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Infrared spectra and conformations of 2,3-dimethyl- 2,3-dinitrobutane and 2,2,3,3-Tetranitrobutane

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Abstract—The following molecules: $MeC(NO_2)_2Me$, $NO_2Me_2C—CMe_2NO_2$ and $(NO_2)_2MeC—CMe(NO_2)_2$ have been investigated by infrared spectroscopy with the aim of determining whether the title compounds can be characterized by definite conformations. On the basis of a comparison of the C—N valence frequencies within the series the conclusion is drawn that samples of both compounds, studied under various conditions, do not consist of single molecular species having a center of symmetry. Arguments are cited in favour of a *gauche* conformation for 2,3-dimethyl-2,3-dinitrobutane and of an equilibrium mixture of *trans-gauche* isomers for 2,2,3,3-tetranitrobutane, in the solid phases.

ROTATIONAL isomerism has been shown to exist in a number of symmetrically disubstituted butanes having methyl group (CH_3 = Me) and halogens (Cl and Br) as substituents. BROWN and SHEPPARD [1] have made spectroscopic measurements on $Me_2HC—CHMe_2$ and have shown that the plastic solid has a spectrum practically identical with that of the liquid. However, in the really crystalline state the i.r. spectrum indicated that the configuration stable in the lattice has a center of symmetry. PARK and WYN-JONES [2] have examined the Raman and i.r. spectra of $BrMe_2C—CMe_2Br$. They found that, during the preparation of a pressed disk sample of the solid, internal rotation has taken place with some molecules going from the trans to the gauche forms (the normal molecular form being trans in the non-pressed solid). For $ClMe_2C—CMe_2Cl$, KOIDE *et al.* [3] have reported that in the high temperature solid phase (above −112°C) the molecules possess some degree of rotational freedom in the crystalline lattice. The present study of $NO_2Me_2C—CMe_2NO_2$ and $(NO_2)_2MeC—CMe(NO_2)_2$ was undertaken in order to extend the foregoing investigations to nitro-compounds and to look for further indications of the presence of rotational isomerism, by the method of infrared spectroscopy. The analysis of these models, however, turn out to be more difficult than the analysis of ethane type models, in part because they are solid crystals at room temperature, and because the internal molecular arrangement of non-ionic aliphatic nitro-compounds has not so far been firmly established. To provide further guidance in band assignments, $MeC(NO_2)_2Me$ was prepared and its spectrum obtained. The most detailed results were obtained in the spectral range 6–12 μ since this region is well known in the vibrational spectra of nitro-compounds. Therefore, band assignments can be made with confidence on the basis of comparison within the series and by comparison

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[1] J. K. BROWN and N. SHEPPARD, *J. Chem. Phys.* **19**, 976 (1951).

[2] P. J. D. PARK and E. WYN-JONES, *Chem. Comm.* 557 (1966).

[3] T. KOIDE, T. ODA, K. EZUMI, K. IWATANI and T. KUBOTA, *Bull. Chem. Soc. Japan* **41**, 307 (1968).

with the assignments of other simple molecules. It is known, of course, that the assignment of the skeletal deformation frequencies are particularly important in the present work. But in the absence of more empirical informations than are now available it would not be profitable to include such a discussion.

EXPERIMENTAL

2,2-dinitropropane, $MeC(NO_2)_2Me$, was prepared by oxidation of propane pseudonitrole, $Me_2C(NO)NO_2$, in acetic acid solution, with chromic acid [4]. Propane pseudonitrole (dimer) was obtained by Nigaard's method of preparation [5].

2,3-dimethyl-2,3-dinitrobutane, $NO_2Me_2C—CMe_2NO_2$, and 2,2,3,3-tetranitrobutane, $(NO_2)_2MeC—CMe(NO_2)_2$, were prepared by the literature methods [6, 7] with only minor modifications in order to obtain samples of high purity.

The spectra were recorded with Perkin–Elmer (21 and 357) and Leitz (G III) spectrographs, employing the procedure for solid samples = solid deposit samples, paste in vaseline, KBr pressed disks, solutions in CCl_4 and CH_2Cl_2. $MeC(NO_2)_2Me$ is unstable and decomposes under the conditions of pressing. The spectrum of this compound was measured in solution. Low temperature spectra of the KBr disk samples were obtained with the use of a variable temperature cell VLT2 RIIC.

RESULTS AND DISCUSSION

The observed band frequencies are presented in Table 1. Having relatively few experimental data at our disposal, we shall limit ourselves mainly to qualitative discussion. In order to establish reliably the conformations of $NO_2Me_2C—CMe_2NO_2$ and $(NO_2)_2MeC—CMe(NO_2)_2$ it is necessary to have adequate vibrational assignment for both molecules. The calculation of the vibrational frequencies being impossible,

Table 1. Frequencies, cm^{-1}, of bands in infrared spectra of 2,2-dinitropropane, 2,3-dimethyl-2-3-dinitrobutane and 2,2,3,3-tetranitrobutane (6–12 μ region)

$MeC(NO_2)_2Me$	$NO_2Me_2C—CMe_2NO_2$		$(NO_2)_2MeC—CMe(NO_2)_2$			
Solution	Solid	Solution	Solid	Solution	Approximate mode	$C_2H_4(NO_2)_2$ (8)
1577	1550	1550	1603, 1658	1600 (broad)	Asym. NO_2 stretch	1593
	1460	1460				
1442	1450	1455	1440	1440	Asym. CH_3 deformation	
1420	1430					
	1400					
1395	1385	1385	1390		Sym. CH_3 deformation	
1360	1370	1370	1380	1380		
1337	1330	1330	1330	1328	Sym. NO_2 stretch	1402
1320			1300	1297		1343
1235						
1175	1160	1160	1114	1117		
1143	1124	1124				
			870	872	C—N	890
854	850	851	855	856		
839	843	843	837	837		875

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[4] V. MEYER and J. LOCHER, *Ann. Chem.* **180**, 133 (1876).

[5] E. M. NIGAARD, J. H. MCCRACKEN and T. T. NOLAND, *Chem. Abstracts* **39**, 3551 (1945).

[6] L. W. SEIGLE and H. B. HASS, *J. Org. Chem.* **5**, 100 (1940).

[7] CH. E. GABRIEL, D. E. BISGROVE and L. B. CLAPP, *J. Amer. Chem. Soc.* **77**, 1293 (1955).

we are compelled to resort to empirical methods. In addition, we have some knowledge of the fundamental frequencies of dinitroethane, $C_2H_4(NO_2)_2$, (listed in the last column of Table 1) to aid us in our analysis of the $MeC(NO_2)_2Me$ spectrum [8].

According to the theoretical calculation made in reference 8, gem-dinitroalkanes, which are related to $MeC(NO_2)_2Me$ molecule, can have four normal N—O vibrations. In two of these vibrations, with frequencies between 1400 and 1300 cm^{-1}, the N—O bonds of each nitro group oscillate symmetrically in relation to each other ν_s NO_2, but symphasically and antiphasically in relation to the other nitro group. In the two others symphasic and antiphasic antisymmetrical changes in the length of the N—O bonds in each nitro group ν_{as} NO_2 occur, with similar frequencies around 1600 cm^{-1}. Guided by the above considerations it is possible to pick out the N—O valence frequencies after elimination of the frequencies arising from CH_3 deformation modes by comparison within the series and by reference to the literature [9]. Thus, in the $MeC(NO_2)_2Me$ spectrum we have assigned bands observed at 1337 and 1320 cm^{-1} to the two inphase and antiphase symmetrical vibrations ν_s NO_2, and a 1577 cm^{-1} band to the antisymmetrical ν_{as} NO_2 vibrations. The intermolecular vibrational coupling of the two nitro groups, separated by carbon atoms, is expected to weaken rapidly as the number of intervening C—C bonds increases. In this case the symphasic and antiphasic symmetrical vibrations ν_s NO_2 become degenerate and their characteristic frequency may be indistinguishable from that of a single nitro group. This is observed in the spectra of NO_2Me_2C—CMe_2NO_2 at 1330 cm^{-1}. On the other hand, agreement is general regarding C—N stretching frequencies of non-ionic aliphatic nitro-compounds. HASZELDINE [10] has reported the range 920–830 cm^{-1} for mononitroalkanes and the present author has found the range 1060–850 cm^{-1} for dihalogeno-dinitromethanes [11]. Taking these reference values into consideration, we can assign the bands observed in all our spectra between 870 and 830 cm^{-1} to C—N stretching vibrations. The normal frequencies of dinitroethane support this assignment (see Table 1). It is evident that there are strong interactions, in these compounds, between the individual structural elements. The assignment of normal frequencies to specific groups or bonds is only approximate. But in view of general regularities in the appearance of individual absorption bands in the spectra, the correlation is sufficiently good to suggest that the vibrational assignment presented in Table 1 is very reliable. The observed additional frequencies in CH_3 deformation regions in the solids are due to intermolecular interactions in the crystal lattices. Such a phenomenon is well known and has been reported much earlier in the i.r. spectra of a considerable number of crystalline hydrocarbons [12, 9].

Let us turn now to the problem of relating i.r. band frequencies to molecular structures. When Table 1 is examined it is clear that as far as the N—O valence frequencies are concerned, the fundamental spectral characteristics of mononitroalkanes are retained in the spectra of NO_2Me_2C—CMe_2NO_2 which possesses two N—O

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[8] E. M. POPOV and V. A. SHLYAPOCHNIKOV, *Opt. Spectry.* **15**, 174 (1963).

[9] N. SHEPPARD and D. M. SIMPSON, *Quart. Rev.* **7**, 19 (1953).

[10] R. N. HASZELDINE, *J. Chem. Soc.* 2525 (1953).

[11] A. O. DIALLO, *C.R. Acad. Sc. Paris* **272**, 1777 (1971).

[12] R. E. RICHARDS and H. W. THOMPSON, *Proc. Roy. Soc.* (London) **195A**, 1 (1948).

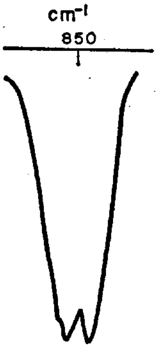

Fig. 1

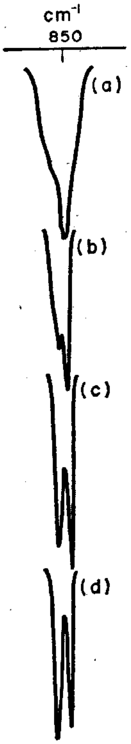

Fig. 2

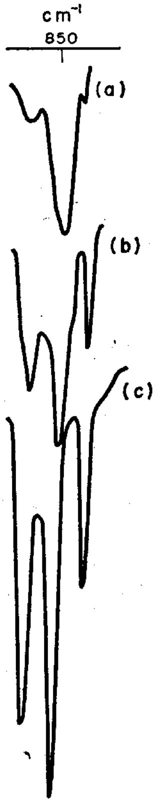

Fig. 3

Fig. 1. C—N absorption bands of 2,2-dinitropropane in CH_2Cl_2 solution.

Fig. 2. C—N absorption bands of 2,3-dimethyl-2,3 dinitrobutane: (a) CH_2Cl_2 solution; (b) KBr disk at room temperature; (c) KBr disk at −80°C; (d) KBr disk at about −180°C.

Fig. 3. C—N absorption bands of 2,2,3,3-tetranitrobutane: (a) CH_2Cl_2 solution; (b) KBr disk at room temperature; (c) KBr disk at about −190°C.

bands and those of $MeC(NO_2)_2Me$ are retained, to a certain extent, in the spectra of $(NO_2)_2MeC$—$CMe(NO_2)_2$. A different pattern, however, is observed concerning the C—N frequencies. The i.r. absorption bands in the ν_{CN} region for the three compounds, studied under various conditions, are presented in Figs. 1, 2 and 3. As can be seen from these figures, the spectra of $MeC(NO_2)_2Me$ and NO_2Me_2C—CMe_2NO_2 are characterized by doublets and those of $(NO_2)_2MeC$—$CMe(NO_2)_2$ exhibit a triplet. Obviously, what we have said above about the N—O valence vibrations cannot be maintained for the C—N valence vibrations. In the i.r. spectrum of $MeC(NO_2)_2Me$, taken for comparison, the C—N stretching frequencies are split apart, most likely, owing to intramolecular vibrational coupling. It is interesting to note that in this spectrum the separation of the two ν_{CN} is the same as observed for dinitroethane (see Table 1). Unfortunately the small amount of experimental data prevents the determination of the molecular symmetry. On the other hand, it is worthy of note that, in Figs. 2

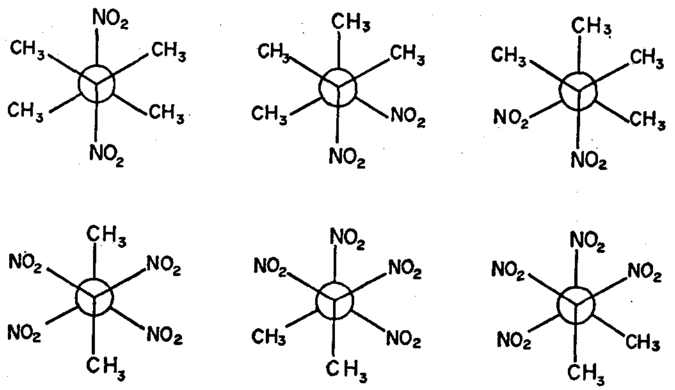

Fig. 4. Newman projections of the staggered rotamers of 2,3-dimethyl-2,3-dinitrobutane and 2,2,3,3-tetranitrobutane.

and 3, the total band splittings are retained by going from solids to solutions. This proves that the multiplicity of the C—N frequencies in the spectra of NO$_2$Me$_2$C—CMe$_2$NO$_2$ and (NO$_2$)$_2$MeC—CMe(NO$_2$)$_2$ is not connected with intermolecular interactions of vibrating bonds in the unit cells of crystals. Hence, we believe that the observed C—N frequencies, in each case, must be interpreted as arising from fundamental vibrations of individual molecules. The possibility presents itself that the observed phenomenon may be interpretable in terms of conformational isomerism. The situation seems to be the same as in many familiar spectroscopic problems. Recourse must be made to comparison of the stereochemical behaviour of our molecules with that of models. But with regard to the subject the uncertainty that the models chosen may be inadequate is always present.

As a basis for the interpretation of the indicated bands, it is reasonable to start with three possible steric isomers (two of which are spectroscopically identical) of NO$_2$Me$_2$C—CMe$_2$NO$_2$ and (NO$_2$)$_2$MeC—CMe(NO$_2$)$_2$, with different relative orientations of the C—N bonds of the molecules, as shown in Fig. 4. Under the approximation of assuming the substituents (CH$_3$ and NO$_2$) as point masses, the molecular configurations in these figures are similar to the *trans* and *gauche* isomers of symmetrically di- and tetrasubstituted ethanes, with C_{2h} symmetry for the *trans* isomers and C_2 symmetry for the *gauche* isomers [13]. The true molecular symmetries cannot actually be higher than these point groups. A study of scale models shows that the most favourable orientations of the planes of the NO$_2$ groups are those in which the projections of the oxygen atoms on a plane perpendicular to the C—C central axis are along the C—N bonds. When these static positions of the NO$_2$ groups are combined with proper orientations of the CH$_3$ groups, the initial C_{2h} and C_2 symmetries are retained for all *trans* and *gauche* molecular configurations without pronounced steric hindrance between non-bonded atoms. Although there is a second conceivable *trans* configuration for NO$_4$Me$_2$C—CMe$_2$NO$_2$ (where the projections of the oxygen atoms on a plane perpendicular to the C—C central bond are equidistant from a line prolonging the C—N bond) the discussion which follows

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[13] S. MIZUHIMA, *Structure of Molecules and Internal Rotation*, Academic Press, New York (1954).

considers only the two molecular models already mentioned. The vibrational types and selection rules expected for these limiting configurations are summarized in Table 2.

Table 2. Vibrational types and selection rules for two limiting stable configurations of NO_2Me_2C—CMe_2NO_2 and $(NO_2)_2MeC$—$CMe(NO_2)_2$

Trans isomers (C_2h)		*Gauche* isomers (C_2)	
Vibrational types	Activity	Vibrational types	Activity
A_g	R.		
A_u	i.r.	A	R., i.r.
B_g	R.		
B_u	i.r.	B	R., i.r.

Instead of looking at all 3 N–6 vibrations, our attention may be focused on the C—N valence frequencies of the molecules. In the trans configurations (C_{2h} point group) the C—N vibrational modes are distributed among the symmetry species as follows: $1A_g + 1B_u$ (NO_2Me_2C—CMe_2NO_2) and $1A_g + 1A_u + 1B_g + 1B_u$ [$(NO_2)_2$-MeC—$CMe(NO_2)_2$]. Actually the i.r. spectra of the former molecule was found to contain two C—N frequencies and those of the latter molecule three C—N frequencies instead of one and two frequencies, respectively, required by the selection rules. On the basis of these differences between predicted and observed spectra one can draw the conclusion that the investigated samples of the molecules do not consist of single molecular species having C_{2h} symmetry. Of course, this is not surprising in view of the complexity of the molecules. Nevertheless, even at this point the analysis has given the useful result that some of the molecules, if not all, have no center of symmetry in the solid state.

The other possibilities, according to our starting hypothesis, are either the all *gauche* conformations or mixtures of *trans-gauche* isomers. For the *gauche* configurations (C_2 point group) all fundamental modes are both Raman and i.r. active. This means that the C_2 isomers have, in principle, twice as many i.r. fundamentals as the C_{2h} forms. In the case of $(NO_2)_2MeC$—$CMe(NO_2)_2$, however, two C—N fundamental vibrations are of type A and the two others of type B. Since the splitting would be expected to be quite small for vibrations of the same symmetry species, the corresponding i.r. bands should hardly be distinguished from each other in practice. If this were the case, one would anticipate the appearance of two C—N bands (one for each vibrational type A and B), whereas three well resolved bands have been found in the spectra of the molecule as can be seen from Fig. 3. It follows from the latter observation that a single *gauche* conformation does not appear to be likely for $(NO_2)_2MeC$—$CMe(NO_2)_2$. Indeed, it is possible to interpret the spectra of the molecule on the basis of a mixture of *trans-gauche* isomers if two C—N fundamental frequencies (one for each isomer) are assumed to coincide. We cannot confirm this suggestion by experimental data at the present time since the corresponding Raman spectra have not been investigated.

In the case of NO_2Me_2C—CMe_2NO_2, the C_2 symmetry cannot be eliminated on purely spectroscopic grounds since the i.r. spectra of the molecule are found to contain just two C—N frequencies, in agreement with the application of selection rules. At this stage, however, we cannot conclude that the *gauche* conformation in the only, or even the principal molecular species in the solid and solution. It is not at all certain that other forms are not present which require more elaborate methods for detection.

In order to clarify the physical nature of the observed bands we have investigated qualitatively the temperature dependence of the vibrational spectra. An illustration of the temperature behaviour of the C—N bands at 850 and 843 cm^{-1} of NO_2Me_2C—CMe_2NO_2 is shown in Fig. 2*. At room temperature the higher-frequency band appears as a strong shoulder on the lower-frequency band (Fig. 2b). As the temperature is lowered the height of the peak of the former band increases gradually while that of the latter band remains about the same (Fig. 2c). At temperature of about −180°C, the relative intensity of the higher-frequency band is greater and the intensity of the lower-frequency band is unchanged within the experimental limits of error (Fig. 2d). At the same time we have noted the appearance of a new band at about 1350 cm^{-1} as well as the splitting of the 1124 cm^{-1} band into two components in the spectrum of the molecule. The changes are not noticeable in the bands corresponding to the N—O vibrations.

The observed variation of relative band intensity with temperature may be due either to redistribution of rotational isomers or to intermolecular interactions. A redistribution of rotational isomers, however, is in itself improbable since the temperature dependence of the intensity is observed for only one component of the C—N bands. Moreover, changes of lattice parameters associated with such an internal transformation are expected to occur near a temperature of transition. (The molecules in crystalline environments being assumed to have discrete orientations). It is possible, therefore, that the temperature dependence of the band intensity is connected with a change of intermolecular interactions. A number of previous experimental studies of crystalline compounds by i.r. and Raman spectroscopy have revealed that the absorption induced by intermolecular interactions is to be regarded as a supplement to the primary absorption band. Likewise, the intensities of the bands can change anomalously with change of temperature and the size of the anomaly may depend on the modes of vibrations involved [14–16].

Decreases in temperature in the condensed state of substances lead to decrease in intermolecular distances which in turn result in the increase of the induced dipole moment caused by the electric field of the surrounding molecules, and thus in an enhancement of spectral band intensities. This is in qualitative agreement with our own experimental observation in the case of the higher-frequency C—N band of NO_2Me_2C—CMe_2NO_2. However, no noticeable alteration in the relative band intensity of the lower-frequency C—N band has been detected in the spectra of the molecule

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* The frequencies of the i.r. absorption bands in the solids, at temperatures down to −180°C, are almost coincident.

[14] M. L. Lisitsa, V. N. Malinko and I. V. Kalinmonova, *Opt. Spectry.* **7**, 386 (1959).

[15] A. S. Lvova and M. M. Sushchinskii, *Opt. Spectry. Suppl. 2, Molecular Spectroscopy*, English Edition, 139 (1966).

[16] P. A. Bazhulin and L. P. Osipova, *Opt. Spectry.* **6**, 406 (1959).

down to −180°C. The different influence of the temperature on the relative intensities of the two C—N bands of the same compound suggests that the bands under consideration correspond to different types of vibration. A reasonable interpretation for this is that the higher-frequency vibration may be of type B and the lower-frequency vibration of type A. If this is the correct explanation of our results, then the observed spectra of $NO_2Me_2C—CMe_2NO_2$ can be interpreted as belonging to a single *gauche* configuration (C_2 point group) without difficulty. In the case of $(NO_2)_2MeC—CMe(NO_2)_2$ the temperature dependence of band intensities provides no new informations on the vibrational character of the molecule.

The simplified models used here make possible only a qualitative interpretation of the experimentally observed i.r. spectra of the molecules. Consequently, the suggested molecular configurations need to be confirmed by Raman studies.