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Vibrational spectra of gem-dinitroparaffins—I
2,2-dinitropropane

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Abstract—Infra-red and Raman spectra of liquid 2,2-dinitropropane (2,2-DNP) have been recorded. A vibrational assignment has been made assuming C_{2V} symmetry of the 2,2-DNP molecule.

Considerations of the vibrational spectra of nitroparaffins have been the subject of numerous investigations mainly referred to the derivatives of nitromethane [1–9]. As far as gem-dinitroparaffins are concerned, the available data cover only some selected regions of the infra-red scale [10–12]. In this laboratory research on gem-dinitroparaffins has been carried out for some time, and a more detailed analysis of the appropriate spectral material became necessary. Owing to its high symmetry, 2,2-dinitropropane (2,2-DNP) was selected, since the simplest gem-dinitroparaffin-dinitromethane was not stable enough to permit obtaining consistent and unequivocal spectral recordings. The structure of 2,2-DNP may be represented by the scheme in Fig. 1. Of course there is a question to what extent the structure proposed reflects actual positions of particular atoms in the molecule. Thus, it may be expected that the angle between the planes of the two nitro groups may differ from tetrahedral [13]. However, the angle and bond-length values recorded in crystalline 2,2-DNP (C—C and C—N = 1·5 Å; N—O = 1·23 Å; C—H = 1·09 Å; $O\overset{N}{\diagup\diagdown}O = 125°$; $H\overset{C}{\diagup\diagdown}H$; $C\overset{C}{\diagup\diagdown}C$ and $N\overset{C}{\diagup\diagdown}N = 109{\cdot}5°$) indicate the angle α value being very close to that of tetrahedral [14]. These observations seem to support the structural concept shown in Fig. 1.

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[3] A. J. Wells and E. B. Wilson, *J. Chem. Phys.* **9,** 314 (1941).
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[13] V. J. Slovetskii, V. A. Shlyapochnikov, S. A. Shevelev, A. A. Fainzilberg and S. S Novikov, *Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk* 330 (1961).
[14] S. C. Abrahams, *J. Chem. Phys.* **21,** 1218 (1953).

Subsequently C_{2V} symmetry should be assigned to molecules of 2,2-DNP although such an assignment does not take into consideration the effects of the rotations of the CH_3 groups about the C—C axis. As shown in Table 1, the thirty nine normal vibrations are distributed 12, 8, 10 and 9 to the representations A_L, A_2, B_1 and B_2 respectively.*

In the Raman spectrum, all the vibrations should be active, while in the infra-red spectrum, the A_2-representation vibrations are inactive.

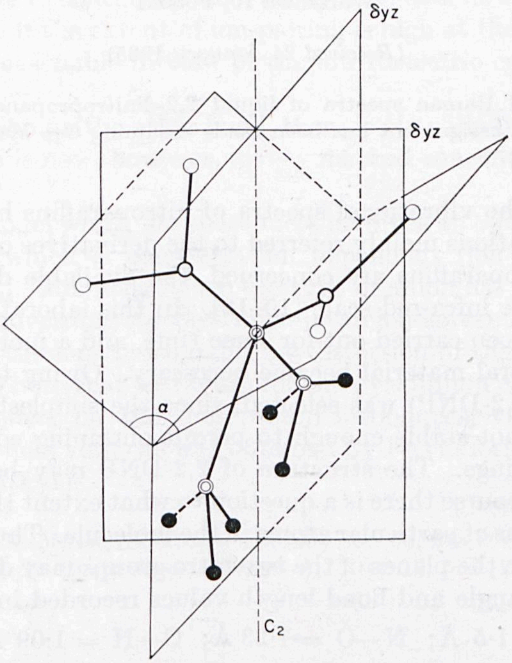

Fig. 1. Spatial arrangement in 2,2-dinitropropane.
◎—carbon; ●—hydrogen; o—nitrogen; ○—oxygen.

EXPERIMENTAL

2,2-Dinitropropane (m.p. 39·5–40°) was obtained according to the known method [15], and its purity was checked by means of gas-chromatography. The infra-red spectra were examined in an UR–10 (Zeiss, Jena) spectrometer with optics in KBr, NaCl and LiF. The substance was examined in molten state at *ca.* 50°C.

The Raman spectra were taken with a "Huet" B–11 quartz spectrograph and registered by a photometric method. The dispersion was 18 Å for 1 mm in the proximity of 4400 Å. The spectra were induced by the 4358 Å line of a low pressure mercury lamp. The exactness was of the order 1–2 cm^{-1}. The substance was in the molten (supercooled) state.

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* All the symbols and markers used in the present paper conform to the notation suggested by HERZBERG [16].

[15] R. B. KAPLAN and H. SHECHTER, *J. Am. Chem. Soc.* **83,** 3535 (1961).

[16] G. HERZBERG, *Infrared and Raman Spectra of Polyatomic Molecules* D. Van Nostrand, New York (1945).

Table 1. Normal vibrations in 2,2-dinitropropane

Description of vibrations \ symmetry	A_1	A_2	B_1	B_2
CH_3asymm. stretching	ν_1	ν_{13}	ν_{21}	ν_{31}
CH_3symm. stretching	ν_2		ν_{22}	
CH_3asymm. bending	ν_3	ν_{14}	ν_{23}	ν_{32}
CH_3symm. bending	ν_4		ν_{24}	
CH_3 rocking	ν_5	ν_{15}	ν_{25}	ν_{33}
C—C stretching	ν_6		ν_{26}	
C—N stretching	ν_7			ν_{34}
NO_2asymm. stretching		ν_{16}	ν_{27}	
NO_2symm. stretching	ν_8			ν_{35}
NO_2 bending	ν_9			ν_{36}
NO_2 rocking		ν_{17}	ν_{28}	
NO_2 wagging	ν_{10}			ν_{37}
NO_2 twisting		ν_{18}	ν_{29}	
C—C—C bending	ν_{11}			
N—C—N bending	ν_{12}			
Skeletal rocking			ν_{30}	ν_{38}
Skeletal twisting		ν_{19}		
CH_3 torsional		ν_{20}		ν_{39}

RESULTS AND DISCUSSION

The infra-red spectrum of 2,2-DNP in the 3500–400 cm^{-1} range is shown in Fig. 2. Analogously in Table 2 are arranged the frequencies of infra-red absorption bands and Raman spectrum lines followed by the assignments proposed.

C—H stretching vibrations

Discussion on the C—H stretching vibrations may be restricted, in general, to asymm. ν_{CH_3} and symm. ν_{CH_3}. Examination of the available data [17, 18] leaves no doubt that interpretation of the C—H stretching vibrations in paraffins is a complex problem. As far as 2,2-DNP is concerned the infra-red spectrum revealed three absorption bands around 3000 cm^{-1} and six in the 2815–2614 cm^{-1} region. In the Raman spectrum, however, only the three bands around 3000 cm^{-1} were recorded.

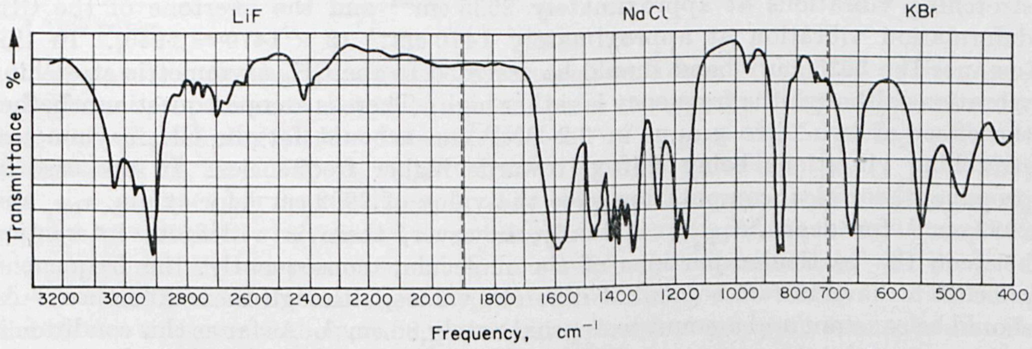

Fig. 2. Infra-red spectrum of 2,2-dinitropropane at approx. 50°C.

In his investigation concerning compounds of the general formula $CH_3CX_2CH_3$

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

[18] R. S. SNYDER and J. H. SHACHTSCHEIDER, *Spectrochim. Acta* **19,** 85 (1963).

where X = Cl or Br, Tobin [19] assigned only one band to the C—H vibrations corresponding to both ν_3 and ν_{22} in our notation, that is to CH_3 symm. stretching vibrations. Accordingly, the appropriate assignments were 2934 and 2922 cm^{-1} in the chloro and the bromo derivative, respectively. The intense band at 2905 cm^{-1} in our spectrum of 2,2-DNP can hardly be assigned to the CH_3 symmetric stretching vibrations, since the corresponding line in Raman spectrum is exceptionally weak. Consequently, it appears that the 2956 cm^{-1} peak could be assigned to the CH_3 symmetric stretching vibrations or alternatively both the 2905 and 2956 cm^{-1} bands could be considered as a doublet due to Fermi resonance between the CH_3 symmetric stretching vibrations at approximately 2935 cm^{-1} and the overtone of the CH_3 deformation vibration at approximately 1470 cm^{-1} ($2 \times 1470 = 2940$). In this instance the 3025 cm^{-1} band should be assigned to the CH_3 asymmetric stretching vibrations although the frequency is rather high. There is an open question whether the effect of two nitro groups in 2,2-DNP can account for the CH_3 asymmetric stretching vibrations being shifted towards higher frequencies. In the case of propane, theoretical computation gave the value of 2902 cm^{-1} for symm. ν_{CH_3} and 2983 cm^{-1} for degen. ν_{CH_3}*. Actually, however, there is a definite interaction between the particular portions of the molecule; consequently, the frequencies referred to have in fact somewhat different values, although their difference $-\Delta\nu$ should be constant and amount to approximately 80 cm^{-1}. As far as this condition is concerned, our interpretation of CH_3 stretching vibration spectrum seems to be satisfactory.

Table 2. Infra-red and Raman frequencies in the spectrum of 2,2-dinitropropane

IR cm^{-1}	Raman cm^{-1}	Assignment	IR cm^{-1}	Raman cm^{-1}	Assignment	IR cm^{-1}	Raman cm^{-1}	Assignment
	200 wb		1164 s	1159 vw	asymm. C—C	2390 vw		
	263 w		1194 s	1185 w		2412 w		
	365 mb	def. NO_2	1258 s	1255 vwb	symm. NO_2			
420 w	415 m	def. NO_2	1342 s	1330 s	symm. NO_2 or def. CH_3			
485 w								
			1367 s	1358 s	symm. NO_2 or def. CH_3	2614 vw		
550 m	543 m	def. NO_2				2665 w		
667 m	660 w	def. NO_2	1388 s	1405 s	def. CH_3	2684 w		
720 vw	722 vw		1417 s	1435 s	def. CH_3	2740 vw		
745 vw			1450 sh	1450 mb		2770 vw		
800 sh			1463 sh			2815 vw		
855 s	846 vs	symm. C—N	1470 s		def. CH_3			
865 s		symm. C—C	1564 sh					
950 sh	944 vw	asymm. C—N	1588 vs	1576 vsb	asymm. NO_2	2905 s	2908 vvw?	
965 w			1610 sh			2956 m	2952 s	symm. CH_3
						3027 m	3017 sb	asymm. CH_3

C—H deformation vibrations

Discussing the case of $CH_3CX_2CH_3$ compounds, we should keep in mind that the totally symmetric (bending) ν_4 and the asymmetric ν_3 vibrations differ considerably

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* Recently Snyder and Schachtscheider [18] carried out extensive normal coordinate calculations for propane and several *n*-paraffins and arrived to figures: as $v_{CH_3} = ca.$ 2967c m^{-1} and symm. $v_{CH_3} = ca.$ 2884 $cm.^{-1}$

[19] M. C. Tobin, *J. Am. Chem. Soc.* **75,** 1788 (1953).

in frequency. There are also three other asymmetric (bending) vibrations ν_{14}, ν_{23} and ν_{32}. We should expect therefore the following absorption bands in 2,2-DNP infra-red spectrum: ν_4 (s-bending); ν_3 (as-bending); ν_{23} and ν_{32} (as-bending), both of similar frequencies. The last CH_3 bending vibration to be discussed here is that denoted as ν_{24}. We may expect that the ν_{24} and ν_4 vibrations fall to the different frequencies.

The data published so far for C—H vibrations of $CH_3CX_2CH_3$ compounds are set up in Table 3; particular vibrations are there denoted by the same symbols as used in Table 1.

Table 3. C—H vibration frequencies in certain $CH_3CX_2CH_3$

Compound νcm^{-1}	$CH_3CH_2CH_3$ [6]	$CH_3CH_2CH_3$ [20]	$CH_3CBr_2CH_3$ [19]	$CH_3CCl_2CH_3$ [19]	$CH_3C(NO_2)_2CH_3$*
ν_3	1451	1470	1376	1387	1470
ν_{14}	1451	1470	1436	1443	
ν_{23}	1465	1487	1434	1443	1417
ν_{32}	1470	1490	1434	1443	1417
ν_4	1370	1382	1179	1187	1388
ν_{24}	1375	1390	1376	1387	1367 or 1342
as ν_{CH_3} stretch.	2946 2967 2968 (16)	2983 calculated (17)	2934	2993	3027
s ν_{CH_3} stretch.	2903 2885 (16)	2902 calculated (17)	2922	2934	2956

* This paper

As may be seen, the ν_4 assignments proposed by TOBIN [19] in 2,2-dichloro- and 2,2-dibromopropane seem not to be correct, since the relevant frequencies are much too low. Considering all the data referred to, we suggest the following tentative assignments in 2,2-DNP: $\nu_3 = 1470$ cm^{-1}; ν_{23} and $\nu_{32} = 1417$ cm^{-1}; $\nu_4 = 1388$ cm^{-1}; $\nu_{24} = 1367$ cm^{-1} or 1342 cm^{-1}. The rocking deformation vibrations ν_5, ν_{15}, ν_{25} and ν_{33} can hardly be referred to as "simple" vibrations of the methyl group. In fact, they are always accompanied by a considerable distortion of the C—C—C skeleton, and, virtually one should speak rather about deformation vibrations of the system taken as a whole, though the share of methyl groups in such vibrations is quite considerable. The available calculations [20] demonstrate that changes in C—C bond length and the C—C—C angle are particularly prominent in the case of ν_{25} and ν_{33} vibrations. No detailed consideration is given to these vibrations in the present paper.

C—C and C—N stretching vibrations

It is noteworthy that both symmetric and asymmetric C—C frequencies do not change much when substituting (H, H), (H, CH_3), (H, NH_2) and (H, OH) for one

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[20] M. A. ELYASHEVICH and B. I. STEPANOV, Doklady Akad. Nauk SSSR **32**, 481 (1941); *Zhurn. Fiz. Khim.* **17**, 145 (1945).

another at the $C_{(2)}$ carbon atom. Very low frequencies proposed in the case of dihalo derivatives are another interesting peculiarity. In the case of 2,2-DNP, we could assign the C—C asymmetric stretching vibration—ν_{26}—to the 1194–1165 cm^{-1} infra-red doublet, and similarly, the corresponding symmetric vibration—ν_6—to the 865–855 cm^{-1} infra-red doublet.

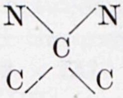
Assignment of the vibrations in question to doublets is not without precedent. For example a similar interpretation has been reported by KOHLRAUSCH [21] in the case of 2-substituted derivatives of propane.

For 2,2-DNP bands should also be present due to asymmetric and symmetric C—N stretching vibrations. In mononitroparaffins, the C—N stretching vibrations have been assigned to the peak around 851 cm^{-1} [6]. Two bands, are to be expected in gem-dinitroparaffins, one of them would probably appear below and the other over 850 cm^{-1}.

None of the reports published thus far gives any data on the frequencies of the C—N stretching vibrations in gem-dinitroparaffins.

The C—N symm. and asymmetric stretching vibrations for tetranitromethane have been assigned as 862 and 958 cm^{-1}, respectively. Unfortunately, owing to the relatively complex structure and high symmetry, the latter compound can hardly be considered a suitable model for 2,2-DNP.

Therefore, there is no evidence to rule out the possibility that the 865–855 cm^{-1} doublet could also be assigned to the symmetric C—N stretching vibration (ν_7). And as regards the C—N asymmetric stretching vibration (ν_{34}), the 965 cm^{-1} band could be considered a possible assignment.

However, we prefer to assign all these bands (1194–1165 cm^{-1}, 865–855 cm^{-1} and 965 cm^{-1}) to skeletal stretching vibrations of the entire  system.

NO_2 stretching vibrations

It should be expected that gem-dinitroparaffins would show four NO_2 stretching vibrations, their frequencies differing from each other to an extent depending on how great is the interaction between the two nitro groups.

Tetranitromethane may be used here again as an illustrative though rather approximate reference model. In the infra-red spectrum of that compound the particularly low frequency of the symmetric NO_2 vibrations 1378, 1348 and 1217cm^{-1} should be pointed out. Only the 1348 cm^{-1} value may be regarded as being fairly close to that observed for the symmetric ν_{NO_2} vibration in a variety of nitrocompounds. The abnormally high frequency of the asymmetric vibrations —1648 and 1618 cm^{-1} is another striking feature in the spectrum of tetranitromethane. The Raman spectra of dichlorodinitromethane and dibromodinitromethane [22], provide another convenient comparison. In that case, the broad and intense bands at 1609 and 1599 cm^{-1} were assigned to as ν_{NO_2} vibrations, the bands at 1324, 1289 cm^{-1} and 1328, 1312 cm^{-1} to symm. ν_{NO_2} vibrations in the chloro and bromo derivatives, respectively.

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[21] K. W. F. KOHLRAUSCH, *Ramanspektren* J. W. Edwards, Ann Arbor, Mich. (1944).

[22] H. WITTECK, *Acta Phys. Austriaca* **1,** 303 (1948).

We suggest that the 1258 cm^{-1} band in the spectrum of 2,2-DNP is to be ascribed to the symmetric NO_2 stretching vibration ν_8. Some doubts arise, however, which band should be assigned to the other symmetric NO_2 vibration ν_{35}. By analogy with other nitro compounds the intense infra-red band at 1342 cm^{-1} might be considered the most probable assignment. On the other hand, however, it should not be overlooked that the corresponding Raman line is relatively weak and that the adjacent intense line at 1367 cm^{-1} would be much more compatible with the symmetry of that vibration.

Having no evidence in favor of either the 1367 cm^{-1} or the 1342 cm^{-1} band, we prefer to leave the question open.

In 2,2-DNP the assignment of the asymmetric NO_2 vibration to the broad and intense band at 1588 cm^{-1} seems to be highly probable. On the other hand, the possible difference in frequencies of the two asymmetric NO_2 vibrations ν_{16} and ν_{27} needs additional explanation. Thus, the vibration would be expected to be inactive in the infra-red but active in the Raman spectrum and that the corresponding Raman line (1576 cm^{-1}) is rather broad and diffuse may be explained by the small difference in frequencies of those vibrations.

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