CONFORMATION OF THIOPHENE ANALOGS OF CHALCONE CONTAINING A NAPHTHALENE RING

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It has been shown on the basis of dipole moment and IR spectroscopic measurements of thiophene-naphthalene analogs of chalcone that the latter exist in the s-cis form in solutions and have a trans configuration of the substitutents at the double bond and a definite position of the thiophene ring.

Dipole moment and IR spectroscopic meansurements have been used in the clarification of the steric structure of 3-(2-thienyl)-1-(1-naphthyl)-prop-2-en-1-one (I), 3-(2-thienyl)-1-(2-naphthyl)prop-2-en-1-one (II), 3-(2-thienyl)-1-(1-naphthyl)prop-1-en-3-one (III), 3-(2-thienyl)-1-(2-napthyl)prop-1-en-3-one (IV), 3-(5-nitro-2-thienyl)-1-(1-naphthyl)-prop-2-en-1-one (V), 3-(5-nitro-2-thienyl)-1-(2-naphthyl)prop-2-en-1-one (VI), 3-(5-nitro-2-thienyl)-1-(1-naphthyl)prop-1-en-3-one (VII), and 3-(5-nitro-2-thienyl)-1-(2-naphthyl)prop-1-en-3-one (VIII). It follows from the experimental dipole moment of thiophene of 0.55 D [1] that the dipole moment of the thiophene ring substituted in position 2 is equal to 1.01 D and is directed at an angle of 40° to the axis joining the center of the thiophene ring with the heteroatom. In an analogous way the dipole moment of 5-nitrothiophene substituted in position 2, equal to 3.78 D and forming an angle of 60° with the axis mentioned,was found from the value of 4.25 D [1] for the dipole moment of 2-nitrothiophene. For other bond moments the following values were used: $C_{sp^2} \leftarrow H\,\mu = 0.7$ D; $C = O\,\mu = 2.26$ D (calculated from the dipole moment of benzaldehyde). The angles between the double and single bonds were taken to be equal to 120° in all cases.

We carried out the calculations by the vector additivity scheme of a whole series of planar structures for each of the ketones (I-VIII), including cis and trans configurations of substituents at the double bond, s-cis and s-trans conformations of conjugated C=C and C=O bonds, and forms due to the asymmetrical structure of the thiophene and naphthalene substitutents. Upon comparison with the experimental results (see Table 1) the calculated figures make it possible to decide on two possible conformations: s-cis and s-trans [Fig. 1, ketones I, III, V, VII]. The low calculated value of their dipole moments (2.44-2.51 D for ketones I-IV and around 2 D for ketones V-VIII) makes it possible to reject all structures having cis conformations of hydrogen atoms at the double bond.

The dipole moment method does not make it possible to make an unequivocal choice between s-cis and s-trans conformations. Further helpful information can be can be obtained from examination of IR spectra. All the ketones investigated have an absorption band in the 980-995 cm^{-1} region (Table 1), the intensity of which varies from medium to high (a typical spectrum is presented in Fig. 2) and which is caused by deformation vibrations of hydrogen atoms in the trans position at the double bond. As a rule, this band is found in the 990-965 cm^{-1} range, but this range is shifted to the frequency region of 1000-980 cm^{-1} [2] upon conjugation with a carbonyl group. Thus, the IR spectra confirm the conclusions made in the investigation of dipole moments that ketones I-VIII are trans isomers with respect to the steric arrangement of substituents at the ethylene bond. Each of the ketones gives two high-intensity bands between 1700 and 1580 cm^{-1}. The high-frequency band at 1641-1661 cm^{-1} (Table 1) must be assigned to stretching vibrations of the carbonyl group, while the low-frequency band (1585-1606 cm^{-1}) belongs to stretching vibrations

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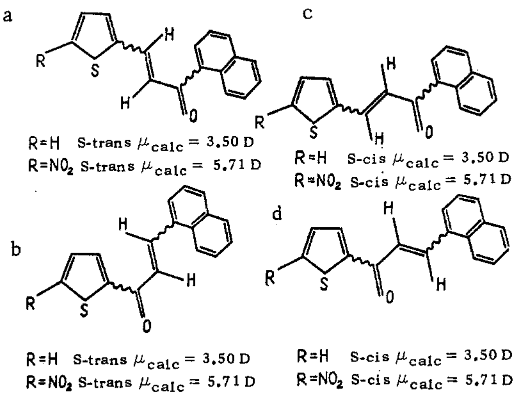


Fig. 1. s-cis and s- trans conformations of ketones I, III, V, and VII.

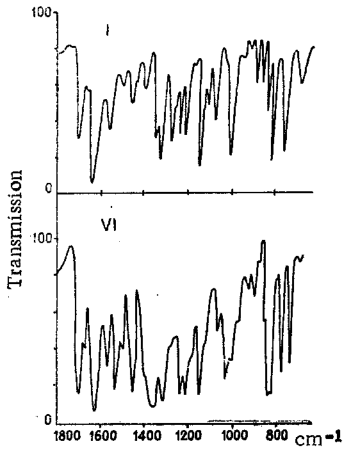
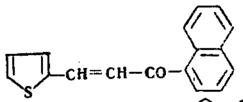
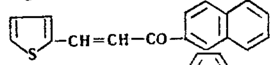
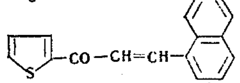
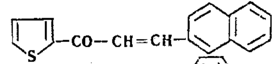
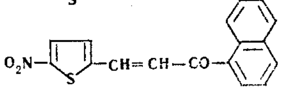
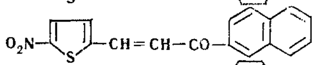
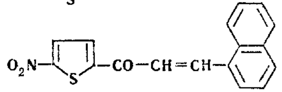
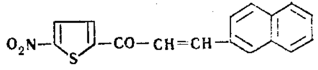


Fig. 2. IR spectra of compounds I and VI.

TABLE 1

Compound	Formula	D		Absorption, cm^{-1}		
		μ_{exp}	μ_{calc}	C=O	C=C	$\underset{H}{C}{=}\overset{H}{C}$
I		3,31	3,50	1652	1589	980
II		3,62	3,50	1657	1600	980
III		3,20	3,50	1641	1585	980
IV		3,62	3,50	1646	1585	982
V		4,96	5,71	1659	1596	983
VI		4,29	5,71	1661	1593	995
VII		4,70	5,71	1648	1606	981
VIII		4,65	5,71	1651	1596	986

of the ethylene bond. For the α, β-unsaturated thiophene ketones studied earlier the absorption regions of carbonyl and double bonds are found at 1635-1670 and 1585-1615 cm^{-1} [3], respectively. Attention is drawn by the fact that the intensity of the stretching-vibration band of the ethylene bond is higher than the intensity of absorption of the carbonyl group. As is known, such a relation between the intensity of C=C and C=O bands is an indication of their s-cis arrangement relative to one another [4, 5]. Of the two possible conformations depicted in Fig. 1, these results make it possible to decide on the s-cis conformation.

Of the two possible structures determined by the asymmetric structure of the thiophene substituent and which we have provisionally called s'-cis and s'-trans (Fig. 3), for ketones III, IV, VII, and VIII the calculations show the appropriateness of that in which the heterocyclic sulfur atom and the carbonyl oxygen are arranged on the same side of the bond connecting the heterocycle and the carbon of the carbonyl group

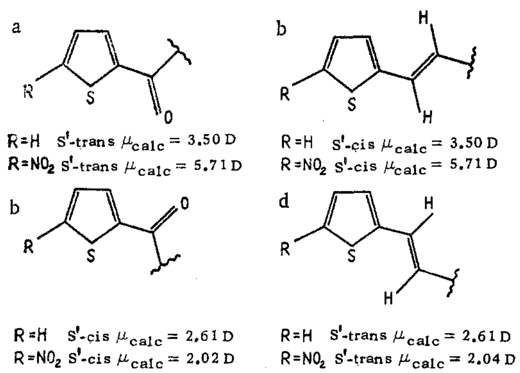


Fig. 3. Conformations due to the asymmetric structure of the thiophene ring.

(Fig. 3a, b), i.e., s'-trans conformation. An opposite arrangement of the heterocycle leads to a structure having a low dipole moment which is rather too low. A similar fact has been reported previously by Lumbroso and Pastour [6]. These authors postulated an s'-trans conformation for α-thiophenealdehyde and α-acetothienone.

The dipole moment method also makes it possible to differentiate s'-cis and s'-trans forms where a C=C double bond is adjacent to the thiophene ring (Fig. 3c, d). A definite answer cannot be given with respect to the arrangement of the naphthalene ring. The method of attachment of the naphthalene ring (in position 1 or 2) and rotation around the bond with the substituent in both thepositionsmentioned does not affect the dipole moment calculated by the vector scheme.

Thus, α, β-unsaturated ketones containing the thiophene and naphthalene rings obtained by crotonic condensation [7] have a transconfiguration of substituents at the double bond, a definite position of the thiophene ring, and an s-cis conformation of the conjugated C=C and C=O bonds.

EXPERIMENTAL

The dielectric contants of dilute dioxane solutions were determined by the method of zero beats. The IR spectra were measured on a UR-10 instrument in tetrachloroethylene solutions.

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