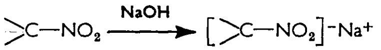
1137. *Spectroscopic Studies. Part I. The Infrared Spectrum and Structure of Sodium Nitromethane.*

By J. Yarwood and W. J. Orville-Thomas.

The infrared spectra of sodium nitromethane and of nitromethane have been studied between 5000 and 250 cm.$^{-1}$. Two possible models for the structure of the nitromethane anion are considered and it is shown that the frequency assignment favours the structure in which an atomic dipole is associated with the carbon atom.

In the presence of alkalis, nitroparaffins form salts. This is in accord with the view, generally held, that CH links, in suitable situations, can be acidic and replaced by metals:



$$>C{-}NO_2 \xrightarrow{\text{NaOH}} [>C{-}NO_2]^-Na^+$$

One would therefore expect sodium nitromethane to have the structure $[H_2C{\cdot}NO_2]^-Na^+$. The infrared spectrum of sodium nitromethane has been examined twice only [1,2] and the results were interpreted as indicating an all-planar structure for the anion (Fig. 1a). Since this is not the only possibility a more extended study has been carried out.

Experimental.—Sodium nitromethane was prepared by Nef's method.[3] Since the salt is insoluble in common spectroscopic solvents the spectrum was obtained from mulls and a

Table 1.

Frequency assignments for sodium nitromethane (in cm.$^{-1}$).

Solid film (from CCl_4)	Nujol mull	Hexachloro-butadiene mull	Strength	Assignment: Jonathan [1]	Assignment: This work
—	—	2957	wsh	—	$2b(CH_2)$
2921 *	—	2923	ms	$\nu_a(CH_2)$	$\nu_a(CH_2)$
2848 *	—	2851	w	$\nu_s(CH_2)$	$\nu_s(CH_2)$
1619	1621	1614	w	—	$b(CH_2) + to\ (CH_2)$
1581	1580	1572	s	$\nu(C{=}N)$	$\nu_a(NO_2)$
1482	—	1482	w	—	$b(CH_2)$
1446	—	1446	ms	$b(CH_2)$	$2w(NO_2)$
1278 1263	1278 1263	1279 1263	s	$\nu_a(NO_2)$	$\nu_s(NO_2)$
— —	1194 1187	— —	vw	$r(CH_2)$	$w(CH_2)$
1033 1018	1033 1019	1033 1018	s	$\nu_s(NO_2)$	$\nu(CN)$
982	984	—	ms	$w(CH_2)$	$tw(CH_2)$
735	736	736	s	$w(NO_2)$	$w(NO_2)$
690 678	689 678	690 678	ms	$b(NO_2)$	$b(NO_2)$
—	536	—	vw	$r(NO_2)$	$r(NO_2)$

* Florube mull.

---

[1] Jonathan, *J. Mol. Spectroscopy*, 1961, **7**, 105.
[2] Fever, Savides, and Rao, *Spectrochim. Acta*, 1963, **19**, 431.
[3] Nef, *Annalen*, 1894, **280**, 267.

solid film deposited by evaporation from a mull. B.D.H. nitromethane was fractionally distilled, the fraction of b. p. 101—101·5° being used.

The infrared spectra were recorded with Grubb-Parsons double-beam grating spectrometers (G.S.2.A, D.M.2) from 5000 to 250 cm.$^{-1}$. The results are given in Tables 1 and 2.

TABLE 2.

Far-infrared spectrum of nitromethane.

Frequency (cm.$^{-1}$)	Assignment	Symmetry class
418	$r(CH_3),B_1–b(NO_2),A_1 = 419$	B_1
375	$b_a(CH_3),B_2–r(CH_3),B_2 = 382$	A_1
350	$b_a(CH_3),B_1–r(CH_3),B_1 = 356$	A_1
287	$b_s(CH_3),A_1 - r(CH_3),B_2 = 297$ $\nu_s(NO_2),A_1–r(CH_3),B_1 = 290$	B_2 B_1

An unsuccessful attempt was made to obtain the Raman spectrum of sodium nitromethane in aqueous solution: the solution was a deep yellow. The Raman spectrum of nitromethane was recorded; it was identical with that already reported.[4]

Models for the Nitromethane Anion.—Two models can be suggested for sodium nitromethane. There is a great deal of evidence that the σ-bonds associated with nitro-groups are coplanar. This view is supported by our analysis of the infrared results and by our molecular-orbital calculations. On this basis the four-atom C·NO$_2$ grouping lies in a plane. The two most probable models are then an all-planar configuration with the carbon atom approximately *sp*^{2}-hybridized (Fig. 1a): this would lead to the possibility of extensive delocalization of the six π-electrons possessed by the system. In the alternative model (Fig. 1b), the carbon atom is approximately *sp*^{3}-hybridized and has two electrons in a hybridized orbital forming an atomic dipole.

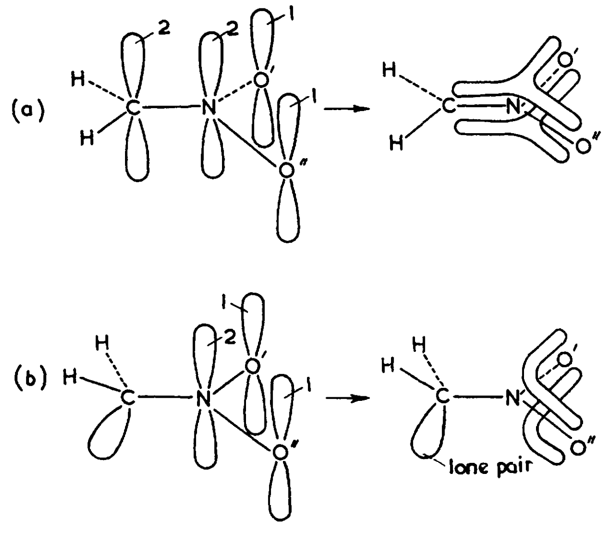


FIG. 1. Two models of the nitromethane anion.

We can differentiate between the alternative models on the basis of the frequencies of the CH$_2$ vibrations. In saturated hydrocarbons[5] the carbons are *sp*^{3}-hybridized and the methylene bands, $\nu_a(CH_2)$, $\nu_s(CH_2)$, and the scissors bending mode, $b(CH_2)$, occur in

---

[4] Smith, Pan, and Nielsen, *J. Chem. Phys.*, 1950, **18**, 706.

[5] Halverson and Williams, *J. Chem. Phys.*, 1947, **15**, 552.

the regions 2926, 2853, and 1465 cm.$^{-1}$ (all $\pm$20 cm.$^{-1}$). However, in molecules with a terminal =CH_2 group where carbon is sp^2-hybridized, the corresponding bands are at 3085, 3025, and 1415 cm.$^{-1}$ (all $\pm$20 cm.$^{-1}$). In keten,[6] in the vapour state, where the attached grouping contains an oxygen atom, the bond-stretching frequencies are even higher, *viz.*, 3166 and 3069 cm.$^{-1}$, whilst the bending frequency decreases to 1388 cm.$^{-1}$.

Bond-stretching CH vibrations are relatively unaffected by changes of state, *e.g.*, for *O*-methylformhydroxamic acid the three CH bands that occur decrease on an average by only 9 cm.$^{-1}$ in going from the vapour to the solid state.[7] The frequencies are also relatively unaffected when the CH bonds occur in an ion: *e.g.*, in the acetaminidinium ion [8] $\nu_s(CH_3)$ has been located at 2880 cm.$^{-1}$. It is possible, then, to take the $\nu(CH_2)$ frequencies as a sensitive measure of the degree of hybridization of the carbon atom (cf. NH_2 frequencies [9]).

The values 2922, 2850, and 1446 cm.$^{-1}$ obtained for the CH_2 vibrations of sodium nitromethane give a clear indication that the carbon atom is approximately sp^3-hybridized and therefore has a non-planar configuration. This being so, the most reasonable model for the nitromethane anion is as in Fig. 1b, the carbon lone-pair forming an atomic dipole and the CN bond being predominantly single in character. The nitro-group with its four π-electrons is expected to be similar in electronic structure to those in the iso-electronic nitramide and other related molecules (see Table 3).

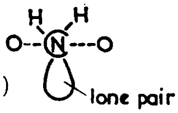
TABLE 3.

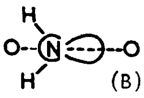
Characteristic frequencies (cm.$^{-1}$) for X·NO_2 vibrations.

X	ν(XN)	$\nu_a(NO_2)$	$\nu_s(NO_2)$	b(NO_2)	r(NO_2)	w(NO_2)	Ref.
F	822	1793	1312	460	570	742	10
OH	886	1710	1320	680	583	765	11
NH_2	1043	1540	1379	709	596	783	12
Me	918	1586	1377	658	477	605	4
CH_2	1033 } 1019 }	1578	1278 } 1263 }	690 } 678 }	536	736	
NMe_2	1016	1568 } 1555 }	1305 } 1298 }	612	—	770	12

The experimental evidence is insufficient to indicate the relative positions of the hydrogen atoms with respect to the NO_2 plane. The extreme configurations would be (A) and (B). The staggered model (A) would probably have the lower energy and thus be more stable

(A)





(B)

than model (B) where repulsion between the atomic dipole and one of the NO bonds is at a maximum. The subsequent discussion will be carried out in terms of structure (A).

Apparently Fever and his co-workers [2] did not study the important CH stretch region: they report bands between 700 and 1600 cm.$^{-1}$ only. Jonathan [1] detected and assigned the ν_a and $\nu_s(CH_2)$ bands but did not discuss the absolute values in terms of the structure of the methylene group.

Frequency Assignment in Sodium Nitromethane.—The sodium nitromethane anion has

---

[6] Arendale and Fletcher, *J. Chem. Phys.*, 1957, **26**, 793.

[7] Parsons, *J. Mol. Spectroscopy*, 1958, **2**, 566.

[8] Davies and Parsons, *Z. phys. Chem.* (*Frankfurt*), 1959, **20**, 34.

[9] Orville-Thomas, Parsons, and Ogden, *J.*, 1958, 1047.

[10] Dodd, Rolfe, and Woodward, *Trans. Faraday Soc.*, 1956, **52**, 145.

[11] Cohn, Ingold, and Poole, *J.*, 1952, 4272.

[12] Davies and Jonathan, *Trans. Faraday Soc.*, 1958, **54**, 469.

twelve fundamental modes of vibration; of these six are associated with the CH_2 group and six are skeletal vibrations.

CH_2 *vibrations.* Frequency values have already been assigned to the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ modes and to the $b(CH_2)$ bending vibration. The remaining vibrations can be described as wagging, twisting, and torsional modes, $w(CH_2)$, $tw(CH_2)$, and $to(CH_2)$. No values have hitherto been assigned to the wagging and twisting modes for a terminal methylene group whose carbon is *ca.* sp^3-hybridized. The order found for $X{\cdot}CH_2{\cdot}Y$ molecules and 1,1-disubstituted ethylenes is $w > tw$. Since these are external modes of vibration their values can be expected to vary widely from molecule to molecule. Lower values are to be expected than in $X{\cdot}CH_2{\cdot}Y$ molecules ($w \sim 1250$, $tw \sim 1200$ cm.$^{-1}$) since the terminal CH_2 group in the nitromethane anion is more flexible, being bonded to one group only. In the spectrum, two weak features, a doublet at 1192—1185 and a peak at 985 cm.$^{-1}$, are thought to arise from the w and $tw(CH_2)$ vibrations. Since the CN bond is predominantly single [$\nu(CN) \sim 1025$ cm.$^{-1}$] the torsional mode, in the lowest-energy levels, will correspond to restricted rotation; the corresponding frequency is therefore expected to be low and beyond the spectral limit studied (250 cm.$^{-1}$). If the band at 1620 cm.$^{-1}$ is assigned to the combination $b(CH_2) + to(CH_2)$, a value of *ca.* 140 cm.$^{-1}$ is obtained for the torsional mode.

Skeletal vibrations.—Three bands associated with bond-stretching vibrations of the " heavy atom " skeleton are expected in the infrared region. Two of these can be described as an antisymmetric and a symmetric stretching mode of the NO_2 group, *viz.*, $\nu_a(NO_2)$ and $\nu_s(NO_2)$; the third, $\nu(CN)$, is more intimately concerned with the stretching of the CN bond.

In the chosen model the CN bond is single and hence the nitro-group, with its four $p\pi$-type electrons, is expected to be very similar in electronic structure to those of the isoelectronic molecules $X{\cdot}NO_2$ ($X = F$, OH, NH_2, or CH_3). The values of corresponding vibrations in these molecules are given in Table 3. On this basis it is relatively straightforward to assign the strong bands centred at 1026, 1580, and 1270 cm.$^{-1}$ to the $\nu(CN)$, $\nu_a(NO_2)$, and $\nu_s(NO_2)$ vibrations. In line with expectation, these bands are amongst the strongest in the spectrum.

The deformation modes of the planar $C-NO_2$ skeleton remain to be accounted for. They consist of the planar bond-bending scissors vibration, $b(NO_2)$, the planar rocking mode, $r(NO_2)$, and the out-of-plane wagging vibration $w(NO_2)$. Again by reference to the isoelectronic series of Table 3 it is possible to allocate frequencies centred at 684, 536, and 736 cm.$^{-1}$ to these vibrations. The proposed frequency assignment is given in Table 1.

If we use the C_{2v} symmetry of the $C-NO_2$ grouping as a basis for classification the vibrations split into the following classes: Class A_1, $\nu(CN)$, $\nu_s(NO_2)$, and $b(NO_2)$; class B_1, $\nu_a(NO_2)$ and $r(NO_2)$; class B_2, $w(NO_2)$. It is interesting that the A_1 bands are all doublets with a spacing of 12—16 cm.$^{-1}$; the B_1 and B_2 bands are single peaks. Splitting of the A_1 bands is probably due to the effect of the crystal field. As expected, the doublets are replaced by single peaks on dissolving the salt in water.

Bond Character.—The bond lengths of sodium nitromethane have not yet been determined. The infrared results indicate, however, that the CN bond is predominantly single, whilst the NO bonds possess a hybrid character. In order to test this qualitative picture a molecular-orbital treatment has been carried out. As a further test of the frequency assignment, bond orders were calculated for the two possible models (Figs. 1a and b). Model (a) has six, and model (b) four, π-electrons distributed as shown in Fig. 1. The L.C.A.O. approximation gives the general molecular orbital:

$$\psi = C_1\phi(C:2p) + C_2\phi(N:2p) + C_3\phi(O':2p) + C_4\phi(O'':2p).$$

For model (b), $C_1 = 0$.

The secular equations were set up by neglecting overlap integrals and resonance integrals between non-adjacent atoms. In accordance with the usual procedure, these equations were solved by expressing all Coulomb, α, and resonance integrals, β, in terms of those of a C atom and a CC bond as found in benzene. In these calculations the values suggested by Anno *et al.*[13] were used. With these parameters the coefficients calculated for the filled molecular orbitals are:

Model (a).				Model (b).		
C_1	C_2	C_3	C_4	C_2	C_3	C_4
0·244	0·683	0·487	0·487	0·669	0·526	0·526
0	0	0·707	−0·707	0	0·707	−0·707
−0·523	−0·508	0·484	0·484			

Coulson's definition[14] leads to values C–N 1·86, N–O 1·17 for the bond orders in model (a), and C–N 1·00, N–O 1·60 for those in model (b).

An interesting and valuable feature of the molecular-orbital assessment is the very different structures predicted for the C–NO_2 grouping in models (a) and (b). The calculated bond orders, in conjunction with the infrared frequency assignments, especially for the $\nu(NO_2)$ and $\nu(CN)$ vibrations, eliminate model (a).

It has generally been accepted that, where the possibility of π-electron delocalization exists, the σ-bonds of terminal XH_2 groups ($X = $ C or N) are coplanar. Such configurations found favour since they allowed maximum overlap between the various $p\pi$-type atomic orbitals, leading to maximum delocalization of π-electrons and hence, it was thought, to minimum energy for the system. This view was supported by early microwave studies which indicated, for example, that formamide[15] had an all-planar structure.

Evidence is now accumulating, however, that the lone-pair electrons of NH_2 are never completely delocalized, even in the most favourable environment. A similar state of affairs exists in the nitromethane anion, *i.e.*, the σ-bonds are pyramidal and the carbon atom possesses lone-pair electrons in an *ca.* sp^3-hybridized orbital (cf. NH_2 groups in amines[9]). This is in sharp distinction to other molecules such as substituted ethylenes and keten where it is well established that the carbon atoms of the CH_2 groups are sp^2-hybridized.

It is believed that this is the first time that a pyramidal configuration with associated atomic dipole has been found for a terminal CH_2 group.

We thank D.S.I.R. for equipment grants and the University of Wales for a Dr. Samuel Williams Studentship (to J. Y.). This research has been sponsored (in part) by the Air Force Cambridge Research Laboratories, OAR, through the European Office, Aerospace Research, U.S.A.F.

THE EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH, WALES.

[*Received, May* 13*th*, 1963.]

[13] Anno, Ito, Shimada, Sado, and Mizushima, *Bull. Chem. Soc. Japan*, 1957, **30**, 638.

[14] Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413; 1951, *A*, **207**, 91.

[15] Kurland, *J. Chem. Phys.*, 1955, **23**, 2202.