Tetrahedron, 1964, Vol. 20, pp. 1519 to 1526. Pergamon Press Ltd. Printed in Northern Ireland

ISOMERIC NITROPROPENES AND THEIR NUCLEAR MAGNETIC RESONANCE SPECTRA

YU. V. BASKOV,*† T. URBAŃSKI, M. WITANOWSKI and L. STEFANIAK
Institute of Organic Synthesis, Polish Academy of Sciences, Warsawa 10, Poland

(*Received* 27 *January* 1964)

Abstract—The NMR spectra of 3-nitropropene, 1-nitropropene and an equilibrium mixture of the two have been analysed. 1-Nitropropene obtained by dehydration of 2-nitro-1-propanol as well as by isomerization of 3-nitropropene is shown to be largely the *trans* isomer. Base-catalysed isomerization of 3-nitropropene leads to an equilibrium of a 3:1 molar ratio of the latter with 1-nitropropene. Correlation between charge distribution in 1-nitropropene (calculated by LCAO method) and the chemical shifts in its NMR spectrum is indicated.

THE three theoretically possible isomeric nitropropenes with a terminal nitro group are:

I $CH_2=CH-CH_2-NO_2$ 3-Nitropropene

IIa CH_3, NO_2, H, H — *cis*-1-Nitropropene

IIb CH_3, H, H, NO_2 — *trans*-1-Nitropropene

Both I and II are known but there is no indication in the literature as to the actual composition of II (two possible geometric isomers), which is usually obtained by dehydration of 2-nitro-1-propanol. In the presence of trace amounts of sodium alkoxides an equilibrium between I and II is established[1] due to isomerization of the nitropropene anion.

A PMR investigation of the nitropropenes has been carried out in order to obtain structural information on II and the equilibrium mixture of I and II.

The NMR spectrum of I is presented in Fig. 1 and Table 1. It is of a complex $ABCD_2$ type, but there are three distinct multiplet groups at $\tau \cong 4$, 4·5 and 5 ppm (relative intensities 1:2:2), attributable to the $=CH-$, $=CH_2$ and $-CH_2-$ protons, respectively. The chemical shifts given were calculated from the first and second spectral moments[2] of the multiplet groups with the assumption that the coupling between the protons at C_1 and C_3 are small in comparison with that across the C_1–C_2 and C_2–C_3 bonds.

$$\underset{\tau = 4{\cdot}42}{\overset{3}{CH_2}}=\underset{\tau = 3{\cdot}80}{\overset{2}{CH}}-\underset{\tau = 5{\cdot}13}{\overset{1}{CH_2}}-NO_2$$
$$\tau = 4{\cdot}49$$

* Paper LXIII from the series "Aliphatic Nitro Compounds"

† On leave from Department of Organic Chemistry, Hertsen Pedagogical Institute, Leningrad D-80, U.S.S.R.

[1] Yu. V. Baskov and V. V. Perekalin, *Dokl. Akad. Nauk SSSR*, **136**, 1075 (1961).

[2] W. Anderson and H. M. McConnell, *J. Chem. Phys.* **26**, 1496 (1957).

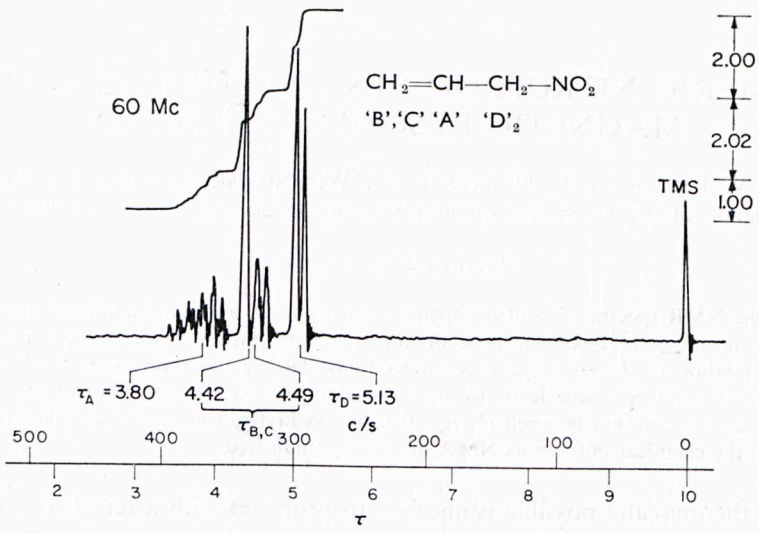


FIG. 1

TABLE 1. 60 Mc NMR SPECTRUM OF 3-NITROPROPENE ($ABCD_2$ system)

CH_2=CH—CH_2—NO_2

'B''C' 'A' 'D'

	ν_i c/s from TMS	L_i normalized ($\Sigma L_i = 5{\cdot}00$)		ν_i c/s from TMS	L_i normalized ($\Sigma L_i = 5{\cdot}00$)
"A"	397·0	0·04	"B", "C"	338·0	1·30
	390·3	0·04		326·8	0·42
	388·2	0·03		318·6	0·28
	385·5	0·03			
	382·0	0·04	"D_2"	295·0	1·08
	381·2	0·04		289·0	0·92
	378·5	0·06			
	374·0	0·09			
	371·5	0·10			
	368·8	0·09			
	365·8	0·14			
	364·1	0·14			
	358·8	0·03			
	356·7	0·13			

The NMR spectrum of II is shown in Fig. 2 and Table 2. The spectrum is of the ABX_3 type where A and B are the olefinic protons and X_3 are the methyl protons. Preliminary analysis of the spectral moments gave approximate values of chemical shifts and coupling constants.

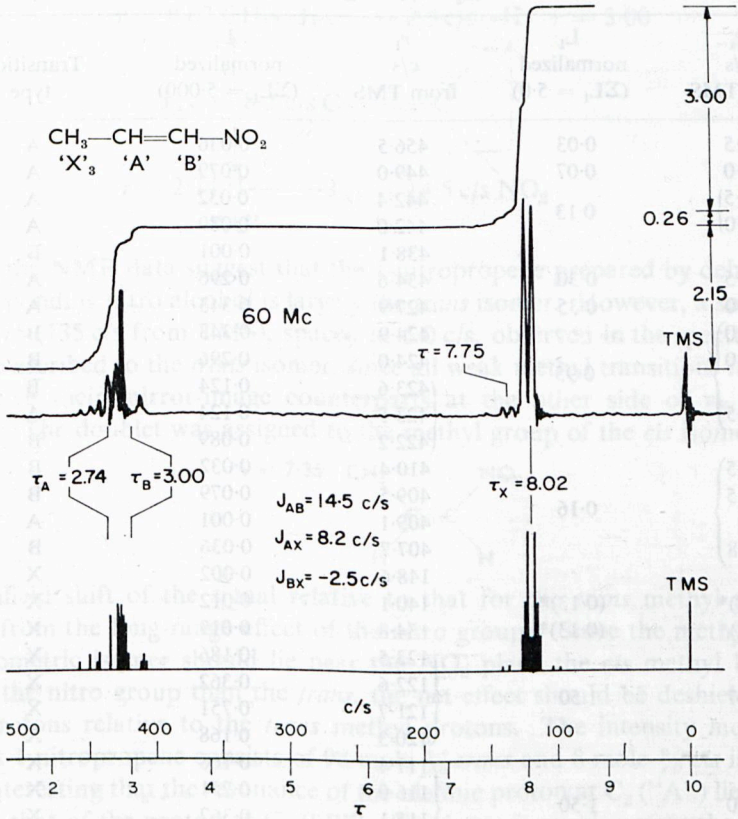


FIG. 2

These were used as first approximations in trial-and-error calculations of the theoretical spectrum. Using appropriate symmetry functions,[3] the ABX_3 matrix was reduced to a set of eight 1×1 and four 2×2 matrices from which energy levels and spin wave functions were readily obtained. Variation of the chemical shifts and coupling constants was carried out until the difference between the calculated and experimental frequencies was reduced to 0·1 c/s. The final values were:

$$\nu_A = 435{\cdot}4 \text{ c/s (from TMS)} \qquad \tau = 2{\cdot}74$$
$$\nu_B = 420{\cdot}3 \text{ c/s} \qquad \tau = 3{\cdot}00$$
$$\nu_X = 118{\cdot}8 \text{ c/s} \qquad \tau = 8{\cdot}02$$
$$J_{AB} = 14{\cdot}5 \text{ c/s} \quad J_{AX} = 8{\cdot}2 \text{ c/s} \quad J_{BX} = -2{\cdot}5 \text{ c/s}$$

[3] J. A. Pople, W. G. Schneider and H J Bernstein, *High Resolution NMR* p. 112. McGraw-Hill, New York (1959).

TABLE 2. EXPERIMENTAL AND CALCULATED 60 MC NMR SPECTRUM OF 1-NITROPROPENE (ABX_3 SYSTEM)

$CH_3—CH=CH—NO_2$

"X_3" "A" "B"

ν_i c/s from TMS	L_i normalized ($\Sigma L_i = 5{\cdot}0$)	ν_i c/s from TMS	L_i normalized ($\Sigma L_i = 5{\cdot}000$)	Transition type
456·5	0·03	456·5	0·036	A
449·0	0·07	449·0	0·079	A
442·5	0·13	442·4	0·032	A
422·0		442·0	0·089	A
		438·1	0·001	B
434·5	0·30	434·6	0·296	A
428·0	0·35	427·9	0·343	A
425·0	0·95	424·9	0·343	B
424·0		424·0	0·296	B
423·5		423·6	0·124	B
		423·5	0·124	A
		422·2	0·089	B
410·5	0·16	410·4	0·032	B
409·5		409·5	0·079	B
		409·1	0·001	A
407·8		407·7	0·036	B
		148·6	0·002	X
(138)*	(0·13)*	140·1	0·012	X
(132)*	(0·13)*	134·8	0·019	X
		123·5	0·186	X
121·7	1·50	122·6	0·362	X
		121·7	0·751	X
		120·3	0·168	X
		117·4	0·168	X
116·0	1·50	116·0	0·751	X
		115·1	0·362	X
		114·2	0·186	X
		102·8	0·019	X
		97·6	0·012	X
		89·2	0·002	X
experimental		calculated for		

$\nu_A = 435{\cdot}4$ c/s $\quad J_{AB} = 14{\cdot}5$ c/s

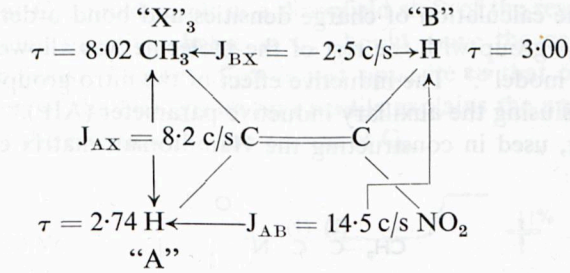
$\nu_B = 420{\cdot}3$ c/s $\quad J_{AX} = 8{\cdot}2$ c/s

$\nu_X = 118{\cdot}8$ c/s $\quad J_{BX} = -2{\cdot}5$ c/s

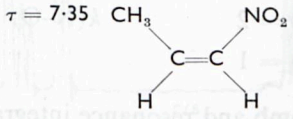
(Ref. $SiMe_4$)

* Assigned to another geometric isomer.

The large value of the coupling constant for the olefinic protons ($J_{AB} = 14{\cdot}5$ c/s) indicates that their relative position is *trans*.[4] The values of $|J_{AX}| = 8{\cdot}2$ c/s and $|J_{BX}| = 2{\cdot}5$ c/s, suggest[4] that A is the proton vicinal to the methyl and that B is vicinal to the nitro group. The complete spectral assignment is then as follows:



Thus, the NMR data suggest that the 1-nitropropene prepared by dehydration of the corresponding nitro alcohol is largely the *trans* isomer. However, a small doublet at $\tau = 7{\cdot}75$ (135 c/s from TMS), spaced at 6·0 c/s, observed in the spectrum (Fig. 2) cannot be ascribed to the *trans* isomer, since all weak methyl transitions in this range should have their mirror-image counterparts at the other side of $\nu_X = 118{\cdot}8$ c/s (Table 2). The doublet was assigned to the methyl group of the *cis* isomer



the downfield shift of the signal relative to that for the *trans* methyl group is as expected from the long-range effect of the nitro group.[5] Since the methyl groups in either geometric isomer should lie near the NO_2 plane the *cis* methyl being much closer to the nitro group than the *trans*, the net effect should be deshielding the *cis* methyl protons relative to the *trans* methyl protons. The intensity measurements show that 1-nitropropene consists of 98 mole % *trans* and 8 mole % *cis* isomers.

It is interesting that the resonance of the olefinic proton at C_2 ("A") lies at a lower field than that of the proton at C_1 ("B"). The latter is much nearer the NO_2 group and should be subject to stronger deshielding due to the inductive and anisotropic effects of the nitro group, as is actually the case in the NMR spectrum of 1-nitropropene[6]

$$\underset{\tau = 7{\cdot}92}{\overset{3}{CH_3}}—\underset{\tau = 5{\cdot}70}{\overset{2}{CH_2}}—\overset{1}{CH_2}—NO_2$$

where the resonance of the protons at C_1 is shifted 2·22 ppm to lower fields relative to that of the protons at C_2. For 1-nitropropane a reverse shift of 0·26 ppm is observed

$$\underset{\tau = 2{\cdot}74}{\overset{3}{CH_3}}—\underset{\tau = 3{\cdot}00}{\overset{2}{CH}}═\overset{1}{CH}—NO_2$$

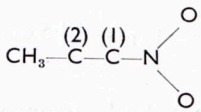
[4] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 85. Pergamon Press, London (1959).

[5] I. Yamaguchi, *Mol. Phys.* **6**, 105 (1963).

[6] W. Hofman, L. Stefaniak, T. Urbański and M. Witanowski, *J. Amer. Chem. Soc.* **86**, 554 (1964).

An explanation of this shift was sought by us in the π-electron distribution over the conjugated system of 1-nitropropene.

The simple LCAO method (neglecting overlap, non-self-consistent field) using empirical[7] parameters h and k for Coulomb ($\alpha_0 + h\beta_0$) and resonance ($k\beta_0$) integrals was employed in the calculation of charge densities and bond orders. Hyperconjugation of the methyl group with the rest of the molecule was allowed for by means of the "heteroatom model".[8] The inductive effect of the nitro group was introduced into the calculations using the auxiliary inductive parameter (AIP).[9] The final set of coefficients h and k, used in constructing the Hamiltonian matrix elements for the system



was as follows:

$$H_{ii} = \alpha_0 + h\beta_0 \qquad H_{ij} = k\beta_0$$

$$h(CH_3) = 2 \qquad k(CH_3\text{–}C_1) = 0{\cdot}7$$

$$h(C_2) = -0{\cdot}2 \qquad k(C_1\text{–}C_2) = 1{\cdot}1$$

$$h(C_1) = +0{\cdot}2 \qquad k(C_2\text{–}N) = 0{\cdot}8$$

$$h(N) = 2 \qquad k(N\text{–}O) = 0{\cdot}7$$

$$h(O) = 1$$

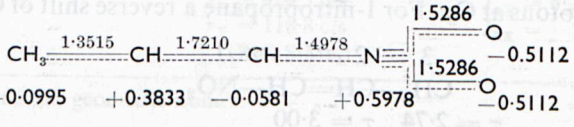
where α_0 and β_0 are the Coulomb and resonance integrals, respectively, for benzene.

The calculated energy levels (E) and coefficients (C) of the corresponding wave functions are given below

			ψ_1	ψ_2	ψ_3	ψ_4
$E_6 = \alpha_0 - 1{\cdot}2977\beta_0$		c_1	0·1140	0·9221	0	0·2950
$E_5 = \alpha_0 + 0{\cdot}2622\beta_0$		c_2	0·1378	0·3134	0	−0·4372
$E_4 = \alpha_0 + 0{\cdot}9695\beta_0$		c_3	0·3074	0·1080	0	−0·6503
$E_3 = \alpha_0 + \beta_0$	occupied	c_4	0·8224	−0·1560	0	−0·0120
$E_2 = \alpha_0 + 2{\cdot}2380\beta_0$	orbitals	c_5	0·3140	−0·0882	$+1/\sqrt{2}$	0·3863
$E_1 = \alpha_0 + 2{\cdot}8335\beta_0$		c_6	0·3140	−0·0882	$-1/\sqrt{2}$	0·3863

$$\psi_i = c_1\varphi_{CH_3} + c_2\varphi_{C_2} + c_3\varphi_{C_1} + c_4\varphi_N + c_5\varphi_O + c_6\varphi_O$$

The resulting calculated net charge densities and bond orders are shown in the following diagram:



Since no interelectronic repulsions are incorporated in the simple LCAO

[7] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* p. 135, Wiley, New York (1961).
[8] F. A. Matsen, *J. Amer. Chem. Soc.* **72**, 5243 (1950).
[9] G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.* **57**, 2086 (1935).

calculations, the resulting net charge densities are usually overestimated, but the general pattern should be true, particularly when using empirical coefficients h and k.

The general correlation between carbon π-electron densities and the NMR chemical shifts of the attached protons is well known.[10,11] Here, the relatively large positive charge at C_2 should result in a downfield shift of the resonance of proton at C_2, while the small negative charge at C_1 should move the corresponding proton signal to higher fields. The net effect is just opposite to that of the inductive and anisotropic effects of the NO_2 group and readily explains the apparently anomalous low-field shift of the resonance of the proton at C_2.

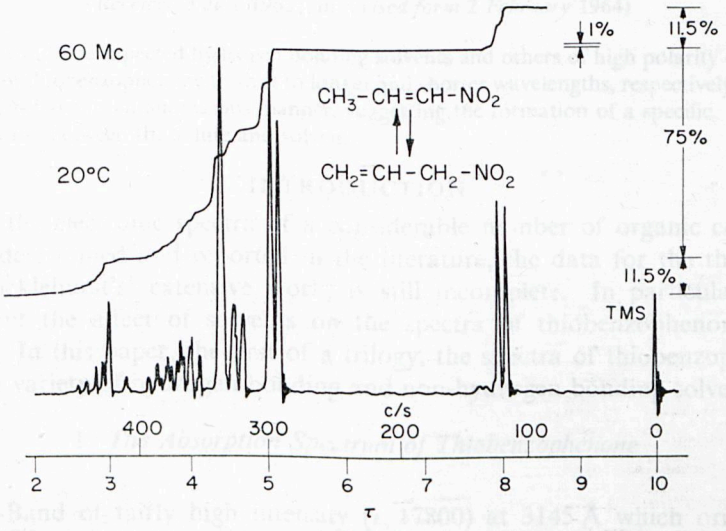
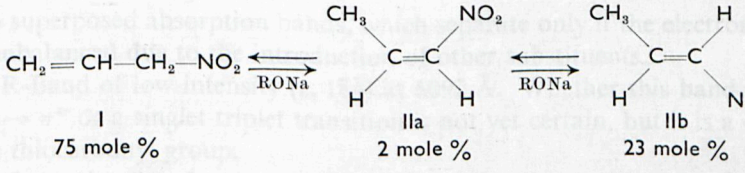


FIG. 3

It is known from literature data[1] that 3-nitropropene is slowly equilibrated with 1-nitropropene in the presence of catalytic amounts of sodium alkoxides. Integration of the NMR spectrum (Fig. 3) of the equilibrium mixture at 20° enabled us to determine the actual composition of the latter.

According to the intensity measurements, the following equilibrium is supposed to exist:



I
75 mole %

IIa
2 mole %

IIb
23 mole %

EXPERIMENTAL

3-Nitropropene was prepared by nitration of allyl bromide with nitrogen tetroxide,[1] 1-nitropropene by dehydration of 2-nitro-1-propanol with phthalic anhydride.[12] Both were purified by eightfold distillation in vacuum under nitrogen atmosphere.

[10] G. Fraenkel, R. E. Carter, A. McLachlan and H. J. Richards, *J. Amer. Chem. Soc.* **82**, 5846 (1960).
[11] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters* No. 14, 468 (1961).
[12] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.* 1471 (1947).

Isomerization of 3-nitropropene was induced by a trace amount of sodium methoxide. The sample was annealed at room temp (20°) through a year and then distilled off in vacuum under nitrogen atmosphere.

The NMR spectra were measured with Varian V-4300 C Spectrometer at 60 Mc and 26 ± 0·3°. Samples were prepared as dilute solutions (5% v/v) in CCl_4. The calibration of the spectra was carried out by the sideband technique with accuracy of ±0·01 ppm (0·5 c/s) for τ-values and 0·2 c/s for relative shifts within multiplets.

The intensities were measured with V-3521 Integrator with accuracy of ±1% of the total integral at a sweep rate of 5 c/s per sec and a radiofrequency field or 25 microgauss as required[13] for reducing below 1% the errors due to neglecting relaxation times.

[13] Varian Technical Information Bulletin, **3**, No. 2 (1960).