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Infrared Absorption Spectra of Aliphatic Nitro-compounds and Their Derivatives

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Data on the infrared spectra of aliphatic nitro-compounds and their salts are discussed and summarised. Relations are established between the position of the nitro-stretching bands in the absorption spectrum and the structure of the radical. A fairly large number of examples are given of the use of infrared spectroscopic data to elucidate the detailed structure of nitro-compounds and their salts, and also to study the behaviour of these compounds in various media. Problems of the assignment of the vibrations in nitro-compounds and in the salts of mononitro- and polynitro-compounds are examined. Possible uses of the infrared relations to identify and analyse nitro-compounds and their derivatives are illustrated. The bibliography contains 237 references.

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I. INTRODUCTION

The rapid development of the chemistry of aliphatic nitro-compounds and improvements in the technique of obtaining infrared absorption spectra have led to the accumulation of much factual information on the infrared spectra of nitro-compounds. However, this information is scattered among numerous papers, and no monographs or reviews have hitherto been published on this topic. The present Review discusses and summarises existing data on the infrared spectra of aliphatic nitro-compounds and their salts, and the relations found are used to elucidate the detailed structure of nitro-compounds and to identify them.

II. ASSIGNMENT OF MAIN ABSORPTION BANDS OF NITRO-COMPOUNDS

What are probably the first papers on the infrared spectra of nitro-compounds[1-4] do not discuss the problem of assigning the absorption bands to definite vibrations. From 1940 several papers appeared[5-11] whose authors assigned bands by comparing the infrared and the Raman spectra (intensity and degree of depolarisation) of nitromethane[5-10], its derivatives[6,7,10], and its homologues[5-7,11]. During the same period stretching vibrations of nitro-groups and the carbon–nitrogen bond in certain nitroalkanes and their halogeno-derivatives were assigned by Wittek[12,13] on the basis of the Raman spectra. A later paper by Wittek[14] makes assignments also in polynitroalkanes. Assignment is a fundamental problem in the calculations and in various correlations between structure and spectral characteristics, etc. This makes it clear why papers have hitherto appeared with complete[15-26] or partial[27-33] (stretching vibrations of the nitro-group and the carbon–nitrogen bond—sometimes only stretching vibrations of the nitro-group) assignment of the bands observed in the spectra of nitro-compounds.

Analysis of the papers[19-21,26-38] shows that the antisymmetric stretching vibration ν_{as} of the nitro-group in a series of aliphatic nitro-compounds and their derivatives appears as an intense band in the range 1640–1535 cm^{-1}. Splitting of this band is observed[16,29,42] only with tetranitromethane†. Other absorption bands are usually absent from this range‡, so that the assignment of ν_{as} presents no difficulty. The symmetric stretching vibration ν_s of the nitro-group appears in the range 1385–1280 cm^{-1}, which contains other bands, and there is no generally accepted view concerning the assignment of this vibration. Thus Wittek[13], and following him Iogansen and Litovchenko[29], assign two bands in nitromethane and some of its homologues to ν_s, assuming that the appearance of two bands is due to mechanical interaction between deformation vibrations of the methyl group δCH_3 and the symmetric stretching vibration of the nitro-group. The chief argument of these authors is that the Raman spectrum contains two fairly intense and equally polarised ($\rho \simeq 0.4$) bands in the range 1410–1365 cm^{-1}. In the Reviewer's opinion the assignment of the two bands to ν_s of the nitro-group is unjustified. Such assignment involves the assumption that the intensity of the deformation vibration δCH_3 or δCH_2 is independent of the introduction of electronegative substituents. This is not observed. The introduction into a molecule of strongly electronegative groups such as nitrate[43], sulphonyl chloride[44], etc.[21] produces the same

† The splitting of ν_{as} observed in the spectrum of trinitroethanol[29] is not confirmed by other workers[39-41].

‡ Aliphatic–aromatic trinitromethyl derivatives form an exception[31].

effect as that of the nitro-group: a quite intense polarised ($\rho \simeq 0.4$) band appears in the region of 1400 cm^{-1}, although there can be no question of any mechanical interaction in the case of nitrates, sulphonyl chlorides, etc. It is not surprising, therefore, that other workers[5,6,8-10,15,19-22,27,31,32,34,35,45], including Wittek in a later paper[14], assign only one, lower-frequency band to ν_s in nitromethane and its homologues. The correctness of this assignment is confirmed by experimental data on the infrared spectra of nitromethane labelled with ^{18}O [46]: the introduction of "heavy" oxygen into nitromethane produces a shift in only one, the longer-wavelength band (from 1375 to 1357 cm^{-1}), while the band at 1396 cm^{-1} remains unchanged.

The origin of the splitting of ν_s of the nitro-group in *gem*-dinitro- and 1,1,1-trinitro-compounds is less certain. One absorption band in the infrared spectra of these compounds is usually assigned to ν_s[28,31,32,34,35,37-41,47-59]. Several authors, however, assign two bands to ν_s of the nitro-group[14,25,29,30,60], such assignment again being based on the Raman spectra. The second band in the infrared spectra§ often appears as a shoulder[25]. Furthermore, theoretical calculation has shown[60] that only a small part of the splitting (which totals 50–60 cm^{-1}) can be attributed to mechanical interaction. (Most authors[14,25,29] explain the splitting of ν_s of the nitro-group by mechanical interaction of the vibrations.) It seems to the Reviewer that Raman spectral data cannot be used unequivocally for interpreting ν_s of the nitro-group. Thus the Raman spectrum of chloropicrin contains two intense bands (1306 and 1345 cm^{-1})[12] having similar degrees of depolarisation ($\rho \simeq 0.5$). Nevertheless, in this case all authors assign only one of these bands to ν_s[12,14,17,18,26,27]. Hence the appearance of a second intense polarised band ($\rho \simeq 0.40$) in the Raman spectrum is still not an unambiguous criterion that it is due to a symmetric stretching vibration of the nitro-group.

Assignment of the remaining absorption bands to definite modes of vibration can be found in Refs. 9, 10, 18–26, and 42, but these bands are rarely used in everyday practice, and therefore will not be discussed here.

Useful information on the general form of the infrared spectra of certain nitro-compounds or on the ranges of absorption characteristic of the nitro-group can be found in Refs. 61–68.

III. CALCULATION OF MECHANICAL MODEL OF VIBRATIONS OF NITROALKANES. ELECTRO-OPTICAL PARAMETERS OF NITROMETHANE

The first calculations of the vibration modes of nitroalkanes were made independently in three papers[7-9]. Mathieu and Massignon[7] and Bogdan and Stefănescu[8] calculated for a planar tetra-atomic model of $C-NO_2$ with symmetry C_2. In both cases the frequencies obtained agree well with experiment. Wells and Wilson's[9] calculation regarded nitromethane as two non-bonded groups NO_2 and CH_3, having symmetry C_{2v}. Two years later Wilson[10] refined this calculation, having supplemented the experimental data with the spectrum of trideuteronitromethane; he assumed that neither the geometry nor the potential function of the molecule is changed when hydrogen is replaced by deuterium.

Popov and Shlyapochnikov[60,69] have recently made a fundamental calculation for nitroalkanes (nitromethane, nitroethane, 1,1-dinitroethane, and trinitromethane). They computed the frequencies and modes of the normal vibrations for the mononitroalkanes[69], and determined the sensitivities of the frequencies to variation in the force constants. They conclude[69] that vibrations of the $C-NO_2$ fragment are uncharacteristic in frequency and in mode. The most characteristic is the ν_{as} vibration of the nitro-group. This conclusion does not agree with the views of Müller and Nagarajan[70], who conclude, though from a simpler calculation of a planar tetra-atomic model of $C-NO_2$, that the methyl group has little effect on the skeletal vibrations of the $C-NO_2$ grouping.

The mechanical problem for the 1,1-dinitroethane and trinitromethane molecules has not, in the view of the authors themselves[60], been solved with sufficient accuracy. Nevertheless, their analysis leads them to the conclusion that the force field of the $C-NO_2$ group undergoes no great change on passing from nitromethane to the above molecules. Interaction of the nitro-groups in polynitroalkanes does not directly affect the elastic properties of the nitro-group, but is apparent only on adjacent CN bonds¶.

Solution of the mechanical problem for the nitromethane molecule[69] and experimental data on the absolute integrated intensities of the infrared bands of nitromethane and trideuteronitromethane vapours enabled Popov and Shlyapochnikov[71,72] to determine the electro-optical parameters of the nitro-group—the dipole moments of the bond and their derivatives with respect to the vibrational coordinates. From the results it is concluded[71,72] that the dipole moment of nitromethane is determined in considerable measure by that of the carbon–nitrogen bond (μ_{CN} = 1.8 D). Somewhat later an analogous electro-optical problem for nitromethane was solved by Singh[73]. However, he considers that the differences between dynamic and static dipole moments are due to errors in the calculations, and that the agreement between them can be improved by taking into account the suggestions made by Sverdlov[74,75].

IV. INTENSITY OF ABSORPTION BANDS OF NITRO-COMPOUNDS

As already noted, the nitro-stretching bands are quite intense: the molar extinction coefficient ϵ (M^{-1} cm^{-1}) for the ν_{as} band in nitroalkanes is ~ 500 [28,29,76-79] per nitro-group, whereas ϵ for ν_s of the nitro-group is ~ 100 [28,29,78]. The appearance of conjugation is accompanied by some decrease in $\epsilon\nu_{as}$, whereas $\epsilon\nu_s$ increases[28,29,80]. Data on the integrated intensities† of the nitro-stretching vibrations (ν_{as} and/or ν_s) will be found in Refs. 29, 56, 60, 73, 80, 83–86‡. The integrated intensity A_{as} of the antisymmetric vibration of the nitro-group is found to be additive[29,60,91], varying little with the structure of the radical.

§ Unfortunately the type of spectrum (infrared or Raman) is not indicated in Ref. 30, nor the intensity and degree of depolarisation of the bands.

¶ The invariability of the elastic properties of the nitro-group is not confirmed (see below) by the dependence of ν_{as} for the nitro-group on the inductive effect of the substituent[31].

† For the theory of integrated intensities, their experimental determination, and conversion coefficients between various intensity scales see, for example, the reviews[81,82].

‡ Data on the integral intensities of the nitro-stretching vibrations in nitro-aromatic compounds will also be found in Refs. 87–90.

On the other hand, the intensity A_S of the symmetric vibration depends substantially on the structure of the radical[29,80,83,86,91], and several workers have suggested[83,86,91] that A_S should be used as a measure of conjugation between the nitro-group and the rest of the molecule in conjugated and aromatic nitro-compounds.

Intensities of other bands have been measured only for nitromethane (at ~ 1105[92], 915[73,92], and 656[73] cm^{-1}). The temperature variation in the intensities of two bands (1103 and 917 cm^{-1}) of nitromethane has also been investigated[92].

V. EFFECT OF STATE OF AGGREGATION AND SOLVENT ON INTENSITY AND POSITION OF ABSORPTION BANDS OF NITRO-COMPOUNDS. HYDROGEN BONDS

The effect of the solvent on the position of the nitro-stretching bands has been examined in only four papers[78,84,93,94]. All the authors conclude that solvents produce only slight shifts in the frequencies of both bands§. More detailed examination of the effect of the solvent on the position of the absorption bands indicates a fairly substantial effect on ν_{as} with change in the state of aggregation (transition from the gaseous state to the liquid) and on passing from the gaseous state to solutions, but this effect reduces to zero as nitro-groups accumulate on the same carbon atom. Nevertheless, the values of ν_{as} and ν_S of the nitro-group are almost unaffected in "inactive"¶ solvents[31]. Values of ν_S diminish somewhat on passing from liquid mononitro-compounds to their solutions. Table 1 gives examples illustrating the influence of the solvent on the frequencies of the nitro-group.

The integral intensity of the absorption bands due to the nitro-group also is almost unaffected by the solvent[79,84]. It is interesting that, in contrast to the frequencies, the intensity of the antisymmetric nitro-stretching vibration A_{as} in nitromethane is the same, within the limits of experimental accuracy, in the gas and in solution: $A_{as,soln}/A_{as,gas} = 1.04 \pm 0.06$.[85]

Study of the intramolecular† and the intermolecular hydrogen bonding of nitro-alcohols and nitro-amines, and also of intermolecular hydrogen bonding between various proton-donors and nitro-compounds, is very closely linked with questions of the effect of the solvent on the vibration frequencies of nitro-compounds.

Urbanski[97-100] assumed that nitro-alcohols and nitro-amines form six-membered rings by interaction of the nitro-group with the hydroxyl or the amino-group. He considered that this hypothesis was supported by the displacement of the nitro-stretching vibrations to lower frequencies on the introduction of hydroxymethyl or an amino-group. This effect was intensified by the introduction of two or three hydroxy-groups. Later investigators have assumed that such an effect[31,36,39,40,78,84], if it exists at all, is usually‡ too small to be determined from the positions of ν_{as} and ν_S for the nitro-group. In the application of infrared spectroscopy to the study of hydrogen bonds in a series of nitro-compounds, therefore, the variation in the position, form, intensity, and half-width of the absorption band due to A–H stretching vibrations was determined (AH being a proton-donor compound)[39,40,78,102-108]. The investigations show that the nitro-group is a weak acceptor of hydrogen atoms[40,78,102,103,105,107].

Table 1. Position of nitro-stretching bands for nitromethane and its derivatives in different states of aggregation and solvents.

Compound	Solvent (state)	Frequencies, cm^{-1}			
		ν_{as}	$\nu_{as} - \nu_{as,av}$	ν_S	$\nu_S - \nu_{S,av}$
CH_3NO_2 [a]	gas	1582 [9,60]	19	1384 [9,60]	11
	gas	1586 [15]	23	1377 [15]	4
	liquid	1567 [34]	4	1379 [34]	6
	liquid	1563 [93]	0	1376 [93]	3
	n-butylamine	1548 [93]	−15	[b]	—
$CH_3CH(NO_2)_2$ [d]	gas	1593 [60]	12	1343 [60 c]	10
	liquid	1582 [52]	1	1331 [52]	−2
	CCl_4	1581 [29]	—	1333 [29 c]	—
$HC(NO_2)_3$ [d]	gas	1600 [60]	−8	1305 [60 c]	6
	liquid	1597 [34]	−11	1307 [34]	8
	CCl_4	1608 [40]	—	1299 [40]	—
$C(NO_2)_4$ [e]	gas	1648 [42]	6	1278 [42]	11
		1618 [c]	5		
	liquid	1648 [42]	6		
		1618 [c]	5	1272 [42]	5
	$CHCl_3$	1642 [29]	—		
		1613 [c]	—	1267 [29]	—

(a) The frequencies $\nu_{as,av}$ and $\nu_{S,av}$ have been taken as 1563 and 1373 cm^{-1} respectively, the mean values for a solution of nitromethane in carbon tetrachloride[46,78,84,93].

(b) Region of strong absorption by the solvent.

(c) The authors assume that ν_S is split, and they give values for two bands (see above). Only the longer-wavelength component has been taken here.

(d) The means $\nu_{as,av}$ and $\nu_{S,av}$ have been taken to be the corresponding values of ν_{as} and ν_S for the compounds in carbon-tetrachloride solution.

(e) The means $\nu_{as,av}$ and $\nu_{S,av}$ have been taken to be the corresponding values for a solution of tetranitromethane in chloroform.

On the basis of infrared data Flett assumed[104] that 2-nitroethanol contained only intermolecular hydrogen bonds, whereas Krueger and Mettee consider[103] that an intramolecular hydrogen bond is formed between hydroxy- and nitro-groups in 2-nitro-alcohols, which stabilises the gauche form relative to the *trans*-form.

§ Small shifts in the frequencies of the nitro-group under the influence both of different solvents and of the state of aggregation are maintained also in a series of aromatic nitro-compounds[95].

¶ "Inactive" solvents are those which do not form complexes with the compounds under investigation.

† Tichy[96] has reviewed the use of infrared spectroscopy to detect an intramolecular hydrogen bond in organic compounds. However, he pays little attention to the formation of hydrogen bonds in nitro-compounds.

‡ Exceptions can be found in two papers. Ungnade et al.[93] found a shift of 15 cm^{-1} for ν_{as} of the nitro-group in n-butylamine solutions. This effect became considerably weaker on passing to solutions of nitromethane in n-hexylamine, and was completely absent in its solutions in secondary or tertiary alkylamines. The authors of the second paper[101] observed that the position of ν_{as} for the nitro-group remained unchanged on passing from nitro-amines to their hydrochlorides, while the ν_S frequencies changed. This displacement was attributed to formation of an intramolecular hydrogen bond.

Kuhn and his coworkers found[108] that 2-nitroethanol exists both in a *trans*-form and in a gauche form in the gaseous state and in carbon-tetrachloride solution. In the liquid state it is associated by intermolecular hydrogen bonding. It is true, of course, that many assignments in these papers[103,108] are based not on fact but on hypothesis. Urbanski's observation[97-100] of a variation in nitro-stretching frequency is due, in the Reviewer's opinion, to inductive and steric[31] effects (see Section VI). Quantitative results are listed in Table 2.

Table 2. Effect of β-hydroxy-groups on nitro-stretching bands in aliphatic nitro-compounds.

Compound[a]	Solvent (state)	ν_{as}, cm^{-1}	σ*[b]	Eqn.[c]	ν_{calc}, cm^{-1}	$\nu_{as} - \nu_{calc}$, cm^{-1}	ν_s, cm^{-1}	$\nu_s - \nu_s$ nitroalkane, cm^{-1}[d]
$CH_3CH_2NO_2$	$CHCl_3$	1554 [29]	−0.100	(I)	1550	4	1366 [29]	—
$HOCH_2CH_2NO_2$	liquid	1555 [28]	0.20	(I)	1555	0	1370 [28]	−4
$CH_3CHClNO_2$	liquid	1571 [24]	0.95	(II)	1565	6	1355 [24]	—
$HOCH_2CHClNO_2$	liquid	1571 [36]	1.25	(II)	1570	1	1353 [36]	−2
$CH_3CHBrNO_2$	liquid	1567 [24]	0.90	(II)	1564	3	1354 [24]	—
$HOCH_2CHBrNO_2$	liquid	1566 [36]	1.20	(II)	1569	−3	1353 [36]	−1
$CH_3CH(NO_2)CH_3$	liquid	1553 [45]	−0.19	(II)	1547	−6	1357 [45]	—
$HOCH_2CH(NO_2)CH_2OH$	CH_2Cl_2	1560 [40]	0.40	(II)	1556	4	1361 [40]	4
$(CH_3)_3CNO_2$	liquid	1538 [45]	−0.30	(III)	1535	3	1344 [45]	—
$CH_3C(NO_2)(CH_2OH)_2$	CH_2Cl_2	1543 [40]	0.30	(III)	1547	−4	1347 [40]	3
$(HOCH_2)_3CNO_2$	paraffin oil	1555 [39]	0.60	(III)	1553	2	e	—
$(HOCH_2C(NO_2)(C_2H_5)CH_2)_2-\overset{+}{N}H_2Cl^-$	paraffin oil	1563 [100]	0.89	(III)	1559	4	1342 [100]	2
$CH_3C(NO_2)_2CH_3$	liquid	1575 [34]	1.53	(V)	1572	3	1330 [34]	—
$HOCH_2C(NO_2)_2CH_3$	CH_2Cl_2	1577 [39]	1.83	(V)	1576	1	1326 [39]	−4
$HOCH_2C(NO_2)_2CH_2OH$	CH_2Cl_2	1580 [40]	2.13	(V)	1581	−1	1328 [40]	−2

(a) Nitroalkanes given for comparison.

(b) Necessary values of σ* taken mainly from Ref. 109. Value of σ* for the nitro-group taken from Ref. 110; and $\sigma^*_{RNH_2CH_2^+}$ calculated from values of σ_I.[111]

(c) For equations used in calculation see Table 3.

(d) This column gives the difference between ν_s for the given nitro-alcohol and ν_s for the corresponding nitroalkane.

(e) Values of ν_s not given here, since the papers show a significant lack of consistency in their values[97,98].

This conclusion is supported also by the fact that the absorption band ν_{as} of the nitro-group in nitromethane is almost identical in methanol and in carbon tetrachloride[78], although the latter is an "inactive" solvent, whereas nitromethane forms intermolecular hydrogen bonds with methanol. In other words, the ν_{as} frequency of the nitro-group remains unchanged independent of the presence or the absence of hydrogen bonds, provided that the inductive and steric effects of the nitro-compound remain constant.

β-Nitro-alcohols are capable of partial association in solvents such as carbon tetrachloride[105] or of the formation of stable intermolecular complexes with pyridine[39,106]. In all cases the association constants of the complexes increase with increase in the number of β-nitro-groups[39,105,106].

In concluding this Section we may note several investigations in which nitromethane has been used as solvent, the second component (the proton donor) being water[112-114], phenol[115,116], or a derivative of the latter[116]. Nitromethane has been investigated as solvent also in study of the integral intensity A_{CN} of the C≡N stretching band in benzonitriles and the dependence of A_{CN} on the Hammett σ-constant[117], and also in study of the dependence of the integrated intensity and the half-width of the chloroform band at ~ 760 cm^{-1} on the nature of the solvent[118].

VI. RELATION BETWEEN POSITION OF BANDS DUE TO NITRO-STRETCHING VIBRATIONS AND STRUCTURE OF THE NITRO-COMPOUNDS

A relation between the positions of symmetric and antisymmetric nitro-stretching bands has been sought by several workers. Some have observed[28,95,119,120] a linear relation between ν_{as} and ν_s, although two kinds of straight lines—for electronegative and for electropositive substituents—are present with aromatic nitro-compounds[28,95,120]. Only Flett[90] observes that such a relation does not exist. Iogansen and Litovchenko[91] consider that "the stretching frequencies of the nitro-group correlate poorly with the structure of the molecular residue if they are examined separately and all nitro-compounds are covered". These workers therefore propose to correlate

$$\nu_{av} = \frac{\nu_{as} + \nu_s}{2} \text{ with } \Delta\nu = \nu_{as} - \nu_s.$$

This is regarded[91] as dividing the nitro-compounds into classes, although there is no relation at all between ν_{av} and $\Delta\nu$ (these quantities are discussed below).

Attempts have also been made to find a correlation between ν_{as} of the nitro-group and the effective electronegativity χ of the α-carbon atom[35,121]. A linear relation was demonstrated between these parameters.

Finally, several authors have sought a relation between ν_{as} for the nitro-group and the Hammett and Taft σ-constants[28,31,72,119,120,122-126]. Campbell and Gilow[127] made a theoretical examination of the relation between the σ-values and the shift $\Delta\nu$ in the absorption bands, and discovered the relation

$$\Delta\nu \frac{hC}{2.3\,RT} = -\rho \cdot \sigma - \frac{\Delta(\Delta S)}{2.3\,R} \qquad (1)$$

where h is Planck's constant, C the velocity of light, R the gas constant, T the absolute temperature, ρ a constant, σ the inductive constant of the substituent, and $\Delta(\Delta S)$ a measure of the change in entropy. From this formula a linear relation is to be expected between σ and the shift (in cm^{-1}) in the absorption bands, provided that the term $\Delta(\Delta S)$ is constant. This condition is satisfied if the effect of the solvent is excluded or if it remains constant for a given reaction series. The second, not unimportant condition determines the choice of reaction series. Both conditions were observed in investigations[28,31,72,119,120,122-126] where a linear relation was found between ν_{as} and the Taft and Hammett σ-values. As example Table 3 is taken from a paper[31] in which a large number of nitro-compounds were used to find relations between ν_{as} and the σ*-values.

From the data in Table 3 and the effect of conjugation on the asymmetric nitro-stretching frequency Slovetskii[31] concludes that this frequency is influenced by the inductive and steric effects and also by conjugation. The influence of the steric effect is evident only on passing from nitro-compounds containing one or two α-hydrogen atoms to compounds which do not contain them. The role of the inductive effect has been discussed above. In the simplest cases the effect of conjugation is additive. α-Fluorine atoms exert only an inductive effect. The experimental results[17,18,128-138] do not reveal the presence of a steric or other specific effect.

Analysis of the influence of various factors on the position of the symmetric nitro-stretching frequency in a series of aliphatic nitro-compounds led Slovetskii[31] to the conclusion that the main factor is the steric effect. The shifts in the ν_s frequencies due to the steric effects of different substituents are additive, being dependent on the volume of the substituent but independent of its electron-accepting or donating properties. The inductive effect and the conjugation factor have hardly any influence on the position of ν_s for the nitro-group.

Table 3. Dependence of antisymmetric nitro-stretching frequency ν_{as} on inductive effect σ^* of substituent[31]: $\nu_{as} = \nu_0 + \rho\sigma^*$.

Reaction series[a]	ν_0, cm^{-1}	ρ	Limits ν_{as}, cm^{-1}	Limits σ^*	r[b]	s[c]	Quantity of cpd.
(I) RCH_2NO_2, where R = alkyl, substituted alkyl, or electronegative substituent	1552	16	1578 1546	1.05 −0.15	0.77	4.5	77
(II) $R'R''CHNO_2$, where R', R'' = alkyl, substituted alkyl, electronegative substituent (other than NO_2), or any combination thereof	1550	16	1590 1548	2.15 −0.26	0.85	6.9	74
(III) $R'R''R'''CNO_2$, where R', R'', R''' = alkyl, substituted alkyl, electronegative substituent (other than NO_2), or any combination thereof	1541	20	1610 1534	3.15 −0.37	0.96	6.2	42
(IV) $RCH(NO_2)_2$, where R = alkyl, substituted alkyl, or any electronegative group	1556	13	1608 1570	3.46 1.60	0.85	4.5	24
(V) $R'R''C(NO_2)_2$, where R', R'' = alkyl, substituted alkyl, any electronegative group, or combination thereof	1547	16	1630 1572	5.19 1.53	0.96	3.9	42

(a) All kinds of nitro-compounds, containing any α-substituent other than fluorine, have been used. α-Fluoro-nitro-compounds fall into the reaction series in which a hydrogen atom(s) is present instead of the fluorine atom(s)[31].

(b) r = correlation coefficient.

(c) s = standard deviation.

Thus the positions of the nitro-stretching bands (ν_{as} and ν_s) depend to different extents on steric, inductive, and conjugation effects. Hence the quantities $\Delta\nu = \nu_{as} - \nu_s$[34,91] and $\nu_{av} = \frac{1}{2}(\nu_{as} + \nu_s)$ are fairly random quantities, and it is not surprising, therefore, that no relation was found[91] between them. Contradictory views are held concerning the relation between ν_{as} and ν_s.[28,90,95,119,120]

VII. ABSORPTION BANDS DUE TO ANIONS OF MONO- AND POLY-NITRO-COMPOUNDS§

1. Anions of Mononitro-compounds

The infrared spectrum of the sodium salt of 1-nitropropane was first determined by Mathieu and Massignon[5]. Comparison of the infrared and Raman spectra of these compounds enabled the strong band at 1586 cm^{-1} to be assigned to the C=N bond. These workers also noted that the characteristic frequencies of the nitro-group and also of the carbon–nitrogen single bond disappear on passing from 1-nitropropane to its sodium derivative.

A complete assignment of the infrared absorption bands due to salts of nitromethane[139-141] and 2-nitropropane[139] has been made much more recently. Jonathan[139] concludes from the spectral data that the anions have a planar structure with the carbon–nitrogen bond order close to 2: $[CH_2{=}NO_2]^-Na^+$ and $[(CH_3)_2C{=}NO_2]^-Na^+$. Such a structure is supported by all the spectral data and by molecular-orbital calculation. Brookes and Jonathan[140] used the sodium salt of trideuteronitromethane and improved the assignments of ν_s of NO_2^- (the charged nitro-group) in the infrared spectrum of the sodium derivative of nitromethane. Yarwood and Orville-Thomas[141] consider, contrary to the opinion of Jonathan and Brookes[139,140], that the carbon–nitrogen bond in this sodium derivative is close to a single bond and that the anion has a non-planar structure. The authors[141] arrive at this view—erroneous¶ in the Reviewer's opinion—as a consequence of the unsubstantiated statement that the position of carbon–hydrogen stretching vibrations depends solely on the type of hybridisation. All the other investigators[143-148] have found, in the infrared spectra of salts of mononitro-compounds, bands corresponding to a C=N double bond. Moreover, Buczkowski and Urbanski[144] even found two bands (~ 1660 and 1600 cm^{-1}) corresponding to C=N stretching vibrations in the salts of primary nitroalkanes, on which they based the hypothesis that the salts are able to exist in two isomeric *cis*- and *trans*-forms. However, this view is not consistent with the experimental results† (the positions of the absorption bands due to a C=N bond differ by ~ 15 cm^{-1},[149] not by 60 cm^{-1}, in *cis–trans* isomers). Furthermore, account must be taken of the hygroscopic nature of the salts of mononitro-compounds‡ and of the possible appearance of a band at ~ 1660 cm^{-1} due to bound or absorbed water[150].

The conditions of preparation of specimens for determining their infrared spectra were not specified in Ref. 144. Feuer et al.[145] made assignments of stretching vibrations of the charged nitro-group NO_2^- in the salts of nitroalkanes, α-nitro-ketones, and α-nitro-nitriles, and Kerber and Chick[147] in a nitrocyclopentadiene salt. Table 4 gives assignments in salts of mononitro-compounds made by various workers.

2. Anions of Polynitro-compounds

Brown[28] assigned two absorption bands in the infrared spectrum of the potassium salt of dinitroethane to stretching vibrations of the charged dinitromethyl group

§ We apply the term polynitro-compounds to compounds having at least two nitro-groups attached to the same carbon atom.

¶ The planar structure of the nitromethane anion and the presence of a C=N double bond (the presence of vinyl hydrogen atoms) is supported by the results of another independent method—nuclear magnetic resonance spectroscopy[142].

† The *cis–trans* isomerism of salts of mononitroalkanes in solution is not confirmed by n.m.r. spectroscopy[142].

‡ Jonathan[139] emphasises that the salts which he studied were hygroscopic, and therefore the infrared spectra of the sodium salt of nitromethane varies substantially between specimens prepared with and without the use of a drying chamber.

(ν_{as} = 1242 and ν_s = 1151 cm^{-1}). Later investigators[37,49,53,151-153] note that, on passing from polynitro-compounds to their salts, bands characteristic of nitro-stretching vibrations (see above) disappear from the infrared spectra, while several new bands appear at ~ 1480, ~ 1200, and 1120 cm^{-1}. The appearance of these bands is attributed to vibrations of the dinitromethyl anion[37,49,53,151-153] and of the anion of trinitromethane[151-153], but no assignments are given. Kaplan[154] made empirical assignments for salts of polynitro-compounds by analogy with the covalent nitro-group. He assigned the band at 1269 ± 9 cm^{-1} to antisymmetric N–O stretching vibrations, and that at 1173 ± 10 cm^{-1} to the symmetric vibrations. Kamlet et al.[155] and Lippincott et al.[156] made more justified assignments of bands to vibrations of the dinitromethyl anion using the spectrum of potassium deuterodinitromethane. The latter authors[156] also adduce data on the Raman spectra of the dinitromethane anion and its deuterated analogue. Comparison of the assignments[28,154-159] shows that they do not completely coincide. A somewhat special position in this series is occupied by the work of Singh[157], whose assignments differ from those proposed by other workers[155,156] for the spectrum of potassium dinitromethane.

Slovetskii et al.[158] conclude from infrared band intensity data that the above bands are due to di- and tri-nitromethyl groups, and can be classed as group absorption bands of the corresponding anions. However, the results available at present do not enable a complete assignment to be made in the vibrational spectra of anions of polynitro-compounds. It has been concluded[159] on the basis of calculation that almost all frequencies of polynitro-carbanions are non-characteristic, 2–5 angles and bonds being involved in each vibration. Yet the calculation[159] involved force constants and in some cases bond lengths and angles of the unionised nitroalkanes, which evidently diminishes the reliability of the results. The suggested[158] specific character of the group bands due to the anions of *gem*-dinitro-compounds and trinitromethane is supported by published data[37,154,159,160]: even the presence of conjugation has hardly any effect on the position of these bands§.

Studies have been made of the effect of the solvent on the infrared spectra of the anions of *gem*-dinitroalkanes and trinitromethane[162-164]¶. Integrated and peak intensities have been measured, and determinations also made of the half-width and the exact position of the group absorption bands due to the trinitromethyl, dinitromethyl, and *gem*-dinitroethyl anions both in the crystalline state (compressed with potassium bromide) and in protic and aprotic solvents.

The investigation showed that, for a given anion, the solvent, the possible formation of ion pairs, and the nature of the cation do not influence the integrated intensity or the shape of the bands. Nor does the nature of the cation affect the position of the bands in solutions. However, change in the state of aggregation—transition from the crystalline salt to its solutions—and in the solvent affects the position of the group absorption bands, this effect being different with different bands. The character of the frequency shift as a function of the nature of the solvent led to the conclusion[162,163] that this shift was due to specific solvation of the polynitro-carbanions.

Briefly summarising available data, we can say that, in the salts of mononitro-compounds, the presence of a C=N bond has been shown fairly convincingly, and reliable assignments have been made of the frequencies due to the CNO_2^- grouping. In the salts of polynitro-compounds, however, only the group frequencies have been reliably assigned. The assignments in anions even of the same polynitro-compounds are contradictory, and require further investigation.

Table 4. Assignments of $C{=}NO_2^-$ stretching vibrations (cm^{-1}) in salts of mononitro-compounds.

Sodium salt of	Solvent (state)	C=N bond	N–O in NO_2^- as	N–O in NO_2^- s	Ref.
1-Nitropropane	paraffin oil	1586 1650 1599 1600	a a 1289	a a 1170	5 144 145
Nitromethane	emulsion in CCl_4	1618	1277 1261	1031 1016	139
	paraffin oil	1582	1272 1261	983	140
	paraffin oil	b	1580	1278 1263	141
		1587	1272	1174	145
Trideuteronitromethane	paraffin oil	1553	1233 1217	899	
2-Nitropropane	ethanol	1604	a	a	143
	paraffin oil	1608	1176 1166	944	139
		1605	1295	1168	145
Primary mononitro-alkanes	paraffin oil	1665—1635 1609—1589 1603—1587	a 1316—1272	a 1175—1555	144 145
Mononitro-compounds (K salts)	paraffin oil	a 1663—1592	1253—1205 a	1156—1124 a	145 146
Nitrocyclopentadiene	paraffin oil	1548	1368	1192 1175	147
α-Nitromethylbenzyl alcohol	paraffin oil	1560	c	c	148

(a) No assignments are given for these vibrations.

(b) The authors deny the presence of a double bond in the salt.

(c) The paper gives several absorption bands—at 1330, 1270, 1139, 1117, 988, and 955 cm^{-1}—which the authors attribute to antisymmetric and symmetric stretching vibrations of the NO_2^- group.

VIII. USE OF INFRARED-SPECTROSCOPIC METHODS TO ESTABLISH THE STRUCTURE OF ORGANIC NITRO-COMPOUNDS

1. Analytical Application

Consideration of the infrared spectra of nitro-compounds and their salts indicates that the main differences in the spectra which are suitable for analytical purposes occur in the region of nitro-stretching vibrations and group absorption bands due to nitro-carbanions. These differences consist in a certain regularity in the position and intensity of the bands depending on the structure of the compounds.

§ Conjugation in potassium bromodinitromethane is confirmed by X-ray examination[161].

¶ Shokhor et al.[164] do not give experimental data, but merely mention that the infrared spectra of solutions of the alkali-metal salts of trinitromethane exhibit a close similarity independently of the cation and the solvent.

Thus primary and secondary nitroalkanes can be distinguished from tertiary nitroalkanes by the bands due to antisymmetric and symmetric stretching vibrations of the nitro-group, and primary from secondary compounds by the symmetric nitro-stretching band[28,34,45].

A detailed examination of published data[165-189] supports this conclusion, with substances belonging to this group which have functional substituents quite remote from the nitro-group (in any case so long as the inductive effect does not operate[31]). The accumulation of nitro-groups on the same carbon atom leads to shifts in the antisymmetric and symmetric vibrations of the nitro-group to higher and lower frequencies respectively[34], which can also be utilised for analytical purposes[27,28,34,59,182,183,190-194]. Another extremely interesting fact is that the difference in frequency between antisymmetric and symmetric nitro-stretching vibrations ($\Delta\nu = \nu_{as} - \nu_s$) is also characteristic[34,91], having approximate values of 180, 250, and 300 cm^{-1} for mononitroalkanes, *gem*-dinitroalkanes, and 1,1,1-trinitroalkanes respectively. Hence this difference also can be used to distinguish among mono-, di-, and trinitro-compounds. However, the difference ceases to be characteristic when we pass to nitro-compounds having a halogen atom or other functional group in the α-position. In this case considerably greater assistance for analytical purposes may be obtained from the dependence of the position of the stretching bands on the structure of the nitro-compounds (see Section VI), in particular the relation between ν_{as} and the σ^*-values[31]. Table 5 gives as examples a few calculations of ν_{as} (based on the equations in Table 3) and of ν_s. For further details see Slovetskii's paper[31].

Table 5. Calculation of positions of ν_{as} and ν_s bands of nitro-group[a].

Compound	State solvent	ν_{as}, cm^{-1}	σ^*[b]	Eqn. (Table 3)	$\nu_{as,calc}$, cm^{-1}	$\nu_{as} - \nu_{calc}$, cm^{-1}	ν_s, cm^{-1}	$\nu_{s,calc}$, cm^{-1}
$CH_2FCH_2NO_2$	liq.?	1557 [195]	0.40	(I)	1558	−1	1370 [195]	1370
$(C_6H_5)_2CCH(NO_2)COOC_2H_5$	CCl_4	1565 [196]	1.04	(II)	1567	−2	1356 [196]	1359
$(CH_3)_2C(NO_2)CH_2ONO_2$	liq.	1550 [197]	0.28	(III)	1547	3	1349 [197]	1346
$CH_3C(NO_2)(CH_2ONO_2)_2$	liq.	1563 [198]	0.86	(III)	1558	5	1350 [198]	1346
$(C_2H_5O_2C)_2C(NO_2)CH_2OH$	liq.	1572 [199]	1.82	(III)	1577	−5	—	—
$H(NO_2)_2CCOOC_2H_5$	liq.?	1588 [200]	2.54	(IV)	1589	−1	—	—
$NC(NO_2)_2CCOOC_2H_5$	liq.?	1610 [200]	3.84	(V)	1608	2	—	—

(a) Experimental data on the positions of the nitro-stretching vibrations can be found in Refs. 201–218 and also in the papers cited earlier.

(b) Values of σ^* taken from Palm's paper[109], and those of σ^* for nitro and nitrate groups from Slovetskii and Fainzil'berg's paper[110]. Several of the σ^*-values can be calculated from those given for σ_I in Charton's paper[111].

A second extremely important fact for the identification of nitro-compounds is the small effect of structure on the integrated intensity of the antisymmetric nitro-stretching vibration[79,91]. This observation can be exploited to determine the number of nitro-groups in compounds of unknown structure[91].

Sometimes there is no need to measure the integrated intensity of a band, a comparison of relative intensities being sufficient, e.g. of ν_{as} and ν_s for the nitro-group[91] or of ν_{as} for two different groups[183]. On the other hand, the intensity of the ν_s band of the nitro-group is considerably dependent on conjugation[29,83,91], another fact which is useful for establishing the structure of nitro-compounds. Furthermore, infrared spectroscopy can be recommended for determining the quantitative composition of mixtures of nitromethane with its simple homologues and analogues—nitroethane, 1-nitropropane, and 2-nitropropane[219].

The transition from nitro-compounds to their anions is accompanied by disappearance of the bands characteristic of the nitro-group and the appearance of a series of bands due to the anions (see Section VII). It must be stressed that the spectrum of polynitro-carbanions is quite characteristic both in its general form and in intensity[162]. The integrated intensities of the strongest bands reach (5–6) × 10^4 cm^{-2} M^{-1} [162] (practical system of units[81,82]). In other words, the presence of an anion can be identified quite reliably from the presence of group absorption bands and measurements of their intensity.

In conclusion we note that, whether in the free form or as the anion, the dinitromethyl group has the same spectral characteristics in the aromatic and heterocyclic series as in the aliphatic series.

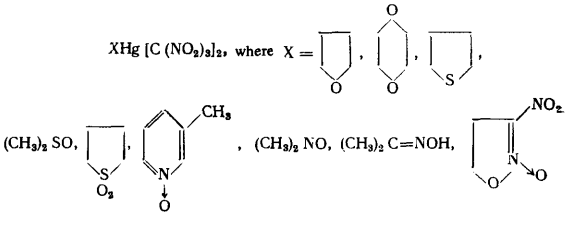
We shall discuss below some examples of the application of infrared spectroscopy to establishing the structure of and elucidating the chemical changes undergone by nitro-compounds and their salts.

2. Structure of Mercury "Salts" of Trinitromethane and Fluorodinitromethane

Infrared spectroscopy has been used to study the structure of the so called mercury salts of trinitromethane and fluorodinitromethane[163,220]. The results confirm that in the crystalline state both "salts" are true organometallic compounds: the spectrum contains bands at 1598, 1312, and 798 cm^{-1} [163,220] corresponding to the trinitromethyl group, and at 1580, 1315, and 835 cm^{-1} [163] corresponding to the fluorodinitromethyl group, while bands characteristic of the corresponding polynitro-carbanion or the covalent aci-form are absent. Bands corresponding to the trinitromethyl anion appear in the infrared spectra of aqueous and dimethylformamide solutions of bistrinitromethylmercury; the proportion of the ionised form diminishes with increase in the concentration of the compound, and may become almost zero on addition of a sufficient amount of the cation involved—Hg^{2+} (as mercuric nitrate)[163]. From these results it is concluded[163,220] that in the crystalline state the so called mercury salts of trinitromethane and fluorodinitromethane are true organometallic compounds, which are capable, under the influence of ionising solvents (protic and aprotic), of dissociating directly into ions without formation of an aci-form.

3. Complexing Power of Bistrinitromethylmercury

Chemical means have been used to isolate the complexes



Study of their infrared spectra showed the presence of frequencies characteristic of the trinitromethyl group—1600 ± 5, 1300 ± 5, and 800 cm^{-1}. [221]

4. Structure of Silver Salts of Polynitroalkanes

Infrared spectroscopy has been used to study the structure of the silver salts of trinitromethane[164,222], dinitroacetonitrile[222,223], dinitromethane[222], and 1,2-dinitroethane[222]. Comparison with the infrared spectra of the mercury and alkali-metal salts of the corresponding polynitro-compounds in the crystalline state have revealed the ionic structure of the silver salts, which are analogues of the alkali-metal salts and differ from the mercury derivatives, which are true organometallic compounds.

In solutions a quite different situation is found. In aqueous solutions of silver salts of polynitro-compounds Slovetskii and his coworkers[222,223] found that equilibrium was established between the true organometallic compound and the ionic form of the salt. The same conclusion was reached[222,223] from the appearance of bands (in the ranges 1610–1580 and 1330–1300 cm^{-1}) due to covalent tri- and di-nitromethyl groups on the addition of the corresponding cation Ag^+ (as silver perchlorate) to the solution or in the spectra of concentrated solutions (e.g. 20 M [sic] aqueous silver trinitromethane). From the infrared spectra it would seem that no other intermediate forms, such as an aci-form, are involved.

Shokhor et al.[164] studied the silver salt of trinitromethane in water and in various non-aqueous solvents. They found that in water the salt has an ionic structure. As the dielectric constant of the solvent decreases, however, the configuration of the trinitromethyl anion changes, and in benzene and dioxan solutions a band due to the covalent silver salt appears (at 1615 cm^{-1}). The appearance of a covalent form is consistent with the experimental data[222], but the change in configuration of the anion contradicts them. Thus the presence of equilibrium between ionic salt and organometallic compound[222] leads to a similar effect observed by Shokhor et al.[164]—diminution in intensity of the band at 1490 cm^{-1} and increased intensity of that at ~ 1600 cm^{-1}—while the dielectric constant of the solution does not decrease in this work[222]. It is not altogether clear why Shokhor et al.[164] find a displacement of the band in the range 1540–1560 cm^{-1}. This may perhaps be due to strong absorption by the solvent in this range. Unfortunately, these workers[164] give no data on cuvette thicknesses, and it is therefore difficult to assess the correctness of their results.

5. Structure of Salts of Polynitro-compounds with Organic Cations. Inner Salts

Infrared spectral data have been used several times[37,224-228] to assess the structure of salts formed by polynitro-compounds with organic cations.

Slovetskii et al.[224] investigated the salts formed by trinitromethane with 4-amino-1,2,4-triazole bases. The infrared spectra showed that in the crystalline state the salts had an ionic structure, the trinitromethane being present as an anion. This is confirmed by the presence of bands characteristic of the trinitromethyl anion (approximately at 1520, 1280, and 1180 cm^{-1}) and by the absence of bands characteristic of nitro-stretching vibrations in the trinitromethyl group (~ 1600 and ~ 1300 cm^{-1}). It was then concluded from the infrared spectra of the salts that the mobile [hydrogen] atom of trinitromethane reacts with two molecules of 4-amino-1,2,4-triazoles to form the so called "ionogenic structures"†. Examination of the region of amino-stretching vibrations showed that the transition from the free 4-amino-1,2,4-triazoles to their trinitromethyl salts was accompanied by displacement of the N–H stretching vibrations to higher frequencies, whereas protonation of the amino-group would have led to lower frequencies. In other words, this fact supports the view that the amino-group is not involved in salt formation. This is further confirmation, in the opinion of the authors[224], that the proton interacts only with the triazole ring in the crystalline salts of 4-amino-1,2,4-triazole.

From an infrared study Glowiak[225] concluded that the benzenediazonium "salt" of trinitromethane had an ionic structure. In the Reviewer's opinion this conclusion does not follow from the data given by this author[225]. In fact, Glowiak observed bands at 1629, 1374, and 1294 cm^{-1}, close to the bands—at 1623, 1372, and 1294 cm^{-1}—in chlorotrinitromethane and differing considerably from those—at 1529, 1418, 1302, and 1263 cm^{-1}—in the potassium salt of trinitromethane. His line of argument is that the chlorine atom in chlorotrinitromethane is appreciably positive in character, whereas the trinitromethyl group is negative. He regards the situation as similar in trinitromethylbenzenediazonium. One can agree with Glowiak's first assertion[225], that the spectra of chlorotrinitromethane and trinitromethylbenzenediazonium are closely similar. However, the opposite conclusion follows from this: since chlorotrinitromethane is a covalent compound‡, the benzenediazonium "salt" of trinitromethane is also a covalent compound—trinitromethylazobenzene. This conclusion is confirmed by comparing the spectrum of trinitromethylbenzenediazonium with that of the potassium salt of trinitromethane, which is known to be ionic.

The structure of inner salts has been established quite reliably from the infrared spectra for 1-guanidino-2,2-dinitroethane[226] and 2-dinitromethylpyridine[37] in the crystalline state. Zeldine and Shechter[226] reached this conclusion from the absence of the 1587 cm^{-1} band characteristic of the dinitromethyl group. Slovetskii et al.[37] deduced the formation of the internal salt 2-dinitromethylpyridine from the presence of absorption bands characteristic of the dinitromethyl anion (strong 1500, very strong and broad 1235, and strong 1130 cm^{-1}) and the absence of bands at 3000 and at 1575 and 1330 cm^{-1} characteristic of stretching vibrations of C–H and N–O respectively in the dinitromethyl group.

6. Structure of Dinitroacetonitrile Tetrahydrate and its Derivatives

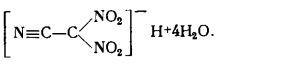
Slovetskii et al.[72,223] used infrared spectroscopy to confirm the structure of dinitroacetonitrile tetrahydrate. This investigation was of fundamental value for the problem of tautomerism in polynitro-compounds.

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† Until the publication of Ref. 224 the formation of an "ionogenic structure" had been observed by Otting[227] only with 1,2,4-triazoles in which the 4-position was unsubstituted.

‡ That chlorotrinitromethane is a covalent compound is confirmed by various kinds of data, e.g. infrared spectroscopy[35], dipole moments[228], etc. Moreover, measurements indicate[228] that the dipole moment of the C–Cl bond is 0.23 D with the negative end of the dipole on the chlorine atom.

The infrared spectrum of the tetrahydrate proved to be identical with those of the sodium and silver salts but different from that of the *O*-methyl ether. This ether was utilised[72,223] as a fixed model compound having the same structural units—the nitro-group in its true form, the presence of a C=N bond, and the absence of a nitro-group in a charged state—as should have been present in a covalent aci-form. From the results obtained it was concluded that crystalline dinitroacetonitrile tetrahydrate had the ionic structure



Another possible ionic structure for the crystalline tetrahydrate—an internal salt—is inconsistent with the infrared spectral data[223].

7. Study of Structure of Salts of 1,1-Dinitroalkanes and Trinitromethane

Slovetskii and his coworkers[151,152] were the first to use infrared spectroscopy to study the structure of salts of polynitro-compounds. From the spectra of a large number of salts (potassium, sodium, ammonium, and lithium) of *gem*-dinitroalkanes and trinitromethane it was found[151,152] that bands corresponding to the C=N bond and also to the nitro-group in true nitro-compounds were absent from the spectra of the anions. This led to the conclusion[151,152] that the salts of 1,1-dinitroalkanes and trinitromethane contain no C=N bond (unlike the salts of mononitroalkanes[5,139,140,143-148]) and no uncharged nitro-groups, in contrast to the true form of nitro-compounds. Hence the conclusion is drawn[151,152] that all the nitro-groups in salts of polynitroalkanes are equivalent and are equally involved in formation of the anion. It is found furthermore[152] that replacement of the cation (potassium, sodium, ammonium) in the crystalline salts has little effect on the absorption bands of the anion, and from 1,1-dinitropropane onwards there are no changes at all in the spectra with different cations.

Subsequent work has shown that the spectral characteristics of the dinitromethyl anion are the same in salts of aromatic and heterocyclic derivatives[37] as in the aliphatic series. Hence the equivalence of the nitro-groups in anion formation is preserved in the aromatic and heterocyclic dinitromethyl derivatives. The equivalence of the nitro-groups in the anion is maintained in salts of dinitroacetonitrile[72,223] and also on passing to solvated anions[158,163], the configuration of the anions being almost unchanged in the crystalline salt and in solution. This conclusion is confirmed by Mel'nikov et al.,[229] who have compared experimental data on the infrared and Raman spectra of the salts of dinitromethyl derivatives, and consider that the configuration of the anions in solution differs little from the configuration in the crystal. Lippincott et al.[156] regard the infrared and Raman spectra of the potassium salts of dinitromethane and its deuterated analogue as indicating that the dinitromethane anion has a planar structure with equivalent nitro-groups.

Singh[157] assumes that the nitro-groups in the dinitromethane anion are not equivalent. However, he supports this structure with several rather artificial assignments, e.g. vibrations of the nitro-group at 1360 and 1125 cm^{-1} instead of ~ 1550 and 1380 cm^{-1}, the C=N frequency 1445 instead of 1650 cm^{-1} as usual, etc. The artificiality of the assignments and in several cases the errors in interpreting the spectrum§ cast doubt on the correctness of the structure ascribed to the dinitromethane anion.

A very large amount of experimental information on the infrared spectra of the salts of polynitro-compounds is given by Kamlet et al.[155] In their opinion 1,1-dinitrocarbanions need not necessarily have equivalent N–O bonds. In particular, the "cationic effect" may lead to non-equivalence of the nitro-groups and hence to broadening or splitting of the absorption bands. It must be stressed that no bands which could have been assigned to a covalent nitro-group are found in any of the spectra of the 32 salts investigated[155].

Non-equivalence of the nitro-groups owing to their rotation about the C–N bond with increase in the order of the N–O bonds and a corresponding increase in the ν_{as} and ν_{s} frequencies to values approaching those of unionised aliphatic mononitro-compounds are assumed only by Shokhor et al.[164] They base this conclusion on the appearance of a band in the range 1600–1500 cm^{-1} in the spectra of alkali-metal salts (from lithium to caesium) of trinitromethane and methyl dinitroacetate and the appearance of a shoulder in the range 1320–1310 cm^{-1} in the case of the trinitromethane salts. However, later work[158,163] has shown that the appearance of a band in the region of 1550 cm^{-1} in the spectrum of the trinitromethane anion is due to splitting of the band at ~ 1515 cm^{-1}. No other bands characteristic of the $C-NO_2$ grouping are observed in the spectra, even in the region of the symmetric nitro-stretching vibration. Incidentally, the equivalence of the nitro-groups in the anions of polynitro-compounds in solution is confirmed by ^{14}N n.m.r. results[230].

8. Some Other Cases of the Use of Infrared Spectra to establish the Structure of Nitro-compounds

By analogy with the structure of anions of *gem*-dinitro-compounds it might be expected that in polynitroimidazoles, e.g. in 4,5-dinitroimidazole, both nitro-groups would be equally involved in formation of the anion. Epishina et al.[231] established from the infrared spectra that with nitroimidazoles anion formation always occurs at one nitro-group with conversion of the imidazole into an isoimidazole ring.

Infrared spectroscopy has been used also to establish the structure of α-nitro-ketones[144,232]. Acyclic α-nitro-ketones are shown to exist in the keto-form, whereas the alicyclic compounds exhibit a tendency to enolisation (up to 30%). Shlyapochnikov et al.[233,234] concluded from the infrared and Raman spectra that in halogenated trinitromethane derivatives the NO and C–Hal bonds are conjugated.

Ivanov and his coworkers have been able to show by means of infrared spectroscopy that the product of the self-condensation of 1,1-dinitroalkanes is a nitrolic ester[56]. They have also completely confirmed the structure of the *O*-ethyl ethers of dinitromethane and trinitromethane[38].

Slovetskii et al.[34] used infrared spectral data to show the effect of one, two, and three nitro-groups on the antisymmetric stretching vibration of C–H in the methyl group. This effect can be traced as far as the fourth

§ Singh[157] did not observe the intense C–H stretching band in the dinitromethane anion[155,156], explaining this fact, and also the unusual assignment, in terms of the theory of resonance.

carbon atom in the case of mononitroalkanes, the fifth in *gem*-dinitroalkanes, and the sixth in 1,1,1-trinitroalkanes.

Einberg[235] used infrared spectral data to assess the structure of 5-dinitromethyltetrazole and its mono- and di-salts. Although the assignments of bands to vibrations of the nitro-groups in the salts can be disputed, his conclusion that the hydrogen atom in the dinitromethyl group is more mobile than the hydrogen atom of the tetrazole ring is not open to doubt.

Table 6. Frequencies characteristic of different types of nitro-compounds*.

Compound	Frequency, cm^{-1}		$\Delta\nu = \nu_{as} - \nu_s$, cm^{-1}	Ref.
$R'CH_2NO_2$	1554±6;	1382±6		34
$R'R''CHNO_2$	1550.5±2.5	1360.5±3.5	180	34
$R'R''R'''CNO_2$	1538.5±4.5	1348.5±4.5		34
$R'HC(NO_2)_2$	1578.5±3.5	1329±2	~250	34
$RC(NO_2)_3$	1600±3	1302.5±4.5	~300	145
$[R'RC(NO_2)]^-M^+$	1253—1205	1156—1124	—	152
$[RC(NO_2)_2]^-M^+$	~1480, ~1210, ~1120		—	152
$[C(NO_2)_3]^-M^+$	~1520, ~1280, ~1180		—	

* R′, R″, R‴ = Alk; R = H or Alk; M^+ = cation. When electronegative substituents are present, the frequencies vary in conformity with Table 3 and Section VI.

Kamlet and Kaplan[236] ascertained by means of infrared spectroscopy the presence of a dinitromethyl anion in a Michael reaction product of unknown structure. Lindenmeyer and Harris[237] detected a low-temperature isomorphous transition in crystalline tetranitromethane.

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In conclusion the Reviewer would like to emphasise yet again the variety of problems and methods of attack in establishing the structure and mutual influence of atoms and groups in nitro-compounds which have been solved by means of infrared spectroscopy. The range of problems begins with establishing the structure of unknown compounds, investigating the effects of conjugation and dissociation processes, and terminates in studying the fine structure of nitro-carbanions and analogues of aci-forms, investigating the specific interaction of anions with the solvent, etc.

The advances made in the technique of obtaining infrared spectra—the use of such acid-stable optical materials as germanium, the improvement of instruments, increase in their accuracy and extension to longer wavelengths of the spectral range recorded—all this considerably broadens the already great possibilities of infrared spectroscopy for solving theoretical and practical problems in organic chemistry.

Table 6 gives the regions of vibration of the nitro-group which are suitable for the identification of nitro-compounds of unknown structure.

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