INTRAMOLECULAR HYDROGEN BONDS AND FERMI RESONANCE IN *N*-SUBSTITUTED *N′*-(2-FLUOROBENZOYL)THIOUREA DERIVATIVES

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Received December 28, 1992
Accepted October 29, 1993

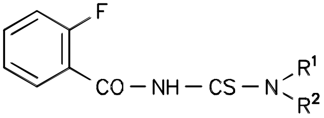
The presence of intramolecular NH...O=C bonds was proved in *N*-substituted *N′*-(2-fluorobenzoyl)-thiourea derivatives by analysis of their infrared spectra. The intramolecular vibrational effects bring about a shift of the ν(NH) vibrational band to lower frequencies to the extent that the band gets into a vicinity to the δ(NH) overtone and Fermi resonance occurs between them. In addition, the ν(NH) vibration is also affected by Fermi resonance with the ν(CO) + δ(NH) combination. Double absorption bands were observed in the ν(CO) region for some of the derivatives. Based on perturbation theory applied to three-level interactions and using the Langseth and Lord equations, the band frequencies corrected for Fermi resonance were calculated and the hydrogen bond strength was examined in the compounds studied.

Hydrogen bonds affect the properties of organic substances[1], and recognition of the hydrogen bond nature can be of advantage when solving reactivity, structure and stereochemistry problems for such substances. Infrared spectroscopy is a simple and reliable method for identifying hydrogen bonds.

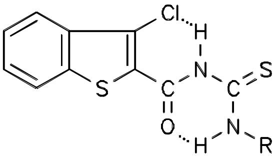
Previously[2] we examined hydrogen bonds with respect to their effect on the photochemical reactions of *N*-(3-chloro-2-benzo[*b*]thienocarbonyl)- and *N*-(2-benzo-[*b*]thienocarbonyl)-*N′*-monosubstituted thiourea derivatives as compared to the analogous *N′*,*N′*-disubstituted derivatives. Their different reactivity was ascribed to the effect of the different spatial structures due to the occurrence of intramolecular hydrogen bonds. For *N*-substituted *N′*-benzoyl- and *N′*-(2-chlorobenzoyl)thiourea[3] we also sought an analogy of hydrogen bond formation and their effect on the reactivity.

When examining the IR spectra of *N*-substituted *N′*-(2-fluorobenzoyl)thiourea we observed, in addition to the occurrence of hydrogen bonds, anomalous splitting of the NH and CO bands. So far, no detailed information concerning this splitting and its relation to hydrogen bonds in the compounds under study exists. In the IR spectra of all the compounds examined (*I* – *VIII*), absorption bands only belonging to the free amide NH group appear in the 3 428 – 3 416 cm^{-1} region (Table I). This indicates that our initial assumption of the occurrence of NH...halogen intramolecular hydrogen bonds, such as exist in the analogous thiourea *IX* (ref.[2]), is wrong. The formation of NH...Cl hydrogen bonds in the region of 3 371 – 3 360 cm^{-1} in the compounds may be explained in terms of a higher electron density at the chlorine atom due to the electron donor effect of sulfur in the thiophene ring and to a hindrance to the rotation of the thiourea part about the Ar–C single bond. In addition, the form *X* is conceivable in all of the compounds.

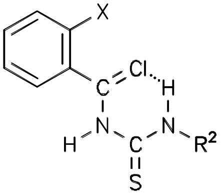
We suppose that this is not so in the case under study because of the repulsion between the electronegative halogen atom and the carbonyl group[2,3]. The spectra of substances *I* – *VI* also exhibit absorption bands in the 3 296 – 3 228 cm^{-1} region (Table I), which we attribute to intramolecular hydrogen bonding between the hydrogen atom of the thioamide NH group and the oxygen atom of the carbonyl group[2,3]. The concentra-



I, $R^1 = R^2 = H$
II, $R^1 = H$; $R^2 = C_3H_7$
III, $R^1 = H$; $R^2 = C_6H_5$
IV, $R^1 = H$; $R^2 = 4\text{-}CH_3\text{-}C_6H_4$
V, $R^1 = H$; $R^2 = 4\text{-}Cl\text{-}C_6H_4$
VI, $R^1 = H$; $R^2 = 4\text{-}Br\text{-}C_6H_4$
VII, $R^1 = R^2 = C_2H_5$
VIII, $R^1 = R^2 = C_6H_5$



IX, R = C_2H_5 or C_6H_5



X, X = halogen, R^2 = alkyl, aryl

tion independence of the intensity ratio of those bands as well as the absence of another band of the free NH group at low concentrations also indicates that the compounds mostly occur in the six-membered ring form. Owing to the absence of the NH...halogen intramolecular hydrogen bond, the aromatic ring with fluorine in position 2 is probably tilted from the plane of the six-membered ring which includes the NH...O=C intramolecular hydrogen bond. The shift of the bands belonging to the stretching vibrations involved in the NH...O=C intramolecular hydrogen bond for compounds *I* – *VI* is consistent with the ^{1}H NMR spectral patterns where the signal of this proton is shifted downfields (9.8 – 12.72 ppm, Table I). In the 3 220 – 3 112 cm^{-1} region the IR spectra also exhibit absorption bands which are probably due to Fermi resonance. We suggest that, as a result of the above intramolecular vibrational effects, the ν(NH) band frequency decreases to the extent that it gets in a close vicinity to the δ(NH) overtone and Fermi resonance occurs between them[4 – 6]. Moreover, the NH stretching vibration is also affected by Fermi resonance with the ν(CO) + δ(NH) combination, hence, the interaction involves three vibrations. Fermi resonance was confirmed by measurements in chloroform as a polar solvent. While the positions of the Fermi resonance-involving bands remained nearly unaffected, their intensities changed. It is also well known that Fermi resonance can play a major part not only in strong hydrogen bonds but also in relatively weak hydrogen bonds[7 – 10]. This implies that if we want to assess the hydrogen bond strength we must obtain frequencies of the absorption bands free from the

TABLE I
Observed IR band frequencies (ν, cm^{-1}) and ^{1}H NMR chemical shifts (δ, ppm) in the NH ranges for compounds *I* – *VIII*

	$\nu(NH)_{nb}$	Fermi triplet[a]			ν(C=O)		δ	
		Branch I	Branch II	Branch III				
I[b]	3 424	3 296	–	3 172	1 692	1 684	9.30	9.80
II	3 428	3 260	3 220	3 192	1 672		9.57	10.55
III	3 420	3 228	3 170	3 126	1 676		9.30	12.40
IV	3 420	3 228	3 168	3 128	1 674		9.62	12.35
V	3 420	3 228	3 168	3 120	1 674		9.70	12.55
VI	3 420	3 228	3 168	3 112	1 674		9.72	12.72
VII	3 416	–	–	–	1 692	1 704	8.50	
VIII	3 420	–	–	–	1 698	1 704	8.60	

[a] Due to interaction of $\nu(NH)_b$, 2 δ(NH) and ν(C=O) + δ(NH); no branch II observed in compound *I*, no branches II and III observed with compounds *VII* and *VIII* (which lack the corresponding hydrogen for branch I); [b] this is the sole compound to contain an NH_2 group, whose asymmetric vibration appears at 3 488 cm $^{-1}$, the symmetric vibration is affected by Fermi resonance.

effect of Fermi resonance, because only such frequencies will be dependent on the force constant solely[11]. For this reason we applied relations based on perturbation theory for cases involving three-level interactions[12] and calculated the approximate band frequencies corrected for Fermi resonance (Table II). The extent of this effect depends on that of the interaction[12,13] between the frequencies of bands that are involved in the resonance. We found that the most intense band in the Fermi triplet is associated with the branch that, after elimination of the resonance, belongs to the ν(NH) stretching vibration. The other side branch is associated with the overtone of the NH bending vibration, whereas the centre of the triplet is constituted by a "less variable" band belonging to the ν(CO) + δ(NH) combination vibration. Data in Table II also indicate that the differences between the wavenumbers of the side branches are higher that those corresponding to the unperturbed wavenumbers. Such behaviour is characteristic of two absorption bands that are in a mutual Fermi resonance which results in a repulsion of the perturbed wavenumbers. From this we deduce that the largest interaction between

TABLE II
Wavenumbers (cm^{-1}) of IR bands in the NH stretching region corrected for Fermi resonance by application of perturbation theory[12] to the three-level interaction

Compound	Fermi triplet components after band separation[a]			Wavenumbers after correction				
	Branch I	Branch II	BranchIII	ν(NH)$_b$	ν(C=O) + δ(NH)		2 δ(NH)	
				Calc[b]	Calc[b]	Sum[c]	Calc[b]	Sum[d]
I	3 303 (2.5)	–	3 179 (3.1)	3 248[e]	–	–	3 234[e]	3 156
II	3 261 (4.6)	3 206 (0.1)	3 170 (0.5)	3 253	3 197	3 224	3 187	3 104
III	3 222 (4.4)	3 168 (0.6)	3 128 (0.5)	3 209	3 161	3 222	3 148	3 100
IV	3 221 (4.3)	3 164 (0.6)	3 127 (0.4)	3 208	3 158	3 224	3 146	3 100
V	3 206 (4.8)	3 162 (0.6)	3 126 (0.3)	3 197	3 155	3 224	3 142	3 100
VI	3 220 (3.8)	3 154 (0.8)	3 107 (0.5)	3 200	3 148	3 224	3 133	3 100

[a] Integrated intensities ($l\ mol^{-1}\ cm^{-2}$) are given in parentheses; [b] calculated by perturbation theory; [c] sum of the observed ν(C=O) + δ(NH) wavenumbers; [d] two-fold multiple of the observed δ(NH) wavenumber; [e] calculated by the equation of Langseth and Lord.

the frequencies of the bands which are affected by Fermi resonance involves the ν(NH) stretching vibration and the δ(NH) overtone. Since Fermi resonance with the combination vibrations does not occur in compound *I*, the extent of interaction between the $\nu(NH)_b$ vibration and the δ(NH) overtone is higher in this compound than in the remaining derivatives (Table II).

The very strong absorption bands of the carbonyl stretching vibrations lie within the range of 1 698 – 1 672 cm^{-1} for all of the compounds. For some of them, viz. *I*, *VII* and *VIII*, double absorption bands were also observed in that region. These can be due to Fermi resonance of the carbonyl group with the overtone of a lower-frequency fundamental vibration[14,15], probably the Ph–C stretching[16]. The splitting of the absorption bands is not a manifestation of the occurrence of conformation isomers in the substances in question.

After obtaining vibrational frequencies corrected for the effect of Fermi resonance, we can assess the hydrogen bond strength. Table II demonstrates that derivatives *I* and *II* form weaker intramolecular hydrogen bonds of the NH...O=C type than the other thioureas. This is due to the +*I* effect of the groups which reduce the acidity of the thioamide group hydrogen, in contrast to the compounds *III* – *VI* where the aryl substituents increase the hydrogen acidity and thereby the hydrogen bond strength. The hydrogen bond strength is only slightly affected by the substituents bonded to the aromatic ring in the *para* position.

EXPERIMENTAL

The infrared absorption spectra were measured on a Specord M 85 spectrometer (Zeiss, Jena) within the 3 600 – 800 cm^{-1} region. The measurements were accomplished at room temperature using a variable optical pathlength cell (0.1 – 0.5 cm) at concentrations of 0.003 – 0.015 mol l^{-1}. Tetrachloroethylene and chloroform served as solvents. The absorption intensities of the Fermi triplet components were determined after resolution of the overlapping bands. The ^{1}H NMR spectra were measured in deuteriochloroform on a Tesla BS 487 A instrument (80 MHz) using tetramethylsilane as the internal standard. Compounds *I* – *VIII* were prepared following ref.[17].

The authors wish to thank Professor M. Horak for valuable advice and stimulating comments on this paper.

REFERENCES

1. Tichy M.: Adv. Org. Chem., Meth. Resul. *5*, 115 (1965).
2. Hritzova O., Kutschy P., Imrich J., Schoffmann Th.: Collect. Czech. Chem. Commun. *52*, 2673 (1987).
3. Hritzova O., Koscik D.: Collect. Czech. Chem. Commun. *56*, 880 (1991).
4. Wolff H.: J. Chem. Phys. *52*, 2800 (1970).
5. Wolff H., Ludwig H.: Ber. Bunsenges. Phys. Chem. *70*, 474 (1966).
6. Wolff H., Horn D.: Ber. Bunsenges. Phys. Chem. *71*, 467 (1967).

7. Hadzi D.: Pure Appl. Chem. *11*, 435 (1965).
8. Hadzi D.: Chimia *26*, 7 (1972).
9. Claydon M. F., Sheppard N.: Chem. Commun. *1969*, 1431.
10. Wojcik M. J.: J. Mol. Struct. *62*, 71 (1980).
11. Miyazawa T.: J. Mol. Spectrosc. *4*, 168 (1960).
12. Nyquist R. A., Fouchea H. A., Hoffman G. A., Hasha D. L.: Appl. Spectrosc. *45*, 860 (1991).
13. Wolff H., Horn D.: Ber. Bunsenges. Phys. Chem. *72*, 419 (1968).
14. Jones R. N., Angell C. L., Ito T., Smith R. J. D.: Can. J. Chem. *37*, 2007 (1959).
15. Bond R. P. M., Cairns T., Conolly J. D., Eglinton G., Overton K. H.: J. Chem. Soc. *1965*, 3958.
16. Rao C. N. R., Venkataraghavan R.: Spectrochim. Acta *18*, 273 (1962).
17. Koscik D., Kutschy P., Dzurilla M., Surkalova I., Imrich J.: Chem. Papers, in press.

Translated by P. Adamek.