INFRARED SPECTROSCOPY, DIPOLE MOMENT, AND STRUCTURE STUDY OF BENZOYL ISOTHIOCYANATES

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Infrared spectra and dipole moments of 4-substituted benzoyl isothiocyanates were studied. The wavenumbers of the v_{as}(NCS) bands as well as logarithms of their integral intensities were found to correlate linearly with the Hammett σ constants. The results indicate that in benzoyl isothiocyanates, mesomeric interaction of the NCS group with the CO group is rather pronounced, while the aromatic part interacts with the —CONCS group predominantly *via* the π-electron inductive effect. The dipole moments of benzoyl isothiocyanates and acetyl isothiocyanate reveal an appreciable electron acceptor character of the —CONCS group displaying the —M effect. The group was found to be present in the Z conformation with the dihedral O=C—N=C angle of ~60°.

In the previous works[1-4] we have studied the synthesis, structure, and reactions of cinnamoyl isothiocyanates. Benzoyl isothiocyanates, which represent the fundamental type of aromatic acyl isothiocyanates, have not been so far studied thoroughly from the point of view of their structure and spectral properties, probably owing to their high reactivity and considerable instability in polar media. Investigating the infrared spectra of these compounds, Hamm and Willis[5] found the v_{as}(NCS) absorption band to be markedly shifted to lower wavenumbers as compared with phenyl isothiocyanates, due to mesomeric interaction of the NCS group with the CO group. No dipole moment data on benzoyl isothiocyanates are at present available from the literature.

In the present work we study the infrared spectra and dipole moments of 4-substituted benzoyl isothiocyanates in order to elucidate the structure and polar nature of the —CONCS group bonded to the aromatic ring.

EXPERIMENTAL

Chemicals: Benzoyl isothiocyanate[6] (*I*), b.p. 77—78°C/0·34 Torr; 4-methylbenzoyl isothiocyanate[7] (*II*), b.p. 107—109°C/0·5 Torr; 4-methoxybenzoyl isothiocyanate[8] (*III*), b.p. 110 to 112°C/0·25 Torr, m.p. 28—30°C; 4-dimethylaminobenzoyl isothiocyanate[9] (*IV*), m.p. 63—64°C; 4-chlorobenzoyl isothiocyanate[10] (*V*), m.p. 46—47°C; 4-cyanobenzoyl isothiocyanate (*VI*), m.p. 54—55°C, prepared according to Johnson and Chernoff[6]. For $C_9H_4N_2OS$ (188·2) calculated/

found: C 57·43%/57·40%, H 2·14%/2·28%, N 14·88%/14·71%; 4-nitrobenzoyl isothiocyanate[9] (*VII*), b.p. 192—194°C/15 Torr, m.p. 90—92°C; acetyl isothiocyanate[11] (*VIII*), b.p. 132—134°C/ 760 Torr. With regard to their considerable instability, the substances examined had to be prepared freshly before each measurement.

Spectral Measurements

Infrared absorption spectra were scanned in the region of 2 300—1 600 cm⁻¹ on a double beam prism spectrophotometer UR 20 (Zeiss, Jena) using a slave recorder (Zweitschreiber). 0·05M solutions in chloroform were measured in NaCl cells, thickness 0·4 mm. The instrument was calibrated by means of a polystyrene foil. Integral intensities, B, for the $\nu_{as}(NCS)$ band were measured in the range of 2 200—1 800 cm⁻¹ with an LiF prism and spectral slit 2·5 cm⁻¹. The absorbance curves were evaluated by applying the baseline method[12] and integrated planimetrically[13] in the limits of $\pm$150 cm⁻¹ from the absorption maximum. The integral intensities were calculated as $B = (2·303/cd)\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A_{\tilde{\nu}} d\tilde{\nu}$, where $A_{\tilde{\nu}}$ is the absorbance, $\tilde{\nu}$ the wavenumber (cm⁻¹), c concentration (mol l⁻¹), and d the sample thickness (cm). The integral intensities of the $\nu(C{=}O)$ bands were measured in the range of 1 800—1 600 cm⁻¹ using an NaCl prism and spectral slit width 7 cm⁻¹, and calculated as $B = 2·303 . a . \Delta\tilde{\nu}_{1/2}$, where a is the absorptivity (1 mol⁻¹ cm⁻¹) and $\Delta\tilde{\nu}_{1/2}$ the half band width (cm⁻¹). The concentration of the solutions was $5 . 10^{-2}$ mol l⁻¹.

Dipole Moments

The dipole moments were measured in benzene solutions, concentration $1—7 . 10^{-3}$ mol l⁻¹, at 20 $\pm$ 0·5°C. The dielectric constants of the solutions were determined on an instrument Dipolmeter DM 01 (Wissenschaftliche-Technische Werkstätten, Weilheim) with the accuracy of 0·0001, and the refractive indices on an Abbe immersion refractometer (Zeiss, Jena). The densities were determined in 10 ml pycnometers for volatile substances. The other measurement conditions are given in the previous paper[3].

The experimental dipole moments were calculated according to Halverstadt and Kumler[14] with correction for atomic polarization of 5—15% R_D. The values of the bond moments, group moments, bond lengths and angles used during the dipole moment calculations are given in[3,15].

RESULTS AND DISCUSSION

All the benzoyl isothiocyanates exhibit, in accordance with the observations of Hamm and Willis[5], a broad intense absorption band in the range of 2 050—1 900 cm⁻¹, which can be attributed to the $\nu_{as}(NCS)$ vibrations. Their spectral parameters are given in Table I. A splitting of the band to two (to three in the case of the nitro derivative) components is characteristic of all the benzoyl isothiocyanates except for the 4-dimethylamino derivative. The correlation was applied to the lowest-frequency components (obtained by the band separation technique[16]), as they exhibit the highest substituent sensitivity. Linear correlations were found between the $\nu_{as}(NCS)$ and $\nu(C{=}O)$ wavenumbers as well as logarithms of the integral intensities, log $B(\nu_{NCS})$ and log $B(\nu_{CO})$, and the Hammett σ_p constants (Table I, Figs 1 and 2). The different signs of the slopes of the dependences indicate that the substituent effect brings about

TABLE I

Band Positions (cm^{-1}), Half Band Widths (cm^{-1}), Absorptivities (1 mol^{-1} cm^{-1}), and Apparent Integral Intensities (10^3 1 mol^{-1} cm^{-2}) of Bands of 4-Substituted Benzoyl Isothiocyanates

Compound	ν(C=O)				ν_{as}(N=C=S)			
	$\tilde{\nu}$	$\Delta\tilde{\nu}_{1/2}$	a	B^a	$\tilde{\nu}$	$\Delta\tilde{\nu}_{1/2}$	a	B^b
I	1 693	43·55	550	55·16	1 947	108·0	657	142·7
					1 986		800	
II	1 692	46·41	550	58·78	1 947	103·0	633	135·4
					1 993		800	
III	1 691	48·00	528	58·36	1 949	109·0	505	129·0
					1 987		657	
IV	1 687	53·90	422	65·94	—	112·0	—	111·5
					1 977		633	
V	1 696	42·84	535	52·78	1 940	116·0	800	149·2
					1 982		888	
VI	1 699	37·40	522	44·96	1 932	116·0	706	154·1
					1 987		680	
VII	1 700	35·70	511	42·01	1 930	113·0	708	172·5
					1 954		738	
					1 990			
VIII	1 713	—	—	—	1 968	—	—	—
					2 000			

^{a} $2·303a . \Delta\tilde{\nu}_{1/2}$; ^{b} $(2·303/cd) \int A \, d\tilde{\nu}$.

FIG. 1

Dependence of the Position and Integral Intensity of the ν(C=O) Band of the Benzoyl Isothiocyanates $I-VII$ in Chloroform Solutions on the Hammett σ_p Constants of the Substituents

○ $\tilde{\nu}$ vs σ_p, $\varrho = 8·258$, $r = 0·996$; ● log B vs σ_p, $\varrho = -0·120$, $r = 0·982$. The σ_p values were taken from[21].
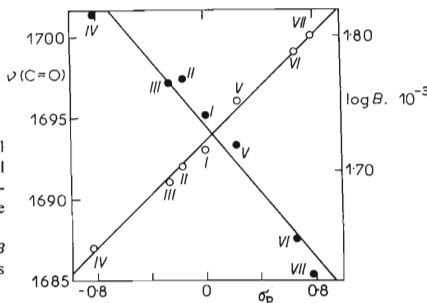
opposite electron displacements at the bonds of the two groups. With regard to the occurrence of the mixed conjugation type in the compound in question (substituents —CO, NCS—CO), it was interesting to find out which of them is the dominant one (Scheme 1, structure A, B). For this purpose we compared the analogous series of

SCHEME 1

cinnamoyl isothiocyanates: here only a very slight change in the position of the v_{as}(NCS) band in dependence on the substituent was observed, whereas for the plot of the v(C=O) wavenumber *versus* σ_p a linear correlation was obtained with the reaction constant higher than for the benzoyl isothiocyanates ($\varrho = 10.24$). This shows that in benzoyl isothiocyanates, in contrast to cinnamoyl isothiocyanates, the mesomeric interaction of the NCS group with the C=O group prevails, while the aromatic ring interacts with the —CONCS group predominantly *via* the π-electron inductive effect (structure B).

In accordance with this assumption are also the results of study of integral intensities of the v(C=O) and v_{as}(NCS) bands. From the comparison of the reaction constants of the two groups it follows that electron acceptor substituents increase the integral intensities of the former band and decrease those of the latter band; this is related with the reverse change of the dipole moments and hence of bond orders of the functional groups in question effected by the substituent.
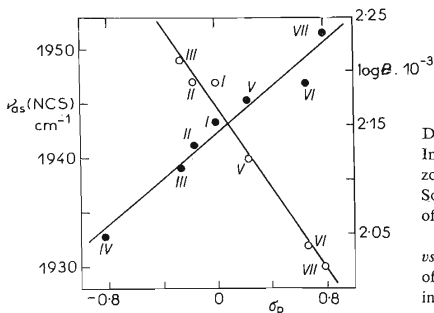

FIG. 2

Dependence of the Position and Integral Intensity of the v_{as}(NCS) Band of the Benzoyl Isothiocyanates $I—VII$ in Chloroform Solutions on the Hammett σ_p Constants of the Substituents

○ $\tilde{v}$ vs σ_p, $\varrho = -18.72$, $r = 0.993$; ● log B vs σ_p, $\varrho = 0.105$, $r = 0.976$. The position of the band of the derivative IV was not included in the correlation.

The experimental and calculated dipole moments of the compounds under study are given in Table II. Similarly as cinnamoyl isothiocyanates, benzoyl isothiocyanates can occur in two conformations, Z and E. From the experimental data of Table II it follows that while for the compounds *I, II,* and *V* the Z conformation predominates, a conformation between Z and E can be expected for the derivative *VII*. This finding is in accordance with the infrared spectral results, which suggest a particularly pronounced mesomeric interaction of the ―CONCS group to be expected in the case of strong electron acceptor substituents, such as nitro group; in this case the nitrogen atom of the NCS group acquires rather the character of an sp hybrid, which results in an increase of the C―N―C angle. The conformation of benzoyl isothiocyanates has been confirmed also graphically[17,18]. From Fig. 3, benzoyl iso-thiocyanates are seen to occur in the Z conformation, similarly as cinnamoyl isothio-cyanates, with the dihedral angle of ~60°.

In the case of 4-methoxybenzoyl isothiocyanate, we attempted to determine analogously the molecular geometry, assuming the rotation of the methoxy group around an axis parallel to the connecting line -O-aromatic ring-C to be hindered and the group to be fixed in the plane of the aromatic ring, due to the marked mesomeric interaction of the methoxy group with the ―CONCS group. As obvious from Fig. 4, in the molecule of this compound the ―CONCS group possesses the conformation Z, with the dihedral angle of ~60°, while the methoxy group can be present in both conformations, E and Z, in the ratio 1 : 1 (Scheme 2, structures E, F).

TABLE II

Polarization Values (cm^3) and Dipole Moments (D) of Benzoyl Isothiocyanates Determined in Benzene Solutions at 20°C

Compound	α_ε	α_{n^2}	β_x	∞P_2	R_D	μ, 5%	μ, 15%	μ (calc.)	
								Z	E
I	16·11	0·614	0·402	277·7	51·8	3·28	3·24	3·80	1·03
II	18·69	0·651	0·557	315·1	52·4	3·54	3·50	4·15	1·30
III	23·25	0·730	0·695	382·8	54·8	3·96	3·92	4·13	2·23
								4·50	1·33
V	6·75	0·755	0·860	139·5	51·7	2·02	1·96	2·23	1·06
VII	4·47	0·399	0·880	109·3	49·5	1·66	1·59	0·80	3·30
VIII	6·76	0·003	0·248	123·3	26·6	2·16	2·13	—	—

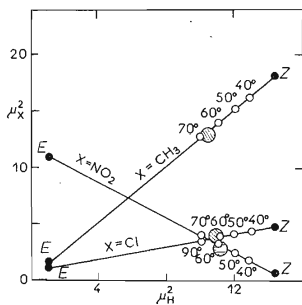C (E, E)

D (Z, E)

E (Z, Z)

F (E, Z)
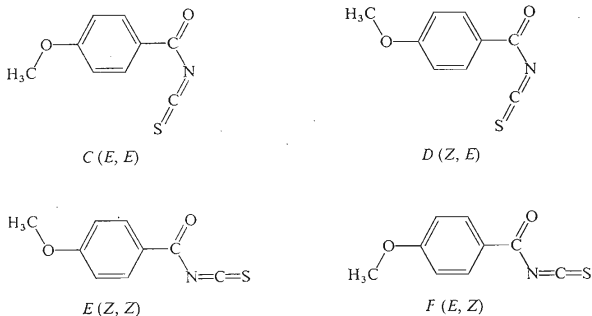
SCHEME 2

FIG. 3

Graphical Comparison of Calculated and Experimental Dipole Moments of Benzoyl, 4-Chlorobenzoyl, 4-Methylbenzoyl, and 4-Nitrobenzoyl Isothiocyanates

The abscissa represents μ_H^2 for the nonsubstituted compound and the ordinate μ_x^2 for the 4-substituted derivatives. ● calculated values for the E and Z conformers (angle 140°), ◎ experimental values.
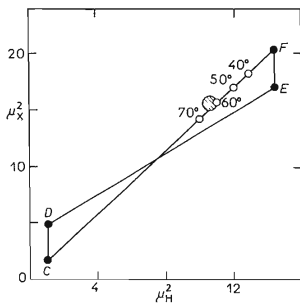
FIG. 4

Graphical Comparison of Calculated and Experimental Dipole Moments of Benzoyl Isothiocyanate and 4-Methoxybenzoyl Isothiocyanate

Comparison of squares of dipole moments of benzoyl isothiocyanate and 4-methoxybenzoyl isothiocyanate. ◎ experimental value, ● calculated values for the conformations C—F. Abscissa represents the nonsubstituted compound, the ordinate the substituted derivative.

Applying the graphical method suggested by van Voerden and Having[19] to the measured values of dipole moments, the group moment of the —CONCS group was calculated to be 3·29 D, the angle $\theta \sim 16°$ to the line connecting the C_1—C_4 carbon atoms of the benzene ring. We attempted to estimate the mesomeric interaction of the —CONCS group with the aromatic ring by employing the differences between the dipole moments of acetyl and benzoyl isothiocyanates (Table II). The value obtained, $\mu_M = -1·12$ D, suggests and appreciable $-M$ effect of the—CONCS group, while the NCS group of phenylisothiocyanate exhibits $+M$ effect[15,20].

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