

# Infrared spectra of heterocumulenes. IV. The influence of substituents on the $\nu_{\text{as}}(\text{NNN})$ bands of some substituted phenyl azides

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The influence of substituents on wavenumbers, integrated absorption intensities, and half-band widths of the  $\nu_{\text{as}}(\text{NNN})$  bands of nine substituted phenyl azides has been discussed. A linear relationship between integrated absorption intensities ( $\log A$ ) and Hammett  $\sigma$  and  $\sigma^+$  substituent constants of electron-withdrawing substituents has been observed ( $\rho = 0.201$  and  $\rho^+ = 0.201$ , respectively). It has been found that the azide group is of dual electron nature.

It has been known that the wavenumbers of the bands corresponding to the asymmetrical stretching vibrations of the azide group,  $\nu_{\text{as}}(\text{NNN})$ , are observed in the range of  $2100\text{--}2170\text{ cm}^{-1}$  [1–3], depending on the nature of the attached group; e.g. aliphatic azides absorb near  $2100\text{ cm}^{-1}$ . However, a shift of the  $\nu_{\text{as}}(\text{NNN})$  band to higher wavenumbers ( $2130\text{--}2160\text{ cm}^{-1}$ ) is observed if the azide group is attached to an atom having the double bond. Sheinker *et al.* [3] studied the infrared spectra of a large number of variously substituted azides (from phenyl azides only phenyl azide and *m*-nitrophenyl azide were studied). They reported that integrated absorption intensities of the  $\nu_{\text{as}}(\text{NNN})$  bands are more sensitive to the nature of the substituents than the wavenumbers of the bands. These authors quoted for the integrated absorption intensities in the spectra of aliphatic and aromatic azides the values near  $4.5 \times 10^4$  and  $6.7 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-2}$ , respectively. They also have found that by attaching the azide group to the multiple bond integrated absorption intensities depend on the electron properties of the substituents. From their observations it appears that the azide group is electron-donating in nature. However, if the azide group is in the interaction with a strong electron-donating substituent, then the electron-withdrawing nature of this group is dominant.

In this paper characteristic spectral data of the  $\nu_{\text{as}}(\text{NNN})$  bands of nine substituted phenyl azides are studied.

## Experimental

All azides studied were prepared by the reaction of the appropriate diazonium salts with hydroxylamine according to [4]. With respect to a large instability, azides possessing electron-donating groups were not prepared. Liquid azides were redistilled under reduced pressure and solid azides crystallized from ethanol, both immediately before use. Their physical constants were in accord with those reported in literature [5].

Infrared spectra of the compounds studied were recorded with a UR-20 (Zeiss, Jena) instrument in  $\text{CCl}_4$ . Recording conditions as well as the calculation of integrated absorption intensities were described previously [6].

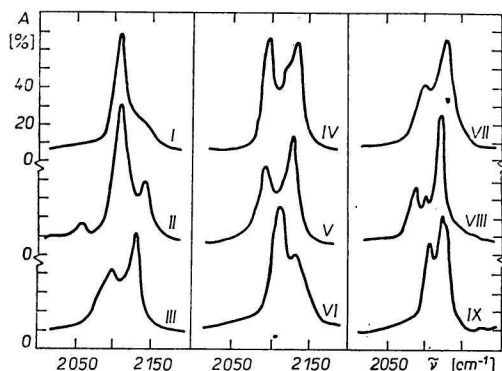


Fig. 1. Infrared band contours of substituted phenyl azides.

Table 1

$\nu_{\text{as}}(\text{NNN})$  Bands of substituted phenyl azides ( $\text{XC}_6\text{H}_4\text{N}_3$ )

No.	X	$\tilde{\nu}_1$	$\epsilon$	$\tilde{\nu}_2$	$\epsilon$	$\tilde{\nu}_3$	$\epsilon$	$\Delta\nu_{1/2}$	$A \cdot 10^{-4}$
I	4-CH <sub>3</sub> O	2125	182	2107	844	2070	48	20	7.3
II	4-CH <sub>3</sub>	2140	293	2107	1112	2055	82	24	7.0
III	H	—	—	2130	583	2095	303	48	6.6
IV	4-Cl	2133	442	2122	296	2097	463	55	5.3
V	4-Br	—	—	2128	582	2092	349	55	5.5
VI	4-HOOC	2132	403	2112	948	—	—	39	6.5
VII	4-C <sub>2</sub> H <sub>5</sub> OOC	—	—	2127	742	2098	322	45	7.1
VIII	4-NO <sub>2</sub>	2122	986	2104	219	2089	283	18	7.1
IX	3-NO <sub>2</sub>	2122	795	2108	534	—	—	35	6.3
		2127	726	—	—	—	—	—	—

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

### Results and discussion

From the i.r. spectra (Fig. 1) it can be seen that all phenyl azides studied except chloro and nitrophenyl azides display the  $\nu_{\text{as}}(\text{NNN})$  band split into a doublet. In the case of compounds IV, VIII, and IX this band is split into a triplet. The complex nature of the bands can be explained in terms of the Fermi resonance [2, 7–9]. The wavenumbers of the bands corresponding to the maximum of absorption are not characteristically influenced by the nature of the substituents (Table 1). The structure of the azide group can be expressed in the best way by a formula *a* in which the cumulative system of double bonds is stabilized by the electron-donating power of substituents, whereas in the case of electron-withdrawing substituents the interaction of a free electron pair located on the nitrogen atom with a  $\pi$ -electron system of the benzene ring *b* can be considered (Scheme 1).



Scheme 1

Molar absorptivities of the  $\nu_{\text{as}}(\text{NNN})$  bands belonging to the maximum of the absorption are observed approximately in the same range (Table 2) as those of the  $\nu_{\text{as}}(\text{XYZ})$  bands of diphenylketene imines [10] and diphenyldiazomethanes [11]. Half-band widths of the complex bands are in the range of 20–55  $\text{cm}^{-1}$  and they are in azides possessing electron-donating substituents approximately half those in azides having electron-withdrawing substituents (Table 1).

Table 2

 $\nu_{\text{as}}(\text{XYZ})$  Bands of some heterocumulenes

Heterocumulenes	$\nu_{\text{as}}(\text{X}=\text{Y}=\text{Z})$	$\epsilon_{\text{max}}$	$A \cdot 10^{-4}$	$\rho^+$	$n$
Diphenylketene imines [10]	1980–2003	605–893	5.5–25.7	+0.127	7
Diphenyldiazomethanes [11]	2031–2046	501–1015	1.7–4.9	+0.126	6
Phenyl azides	2055–2140	463–1112	6.6–7.1	+0.201 <sup>a</sup>	9
Carbodiimides [6]	2040–2187	930–2004	14.4–25.7	+0.247	7

$n$  — number of compounds in the correlation.

$\rho^+$  — calculated from the plot of  $\log A$  against  $\sigma^+$ .

<sup>a</sup> — only derivatives containing electron-withdrawing substituents were taken into the correlation.

Integrated absorption intensities of the bands are observed in the range of  $5.3 \times 10^4$ – $7.3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-2}$  and they are with phenyl and *m*-nitrophenyl azide in agreement with [3]. The range of integration was 160  $\text{cm}^{-1}$  (80  $\text{cm}^{-1}$  on both sides from the maximum of absorption).

In considering the variations of integrated absorption intensities ( $A$ ) of the  $\nu_{\text{as}}(\text{NNN})$  bands, it has been found that a roughly linear relation exists between  $\log A$  and the Hammett  $\sigma_p$  and  $\sigma_p^+$  constants ( $\rho = 0.201$ ,  $r = 0.805$  and  $\rho^+ = 0.201$ ,  $r = 0.914$ , respectively). Integrated absorption intensities of the  $\nu_{\text{as}}(\text{NNN})$  bands in the spectra of azides having electron-releasing groups (compounds *I* and *II*) were not taken into correlation as those are roughly the same as observed with azides possessing strong electron-withdrawing substituents. However, it can be assumed that the NNN group in azides examined is equally influenced by electron-releasing as well as electron-withdrawing substituents. If a statistically found relation [12] holds, that is, a positive slope  $\rho$  is found when the groups involved are electron-releasing by which integrated absorption intensities of the  $\nu_{\text{as}}(\text{XYZ})$  bands increase with the increasing electron-withdrawing power of the substituents and a negative slope is observed with electron-withdrawing groups involved by which integrated absorption intensities decrease with the increasing electron-withdrawing power of the substituents, a dual electron nature of the azide group of aromatic azides can be considered.

From integrated absorption intensities of the  $\nu_{\text{as}}(\text{NNN})$  bands (Table 1) it follows that with azides having electron-releasing substituents the azide group exhibits an electron-withdrawing ability and that having electron-withdrawing substituents does the reverse. These observations are in accord with conclusions described in [3].

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