

# Infrared spectra of heterocumulenes. VI. Characteristic wavenumbers and intensities of the bands of isocyanates, isothiocyanates, and isoselenocyanates

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Received 2 April 1973

Infrared spectral data of three different groups of heterocumulenes are reported. A linear dependence of integrated absorption intensities of the  $\nu_{as}(X=Y=Z)$  bands on Hammett substituent constants with a positive slope has been found. On the basis of wavenumbers, half-band widths as well as integrated absorption intensities of the  $\nu_{as}(X=Y=Z)$  bands the structure of the cumulative system of  $X=Y=Z$  bonds is discussed.

It has been known that in the spectra of heterocumulenes very strong absorption bands assigned to the asymmetric stretching vibration of the  $X=Y=Z$  bonds are observed in the range of  $1900-2300\text{ cm}^{-1}$  [1-4]. Some heterocumulenes, such as isocyanates [1, 3, 5] and isothiocyanates [6-9] have been investigated in detail. The wavenumber of the  $\nu_{as}(N=C=O)$  band of isocyanates is relatively little influenced by the nature of the substituent as well as by the change of the state when compared with other heterocumulenes. *Caldow* and *Thompson* [5] have reported a range of  $2240-2285\text{ cm}^{-1}$  for isocyanates they examined. Only in case the NCO group is attached to the carbonyl group, a shift to lower wavenumbers of the  $\nu_{as}(N=C=O)$  band is observed at  $\sim 2220\text{ cm}^{-1}$ . Integrated absorption intensities of these bands are observed in the range of  $14-17 [10^{-4}\text{ l mol}^{-1}\text{ cm}^{-2}]$ . The wavenumbers of the  $\nu_{as}(NCS)$  bands of aromatic isothiocyanates can be observed in the  $2000-2120\text{ cm}^{-1}$  region [5-9] and they are significantly influenced by the nature of the substituents in such a way that they are shifted to lower wavenumbers with the increasing electron-withdrawing power of the substituents. A linear dependence of the  $\nu_{as}(NCS)$  on Hammett constants with a positive slope  $\rho$  has been found in a large series of substituted phenyl isothiocyanates. Integrated absorption intensities of the  $\nu_{as}(NCS)$  bands in the range of  $13-20 [10^{-4}\text{ l mol}^{-1}\text{ cm}^{-2}]$  for some aromatic isothiocyanates are reported in [5, 7].

Only little information has been available in literature on infrared spectral data of isoselenocyanates [10, 11]. Broad bands of complex shape are observed on the spectra of these compounds in the range of  $2020-2130\text{ cm}^{-1}$  having high integrated absorption intensities  $15-20 [10^{-4}\text{ l mol}^{-1}\text{ cm}^{-2}]$ . As different values of integrated absorption intensities of the  $\nu_{as}(X=Y=Z)$  bands are reported in literature, it is difficult to compare the apparent and intrinsic integrated absorption intensities. In this work we report true integrated absorption intensities of the  $\nu_{as}(X=Y=Z)$  bands of three groups of heterocumulenes: isocyanates, isothiocyanates, and isoselenocyanates. The structure of the  $X=Y=Z$  group in these compounds is discussed.

## Experimental

All heterocumulenes studied were prepared according to the following literature: isothiocyanates [13], isocyanates [14], and isoselenocyanates [10]. The compounds studied were recrystallized from a suitable solvent or redistilled under reduced pressure before use. Their physical constants agreed with those reported in literature. Infrared spectra were recorded with a UR-20 (Zeiss, Jena) instrument in the range of 1900—2300  $\text{cm}^{-1}$ . Recording conditions as well as integrated absorption intensities of the  $\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$  bands are the same as those described previously [12]. Integrated absorption intensities of the  $\nu_{\text{as}}(\text{NCS})$  bands were determined by an extrapolation method. The range of integration was 140  $\text{cm}^{-1}$  (with isocyanates and isoselenocyanates) and 150  $\text{cm}^{-1}$  (with isothiocyanates) on both sides from the maximum of absorption.  $\text{CCl}_4$  (spectroscopic grade) was used.

## Results and discussion

The highest wavenumbers of the  $\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$  bands are observed with isocyanates (Table 1; Fig. 1), which can be explained by the fact that the highest electron density is on the  $\text{N}=\text{C}$  bond in consequence of the electron-withdrawing ability of the oxygen

Table 1

Characteristic data of the  $\nu_{\text{as}}(\text{N}=\text{C}=\text{O})$  bands of some 4-substituted phenyl isocyanates

No.	X	$\tilde{\nu}_1$	$\epsilon$	$\tilde{\nu}_2$	$\epsilon$	$\tilde{\nu}_3$	$\epsilon$	$\Delta\nu_{1/2}$	$A \cdot 10^{-4}$
I	$\text{CH}_3\text{O}$	2277	885	2268	788	2233	159	40	12.0
II	$\text{CH}_3$	2279	1147	2242	241	—	—	40	12.9
III	H	2282	665	2263	1079	2208	102	47	14.7
IV	Cl	2298	346	2277	1302	2243	169	35	13.9
V	$\text{Br}^*$	—	—	2269	—	—	—	—	14.9
VI	$\text{NO}_2^*$	—	—	2269	—	—	—	—	17.1

\* Values from [5].

$\tilde{\nu}$  and  $\Delta\nu_{1/2}$  in  $\text{cm}^{-1}$ ;  $\epsilon$  in  $\text{l mol}^{-1} \text{cm}^{-1}$ ;  $A$  in  $\text{l mol}^{-1} \text{cm}^{-2}$ .

atom. Half-band widths as well as integrated absorption intensities of the  $\nu_{\text{as}}(\text{N}=\text{C}=\text{O})$  bands are the lowest when compared with the spectral data of other heterocumulenes. The true integrated absorption intensities  $A$  of the  $\nu_{\text{as}}(\text{N}=\text{C}=\text{O})$  bands of the isocyanates

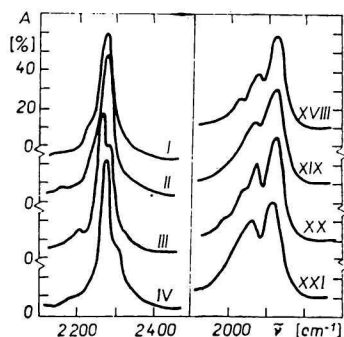
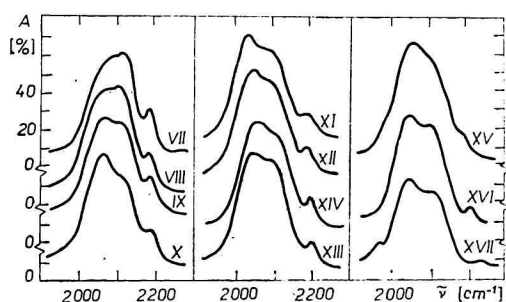


Fig. 1. Infrared band contours of the  $\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$  bands of some aromatic isocyanates and isoselenocyanates.

investigated are observed in the range of 12–17 [ $10^{-4}$  l mol $^{-1}$  cm $^{-2}$ ] and they are more influenced by the nature of the substituents than the wavenumbers of the bands (see Table 1). Furthermore, it can be seen that integrated absorption intensities increase with the increasing electron-withdrawing power of the substituent. With these compounds a linear dependence of  $\log A$  on Hammett  $\sigma_p$  and  $\sigma_p^+$  substituent constants has been found ( $\rho = 0.129$ ,  $r = 0.924$  and  $\rho^+ = 0.100$ ,  $r = 0.971$ , respectively). The strongest  $\nu_{as}(\text{N}=\text{C}=\text{S})$  bands are observed in the spectra of all phenyl isothiocyanates at the lowest wavenumbers (Fig. 2). Molar absorptivities ( $\epsilon$ ) of the first two bands are relatively small ( $\epsilon = 370 \rightarrow 560$  l mol $^{-1}$  cm $^{-1}$ ) and they are the lowest in comparison with those of other heterocumulenes studied (Table 2). However, the greatest half-band widths,

Fig. 2. Infrared band contours of the  $\nu_{as}(\text{N}=\text{C}=\text{S})$  bands of some aromatic isothiocyanates.



$\Delta\nu_{1/2}$ , are observed with isothiocyanates ( $\Delta\nu_{1/2} = 134 \rightarrow 149$  cm $^{-1}$ ) pointing to the high degree of vibrational couplings. The true integrated absorption intensities of the  $\nu_{as}(\text{N}=\text{C}=\text{S})$  bands of the isothiocyanates studied are observed in the range of 13  $\rightarrow$  19 [ $10^{-4}$  l mol $^{-1}$  cm $^{-2}$ ] and they increase (except for *m*-substituted derivatives) with the increasing electron-withdrawing power of the substituents. Just as in the case of isocyanates, the linear dependence of  $\log A$  on Hammett substituent constants ( $\sigma_p$  and  $\sigma_p^+$ ) has been observed with phenyl isothiocyanates ( $\rho = 0.147$ ,  $r = 0.874$ ,  $\rho^+ = 0.077$

Table 2

Characteristic data of the  $\nu_{as}(\text{N}=\text{C}=\text{S})$  bands of some substituted phenyl isothiocyanates.

No.	X	$\tilde{\nu}_1$	$\epsilon$	$\tilde{\nu}_2$	$\epsilon$	$\tilde{\nu}_3$	$\epsilon$	$\Delta\nu_{1/2}$	$A \cdot 10^{-4}$
VII	4-(CH $_3$ ) $_2$ N	2189	146	2125	445	2100	445	134	12.9
VIII	4-C $_2$ H $_5$ O	2187	122	2110	412	2073	424	140	12.9
IX	4-CH $_3$	2184	137	2115	423	2062	497	134	13.8
X	H	2184	113	2115	376	2060	544	134	15.5
XI	4-Cl	2192	82	2091	423	2042	547	137	16.4
XII	4-Br	2190	97	2095	451	2048	547	144	17.9
XIII	4-C $_2$ H $_5$ OOCC	2196	82	2093	486	2040	563	145	18.6
XIV	4-CH $_3$ COO	2194	96	2105	406	2053	500	140	14.9
XV	3-HO	2184	78	2150	226	2062	523	149	16.1
				2093	454				
XVI	3-Br	2198	62	2090	458	2040	542	142	17.9
XVII	3-HOOC	2222	24	2108	295	2043	371	149	13.7

$\tilde{\nu}$  and  $\Delta\nu_{1/2}$  in cm $^{-1}$ ;  $A$  in l mol $^{-1}$  cm $^{-2} \times 10^4$ .

Table 3

Characteristic data of the  $\nu_{\text{as}}(\text{N}=\text{C}=\text{Se})$  bands of some 4-substituted phenyl isoselenocyanates

No.	X	$\tilde{\nu}_3$	$\epsilon$	$\tilde{\nu}_2$	$\epsilon$	$\tilde{\nu}_1$	$\epsilon$	$\Delta\nu_{1/2}$	$A \cdot 10^{-4}$
XVIII	$(\text{CH}_3)_2\text{N}$	2130	663	2080	331	2032	162	90	15.2
XIX	$\text{C}_2\text{H}_5\text{O}$	2126	705	2072	383	2032	214	105	17.4
XX	$\text{CH}_3$	2121	807	2072	529	2032	299	105	19.3
XXI	Cl	2113	705	2065	518	2027	356	130	19.9

$\tilde{\nu}$  and  $\Delta\nu_{1/2}$  in  $\text{cm}^{-1}$ ;  $A$  in  $\text{l mol}^{-1} \text{cm}^{-2} \times 10^4$ .

and  $r = 0.857$ ). Infrared spectral data of isoselenocyanates are very similar to those of isothiocyanates (Table 3); however, the strongest  $\nu_{\text{as}}(\text{N}=\text{C}=\text{Se})$  bands are observed in all the cases at the highest wavenumbers (Fig. 1). The wavenumbers of the  $\nu_{\text{as}}(\text{N}=\text{C}=\text{Se})$  bands of the isoselenocyanates investigated are observed in the range of 2027–2130  $\text{cm}^{-1}$ . These bands are shifted, like those of isothiocyanates, to lower wavenumbers with the increasing electron-withdrawing power of the substituent. The bands at the lowest wavenumbers ( $\sim 2030 \text{ cm}^{-1}$ ) are independent of the nature of the substituent. These bands can be assigned to the overtones of some fundamentals. The other two intense bands at higher wavenumbers can be, as with isocyanates and isothiocyanates, considered as a Fermi resonance doublet with an average wavenumber  $\sim 2100 \text{ cm}^{-1}$ . Integrated absorption intensities of the  $\nu_{\text{as}}(\text{N}=\text{C}=\text{Se})$  bands are influenced by the substituents similarly as is the case with isothiocyanates. As with the above-mentioned heterocumulenes a linear relationship has likewise been observed between  $\log A$  and the  $\sigma_p$  substituent constants with a positive slope ( $\rho = +0.140$ ). Kristian and Suchár [11] reported the slope  $\rho = +0.12$  found from the  $\log A - \sigma$  plots of some aromatic isoselenocyanates. However, these authors made no corrections for the area outside the absorption band. From the comparison of the slopes of the  $\log A - \sigma$  plots of the three types of heterocumulenes (Table 4) it appears that the NCO, NCS, and NCSe groups are influenced by the nature of the substituent approximately in the same way. If we admit the validity of the statistically found relation [15] according to which the slope of the plots  $\log A - \sigma_p$  has a positive value in the cases when the group involved is electron-donating, then the structure of the characteristic groups of the heterocumu-

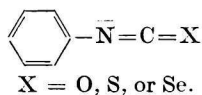
Table 4

Infrared spectral data and tangents ( $\rho$ ) from the plots of integrated absorption intensities of the  $\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$  bands against  $\sigma$  and  $\sigma^+$  constants of some heterocumulenes

Heterocumulenes	Group	$\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$	$A$	$\Delta\nu_{1/2}$	$\sigma_p$	$\rho$	$\sigma^+$	$n$
Isocyanates	$-\text{N}=\text{C}=\text{O}$	2208–2298	12.0–17.1	35 → 40	—	0.129	0.100	6
Isothiocyanates	$-\text{N}=\text{C}=\text{S}$	2040–2222	12.9–18.6	134 → 149	0.38	0.147	0.077	11
Isoselenocyanates	$-\text{N}=\text{C}=\text{Se}$	2027–2126	15.2–19.9	90 → 130	0.31	0.140	0.065	4

$n$  — number of compounds included in the correlation.

lenes investigated can be expressed by a formula possessing cumulative double bonds and the lone electron pair situated on the nitrogen atom (Scheme 1).



*Scheme 1*

In the case of the structure of the NCX group with the triple bond between the nitrogen and carbon atoms the wavenumber of the  $\text{N}\equiv\text{C}$  bond should be observed at higher wavenumbers, similarly as with thiocyanates, cyanides, and similar compounds.

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Translated by Š. Kováč