

Infrared spectra of heterocumulenes. VIII.*

Nature of the $\nu_{as}(\text{NCS})$ complex band of aromatic isothiocyanates

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Characteristic data of the $\nu_{as}(\text{NCS})$ complex band of some aromatic isothiocyanates have been studied and the origin of the splitting of these bands is discussed using perbromophenyl isothiocyanate as a model compound.

Изучаются характеристические спектральные данные сложной полосы $\nu_{as}(\text{NCS})$ некоторых ароматических изотиоцианатов. На примере пербромфенилизотиоцианата обсуждается причина расщепления этих сложных полос.

It is known that organic isothiocyanates exhibit strong and characteristic absorption bands at around 2100 cm^{-1} which are always split [2—6]. The complex nature of these bands has been explained for the first time by *Badger* [2] in terms of Fermi resonance between the 2100 cm^{-1} and an overtone of the band at 1080 cm^{-1} . This explanation seems to be correct for aliphatic isothiocyanates mainly because the band at 1080 cm^{-1} is absent from the spectrum of methyl thiocyanate — an isomeric compound, and no splitting of the band at 2160 cm^{-1} is observed. Analogously, the splitting of the $\nu_{as}(\text{NCS})$ band was also explained for phenyl isothiocyanate. A series of aromatic isothiocyanates was studied in more detail [6] and the splitting of the $\nu_{as}(\text{NCS})$ band was explained as a Fermi resonance between $\nu_{as}(\text{NCS})$ and combination vibration at $\tilde{\nu} = 2094\text{ cm}^{-1}$. Fundamental vibrations of the bands concerned were observed at $\tilde{\nu} = 927\text{ cm}^{-1}$ and $\tilde{\nu} = 1167\text{ cm}^{-1}$, respectively. The bands at 927 and 1167 cm^{-1} are observed in the spectra of all isothiocyanates and were assigned to the symmetrical vibration of the NCS group, $\nu_s(\text{NCS})$, and to the in-plane deformation vibration, $\beta(\text{CCH})$.

Experimental

All the studied isothiocyanates were prepared by the thiophosgene method [7]. They were purified just before use by distillation or crystallization, and their melting points were in

* For Part VII see Ref. [1].

accord with literature. Infrared spectra were recorded with a UR-20 Zeiss instrument in the region of 2300—1900 cm^{-1} . Recording conditions are given in [8]. Integrated absorption intensities of the components of the $\nu_{\text{as}}(\text{NCS})$ complex band were determined by the Ramsay method [9]. The separation of the $\nu_{\text{as}}(\text{NCS})$ band of phenyl isothiocyanate into its components was carried out by the least-square method using a program on the Hewlett—Packard 9100 B calculator.

Results and discussion

The splitting of the band at $\sim 2100 \text{ cm}^{-1}$ has been regarded as peculiar to the spectra of isothiocyanates. Nowadays it is known that nearly all heterocumulenes absorbing in the region of 2300—1900 cm^{-1} have the $\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$ bands split [6, 10—12]. With respect to the difficulty with which a graphical separation of the $\nu_{\text{as}}(\text{NCS})$ complex band into its four components is connected, a mathematical separation has been used. It was assumed that also for components of this complex band (it contains four components, however, the fourth one $\tilde{\nu}_4$, very weak at 1950 cm^{-1} , was neglected for simplification) must hold the Lorentz function. The equation which was necessary to be solved can be written as follows

$$A = \frac{a_1}{(\tilde{\nu} - \tilde{\nu}_1)^2 + b_1^2} + \frac{a_2}{(\tilde{\nu} - \tilde{\nu}_2)^2 + b_2^2} + \frac{a_3}{(\tilde{\nu} - \tilde{\nu}_3)^2 + b_3^2}$$

where A is absorbance of the band, a , b are constants, $a/b^2 = A\tilde{\nu}_{\text{max}}$, $2b = \Delta\nu_{1/2}$, $\tilde{\nu}$ is a calculated wavenumber of the band, and $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$ are wavenumbers of the maxima of the components of the complex band.

As seen from Fig. 1 the calculated and experimental curves fit well. For the components of the complex band the following characteristics were obtained

	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$
$\tilde{\nu} [\text{cm}^{-1}]$	2190	2110	2060
$\varepsilon_{\nu} [\text{l mol}^{-1} \text{ cm}^{-1}]$	68	287	456
$\Delta\nu_{1/2} [\text{cm}^{-1}]$	30	60	60
$A [10^{-4} \text{ l mol}^{-1} \text{ cm}^{-2}]$	0.74	6.2	9.88

Integrated absorption intensity A and the half-band width $\Delta\nu_{1/2}$ for the whole complex band was reported to be $A = 15.5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-2}$ and $\Delta\nu_{1/2} = 134 \text{ cm}^{-1}$ [13]. From molar absorption coefficients and integrated absorption intensities of these bands it can be seen that the bands at 2110 and 2060 cm^{-1} form the Fermi doublet whilst the band at 2190 cm^{-1} is an overtone, which is in good

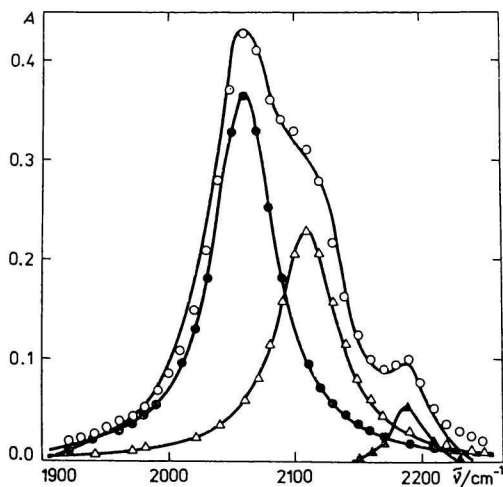


Fig. 1. Separation of the $\nu_{as}(\text{NCS})$ band of phenyl isothiocyanate.

△ Experimental curve; ▲ absorption bands assigned to the overtone; ○ points obtained by superposition of three curves calculated according to the Lorentz relation; ● bands forming the Fermi doublet.

Table 1

Components of the $\nu_{as}(\text{NCS})$ band of X-substituted phenyl isothiocyanates

Compound	X	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	$\tilde{\nu}_4$
		(ϵ)	(ϵ)	(ϵ)	(ϵ)
I	H	2184 (113)	2115 (376)	2060 (544)	1950 (26)
II	4-Bromo	2190 (97)	2095 (451)	2048 (547)	1962 (61)
III	3-Bromo	2198 (62)	2090 (458)	2040 (542)	1962 (68)
IV	2-Bromo ^a	2192 (33)	2120 (167)	2058 (348)	2000 (75)
V	2,4-Dibromo ^b	2186 (51)	2111 (385)	2054 (791)	1997 (205)
VI	2,4,6-Tribromo ^c	—	2102 (385)	2056 (890)	2018 (422)
VII	2,3,4,5,6-Pentabromo ^d	—	2095 (264)	2052 (532)	1984 (84)

$\tilde{\nu}$ in cm^{-1} ; ϵ in $\text{l mol}^{-1} \text{cm}^{-1}$.

Additional bands $\tilde{\nu}(\epsilon)$: a) 2226 (18); b) 2223 (45); c) 2216 (51); d) 2220 (14).

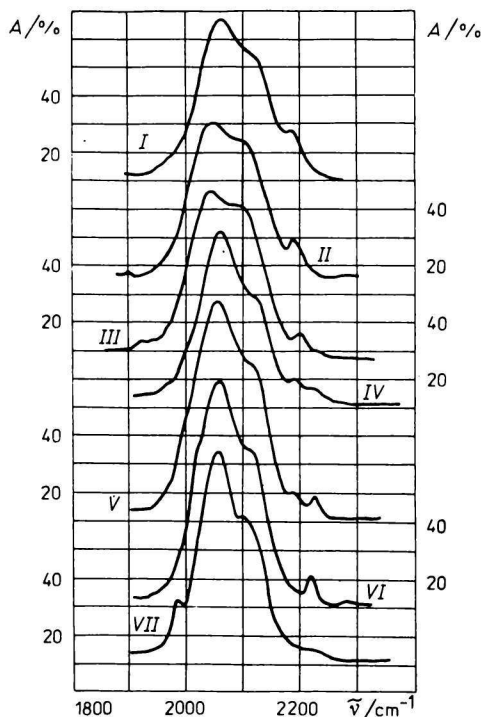


Fig. 2. Absorption bands of some substituted phenyl isothiocyanates.

agreement with the work [6]. To clarify the nature of the splitting of the $\nu_{\text{as}}(\text{NCS})$ band we prepared perbromophenyl isothiocyanate and interpreted its i.r. spectrum. In the spectrum of this compound, although the C—H bands are missing, the $\nu_{\text{as}}(\text{NCS})$ very intense split band is observed pointing out that the explanation of the band splitting by the interaction of $\nu_{\text{as}}(\text{NCS})$ with $\beta(\text{CCH})$ bands has not general validity [6]. For comparison wavenumbers and molar absorption coefficients of the $\nu_{\text{as}}(\text{NCS})$ bands of some aromatic isothiocyanates are given in Table 1 and the shapes of the bands are illustrated in Fig. 2. In the spectra of all isothiocyanates studied Fermi doublets are observed (in Table 1 denoted as $\bar{\nu}_2$ and $\bar{\nu}_3$; $\Delta\bar{\nu} = \bar{\nu}_2 - \bar{\nu}_3 = 30\text{--}60\text{ cm}^{-1}$). Moreover, in the spectra of all isothiocyanates substituted in position 2 and 6, respectively, a shoulder at 2220 cm^{-1} is observed. The band at 2184 cm^{-1} previously assigned to an overtone with phenyl isothiocyanate, was not observed in the case of symmetrical tri- and pentabromo derivatives, respectively. The overtone at 1997 cm^{-1} observed in the spectra of 2,4-dibromo and 2,4,6-tribromo derivatives was too intense, which is not easy to explain.

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References

1. Stankovský, Š. and Kováč, Š., *Tetrahedron* 29, 4175 (1973).
2. Badger, R. M., *J. Chem. Phys.* 5, 178 (1937).
3. Williams, D., *J. Chem. Phys.* 8, 513 (1940).
4. Caldow, G. L. and Thompson, H. W., *Spectrochim. Acta* 13, 212 (1958).
5. Lieber, E., Rao, C. N. R., and Ramachandran, J., *Spectrochim. Acta* 13, 296 (1958).
6. Ham, N. S. and Willis, J. B., *Spectrochim. Acta* 16, 279 (1960).
7. Dyson, G. M. and George, H. J., *J. Chem. Soc.* 125, 1702 (1924).
8. Stankovský, Š. and Kováč, Š., *Chem. Zvesti* 28, 230 (1974).
9. Ramsay, D. A., *J. Amer. Chem. Soc.* 74, 72 (1952).
10. Stankovský, Š. and Kováč, Š., *Chem. Zvesti* 28, 247 (1974).
11. Lieber, E., Rao, C. N. R., and Thomas, A., *Spectrochim. Acta* 19, 1135 (1963).
12. Meakins, G. D. and Moss, R. J., *J. Chem. Soc.* 1957, 993.
13. Foffani, A., Pecile, C., and Ghersetti, S., *Tetrahedron* 11, 285 (1960).

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