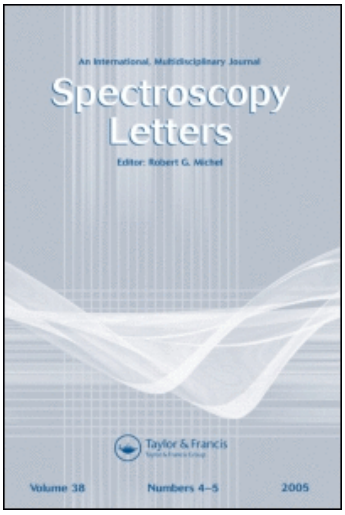

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IR-SPECTRAL STUDY OF 4'-SUBSTITUTED PHENYLTHIOLBENZOATES IN SOLUTION

Key words: Penylthiolbenzoates, IR-spectra, Conformational equilibrium in solution

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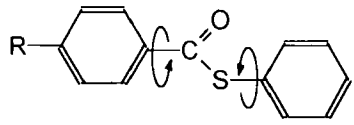
ABSTRACT

A doublet structure of the C=O stretching band in the IR-spectra of 4'-methoxy-, 4'-methyl- and 4'-cyanophenylthiolbenzoate is proved. The solvatochromic effect on the intensities of both components suggests an equilibrium between two conformers with different dihedral angle determined by the plains of the benzene rings. The choice of the studied compounds is influenced by the fact that they are structural fragments of liquid crystals. The characterization of their rotameric preference in solution provides additional information about the influence of the terminal groups on the conformational mobility of the phenylthiolbenzoate skeleton as well as on the polarizability of the molecule.

INTRODUCTION

The IR-spectral studies on a series of 4'-substituted phenylthiolbenzoates (see Scheme **I**), show a splitting of the C=O stretching band which is not observed in the spectrum of the unsubstituted compound as well as the respective phenylbenzoates.[1] In oposite to the corresponding *ortho*- and *meta* derivatives, this splitting cannot be explained by a field effect[2] or sin-anti-conformational equilibrium between the substituent R and the C=O group.[3] The possibility of E,Z-conformational equilibrium depending on the rotation around the C-S bond is low too. Such an equilibrium is proved for the phenylthiolformate,[4] but the studies of the dipole moments of ethylthiolbenzoates[5] and phenylthiolbenzoates[1] show that the substitution of the formyl hydrogen atom by an aryl group shifts the equilibrium to the Z-conformer.

In the present work the C=O stretching region in the IR-spectra of 4'methoxy-, 4'-methyl- and 4'-cyanophenylthiolbenzoate (Scheme **I**:, R = OCH_3, CH_3 and C≡N) is studied in a series of aprotic solvents of increasing polarity. The results obtained suggest an equilibrium between two conformers with a different dihedral angle between the benzene rings (Scheme **I**).



I

The studied compounds are structural fragments of liquid crystal[6-8] and the study of their conformational preference in solution provides additional information about the effect of the terminal group on the conformational flexibility of the phenylthiolbenzoate skeleton as well as on the polarization of the respective compounds.

EXPERIMENTAL

4'-Methoxy-, 4'-methyl-, and 4'-cyanophenylthiolbenzoate are obtained using the described method.[9] The IR-spectra are recorded on a Perkin Elmer 983G spectrometer at 1.10^{-1} M concentration and path length of 0.018 cm. The spectral data are obtatined by six accumulations of the signals. The integral absorbances are calculated by means of a program for separation of overlapping bands.[10] The UV-spectra are recorded on a Specord UV-VIS spectrometer in cyclohexan (Uvasol, Merck), concentration 10^{-4} M, path length 0.5 cm.

All solvents (Table 1) were redistilled and dried over molecular sieves. The purity grade, and, in particular, the amount of water were controlled by monitoring the corresponding IR-region.

RESULTS AND DISCUSSION

The IR-spectra of the studied 4'-substituted phenylthiol-benzoates show a raising intensity of the low frequency C=O stretching band with the increase of solvent polarity (Table 2).

The possibility of this effect to arise from conformational equilibrium is considered taking into account that: **(i)** the used aprotic solvents are characterized by non-specific solvent interactions with the solute molecules, and **(ii)** their dielectric constants $\varepsilon^S \leq 8$, i.e., the additional electronic polarization of the solute induced by the reaction field of the solvent can be neglected.[12,13]

Under the above conditions the following equation is valid:[13]

$$\Delta G^S_{L,H} = \frac{\Delta\mu^2_{L,H}}{r^3_{eff}} \varphi(\varepsilon^S) + \Delta G^V_{L,H} \qquad (1)$$

It gives the relation of the free energy difference $(\Delta G^S_{L,H})$ between high (**H**)- and low (**L**)-frequency conformers in the solvent, *S*, with the solvent polarity parameter $\varphi(\varepsilon^S) = (\varepsilon^S - 1)/(2\varepsilon^S + 1)$; [14] $\Delta\mu_{L,H}$ and $\Delta G^V_{L,H}$ are the differences between the permanent dipole moments

TABLE 1

Solvents and their dielectric constants

No.	Solvent	ε^S
1	Carbon tetrachloride	2.24 [a]
2	Benzene	2.28 [a]
3	Tetrachloroethylene	2.30 [b]
4	Trichloroethylene	3.41 [a]
5	Chloroform	4.81 [a]
6	1,1,2,2-Tetrachloroethane	8.20 [a]

[a] Ref. **11**; [b] Ref.**10**: p. 183.

and the free energies in the vapour of **H** and **L**, respectively; r_{eff} is the effective (Onsager) radius of the molecule.

Therefore, the presence of conformational equilibrium (**H** ⇌ **L**) suggests a linear relationship between $\Delta G^S_{L,H}$ and $\varphi(\varepsilon_s)$. The values of $\Delta G^S_{L,H}$ are obtained from the IR-spectra of the solute in the respective solvents:

$$\Delta G^S_{L.H} = -RT \ln[(a_H/a_L).(A^S_L \; A^S_H)] \qquad (2)$$

where A^S_L and A^S_H are the integral absorbances of the low- and high-frequency C=O band, a_L and a_H are the corresponding molar absorptivities (cm.mmol^{-1}). The values of a_L, a_H and their ratio can be determined using the relation:

$$A^S_H = -(a_H / a_L).A^S_L + a_H bc_0 \qquad (3)$$

where $c_0 = const$ is the total molar solute concentration and b is the path length (in cm). The linear relation between A_H^S and A_L^S suggests that the a_H / a_L-ratio is independent of the solvent, which is the condition for the applicability of Eqn. (3) and generally of the used quantitative method.

The integral intensities A_H^S and A_L^S in various solvents are given in Table 2 and these data are substituted in Eqn. (3). A linear correlation is observed for the OCH_3- and CH_3-substituted compounds (Table 3); Fig. 1 shows the relation $A_H^S = f(A_L^S)$ for 4'-methylphenylthiol-benzoate.

According to the statistical analysis of the 4'-cyano-phenylthiolbenzoate data the solvents could by arranged around two parallel lines (Table 3) with nonoverlapping values of the mean square error of the intercepts (13.16 ± 0.54 and 15.56 ± 0.38 respectively). This arrangement can be explained with the local field effect of the medium and it is observed when the solute molecule is conformationally mobile.[15] Since the distribution of the solvents in parallel lines follows exactly from the relation $a_H / a_L = const$, i.e., Eqn. (3) is applicable in this case too.

According to Eqn. (2), the room temperature eqilibrium constants and $\Delta G_{L,H}^S$ (Table 2) are calculated from the A_L^S / A_H^S- and a_H / a_L- values (Table 3). They are correlated with the $\varphi(\varepsilon_S)$-parameters of the medium in Eqn. (1). The slopes ($\Delta\mu^2 / r^3_{eff}$) and the intercepts ($\Delta G_{L,H}^V$) of the corresponding lines are given in Table 3. On the basis of these results the following conclusions can be drawn:

1. With increasing of the solvent polarity the equilibrium is shifted to the **L**-conformer; i.e., the latter is characterized by a higher dipole moment. This indicates that the observed equilibrium is not of the E,Z-conformational type discussed above in which the low frequency C=O band corresponds to the Z-rotamer.[16] Since in phenylthiolbenzoates this rotamer has a lower dipole moment,[1] in opposite to our observation the intensity of the low frequency maximum should decrease in more polar media.

TABLE 2

A_H^S-, A_L^S- and $\Delta G_{L,H}^S$ (kJ mol^{-1})-values of the studied compounds in different solvents

Solvent		Substituent								
	$\varphi(\varepsilon_s)$	4 - OCH_3			4 - CH_3			4 - CN		
No[a]	x 10^2	A_H^S	A_L^S	$\Delta G_{L,H}^S$	A_H^S	A_L^S	$\Delta G_{L,H}^S$	A_H^S	A_L^S	$\Delta G_{L,H}^S$
1	22.61	3.72	10.89	-2.37	4.15	9.20	-1.09	10.97	3.32	2.22
2	23.06	3.07	10.08	-2.66	3.88	9.41	-1.31	10.11	2.24	3.06
3	23.21	3.58	9.46	-2.12	4.94	8.13	-0.35	10.47	3.94	1.75
4	30.81	1.76	11.66	-4.39	2.71	11.34	-2.67	9.10	3.39	1.78
5	35.87	0.86	12.22	-6.29	1.44	13.05	-4.58	5.57	5.86	-0.79
6	41.38	0.51	13.08	-7.73	1.02	13.61	-5.53	5.43	7.56	-1.49

[a] See Table 1.

TABLE 3

a_H / a_L-, $\Delta\mu^2 / r^3_{eff}$- and $\Delta G_{L,H}^V$ (kJ mol^{-1}) -values of the studied compounds

Compound	a_H / a_L	$\Delta\mu^2 / r^3_{eff}$	$\Delta G_{L,H}^V$
4-OCH_3	0.89 ± 0.06[a] (r = 0.992)	29.21± 1.49 (r = 0.995)	4.35 ± 0.45
4-CH_3	0.70 ± 0.01 (r = 0.998)	25.77 ± 2.54 (r = 0.981)	5.01 ± 0.77
4-CN	1.28 ± 0.13[b] (r =0.995) 1.34 ± 0.07[c] (r = 0.998)	21.27 ± 4.15[d] (r = 0.932)	7.36 ± 1.26[d]

[a] without solvent **1**; [b] solvents **2,4** and **5**; [c] solvents **1,3** and **6**;
[d] at an average value of the a_H / a_L- slope = 1.31

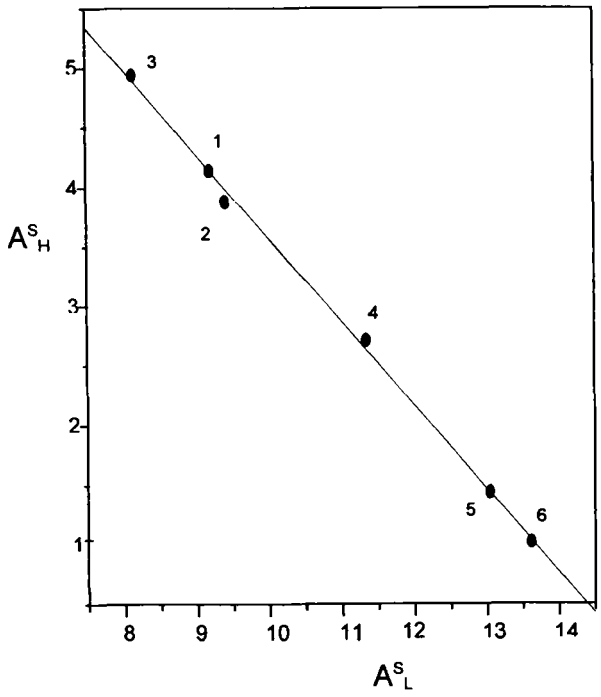


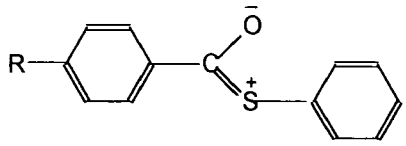
Fig.1. $A_H^S = f(A_L^S)$-plot for 4'-methylthiolbenzoate
The numbering of the solvents is given in Table 1.

2. The $\Delta\mu^2_{L,H} / r^3$-values decrease in the order OCH_3 > CH_3 > C≡N, the value of the cyano derivative being comparatively lower (Table 3). Taking into account that the replacement of the substituents do not actually change the effective molecular volume r^3_{eff} (see Eqn. 1), this result shows that the conformational transition in compounds with electron donor CH_3- and especially OCH_3-substituent leads to a greater change of the $\Delta\mu_{L,H}$.

3. The $\Delta G^V_{L,H}$-value for 4'-cyanophenylthiolbenzoate is about 1.5 as high as the values for the CH_3- and OCH_3- substituted compounds. This fact suggests that the electron acceptor ability of the cyano group favours the stabilization of the **H**-conformer.

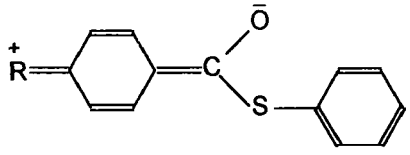
The above results confirm the assumption about a conformational equilibrium between conformers of different dihedral angle between the benzene rings.[1] The existence of this equilibrium in compounds of similar structure is proved for *meta*- and *para*-terphenyls, since experimental[17,18] and quantum chemical results[19] reveal the presence of two energy minima. They correspond to the equilibrium between conformers with a non-planar and planar disposition of the terminal benzene rings. From this point of view, the effect of the 4'-substituents on the conformational equilibrium in the investigated phenylthiol-benzoates can be explained in the following manner.

It is known that the substitution of the oxygen atom by sulfur leads to an increase of the statistical weight of the resonance structure (**II**) in the real electronic density distribution of thiolesters. It is assumed that this effect is the reason for the increased mesogenic ability of these compounds, compared to their oxygen analogues.[7] The influence of structure (**II**) on the IR-characteristic frequencies in thiolesters is discussed in detail.[20] The stabilization of this structure explains the decrease of the C=O stretching frequency, compared to that of oxyesters.

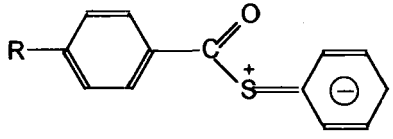


II

The introduction of the electron donor CH_3- or OCH_3-substituents in 4'-position leads to increasing contribution of the resonance structure (**III**). This concurrent effect results in an increase of the order not only of the C-Ph bond (see **III**), but also of the S-Ph bond, since the decrease of the relative part of structure (**II**) increases the conjugation between the sulfur atom and the benzene ring of the thiol fragment, i.e., the participation of structure (**IV**) increases as well.



III



IV

Due to conjugation with the carbonyl group, electron acceptor substituents such as cyano group in 4'-position have no adverse effect but only reduce the contribution of structures (**III**) and (**IV**). This assumption is confirmed experimentally by the UV-spectra of the studied phenylthiolbenzoates. The charge transfer band of the cyano derivative at 245 nm as well as these of the compounds with electron donor substituents (Fig. 2) are shifted batochromically compared to the spectrum of the unsubstituted compound ($\lambda_{max} = 237$ nm).

Therefore, electron donor substituents in 4'-position favour the resonance structure (**III**) and partly (**IV**) stabilizing the flat geometry of the phenylthiolbenzoate molecules and increasing their dipole moments. These phenomena characterize the **L**-rotamer in solution. In the cases of the investigated OCH_3- and CH_3-derivatives, this accounts for a stronger conformational preference (lower value of $\Delta G^{v}_{L,H}$) and for a greater change of $\Delta\mu_{L,H}$ (Table III). As mentioned above, the electron acceptor influence of the cyano group decreases the effective contribution of structures (**III**) and (**IV**) relieving the rotation around the Ph-C and S-Ph bonds (see Scheme **I**). This decreases the conformational preference (greater value of $\Delta G^{v}_{L,H}$ - Table III) and increases the conformational mobility. The last assumption corresponds to the data about the $A^{S}_{H} = f(A^{S}_{L})$-relationship for 4'-cyanophenyl-

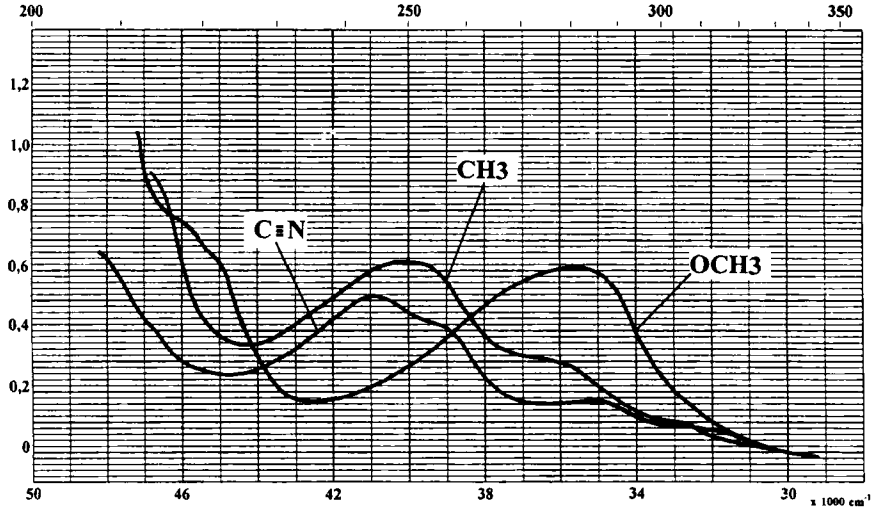
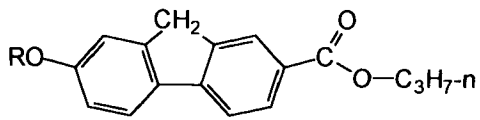


Fig.2. UV- spectra of the investigated 4'-substituted phenylthiolbenzoates

thiolbenzoate (see above). The final result is the shifting of the equilibrium to the **H**-rotamer with non-parallel disposition of the benzene rings. This is in agreement with X-Ray diffraction study of 4-n-pentyl-4'-cyanophenylthiolbenzoate.[8]

These conclusions support the available data about the mesogenic ability of the thiolesters. A homologous series of mesomorphic 4-n-alkyl-phenyl-4'-n-akyl- or alkoxy- thiolbenzoates are described[6,7] and it is proved that the alkoxy group in 4'-position favours the formation of smectic phase.[7] The influence of the coplanarity of the benzene rings on the properties of the mesophase is discussed for liquid crystalline compounds with similar to the phenylthiolbenzoates structure.[21] Particularly, the n-propyl-7-alkoxy-



V

fluorene-2-carboxylates (Scheme **V**) exhibit smectic mesophases of greater thermal stability than those of the analogous biphenyl esters.[21] It is due to the flat structure of the biphenyl sceleton stabilized by the bridging CH_2-group of the fluorene fragment (Scheme **V**) which increases the dipole moment and the polarizability of the ester molecules raising the mesogenic ability too.

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