

THE STRETCHING FREQUENCY OF THE $-N=N-$ GROUP*

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Our search for the stretching frequency of the azo-groups, presented in five papers to this *Journal* (Le Fèvre, O'Dwyer, and Werner 1953; Le Fèvre, Sousa, and Werner 1956; Le Fèvre *et al.* 1957; Le Fèvre and Werner 1957; and Le Fèvre *et al.* 1958) and covering about 90 $N=N$ containing molecules, led to the conclusion that $\nu_{N:N}$ lies between 1400 and 1450 cm^{-1} in the simpler azoaryls. This has recently been confirmed by Kübler, Lüttke, and Weckherlin (1960) by comparing the spectra of five pairs of compounds related as $R-^{14}N=^{14}N-R$ and $R-^{14}N=^{15}N-R$. The $-N:N-$ frequencies thus identified agree satisfactorily with those noted by us in the following table:

Molecule	Kübler, Lüttke, and Weckherlin (1960) (KBr disks) (cm^{-1})	Sydney Group (Nujol mulls) (cm^{-1})
<i>cis</i> -Azobenzene	1511	1508
<i>p</i> -Amino- <i>trans</i> -azobenzene	1418	1412
<i>p</i> -Dimethylaminoazobenzene ..	1410	1412 (for <i>p</i> - <i>N</i> -MeEt-azo- benzene)
<i>p</i> -Hydroxyazobenzene	1416	1419
Diazoaminobenzene	1416	{ 1400 1432
Ag derivative of diazoaminobenzene	1362	1358

Recognizing that $\nu_{N:N}$ should decrease from *cis*-azobenzene to the more conjugated *trans*-isomer, $\nu_{N:N}$ in the latter can be accepted as 1442 cm^{-1} , indicated by the Raman displacements listed by Stammreich (1950).

The $-N=N-$ Frequency in Aliphatic Azo-Compounds

There remains the question: what is $\nu_{N=N}$ in the absence of conjugation? It would probably be higher than 1511 cm^{-1} and might in fact correspond to the absorption at 1576 cm^{-1} , noted by West and Killingsworth (1938) in the Raman, but not the infrared, spectrum of azomethane, and which was assigned by Herzberg (1945) to $\nu_{N:N}$. On this basis the transparency of azomethane in the infrared region between 1500 and 1600 cm^{-1} is due to the centro-symmetry of the molecule.

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Accordingly, the unsymmetrical methyl isopropyl-di-imide, Me.N:N.CHMe_2 , has been investigated; as a liquid film it absorbs at 1574 cm^{-1} (Table 1, 3rd col.). Azoisopropane, $\text{Me}_2\text{CH.N:N.CHMe}_2$, which displays a very weak infrared absorption at 1572 cm^{-1} , gives a relatively strong Raman displacement, recorded by our equipment at 1565 cm^{-1} (Table 1, cols. 4 and 5).

TABLE 1
INFRARED BANDS AND RAMAN DISPLACEMENTS (AS CM^{-1})

Me.N=N.Me		Me.N=N.Pr^β	$\text{Pr}^\beta.\text{N=N.Pr}^\beta$	
Infrared*	Raman*	Infrared	Infrared	Raman
	548(w) 593(s)			283(3) 520(3)
700 730			811(m)	887(4)
	922(m)	{ 924(w) 955(w) 981(m)	{ 925(m) 938(m)	918(3) 954(2)
1013(s) 1110(s)	1023(w)	1052(w)	1094(m)	
		{ 1126(s) 1164(s)	{ 1126(s) 1159(s)	1107(2)
	1182(m)	1186(w)	1218(w)	
	1376(s)	1311(s)	1319(s)	1326(5)
1430(vs)		{ 1366(s) 1381(s) 1430(s)	{ 1368(s) 1380(s)	
	1442(vs)	{ 1442(s) 1467(s)	1447(s) 1467(s)	1456(10)
	1576(m)	1574(w) 1722(vw)	1572(vw) 1724(w)	1565(6)
1922(w) 2189(m) 2391(m) 2596(m)				
	2733(w) 2854(w) 2914(vs) 2985(s)	2896(vs) 2960(vs)	2880(vs) 2943(vs)	

* From West and Killingsworth (1938).

Discussion

Unpublished measurements show these aliphatic azo-derivatives to be non-polar, i.e. to contain *trans*-azo-groups. Out of an infinitude of configurations of the isopropyl radicals in $\text{Me}_2\text{CH.N:N.CHMe}_2$, only one will have a centre, and only two a plane, of symmetry; the very weak infrared absorption of this compound is therefore understandable. The four features, at 1576, 1574, 1572, and 1565 cm^{-1} , thus show $\nu_{\text{N:N}}$ to lie between 1565 and 1576 cm^{-1} .

Le Fèvre, O'Dwyer, and Werner (1953) attempted to forecast $\nu_{\text{N:N}}$ by certain empirical equations then in the literature. Since then, another has emerged in effect, since the longitudinal polarizability of a bond appears to be connected both with its stretching frequency (Le Fèvre 1959) and its length (Le Fèvre 1958). Using $r_{\text{N-N}}=1.45 \text{ \AA}$ and $r_{\text{N:N}}=1.24 \text{ \AA}$ as the inter-centre separations of N—N and N=N respectively (from MeNH—NHMe and Me.N:N.Me, *M* 140 and *M* 137 in Chem. Soc. Spec. Publ. No. 11, 1958), the longitudinal polarizability of N=N is 0.213×10^{-23} and $\nu_{\text{N:N}}$ follows as 1629 cm^{-1} . The relationships are sensitive to changes in r , as the following comparisons show:

$r_{\text{N-N}}$	1.45	1.44	1.45	1.44
$r_{\text{N=N}}$	1.24	1.24	1.23	1.25
$10^{23}b_L^{\text{N=N}}$	0.213	0.204	0.219	0.198
$\nu \text{ (cm}^{-1} \text{ calc.)}$	1629	1600	1678	1554

We note, however, that the two lengths are quoted in the source cited as 1.45 ± 0.03 and 1.24 ± 0.05 ; the lower $\nu_{\text{N:N}}$ in azobenzene can easily be predicted from r 's well within these limits.

Materials

These were prepared by oxidation of the corresponding hydrazines by methods described by Ramsperger (1927, 1929) and Lochte, Noyes, and Bailey (1921, 1922).

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