Infra-Red Spectra of Nitric Esters

Part 2.—Rotational Isomerism of Some Esters

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Nitric esters of general formula X—CH₂CH₂—ONO₂, where X is a large substituent (such as Cl, Br, I, CN, NO₂, ONO₂) show splitting of both asymmetric and symmetric vibrations of the O-nitric group. The same phenomenon was observed when the structure of the nitric ester was

X-CH₂-CH-CH₂ | | ONO₂ ONO₂

where X was Cl, ONO_2 . It is suggested that this is due to the rotational isomerism around the C—C bonds in the compounds.

The spectra of crystalline polynitrates of such alcohols as erythritol, mannitol, sorbitol and dulcitol display several peaks in the range of both asymmetric and symmetric vibrations. This is also attributed to the rotational isomerism combined with crystal lattice effects. A supercooled melt of pentaerythritol tetranitrate gives sharp single NO_2 bands supporting the idea of free rotation around its C-O bonds as inferred from the dipole moment study.

Both the NO₂ stretching vibrations (asymmetric and symmetric) of some esters give bands which are split into two components.¹ This is marked in the esters which contain a structural unit (A),



where X is a relatively large substituent, such as ONO_2 , NO_2 , I, Br, Cl, CN, C_6H_5 . Some other esters, such as allyl nitrate and cyclohexyl nitrate give similar splitting of $v_{as}(NO_2)$ and $v_8(NO_2)$.

On the contrary, no splitting of the NO_2 bands was noticed in the spectra of the compounds with a structural unit (B):

$$\begin{array}{c} X - C - ONO_2 \\ | \\ B \end{array} \qquad (X = ONO_2, CN)$$

This led us to the view that the phenomenon of splitting of both the frequencies is produced by rotational isomerism of the compounds (A) due to rotation around the C—C bond, a process which is impossible when the structure is of the type B.

Splitting of the NO₂ stretching vibration bands in some esters was noticed first by Rossmy.² He found both the NO₂ bands—asymmetric and symmetric—were split in the spectrum of ethylene glycol dinitrate. The values for $v_{ab}(NO_2)$ were 1656, 1637 cm⁻¹ and 1290, 1269 cm⁻¹, respectively. According to Rossmy this

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may be due to rotational isomerism. Also Brown ³ noticed splitting of $v_{\rm s}(\rm NO_2)$ bands, but he described it only for 1-nitro-2-methyl-2-propyl nitrate.

In the present paper we report the examination of compounds containing the structural units A and B above. Some of them have already been described.¹ Their spectra are now analyzed and compared with those of a number of other compounds.

EXPERIMENTAL

Preparation and spectra of most of the compounds discussed here were described previously,¹ viz., cyclohexyl nitrate (X), allyl nitrate (XI), benzyl nitrate (XII), 2-phenylethyl nitrate (XIII), 2-hydroxyethyl nitrate (XIV), 2-chloroethyl nitrate (XV), 2-bromoethyl nitrate (XVI), 2-iodoethyl nitrate (XVII), 2-cyanoethyl nitrate (XVIII), acetone cyanohydrin nitrate (IX), 2-nitroethyl nitrate (XX), 2 nitro-2-methylpropyl nitrate (XXI), methanediol dinitrate (XXIV), ethylene glycol dinitrate (XXV), 1,2-propanediol dinitrate (XXVI), 1,3-propanediol dinitrate (XXVII).

The other nitrates were prepared as previously ¹ by direct esterification (method A) and by homogeneous reaction of corresponding bromides with AgNO₃ in acetonitrile (method B). Crystalline polyalcohols were esterified (method A') by dissolving them in HNO₃ (d = 1.4) and precipitating the nitrates with H₂SO₄ (d = 1.8); the nitrates were filtered, washed, dissolved in acetone, precipitated with water and repeatedly crystallized from ethanol. Their purity was tested by the microscopic method of equilibrium melting-point range (20 % and 90 % melt).⁴ With mannitol hexanitrate, two readily interconvertible crystalline forms were obtained (designated A and B) differing in their spectra and X-ray powder diagrams but not in their melting ranges. Similar two forms of dulcitol hexanitrate were found.

TABLE 1

compound	720 D	melting range, °C	method of preparation
3-chloro-1,2-propanediol dinitrate	1.4745		A 1
glycerol trinitrate	1·4732 1·4732 18		Α
glycerol 1.2-dinitrate	1.4682		A. ² B
glycerol 1.3-dinitrate	1.4683		A. ² B
2.3-dihydroxypropyl nitrate		58-2-59-1	
2-nitro-2-methyl-1.3-propanediol			
dinitrate		37.6-38.6	A'
meso-ervthritol tetranitrate		61.0-61.3	A'
pentaerythritol tetranitrate		140.9-141.4	A' 4
D-sorbitol hexanitrate		54.0-54.8	Â'
D-mannitol hexanitrate		112.0-113.0	Â'
dulcitol hexanitrate		94.1-95.2	Â'
myoinositol hexanitrate		132-0-132-5	Â'
	compound 3-chloro-1,2-propanediol dinitrate glycerol trinitrate glycerol 1,2-dinitrate glycerol 1,3-dinitrate 2,3-dihydroxypropyl nitrate 2-nitro-2-methyl-1,3-propanediol dinitrate meso-erythritol tetranitrate pentaerythritol tetranitrate D-mannitol hexanitrate dulcitol hexanitrate myoinositol hexanitrate	compoundn203-chloro-1,2-propanediol dinitrate1-4745glycerol trinitrate1-4732glycerol 1,2-dinitrate1-4682glycerol 1,3-dinitrate1-4682glycerol 1,3-dinitrate1-46832,3-dihydroxypropyl nitrate1-46832-nitro-2-methyl-1,3-propanediol1-4683dinitratemeso-erythritol tetranitratepentaerythritol tetranitrate-sorbitol hexanitrateD-mannitol hexanitrate-mannitol hexanitratemyoinositol hexanitrate-mannitol hexanitrate	compoundnomelting range, °C3-chloro-1,2-propanediol dinitrate1-4745glycerol trinitrate1-4732glycerol 1,2-dinitrate1-4732glycerol 1,3-dinitrate1-4682glycerol 1,3-dinitrate1-46832,3-dihydroxypropyl nitrate58-2-59-12-nitro-2-methyl-1,3-propanediol37-6-38-6dinitrate61-0-61-3pentaerythritol tetranitrate54-0-54-8D-mannitol hexanitrate112-0-113-0dulcitol hexanitrate94-1-95-2myoinositol hexanitrate132-0-132-5

¹ by the action of PCl₅ on glycerol 1,2-dinitrate in chloroform.

² Both the isomeric glycerol dinitrates were obtained by direct esterification with HNO₃ (d 1.5) and separated by crystallization of hydrate of glycerol 1,3-dinitrate ⁵, ¹⁸ (m.p. 26°). ³ By hydrolysis of glycidol nitrate.

⁴ From pure pentaerythritol (free from dipentaerythritol) by esterification with HNO₃ (d = 1.5) and crystallization from acetone.⁶

The infra-red absorption spectra (1750-650 cm⁻¹ range) were measured with a Hilger 800 double-beam spectrometer with NaCl prism.¹ Crystalline nitrates were examined as Nujol mulls. In the spectral range of 1500-1350 cm⁻¹ (Nujol absorption) mulls in CCl₃Br were used. A method of studying the infra-red spectra of supercooled liquid films of unstable crystalline nitric esters was worked out. This was based on the microscopic techniques of melting-point determination for easily decomposed substances.⁴ A well-ground sample of about 10 mg was placed between thin (2 mm) NaCl plates on a preheated Kofler stage so that the melting should occur in 20-30 sec and the temperature would not

	-ONO-	vibrations		(² ON) ⁵⁸ 4		I		120N)#4			Û Î		(N-0)*		%₩(NO2) &(NO ₂)
IXXXX	71	CHIONO	CH ₂ ONO ₂ melt 120°	1648 (vs)		1393 (m)	11	1276 (vs)	11	1036 (m)	1002 (s)	940 (w)	861 (vs)	754 (s)	685 685
	x	03N0-CH1	02N0-CH2 CTYR.	1659} 1647} (vs)	1474 (EI)	1395 (EI)		1287(vs) 1287(vs) 1272(vs)	11	1037 (m)	1002 (s)	938 (w) 936 (eh)	871 (vs) 856 (vs,c)	756 (m)	748 (w)
	2	202 NO2 NO2	melt 20°	1650 (va.c)	1459 (₩) 1430 (₩)	1379 (m)		1290} (vs) 1275 }	1230 (vw)	1090 (vw) 1037 (w)	1008 (m)	983 (₩) 	832 (vie)	747 (w)	(w) 695 (w)
_	XX		cryst.	1671 1634} (vs.c)	1459 (w)	1380 (m)	1342 (w)	1300(s) 1282(vs) 1263(s)	1231 (vw) 	1061 (w) 1035 (m)	985 (I)	920 (m)	881 (vs) 	757 (w)	743 (m) 699 (w)
ARD PREQUENCIES IN CM ⁻¹ XXXIV	XIV	H ₂ ONO ₂	H ₂ ONO ₂ melt 20°	1658 (vs)	1563 (s) 1462 (s)	1405 (m)	1350 (II)	1283 (vs)			1001(m)	929 (vw)	850 (sc) 810 (sc)	749 (m)	719 (vw) 688 (w)
	X	N N N N N N N N N N N N N N N N N N N	CH3 cCH3	1658 1636} (vs) 1636	1462 (II) (I)	1408 1385 1385 1385 1385	1331 1331	$\frac{1300}{1284}$ (vs)	1220 (vw) 1189 (w)	1137 (w) 1035 (s)	1001(m)	968 (W) 935 (W)	875 865 865 840 (s)	753 (s)	719 (w) 707 (w) 685 (w)
Table 2.—Inpra- XXXIII	CXIII	CHJONO2 CHJONO2 CH-OH CH2OH CH2OH CH2OH 1621 (vs) 1638 (vs) 1621 (vs) 1638 (vs) 1456 (w)	DH melt 20°	1638 (vs)		1432 (w) 1382 (vw) 1375 (vw)	11	1282 (vs)	11	1118 (w)	1000(mc)	11	859 (sc)	755 (w)	
	Ŕ		1421 (sh) 1390 (m)	1356 (w) 1316 (vw)	1280 (vs)	1247 (w) 1218 (vw)	1134 (m) 1097 (w)	1026(m)	(m)	883 (sc) 871 (s)	760 (w)	748 (m) 691 (vw)			
	ТХХХ	CHJONO2	CH20NO2	1640 (vs)	 1458 (sh)	1436 (w) 1390 (sh) 1371 (vw)		1283 (vs)	11	1113 (w) 1073 (w)	1001 (m)	11	857 (sc)	755 (m)	
	IXXX	CH20NO2	ĊH₂OH	1657 1640} (vs)		1430 (w) 1391 (vw) 1378 (vw)	1353 (vw)	1287 1275} (vs)	11	1115 (w) 1085 (sh)	1003(E))		850 (vsc)	752 (m)	700 (w)
	XXX	CH20N02 CH-ON02	ĊH2ONO2	1675 1654 1645} (vs)	1457 (w)	1431 (w) 1382 (vw) —	1358 (vw) 	1293 1276} (vs)	11	1068 (w)		() 	840 (s,c)	753 (m)	
	XIXX	CH ₂ CI CH-ONO ₂	CH20N02	1670} 1648} (vs)	1445 (va)	1434 (w) 1380 (vw)	1353 (vw) 	1290} (vs.c) 1274 }	1200 (vw)	1111 (vw) 1058 (w) 1028 (m)	1002 E)	() () () () () () () () () () () () () (878 (sh) 838 (s,c)	750 (w)	(m) 069

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				• •		
-ONO2 vibrations	(⁴ ON) ⁵⁸ 4		(70N) %	*(C0)	(N-O)	1,0V) W Y
ovo	melt 100° 1 1676 (vs,c)	1380	1285 (vs,c) 1195 (v w)	1146 (vw) 1126 (vw) 1050(vw) 1008(s) 1008(s) 928 (w)	850 (sh) 833 (vs) 816 (vs)	730 (m) 727 (m) 716 (w)
	ONO ₂ cryst. 1676 (vs.c)	1380 (w,c)	1285 (va,c) 1195 (vw)	1146 (vw) 1126 (vw) 1080 (w) 1050(vw) 1050(s) 970 (vw) 928 (w)	853 (sh) 830 (vs) 810 (s)	730 (w) 727 (w) 716 (w)
XXXIX CH ₂ ONO ₂ O ₂ NO O ₂ NO CH ₂ ONO ₂ CH ₂ ONO ₂	melt 60° 1660 (vs,c)		1284 } (vs) 1268 }	1008 008 00 (w)	818 (s,c)	737 (w)
	cryst. B 1682(vs)} 1662(vs)}	1460 (w) 1460 (w) 1380 (vw) 1364 (vw) 1338 (vw)	1291(s) 1269(vs)} 		889 864 (s) 806 (s) 80	730 (w) 716 (w) 681 (w)
	cryst. A 1681(va) 1654(va)		1294(s) 1273(m) 1265(s) 1245 (w)	1100 (vw) 	853 (s) 830 (s) 800 (s)	750 (w) 743 (w) 729 (vw)
	meit 80° 1660 (vs,c		1284} (vs) 1269} —		819 (s,c)	747 (w)
XXXVIII CH10N02 02N0 03N0 0N02 CH20N02	cryst. B 1687(ws) 1658(vs) 1637(s)	1467 (w) 1381 (m) 1364 (ww) 1364 (ww)	1292(vs) 1275(vs)} 1227 (vw)	1057 (vw) 1034(m) 1004(m) 964 (w) 932 (w)	873 (s) 817 (s) 812 (s)	752 (w) 737 (w) 687 (vw)
	cryst. A 1683(sh) 1666(vs) 1635(vs)	1472 (w) 1472 (w) 1381 (m) 1361 (vw) 1303 (vw)	1292(vs) 1275(s) 1231 (vw)		8 77 (s) 835 (s) 814 (m) 797 (w)	733 (w) 733 (w)
0N02 20102 20102 20102	melt 20° 1664 (vs,c)	1462 (w) 1462 (w) 1438 (w) 1377 (vw) 1351 (vw)	1287 1272} (vs)		826 (s,c)	75 (*)
	cryst. 1678(vs) 1650(vs)}	1460 (m) 1437 (w) 1378 (w) 1325 (vw)	$\begin{array}{c} 1305\\ 1287\\ 1275\\ 1276\\ 1226\\ 1229\\ (vw) \end{array}$	(w) 1084 (w) 1064 (w) 1051(m) 976 (w) 925 (w) 925 (w)	891 851 840 (3)	750 (w) 739 (w) 715 (w)

exceed that of the melting point by more than 1° . The sample was immediately cooled over 30-40° and thermostatted in the spectrometer. The infra-red frequencies are presented in table 2.

DISCUSSION

$v_{ab}(NO_2)$ and $v_b(NO_2)$ splitting

The following facts should be noted: (i) Splitting was regularly observed in the spectra of the $X-CH_2-CH_2-ONO_2$ type of molecules with large X

Table 2-contd.

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INFRA-RED SPECTRA OF NITRIC ESTERS

substituents: -Cl(XV), -Br(XVI), -I(XVII), -CN(XVIII), $-NO_2(XX)$, $-ONO_2(XXV)$. (ii) No splitting was detected when X was small (-OH, XIV), or the structure was X-C-ONO₂ where X = $-ONO_2(XXIV)$, -CN(XIX). (iii) Both the $v_{as}(NO_2)$ and $v_s(NO_2)$ frequencies were split. Thus it is unlikely that the splitting should result from vibrational coupling of fortuitous superposition of absorption bands. We suggest that the presence of the $v_s(NO_2)$ and $v_s(NO_2)$ doublets is associated with rotational isomerism and that differences of steric effects on ONO_2 groups in individual rotational isomers are responsible for the splitting. The effect of steric hindrance of the nitrate group on its $v_s(NO_2)$ frequency had already been reported.¹

ROTATIONAL ISOMERISM OF NITRIC ESTERS

While rotation around the C—O bond in the —C—ONO₂ system is considered to be free,^{7, 8, 9} nitric esters of the general formula X—CH₂—CH₂—ONO₂ should exist as trans and gauche rotational isomers due to hindered rotation around the



C—C bond, a well-known phenomenon in 1,2-disubstituted ethanes.^{10, 11} This has been supported by a dipole-moment study of nitric esters.¹² Further evidence has been found by us from the γ_r (CH₂) frequencies of ethylene glycol dinitrate (XXV) as compared with those of trans and gauche isomers of carboxylic esters of ethylene glycol.¹³

$$\gamma_r(CH_2)$$
 frequencies $\begin{pmatrix} H & H \\ C & C \end{pmatrix}$

Ac-O-CH₂--CH₂--O-Ac ¹³ trans. 910; 860 cm⁻¹: gauche: doublet at 890 cm⁻¹: O₂NO---CH₂---CH₂---ONO₂ 925; 860 cm⁻¹ doublet at 897 cm⁻¹.

SPECTRAL ASSIGNMENTS TO TRANS AND GAUCHE ISOMERS OF NITRIC ESTERS

There is a significant difference between trans and gauche isomers of X—CH₂— CH₂—ONO₂ in the spatial environment of the ONO₂ group if X is large. The steric effect of close packing X and ONO₂ in gauche isomers depends on the size of the X and this effect should appear in the spectra if our suggestions on the cause of the $v_{as}(NO_2)$ and $v_s(NO_2)$ splitting are valid. Support for this has been found in the $v_{as}(NO_2)$ doublets when X = Cl, Br, I. In this series one component of the doublet does not change its frequency (1640 cm⁻¹) while the frequency of the other rises with the increasing radius of X, so the former is ascribed to the trans and the latter to the gauche isomers.

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X-CH₂-CH₂-ONO₂

по.	v	covalent 14	* as(NO₂) cm ⁻¹		
	X	radius, Å	gauche	trans	
XV	Cl—	0.99	1652	1640	
XVI	Br	1.14	1656	1641	
XVII	J	1.33	1662	1640	

Since our previous study ¹ of the spectra of tert-butyl (VIII) and acetone cyanohydrin (XIX) nitrates led to the conclusion that steric effects on the ONO₂ group raise its $v_8(NO_2)$ frequency, then higher values of this frequency should be expected for gauche isomers.

Both these suggestions were examined from the spectra of 2-nitroethyl nitrate (XX) and 2-nitro-2-methylpropyl nitrate (XXI). The ONO₂ group of the former is sterically hindered only in the gauche isomers, while that of the latter is hindered in all its rotational isomers :



The single $v_{as}(NO_2)$ and $v_s(NO_2)$ bands in the spectrum of XXI have frequencies close to the higher frequencies of the $v_{as}(NO_2)$ and $v_s(NO_2)$ doublets, respectively, in the spectrum of XX:



The following conclusions may be drawn from these observations :

(i) steric effects raise the $v_{as}(NO_2)$ as well as the $v_s(NO_2)$ frequency of the ONO₂ group; (ii) the band splitting in X—CH₂—CH₂—ONO₂ systems is due to rotational isomerism; (iii) the gauche isomers have higher $v_{as}(NO_2)$ and $v_s(NO_2)$ frequencies than the trans isomers.

OTHER SYSTEMS

The spectra of some other nitric esters. which do not belong to the X—CH₂— CH₂—ONO₂ type, can be explained in terms of steric effects and rotational isomerism. Allyl nitrate (XI), which should exist as two rotational isomers with different steric effects on the ONO₂ group (similar systems have already been investigated ¹⁵):



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displays split $v_{ab}(NO_2)$ and $v_b(NO_2)$ absorption bands. With benzyl nitrate (XII) only one conformation is probable:



and this can explain the presence of single $v_{ab}(NO_2)$ and $v_b(NO_2)$ bands in the spectrum.

 $\begin{array}{cccc} & & & & & & & & \\ & & & & & & \\ CH_2 = CH - CH_2 - ONO_2 & 1638 ; 1632 \ cm^{-1} & 1295 ; 1280 \\ & & & - CH_2 - ONO_2 & 1633 & 1282 \end{array}$

The barely detectable splitting of the bands in the spectrum of cyclohexyl nitrate (X), reported by Carrington,¹⁶ may also result from the steric difference between axial and equatorial positions of the ONO_2 group.

SPECTRA OF NITRATES OF POLYHYDRIC ALCOHOLS

Molecules that include the structural element



are characterized by $v_{as}(NO_2)$ and $v_s(NO_2)$ doublets (XX, XXVI, XXXI). As previously, the splitting is explained as the result of steric unequivalence of the ONO₂ groups due to rotational isomerism. In compounds containing the system



no splitting of the frequencies is observed if there is no bulky substituent at the middle carbon atom (XXVII, XXXII.)

The hydroxyl group is too small to exert any appreciable hindrance on the ONO_2 group in the gauche isomers of the system



There is no detectable splitting of the $v_{ab}(NO_2)$ and $v_b(NO_2)$ frequencies in the spectra of compounds XIV, XXXII, XXXIII containing this system.

		$v_{as}(NO_2)$	ν _s (NO ₂)
XXV	CH ₂ -ONO ₂	C C	m -
	CH2-ONO2	1656; 1643	1292; 1271
XIV	CH ₂ —OH		
	CH2—ONO2	1631	1282

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XXVI	CH ₃		
	CH—ONO ₂	1656; 1641	1288; 1274
	CH2-ONO2		
XXXI	CH2—OH		
	CH—ONO ₂	1657; 1640	1287; 1275
	CH2-ONO2		
XXVII	CH2ONO2		
	CH_2	1634	1278
	CH2-ONO2		
XXXII	CH2-ONO2		
	сн—он	1640	1283
	CH2—ONO2		

The number of rotational isomers with non-equivalent ONO_2 groups increases in molecules of the type



with a large X substituent (XXIX, XXX) and so does the multiplicity of the $v_{as}(NO_2)$ and $v_s(NO_2)$ bands.

The spectra of crystalline polynitrates: erythritol tetranitrate (XXXV), Dmannitol (XXXVIII), D-sorbitol (XXXVII) and dulcitol (XXXIX) hexanitrates display groups of several peaks in the $v_{as}(NO_2)$ and $v_s(NO_2)$ ranges. These might be assigned solely to the crystal lattice effects, but on the basis of our previous experiments and the fact that the supercooled melts also give composite bands (broad and less resolved, similar to those of glycerol trinitrate), we suggest that hindered rotation in crystals reduces the number of rotational combinations of --CHONO₂---CHONO₂--- units. In the liquid, the large number of rotational isomers should result in a broadening and blurring of the fine structure of the bands as is actually observed. Support for this idea was found in the spectra of a cyclic compound, myoinositol hexanitrate (XL), where internal rotation around C--C bonds is hindered in both the solid and the liquid. The spectrum of the solid is nearly identical with that of the liquid, particularly in the frequency and overall shape of $v_{as}(NO_2)$ and $v_{s}(NO_2)$ bands. However, the crystal lattice effects should not be neglected, because the $v_{as}(NO_2)$ bands of crystalline pentaerythritol tetranitrate (XXXVI) are

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split, while the melt gives single and symmetric bands in these regions. The environments are identical for each of the four ONO_2 groups in the lattice as shown by X-ray study.¹⁷

FREE ROTATION IN PENTAERYTHRITOL TETRANITRATE

Pentaerythritol tetranitrate is the only nitric ester, the crystal structure of which has been fully investigated by X-ray methods.¹⁷ Booth and Llewellyn ¹⁷ had suggested partly double-bond character of the C—O bonds on the basis of X-ray study, but this was strongly opposed by Mortimer, Spedding and Springall,⁹ who carried out a dipole-moment investigation. The latter authors suggested free rotation around the C—O bonds because of the permanent dipole moment of pentaerythritol tetranitrate in acetone (2.5 D); the fixed symmetric structure would have resulted in a zero dipole moment.

This proof is incomplete as the permanent dipole moment might arise from some unsymmetric conformations of the four ONO₂ groups. Our study of the infra-red spectra, however, has shown that liquid (supercooled) pentaerythritol tetranitrate gives single, symmetric $v_{88}(NO_2)$ and $v_8(NO_2)$ bands, thus implying either free rotation of ONO₂ groups or the fixed symmetric conformation given by Booth and Llewellyn.¹⁷ The latter possibility is excluded on the basis of the dipole-moment study,⁹ so that the combined dipole-moment and spectroscopic results favour free rotation around the C—O bonds in pentaerythritol tetranitrate molecules liberated from the crystal lattice.

XXXVI



for supercooled liquid

Similar bands were found in the spectrum of a supercooled melt of 2-nitro-2-methyl-1,3-propanediol dinitrate (XXXIV).

- ¹ Urbański and Witanowski, Trans. Faraday Soc., preceding paper.
- ² Rossmy, Ber., 1955, 88, 1969.
- ³ Brown, J. Amer. Chem. Soc., 1955, 77, 6341.
- 4 McCrone, Fusion Methods in Chemical Microscopy, (Interscience Publishers, New York, 1957).
- 5 Will, Ber., 1908, 41, 1110.
- 6 Urbański, Roczniki Chem., 1933, 13, 406.
- 7 Brand and Cawthon, J. Amer. Chem. Soc., 1955, 77, 319.
- 8 Pauling and Brockway, J. Amer. Soc. 1937, 59, 13.
- 9 Mortimer, Spedding and Springall, J. Chem. Soc., 1957, 188.
- ¹⁰ Mizushima, Structure of Molecules and Internal Rotation, (Academic Press, New York, 1954).
- 11 Thompson, Advances in Spectroscopy, (Interscience Publishers, New York, 1959), pp. 289-347.
- ¹² De Kreuk, Rec. Trav. Chim., 1942, 61, 819.
- 13 Miyake, J. Amer. Chem Soc., 1960, 82, 3040.
- 14 Pauling, The Nature of Chemical Bond, (Cornell Univ. Press, Ithaca, New York, 1940).
- ¹⁵ Nakagawa, Ichishima, Kuratani, Miyazawa, Shimanouchi and Mizushima, J. Chem. Physics, 1952, 20, 1720.
- 16 Carrington, Spectrochim. Acta, 1960, 16, 495.
- 17 Booth and Llewellyn, J. Chem. Soc., 1947, 837.
- 18 Urbański, Technologia Materiałow Wybuchowych, vol. II., MON, (Warszawa, 1955).