CH_3*	$CH=CH_2$	C≡CH	2-furyl	2-furyl*	C_6H_5
A	2,4	1,5	2,1	1,9	3,1	2,2	2,2
B	2,4	1,5	2,8	3,0	2,1	1,9	2,8
C	2,4	1,5	2,2	1,9	3,1	2,2	2,2
D	1,2	1,5	1,2	1,3	1,6	1,4	1,2
E	1,2	1,5	1,9	1,9	1,3	1,2	1,2
F	1,2	1,5	2,2	1,0	1,6	1,5	1,2
μ_{exp}, D	2,16		2,17	2,34	2,15		2,23

*Dipole moments were calculated taking into account free rotation about the C(2)—C=O (R = CH_2CH_3) and C(α)—C'(2) (R = 2-furyl) bonds.

large extent decrease the electron donating ability of the carbonyl oxygen atom, and thus lower the barrier to internal rotation of the ester fragment in the molecule about the C(2)—C=O bond. For instance, in the case of allyl 2-furoate, the value of μ_{calc} taking this type of rotation into account is 2.22 D, which is also close to the experimental value (Table 1). On the other hand, specific interaction of an aromatic solvent with an ester molecule should lead to the predominance in solution of the more sterically accessible O,O-cis-isomer [1].

Scalar projections (Fig. 1, M 1:2·10^{-8}) make it possible to evaluate qualitatively the presence of steric hindrance in one or another of the possible structures. Based on this type of analysis, the most questionable conclusion would be the presence of a significant concentration of the type B, C, E, and F planar structures for the propargyl, furfuryl, and benzyl 2-furoate ester derivatives (VI-VIII).

Comparison of the dipole moment values of the propyl (III, IX, XI, XIII), allyl (V, X, XII, XIV), and propargyl (VI) esters of furan-2-carboxylic and benzoic acid (XVII, XIX, and XX, respectively) (Table 2) indicates quite clearly that an allyl radical has almost no effect on the μ value of esters, and that introduction of an acetylenic bond leads to a small increase in the polarity of ester molecules, probably as a consequence of the inherent dipole of a C≡CH group (0.78 D [8]), which is comparable in value to the dipole moment of the furan ring (0.74 D [8]).

It is also noteworthy that the μ value of compound VII is lower than that of compound VI. This is apparently due to the difference in the polarizability of the HC≡C and 2-furyl radical substituents, since the inherent group dipole moments of an acetylenic and furyl fragment are almost identical. However, the possibility of a specific solvent effect cannot be dismissed, both on the conformational equilibrium that is established for 2-furoates in solution and on intramolecular interaction among substituent groups in the ester molecules. Theo-

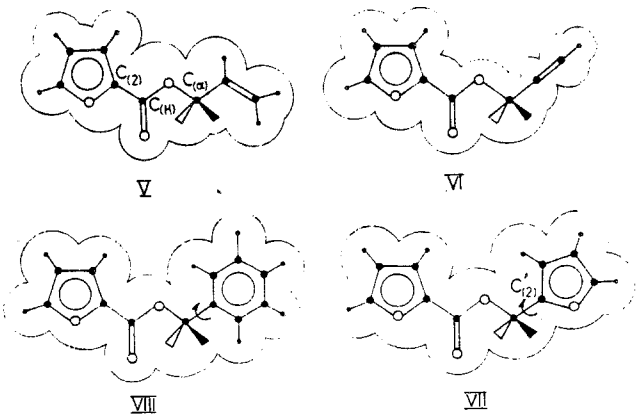

Fig. 1. Scalar projection of O,O-cis-conformers of furan-2-carboxylic acid esters [M (1:2)·10^{-8}].

TABLE 2. Dipole Moments* and IR Spectral Data** for Furan-2-carboxylic and Benzoic Acid Esters

5-X—C_4H_2O—$COOCH_2R$ I—XIV					$C_6H_5COOCH_2R$ XV—XXII			
Compound	X	R***	μ_{exp}	$\nu_{C=O}$, cm^{-1}	Compound	R***	μ_{exp}	$\nu_{C=O}$, cm^{-1}
I	H	H	2,11	1740, 1720	XV	H	1,81	1720
II	H	CH_3	2,13	(1736)	XVI	CH_3	1,79	1722
III	H	C_2H_5	2,16	1738, 1722	XVII	C_2H_5	1,83	1722
IV	H	C_3H_7	2,22	1737, 1716	XVIII	C_3H_7	1,81	1720
V	H	$CH=CH_2$	2,17	(1737)	XIX	$CH=CH_2$	1,80	1726
VI	H	$C\equiv CH$	2,34	1741, 1730	XX	$C\equiv CH$	2,20	1715
VII	H	C_4H_3O	2,15	(1740)	XXI	C_4H_3O	1,97	1721
VIII	H	C_6H_5	2,23	1740, 1725	XXII	C_6H_5	1,67	1723
IX	CH_3	C_2H_5	2,24	(1731)				
X	CH_3	$CH=CH_2$	2,23	(1721)				
XI	C_2H_5	C_2H_5	2,28	(1730)				
XII	C_2H_5	$CH=CH_2$	2,30	(1721)				
XIII	Br	C_2H_5	2,22	1748, 1730				
XIV	Br	$CH=CH_2$	2,20	1740, 1722				

*Dipole moment measurements were made in toluene at 20°C.
**IR spectra were obtained for crushed drops, NaCl plates; the values given in parentheses correspond to the average value of the absorption maximum for a complex band.
***For compounds VII and XXI, R = C_4H_3O, 2-furyl.

retical calculations based on an additive vector scheme revealed that a molecule of compound VII exists predominantly in a type A conformation, with free rotation of the furyl fragment in the alcohol radical about the C(α)—C'(2) bond (Fig. 1, VII).

A benzyl radical exerts oppposite effects in the alcohol portions of 2-furoates versus benzoate esters: although the μ value of the benzyl ester of furan-2-carboxylic acid (VIII) is greater than that of propyl 2-furoate (III), the μ value of benzyl benzoate XXII is lower than that of propyl benzoate XVII (Table 2).

Apparently, therefore, in addition to exerting an electron withdrawing effect on the distribution of electron density in ester molecules, a benzyl radical in 2-furoate derivatives also changes the ratio of conformers in the system, in favor of increasing the concentration of the more polar O,O-cis-isomer. In saturated aliphatic esters there is no free rotation about the C(2)—C=O bond, based on the results of this dipole moment study. These compounds exist in solutions of nonpolar or weakly polar solvents in two conformational forms: O,O-cis (75-85%) and O,O-trans.

The dipole moment values of n-alkyl 2-furoates seem to increase as the length of the hydrocarbon chain of the alcohol radical is increased from CH_3 to C_4H_9 (compounds I-IV, Table 2). In contrast, an n-alkyl alcohol radical in benzoic acid esters does not have a noticeable effect on the dipole moment value of the alkyl benzoate, under the conditions of these measurements. We assume, therefore, that the relative concentration of the O,O-cis ester conformer increases as the length of the alkyl chain in the alcohol portion of a 2-furoate ester increases, due to suppressed rotation about the C(2)—C=O bond.

Substituents located in the 5-position of the furan ring exert a decisive effect on the μ value of a 2-furoate ester. Both alkyl substituents as well as halogen atoms increase the value of μ. The change in the dipole moment of furoate esters upon introduction of a second substituent in the α-position of the ring is apparently associated not only with a change in the geometry of the ring or in the isomer ratio, but also with intramolecular electronic interaction of the substituents in the ring and a change in the anisotropic polarizability of the furoate fragment of the ester molecule.

The results of this study of the conformational structure of furan-2-carboxylic acid ester derivatives clarify to some extent the reasons behind the complex, yet very pronounced, doublet character of the carbonyl group stretching bands in the IR spectra of 2-furoates.

Chadwick and coworkers [5] have attributed the doublet character of these bands in the IR spectra of furan-2-carboxylate methyl, ethyl, and tert-butyl esters to the existence of three-dimensional isomers, in analogy with the behavior of furanyl aldehydes and ketones. At the same time, however, the authors of another paper [9] did not detect any doubling in the bands of 13 furan-2-aldehydes, which they attributed to extremely small differences in the frequencies of the rotational isomers.

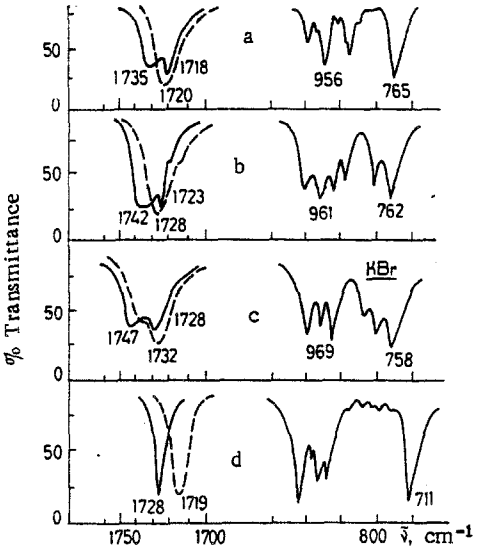

Fig. 2. IR spectra in the 1750-1700 cm^{-1} (—— in CCl_4, --- in $CHCl_3$) and 1100-700 cm^{-1} regions (crushed drop or KBr): a) compound I; b) compound V; c) 5-nitroallyl 2-furoate; d) benzoic acid ester XVII.

It is furthermore known that the isomerization energy of furan carbonyl compounds is more than ten times greater than the isomerization energy of the methyl ester of pyromucic acid (furan-2-carboxylic acid) [5, 10]. It would seem to follow, therefore, that the $\nu_{C=O}$ frequency difference for the two isomers in the IR spectra of ester derivatives should be less than that observed for furfurals or acetylfurans. It should be noted that in the IR spectra of thiophene-2-carboxylate [5] and benzoate esters (compounds XV-XXII) the $\nu_{C=O}$ absorption bands are single and symmetrical. On the basis of these results and discussion, we conclude that the doublet character of these bands in the IR spectra of 2-furoates is not due to the presence of isomers, but rather to the appearance of combination or resonance absorption bands. The possibility of distortion of the carbonyl group stretching bands in ester derivatives as a result of Fermi resonance has been noted previously [11, 12].

In the IR spectra of 2-furoates in $CHCl_3$, the form of the ester $\nu_{C=O}$ absorption band changes significantly; specifically, in comparison with the spectrum in CCl_4 solution, one of the bands of the doublet (the higher frequency end) is shifted 8-15 cm^{-1} to lower frequency, while the other component of the doublet is practically insensitive to the nature of the solvent (Fig. 2). An analogous effect is observed when the IR spectra of the esters are recorded in CCl_4 solution to which an equimolar amount of phenol has been added as a proton donor.

The $\nu_{C=O}$ bands of benzoate esters undergo a bathochromic shift of 8-10 cm^{-1}, and increase in width, but otherwise retain their symmetry.

If we take into consideration the fact that the IR spectra of 2- and 3-monosubstituted furans contain a very characteristic band in the 1720-1740 cm^{-1} region, which consists of a resonance band of two vibrations in the furan heterocycle, with the main contribution coming from the ring breathing vibration in the 960-1100 cm^{-1} region and the γ_{CH} ring out-of-plane deformation in the 720-780 cm^{-1} region [13, 14], then we conclude that the main factor responsible for the complex character of the $\nu_{C=O}$ band in the IR spectra of 2-furoate esters is not the existence of isomers, but rather the appearance of resonance absorption bands.

EXPERIMENTAL

Furan-2-carboxylic and benzoic acid esters were synthesized by esterification of the corresponding acids by alcohols, via a procedure analogous to that described in [15]. The purity of all of the esters was checked by GLC and was found to be always better than 99%.

Dipole moments of benzoate and furan-2-carboxylate esters were measured according to the Debye method. The dielectric susceptibilities of toluene solutions of the esters were measured on a Tangens-2 M dielectrometer at 20 ± 0.2°C, in a constant capacity cell YaZh-3S ($C_{op} = 21 \cdot 10^{-12}$ F) at a frequency of 1.0 MHz.

Dipole moment calculations were made using the Srivastava and Charandas equation [16]: $\mu = A\sqrt{\alpha M}$, where $A = 0.012812\sqrt{3T/[d_1(\varepsilon_1+2)^2]}$ or A = 0.09323 for toluene at 20°C; M is the molecular weight of the substance in kg/mole; α is a coefficient which combines the dielectric susceptibility of dilute solutions ε with the mass fraction of the analyzed substance ω_2, and is

determined using least squares: $\varepsilon = \alpha\omega_2 + \varepsilon_1$; d_1 and ε_1 are the solvent density and dielectric susceptibility; $d_1 = 0.8670$ g/cm^3, and $\varepsilon_1 = 2.3830$ [17].

The ester concentration in the solutions to be analyzed was in the range 0.05 to 0.005 M. Solution dielectric susceptibility values were calculated using a method suitable for the apparatus. The accuracy of the μ measurements, calculated according to the data in [17], was ±0.02 D. Theoretical μ calculations were carried out on the basis of an additive vector scheme with geometric parameters and group dipole moment values taken from [17, 18].

IR spectra of furan-2-carboxylate esters were recorded on an IKS-14A spectrophotometer using crushed drops or KBr plates (for the allyl ester of 5-nitrofuran-2-carboxylic acid, the concentration was 0.3%), or for solutions in CCl_4 or $CHCl_3$ (ester concentration 0.5 M, absorbing cell width 0.1 cm). Recording conditions for the NaCl window region: rate of spectral acquisition 62 cm^{-1}/min, graph paper drive rate 6 mm/min, pen running time 4 sec, 11-division screw slit.

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