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Abstract

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POSITION AND INTENSITY OF THE ABSORPTION BAND OF THE ANTISYMMETRIC STRETCHING VIBRATION OF THE N_3 GROUP IN THE IR SPECTRA OF ORGANIC AZIDES

(Presented by Academician M. M. Shemyakin on 29 VII 1964)

In the literature ([1–3]) it is still considered that the position of the band of the antisymmetric stretching vibration of the azido group, $\nu_{(as)}N_3$,* in the IR spectra of organic azides is localized in the range 2120–2160 cm^{-1}.

At the same time, consideration of the spectra of azides available to us, both in the present study and in an earlier study ([4]), showed that the absorption range of $\nu_{(as)}N_3$ is broader than that given in the cited works ([1–3]) and is approximately confined within 2100–2170 cm^{-1}. The position of $\nu_{(as)}N_3$ within this range is determined by the nature of the group directly adjacent to the azido group. In aliphatic azides, $\nu_{(as)}N_3$ is located in the range 2100–2110 cm^{-1}. Conjugation of the azido group with C=O, C=C, N=C, and SO_2 raises the frequency of the absorption band to 2130–2150 cm^{-1}; conjugation with P=O and P=S, or the presence of an electron acceptor at the α-C atom relative to the N_3 group, raises $\nu_{(as)}$ to 2163–2166 cm^{-1}. In ferrocenyl azide, $\nu_{(as)}$ occupies a position only slightly higher (2113 cm^{-1}) than in aliphatic azides (Table 1).

There are no data in the literature on the integral intensity of the $\nu_{(as)}N_3$ band. We measured these characteristics in the spectra of a number of organic azides of various classes. The calculation of integral intensity was carried out without taking into account wing corrections (over a broad integration range). When the band was split (a rather frequent occurrence for $\nu_{(as)}N_3$), the total intensity was taken.

Our measurements showed that the integral intensity of the $\nu_{(as)}N_3$ band is considerably more sensitive to the nature of the radical bonded to the azido

group than is the frequency. In aliphatic azides, the intensity of $\nu_{(as)}$ has a value of 4.4-4.5 $\cdot 10^4$ $m^{-1} \cdot l \cdot cm^{-2}$. Upon conjugation of the azido group with double bonds, the intensity $A_{(as)}N_3$ changes noticeably. This change may be either toward an increase or toward a decrease in intensity, depending on the electronegativity of the substituents, whereas the frequency upon conjugation with any double bonds, as noted earlier, only increases. In aromatic azides the intensity increases by $\sim 50\%$. Lengthening of the conjugation chain leads to a further increase in intensity. Introduction into the phenyl ring of an electron-acceptor substituent—the nitro group (compound 3)—lowers the intensity. The presence of an electron acceptor at the α-C atom, as well as conjugation with a carbonyl group, causes a decrease in intensity. In compounds in which the azido group is conjugated with a carbonyl, alongside a drop in $A_{(as)}N_3$ there is observed some increase in the intensity of the $\nu_{C=0}$ band (by 0.2 units in comparison with compounds in which, instead of the group

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* The designation of vibrations in the form $\nu_{(as)}N_3$ and $\nu_{(s)}N_3$ is strictly correct only for a group with symmetry $D_{\infty h}$; however, we retain these symbols for designating the characteristic vibrations of the N_3 group in organic azides, where this symmetry no longer exists.

Table 1*

Compound No.	R—	ν, cm^{-1}, in film or paste, *as*	ν, cm^{-1}, in film or paste, *s*	Solvent	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *as*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *s*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, C=O
1	HO—CH_2—CH_2—	2105	1300	CCl_4	4,47		
2	CH_2=CH—CH_2—	2107	1257	CCl_4			
3	$C_2H_5OCOCH_2$—	2108		CCl_4	4,35		2,64
4	$C_6H_5CH_2$—	2103	1260	CCl_4	4,54		

Compound No.	R—	ν, cm^{-1}, in film or paste, *as*	ν, cm^{-1}, in film or paste, *s*	Solvent	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *as*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *s*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, C=O
5	[[structural formula: aromatic ring bearing —CO— substituent]]	2104	1267	CCl_4			
6	[[structural formula: ferrocenyl substituent, Fe between two cyclopentadienyl rings]]	2113	1287	CCl_4	4,76	0,67	
7	C_6H_5—	2135[a]	1297	CCl_4	6,46		
8	$C_6H_5COCH_2$—	2140[a]	1260	CCl_4	6,88	2,80	2,32

Compound No.	R–	ν, cm^{-1}, in film or paste, *as*	ν, cm^{-1}, in film or paste, *s*	Solvent	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *as*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *s*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, C=O
9	[[structural formula: biphenyl system with NO substituent]]	2140[a]	1272	Dioxane	6,89		
10	[[structural formula: biphenyl system with NO_2 substituent]]	2143[a]	1297	Dioxane	6,96		
11	[[structural formula: biphenyl system with N-oxide substituent, $O \leftarrow N$]]	2132[a]	1297	Dioxane	$\frac{13,33}{2} = 6,67$		
12	*n*-NO_2–C_6H_4–	2140[a]	1290				

Compound No.	R–	ν, cm^{-1}, in film or paste, *as*	ν, cm^{-1}, in film or paste, *s*	Solvent	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *as*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *s*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, C=O
13	*m*-NO_2–C_6H_4–	2132[a]		CCl_4	6,23		
14	*o*-NO_2–C_6H_4–	2130[a]	1295				
15	C_6H_5–CH(OH)–CH(HCO)–CH_3	2144[a]					
16	CH_3O–CO–	2134[a]		CCl_4	3,08		3,01
17	$(CH_3)_3C$–O–CO–	2135[a]		CCl_4	3,86		3,37
18	C_6H_5CO–	2137[a]	1242	Dioxane	4,10		2,31
19	$CH_3C_6H_4CO$–	2138[a]	1255	Dioxane	6,41		2,79
20	HO_2C–$CH_2SHgC_6H_4CO$–	2140[a]	1247	Dioxane	5,16		

Compound No.	R–	ν, cm^{-1}, in film or paste, *as*	ν, cm^{-1}, in film or paste, *s*	Solvent	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *as*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *s*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, C=O
21	[[structural formula: ferrocenylcarbonyl substituent, Fe between cyclopentadienyl rings, –CO –]]	2154[a]	1266	CCl_4	3,8	1,8	3,05
22	C_6H_5 –CH –CH –CO – with bridging – CH_2–	2140[b]	1266				
23	C_6H_4 – [[imidazole-type ring: N, NH, C–]]	2150[a]					

Compound No.	R–	ν, cm^{-1}, in film or paste, *as*	ν, cm^{-1}, in film or paste, *s*	Solvent	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *as*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, *s*	Intensity $A \cdot 10^{-4}$, $m^{-1} \cdot l \cdot cm^{-2}$, C=O
24	C_6H_4 – [[diazole-type ring: N, N, C–]]	2136[a]					
25	[[fused aromatic heterocycle with CH_3, N, N –H, C–]]	2150[a]					
26	[[fused aromatic heterocycle with N, N, C–, CH_3]]	2140[a]					
27	CH_3SO_2 –	2143	1200	CCl_4	4,23		
28	CHF_2CF_2 –	2163[b]		CCl_4	2,35		
29	$(C_2H_5O)_2$ –PO –	2166[b]		CCl_4	5,37		
30	$(C_2H_5O)_2$ –PS–	2166[b]	1274	CCl_4	4,64		

* All investigated substances had constants corresponding to literature data; *a*

–splitting of $\nu_{as}N_3$ is observed; values of $\nu_{(as)}N_3$ are given for the most intense band; *b*–data for solution in CCl_4.

N_3 there is a CH_3 group). Thus, in these compounds the azido group manifests itself as a weak electron donor. When an additional strong electron donor is present in the compound (even with conjugation of the azide group with a carbonyl), it acts as an acceptor and the intensity of its band increases. Thus, in the presence of mercury in chloromercuribenzoic acid azide (compound 19), the intensity of the azido-group band increases markedly (to $6.4 \cdot 10^4$ $m^{-1} \cdot l \cdot cm^{-2}$, as compared with $4.1 \cdot 10^4$ $m^{-1} \cdot l \cdot cm^{-2}$ for benzoyl azide), while the intensity of the carbo-

Table 2*

No. comp.	Formula	$\nu_{as}N_3$	$\nu_s N_3$	ν funct. groups	ν_1	ν_2	ν_3	ν_4	ν_5	Possible combination frequencies
3	$C_2H_5OCH_2CH_2N_3$	2108	1294	1744 C–O 1200 C–O		1028				$\nu_{C-O}+\nu_2=2228$ $\nu(s)+\nu_{C=O}=2492$ $\nu(s)+\nu_2=2322$
18	$C_6H_5CH_2CH_2N_3$	2137	1274	1699	1187	995			700	$\nu_1+\nu_2=2182$
16	$CH_3OC_6H_4CH_2N_3$	2134	1245	1632	1321	1032			760	$\nu_1+\nu_2=2170$ $\nu(s)+\nu_3=2170$ $\nu_1+\nu_5=1930$ $\nu_2+\nu_3=1930$

No. comp.	Formula	$\nu_{as}N_3$	$\nu_s N_3$	ν funct. groups	ν_1	ν_2	ν_3	ν_4	ν_5	Possible combination frequencies
12	*m*-$NO_2C_6H_4N_3$	2113	1286	1530	1106	1026	1008	825	731	$\nu_1+\nu_4=2088\nu(s)+\nu_4=2121\nu(NO_2)+\nu_4=21702\nu_1=2288\nu(s)+\nu_4=2111\nu_2+\nu_3=21142\nu_2=22122\nu_3\begin{cases}=2016\\=2052\end{cases}$
30	$(C_2H_5O)_2P(=S)-N_3$	2132	1274		1025	973		828		$\nu(s)+\nu_4=2102\nu(s)+\nu_3=22502\nu_3=2050$
27	$CH_3-SO_2-N_3$	2143	1200	1356	1166		969	780	732	$\nu(s)+\nu_3=2169\nu_{SO_2}+\nu_3=2135\nu_{SO_2}+\nu_4=2130$

* The position of the most intense band is given first; the remaining bands are weaker or are shoulders.

nyl increases by 0.5 unit. In another derivative of mercuribenzoic acid (compound 20), where the donor properties of mercury are lowered by the presence of an HO_2C-CH_2-S group, the intensity of the azide-group band decreases to $5.2 \cdot 10^4$ $m^{-1} \cdot l \cdot cm^{-2}$, but it is still higher than in benzoyl azide. From the

intensities in compounds 29 and 30, where the N_3 group is attached to phosphorus, it is seen that the P=O and P=S bonds are electron donors with respect to the azide group. The value of the intensity of the band under consideration in ferrocene azide increases only slightly (analogously to the increase in frequency) in comparison with aliphatic azides, although a greater rise in intensity might have been expected, since the ferrocene nucleus is usually regarded as a considerably stronger donor than the benzene ring. Apparently this is due to the closeness of ferrocene and the N_3 group in electron-donor ability.

Thus, from the intensity data it follows that the azide group is a weak electron-donor group which, however, is capable of exhibiting noticeable acceptor properties when attached to a sufficiently strong donor.

In considering the IR spectra of azides, splitting of the $\nu_{(as)}N_3$ band is often observed (see Table 2) and ([4], [5]). An attempt was once made to explain this splitting in the case of methyl carbonic acid ester by rotational isomerism ([4]). Lieber in 1963 came to the conclusion ([3]) that

splitting of the $\nu_{(as)}N_3$ band can be explained by Fermi resonance of $\nu_{(as)}N_3$ with combination tones involving symmetric and C–N stretching vibrations and other lower frequencies. Indeed, in all the cases considered by him, when splitting was present the spectra contained intense bands capable of forming a combination tone with a frequency of ~ 2100 cm^{-1}; conversely, in the absence of such bands in the spectrum he did not observe splitting of the $\nu_{(as)}N_3$ band ($C_6H_5CH_2CON_3$, $(CH_3)_2NCH_2N_3$). A similar explanation of the splitting of $\nu_{(as)}N_3$ in the case of methyl azide was given in work ([6]). From this point of view we examined the spectra of azides obtained by us, some of which are presented in Table 2. Consideration of the data in this table shows that in a number of cases the explanation given by Lieber is confirmed. Thus, in compound 3 no splitting is observed, and its spectrum lacks bands that could give combination tones with a frequency of about 2100 cm^{-1}. At the same time, in compounds 18, 16, and 12 splitting is observed (especially strong in 16), and the spectra contain possibilities for the formation of combination tones (see Table 2). However, analysis of the data in Table 2 shows that the spectra of compounds 5, 30, and 27 contain absorption bands that could form a combination tone and produce Fermi interaction, whereas the antisymmetric stretching vibration of the azide group in these cases appears as an individual symmetric band. This is not in agreement with Lieber' s point of view. Probably the presence in the spectrum of bands which, in sum, give combination tones corresponding in frequency, or which have corresponding overtones, is not a sufficient condition for splitting of $\nu_{(as)}N_3$. Evidently, these frequencies must correspond to vibrations capable of interacting with the vibrations of the azide group. Thus, in the spectrum of ferrocenyl azide there are bands that could form a tone with frequencies 2114 and 2111 cm^{-1}, close to $\nu_{(as)}N_3$. However, these bands are associated with vibrations of the unsubstituted cyclopentadienyl ring, and because of this their interaction with the vibration of the azide group cannot be transmitted through the Fe atom, and no splitting of the band is observed. In other cases, the barrier to interaction of

vibrations apparently is phosphorus (compounds 29 and 30) or sulfur (compound 27). In these compounds the $\nu_{(as)}N_3$ band is not split, although possibilities exist for the formation of combination tones. Thus, a condition for splitting of azide bands is not only the presence of vibrations capable of giving the corresponding combination frequencies in the spectrum, but also the absence of obstacles to interaction between $\nu_{(as)}N_3$ and these combination frequencies; such obstacles may be decoupling of vibrations because of their remoteness from one another in the molecule, separation of groups by a heavy atom, and also differences in the symmetry of these vibrations.

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Note: Figure translations are in progress. See original paper for figures.