

SOLVENT EFFECT ON THE STRUCTURE AND INFRARED SPECTRA OF *N*-(3-CHLORO-2-BENZO[*b*]THIENOCARBONYL)-*N'*-ETHYLTHIOUREA

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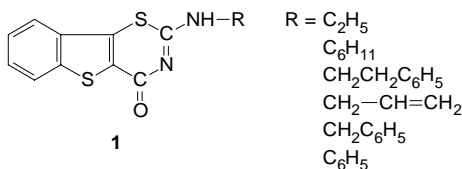
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The solvent effect on the title compound was studied by examining changes in the positions of IR bands belonging to the NH and CO bonds and in the dipole moments in benzene and dioxane solutions. The results are discussed in terms of intramolecular hydrogen bonding and spatial arrangement of the CONHCSNH grouping.

Key words: IR spectra; Hydrogen bonds; Solvent effect; Dipole moment.

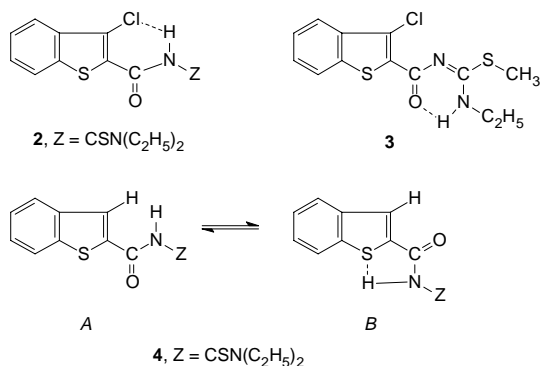
Previously^{1,2} we investigated the photocyclization of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)- and *N*-(2-benzo[*b*]thienocarbonyl)-*N'*-monosubstituted thiourea derivatives and found that if irradiated from a high-pressure mercury discharge lamp, the compounds in acetone solutions give derivatives of benzothienothiazine **1** in yields lower than the analogous *N',N'*-disubstituted thioureas do.



We suggested that this difference in reactivity was due to the different spatial structure of the compounds resulting from the formation of intramolecular hydrogen bonds. Based on the IR spectra of the model compounds *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N',N'*-diethylthiourea (**2**) and *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethyl-*S*-methylisothiourea (**3**), we were able to prove the presence of intramolecular hydrogen bonds of the NH...Cl and NH...O=C type in derivatives of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-monosubstituted thiourea. For *N*-(2-benzo[*b*]thienocarbonyl)-*N',N'*-diethylthiourea (**4**) we observed two conformers, *A* and *B*, due to the rotation

about the $C_{Ar}-C(O)$ line, with a free amidic NH bond and the $NH\dots S$ intramolecular hydrogen bond (Scheme 1).

From a comparison of the wavenumbers belonging to the $NH\dots Cl$ and $NH\dots S$ hydrogen bonds in the model compounds **2** and **4** we deduced that the former hydrogen bond is stronger than the latter.



SCHEME 1

With a view to gaining additional information concerning the reactivity of the thioureas under study, we examined in this work the solvent effect by measuring changes in the IR bands of the NH and CO bonds for *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea. We expected that the interaction of the CONHCSNH group with the solvent would induce an increase/decrease in the probability of occurrence of the six-membered cyclic form². Based on reported data³, we employed van der Waals solvents and solvents which are hydrogen bond acceptors with a view to employing the experimentally discriminated contributions of the various intermolecular interactions for assessment of the solvent effects.

EXPERIMENTAL

N-(3-Chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea was prepared following ref.¹. The solvents were of spectral purity. For the dipole moment measurements, benzene and dioxane were redistilled (b.p. 80 °C and 101.3 °C, respectively) and dried over Nalsit-4 molecular sieve.

The infrared spectra were measured on a Specord M 85 spectrometer (Zeiss, Jena) over the region of 3 600–800 cm^{-1} . The measurements were accomplished at room temperature in an NaCl cell 0.0245 cm optical path length at a concentration of 0.03 mol l^{-1} . Overlapping absorption bands were resolved and the integral absorption intensities of the Fermi triplet components were determined. The integral absorption intensity A_1 served as the criterion of intensity of the observed absorption bands.

The dipole moments were measured in solutions in benzene and 1,4-dioxane at five concentrations within the region of 0.01 to 0.08 mol l^{-1} . The permittivities of the substances studied were measured on a Dipolmeter DM 01 (Wissenschaftlich-technische Werkstätten) with a precision of 0.0001. The measuring frequency for liquids was 2 MHz and the temperature of the system was 20 ± 0.05 °C.

The volume of the thermostatted DFL 2 cell was 4 ml. Densities were measured in 10 ml pycnometers for volatile substances. The dipole moments were calculated by the method of Halverstadt and Kumler⁴ without correction for atomic polarization. Molar refractions R_D were calculated based on the values for benzothiophene⁵ and the increments^{6,7}. The following published standard bond or group increments⁸ (in 10^{-30} C m) were used when calculating the dipole moments by the vector addition approach: H-C_{ar} 0.00, C_{ar}-Cl 5.29, C=O 7.99, C=S 6.66, C-N 1.49, N-H 4.36, C_{al}-H 1.33, benzothiophene⁵ 2.06; bond angles^{9,10}: C(2)-C-O 120°, O-C-N 117°, C-N-C 126°, C-N-H 117°, S-C-N 117°, C-N-C_{al} 120°.

RESULTS AND DISCUSSION

Based on the study of IR spectra of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea in van der Waals solvents and in solvents which are hydrogen bond acceptors (Table I, solvents Nos 1-7 and 8-10, respectively), we found bands due to the intramolecular NH...X bond (X = Cl, S) within the region of 3 387-3 379 cm⁻¹ and bands due to the intramolecular NH...O=C bond within the region of 3 268-3 261 cm⁻¹. The facts that the intensity ratio of those bands is concentration independent and that no additional band belonging to the free NH group is present at low concentrations give evidence that the compound occurs in the six-membered cyclic form solely. In addition to the hydrogen bonds, we also observed anomalous splitting of the absorption bands of the thioamidic NH bond due to Fermi resonance with the δ (NH) overtone and the ν (CO) + δ (NH) combination vibration. By perturbation theory for three-level interactions¹¹ we calculated the band frequencies corrected for the Fermi resonance and the extent of interaction between the absorption band pairs (W_{AB} , W_{AC} , W_{BC} , Table I). We found that the ν (NH...O=C) ground stretching vibrations interact more with the δ (NH) overtone (W_{AB} values in Table I) than with the ν (CO) + δ (NH) combination (W_{AC} values). The very strong bands of the ν (CO) stretching vibrations lie at 1 659-1 653 cm⁻¹; the wavenumbers are also affected by the intramolecular NH...O=C hydrogen bond. Quantitative evaluation of the IR spectra in the regions of the intramolecular hydrogen bonds of the NH and CO groups, with respect to the wavenumber shifts and integral intensities (Table I), showed that the differences in the values in solvents 1-7 and 8-10 are very low $\Delta\nu$ (NH...X) = 3.8 cm⁻¹ and 3.7 cm⁻¹, $\Delta\nu$ (NH...O=C) = 3.2 cm⁻¹ and 4.7 cm⁻¹, $\Delta\nu$ (CO) = 2.5 cm⁻¹ and 0.2 cm⁻¹, respectively; ΔA_1 (NH...X) = 0.32 and 0.24, ΔA_1 (NH...O=C) = 0.30 and 0.28, ΔA_1 (CO) = 0.39 and 0.46, respectively). This suggests that the interaction between the solute molecules and the solvent is very low due to the negligible possibility of action of dispersion forces, dipole interactions, and intermolecular hydrogen bonds. Despite the low changes in the wavenumbers and integral intensities of the bands in the various solvents, the correlations with their constants were of interest. We employed the following parameters to characterize the solvents: dipole moment^{3,12} (μ^2), refractive index¹³ [n^2 or $(n^2 - 1)/(2n^2 + 1)$], permittivity¹³ [$(\epsilon - 1)/(2\epsilon + 1)$], field effect¹³ [$|R| = (\epsilon - 1)/(2\epsilon + n^2)$], electrophilicity E , and nucleophilicity¹³ B . We

TABLE I
IR band positions (cm^{-1}) of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea in various solvents

No.	Solvent	Fermi triplet parameters ^b after band separation ^d			Band positions after resonance removal				W_{AB} W_{AC} W_{BC}			
		$\nu(\text{NH}\dots\text{X})^d$ (X = Cl, S)	band I	band II	band III	$\nu(\text{NH}\dots\text{O}=\text{C})$		$\nu(\text{CO}) + \delta(\text{NH})$		$2\delta(\text{NH})$		
						calc ^c	sum ^d	calc ^c			sum ^d	
1	Tetrachloromethane	3 382.8 (0.63)	3 263.2 (1.24)	3 204.1 (0.12)	3 171.5 (0.10)	1 655.8 (1.70)	3 252.6	3 198.3	3 205.7	3 187.9	3 099.8	20.5
2	Tetrachloroethylene	3 382.9 (0.67)	3 264.0 (1.42)	3 199.2 (0.12)	3 146.4 (0.01)	1 655.5 (1.63)	3 257.4	3 185.7	3 204.1	3 166.5	3 097.2	26.2
3	Trichloromethane	3 379.0 (0.89)	3 267.4 (1.37)	3 206.3 (0.12)	3 148.3 (0.03)	1 653.5 (2.02)	3 259.5	3 191.4	3 202.9	3 171.1	3 098.8	26.5
4	Dichloromethane	3 381.0 (0.73)	3 264.1 (1.44)	3 204.4 (0.13)	3 168.7 (0.08)	1 655.2 (1.80)	3 254.7	3 197.2	3 210.5	3 185.3	3 110.6	21.3
5	1,2-Dichloroethane	3 380.0 (0.57)	3 266.6 (1.14)	3 215.8 (0.14)	3 164.5 (0.08)	1 656.0 (1.78)	3 255.8	3 204.0	3 210.3	3 187.1	3 108.6	24.2
												13.1
												17.5

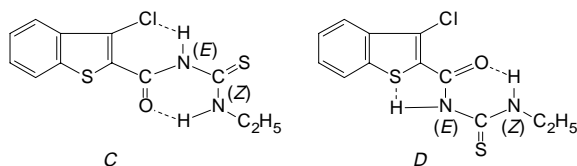
TABLE I
(Continued)

No.	Solvent	Fermi triplet parameters ^b after band separation ^a			Band positions after resonance removal						W_{AB} W_{AC} W_{BC}	
		$\nu(\text{NH}\dots\text{X})^d$ (X = Cl, S)	$\nu(\text{CO})^e$			$\nu(\text{NH}\dots\text{O}=\text{C})$		$\nu(\text{CO}) + \delta(\text{NH})$		$2\delta(\text{NH})$		
			band I	band II	band III	calc ^c	calc ^c	calc ^c	sum ^d	calc ^c		sum ^d
6	Benzene	3 382.1 (0.59)	3 265.8 (1.15)	3 200.0 (0.13)	3 167.5 (0.07)	1 654.9 (1.68)	3 254.6	3 194.9	3 205.7	3 183.8	3 101.6	24.2 14.7 11.6
7	Bromobenzene	3 380.1 (0.78)	3 261.2 (1.27)	3 199.5 (0.13)	3 161.7 (0.06)	1 654.3 (1.97)	3 251.5	3 191.9	3 202.7	3 179.0	3 096.8	23.3 13.2 13.3
8	Acetone	3 387.5 (0.57)	3 266.2 (1.40)	3 211.8 (0.10)	3 176.9 (0.02)	- ^f	3 261.1	3 203.1	-	3 190.7	-	18.6 7.1
9	1,4-Dioxane	3 383.8 (0.33)	3 264.7 (1.28)	3 206.0 (0.23)	3 170.4 (0.08)	1 659.4 (1.72)	3 251.7	3 201.2	3 213.0	3 188.2	3 107.2	12.6 27.2 12.3
10	Acetonitrile	3 385.2 (0.35)	3 267.9 (1.12)	3 209.3 (0.20)	3 159.9 (0.27)	1 659.6 (1.26)	3 246.2	3 201.8	3 223.6	3 189.1	3 128.0	13.5 23.9 22.0 13.9

^a Integral absorption intensities ($1 \text{ mol}^{-1} \text{ cm}^{-2}$) are given in parentheses. ^b Due to the interaction of $\nu(\text{NH}\dots\text{O}=\text{C})$, $2\delta(\text{NH})$ and $\nu(\text{CO}) + \delta(\text{NH})$. ^c Obtained by perturbation calculation. ^d The $\nu(\text{C}=\text{O}) + \delta(\text{NH})$ values obtained by summing up the experimental wavenumbers. ^e Twice the observed $\delta(\text{NH})$ wavenumber. ^f Wavenumber cannot be read.

found no linear independence with the spectral properties of the thiourea studied for any of the solvents 1–7 and 8–10, or 1–10.

From the results (Table I) it can be inferred that, with regard to the cyclic six-membered



arrangement of the CONHCSNH grouping, the structure of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea is as expressed by formula *C* or *D*.

Taking into account published data^{14,15} we attributed the amidic NH band to the *E* planar conformation and the band of the thioamidic NH group to the *Z* planar conformation at the –C–N– bonds.

In order to support the conclusions drawn from the IR spectral patterns we measured the dipole moments of the compound in benzene and in dioxane (Table II). We employed the dioxane effect⁸ to test the presence of intermolecular hydrogen bonds. The difference between the dipole moments in dioxane and in benzene, $\Delta\mu = 0.8 \cdot 10^{-30}$ C m, gave evidence that the solute does not enter any significant interaction with dioxane. This in turn indicates the presence of strong intramolecular hydrogen bonds within the solute molecule. The strength of those hydrogen bonds can also be demonstrated by calculating their force constants¹⁶ from the band positions corrected for the Fermi resonance. For the NH...X and NH...O=C hydrogen bonds the force constants lay within the ranges of $(6.333\text{--}6.365) \cdot 10^2$ N m⁻¹ and $(5.845\text{--}5.899) \cdot 10^2$ N m⁻¹, respectively.

We also attempted to find which of the two conformations *C*, *D* is actually preferred, viz. by comparing the corresponding dipole moments calculated by the vector addition method with the values observed in the benzene solutions (Table II). However, the

TABLE II

Dipole moments μ (in 10^{-30} C m), polarizations *P* and molar refractions R_D (cm³ mol⁻¹) of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea in benzene and 1,4-dioxane at 20 °C

Solvent	α	β	<i>P</i>	R_D	μ_{exp}	μ_{calc}	
						<i>C</i>	<i>D</i>
Benzene	6.51	–0.34	442.85	83.02	13.9		
1,4-Dioxane	9.02	–0.43	486.49	83.02	14.7	13.3	12.4

difference between the two calculated dipole moments is very low ($\Delta\mu_{CD} = 0.9 \cdot 10^{-30}$ C m) and the differences between the experimental and calculated values are not very different either ($\Delta\mu_C = 0.6 \cdot 10^{-30}$ C m, $\Delta\mu_D = 1.5 \cdot 10^{-30}$ C m), so that no reasonable conclusions can be drawn from them.

The results of the IR study, dipole moment measurements, and solvent effect examination, in conjunction with the published data^{17,2}, lead to the conclusion that *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)-*N'*-ethylthiourea occurs in the six-membered cyclic conformation *C*. We suppose that conformation *D* does not play any role due to the repulsive forces between the electronegative chlorine atom and the carbonyl group, as in 3-chloromethyl-2-oxabenzothiazole¹⁷. Moreover, as a consequence of the existence of very strong intramolecular hydrogen bonds, solvent replacement fails to cause any change in the spatial arrangement of the CONHCSNH group and thus in the reactivity of the compound.

REFERENCES

1. Kutschy P., Imrich J., Bernat J., Kristian P., Hritzova O., Schoffmann Th.: *Collect. Czech. Chem. Commun.* 51, 2839 (1986).
2. Hritzova O., Kutschy P., Imrich J., Schoffmann Th.: *Collect. Czech. Chem. Commun.* 52, 2673 (1987).
3. Kleeberg H., Eisenberg Ch., Zinn Th.: *J. Mol. Struct.* 240, 175 (1990).
4. Halverstadt I. F., Kumler W. D.: *J. Am. Chem. Soc.* 64, 2988 (1942).
5. Charles R. G., Freiser H.: *J. Am. Chem. Soc.* 72, 2233 (1953).
6. Vogel A. I.: *J. Chem. Soc.* 1948, 1833.
7. Vogel A. I., Cresswell W. T., Jeffery G. H., Leicester J.: *J. Chem. Soc.* 1952, 514.
8. Exner O.: *Dipole Moments in Organic Chemistry*. Thieme, Stuttgart 1975.
9. Barton D., Ollis D.: *Comprehensive Organic Chemistry*, Vol. 3, p. 440. Pergamon Press, Oxford 1979.
10. Suchar G., Danihel I.: *Collect. Czech. Chem. Commun.* 60, 856 (1995).
11. Nyquist R. A., Fouchea H. A., Hoffman G. A., Hasha D. L.: *Appl. Spectrosc.* 45, 860 (1991).
12. Mc Clellan A. L.: *Tables of Experimental Dipole Moments*. Freeman, San Francisco 1963.
13. Chapman N. B., Shorter J.: *Advances in Linear Free Energy Relationships*, p. 254. Plenum Press, New York 1972.
14. Walter W., Ruess K. P.: *Justus Liebigs Ann. Chem.* 743, 167 (1971).
15. Walter W., Ruess K. P.: *Justus Liebigs Ann. Chem.* 746, 54 (1971).
16. Legon A. C., Millen D. J.: *J. Am. Chem. Soc.* 109, 356 (1987).
17. Perjessy A., Sutoris V.: *Chem. Zvesti* 38, 119 (1984).