medium. The results of this investigation suggest (but do not prove) that the necessary regularity in the salt effect term may well exist. However, the rather large variation in the medium effect for monosubstituted anilines of closely similar structures (see Table VI) makes it seem doubtful that a suitable series of indicators can be found. This conclusion, which applies with equal force to the H_- function in 33.4% methanol, substantiates the earlier finding of deLigny, *et al.*[19] It is likewise consistent with the view of Gutbezahl and Grunwald[5] that useful scales of H_0 and H_- do not exist in ethanol–water mixtures.

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC SYNTHESIS, POLISH ACADEMY OF SCIENCES, WARSZAWA 10, POLAND]

Proton Magnetic Resonance Study of Nitroalkanes

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An attempt was made to explain chemical shifts (at 60 Mc.) of protons in nitroalkanes in terms of the inductive effect of the NO_2 group and the effect of diamagnetic anisotropy of the C–C bonds. The inductive effect was shown to operate as far as the fourth carbon atom in the chain. Some correlations were observed between bond polarization and the diamagnetic anisotropy effect. Rather narrow ranges of chemical shifts of various types of protons in nitroalkanes were found. Analysis of the multiplet pattern and position of the methine signal of nitrocyclohexane showed that the chair form with an equatorial nitro group is the only species of the compound at room temperature. The effect of internal rotation on the chemical shifts of the protons at C-1 is discussed.

Very little literature data are known on the position of n.m.r. signals of protons in alkyl groups bonded to one or more nitro groups. The only substances which have been examined so far are nitromethane,[1–3] nitroethane,[1b,3] nitropropanes,[3] nitrocyclohexane,[4] and some rather complicated alicyclic nitro compounds.[5,6]

We have been interested in the possibility of qualitative and, eventually, quantitative predictions of the chemical shifts, particularly those of α-hydrogen signals in proton resonance spectra of nitroalkanes.

This work presents a discussion of the problem in terms of the inductive effect of the nitro group and the effect of diamagnetic anisotropy of the C–C bonds. The latter seems to be particularly valuable in structural assignments and conformational analysis based on n.m.r. data.

Experimental

The following compounds were examined: nitromethane (I), nitroethane (II), 1-nitropropane (III), 1-nitrobutane (IV), 1-nitropentane (V), 1-nitrohexane (VI), dinitromethane (VII), trinitromethane (VIII), 2-nitropropane (IX), nitrocyclohexane (X), 2-chloro-2-nitropropane (XI), 1,1-dinitroethane (XII), 1,1-dinitropropane (XIII), 2-methyl-2-nitropropane (XIV), and 2,2-dinitropropane (XV).

Compounds I–VI, IX, XI, and XV were commercial C.P. grade products, distilled under reduced pressure. Dinitromethane (VII) was prepared from dibromodinitromethane after Duden.[7] Trinitromethane (VIII) was obtained from its potassium salt made by the action of aqueous solution of $K_4Fe(CN)_6$ on tetranitromethane.[8] Nitrocyclohexane (X) and 2-methyl-2-nitropropane (XIV) were made by the Meyer reaction from the corresponding iodide[9a] and chloride,[9b] respectively. The dinitroalkanes XII[10] and XIII[10] were prepared from the corresponding sodium salts of mononitro compounds according to Shechter and Kaplan.[11] All compounds were vacuum distilled; their purity, tested by the integration of their n.m.r. peaks, was found to be higher than 98%.

The n.m.r. spectra were measured at 60 Mc./sec. using a Varian HR-60 spectrometer with a flux stabilizer, a field homogeneity control unit, and a spinning sample insert. The temperature was maintained at 26 ± 0.3°. Calibration of the spectra was carried out by the side-band superposition method with accuracy of ±0.3 c.p.s. within the 20–100 c.p.s. range and ±0.5 c.p.s. within the 100–500 c.p.s. range, measured from tetramethylsilane internal standard. Peak positions were reported in τ-units = $10.00 - (\nu_{TMS} - \nu_x)/\nu_{TMS} \times 10^6$. The chemical shifts of multiplets were determined at the frequencies of the "first moments"

$$\langle\nu\rangle = \sum \nu_i L_i / \sum L_i$$

(ν_i is the component frequency, L_i the corresponding integral intensity). The coupling constants were measured by the wiggle-beat method with an error of ±0.2 c.p.s. The spectra are presented together with their integral curves in Fig. 1 and 2.

Discussion

Local Diamagnetic Deshielding by Inductive Effect of Nitro Group.—The nitro group, being strongly electron-attracting, decreases local electron density around alkyl protons in nitroalkanes, thus shifting their resonance signals to lower magnetic fields. The effect depends both on the number of nitro groups and on the number of intervening bonds between the proton and the nitro group. This may be seen in the series

	CH_4	CH_3NO_2	$CH_2(NO_2)_2$	$CH(NO_2)_3$
τ, p.p.m.	9.767	5.72	3.90	2.48

and in the spectra of primary, straight-chain nitroalkanes II–VI. The negative inductive effect of the NO_2 group operates significantly as far as to the fourth carbon atom in the chain, permitting the observation of resolved signals of individual methylene groups up to 1-nitrobutane (IV); the first two CH_2 multiplets are clearly distinguished in the whole series.

The same conclusion may be drawn if the chemical shifts of the terminal methyl groups are considered (Fig. 3).

The CH_3 shifts presented on the above diagram may be considered as a measure of the decrease in local electron density around successive carbon atoms in the chain, since the effect of diamagnetic anisotropy of the NO_2 group and additional C–C bonds should not be significant (except in nitromethane) because of the averaging effect of internal rotation. This diagram will be used in the next part of this work for some quantitative predictions regarding polarization of the C–C bonds in nitroalkanes.

The τ-values of the CH_3 peaks of branched-chain nitroalkanes (IX, XIV) lie rather in line with those of straight-chain ones. Positions of the methyl signals

(1) (a) L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953); (b) B. P. Dailey and J. N. Shoolery, *ibid.*, **77**, 3977 (1955).

(2) (a) C. H. Holm, *J. Chem. Phys.*, **26**, 707 (1957); (b) A. L. Allred and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5361 (1957).

(3) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

(4) W. C. Neikam and B. P. Dailey, *ibid.*, **38**, 445 (1963).

(5) W. F. Trager, F. F. Vincenzi, and A. C. Huitric, *J. Org. Chem.*, **27**, 3006 (1962).

(6) A. C. Huitric and W. F. Trager, *ibid.*, **27**, 1926 (1962).

(7) P. Duden, *Ber.*, **26**, 3003 (1893).

(8) F. D. Chattaway and J. M. Harrison, *J. Chem. Soc.*, **109**, 171 (1916).

(9) (a) N. Kornblum, B. Taub, and H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954); (b) N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub, and S. A. Herbert, *ibid.*, **77**, 5528 (1955).

(10) Kindly supplied by Dr. Z. Buczkowski.

(11) H. Shechter and R. B. Kaplan, *J. Am. Chem. Soc.*, **83**, 3535 (1961).

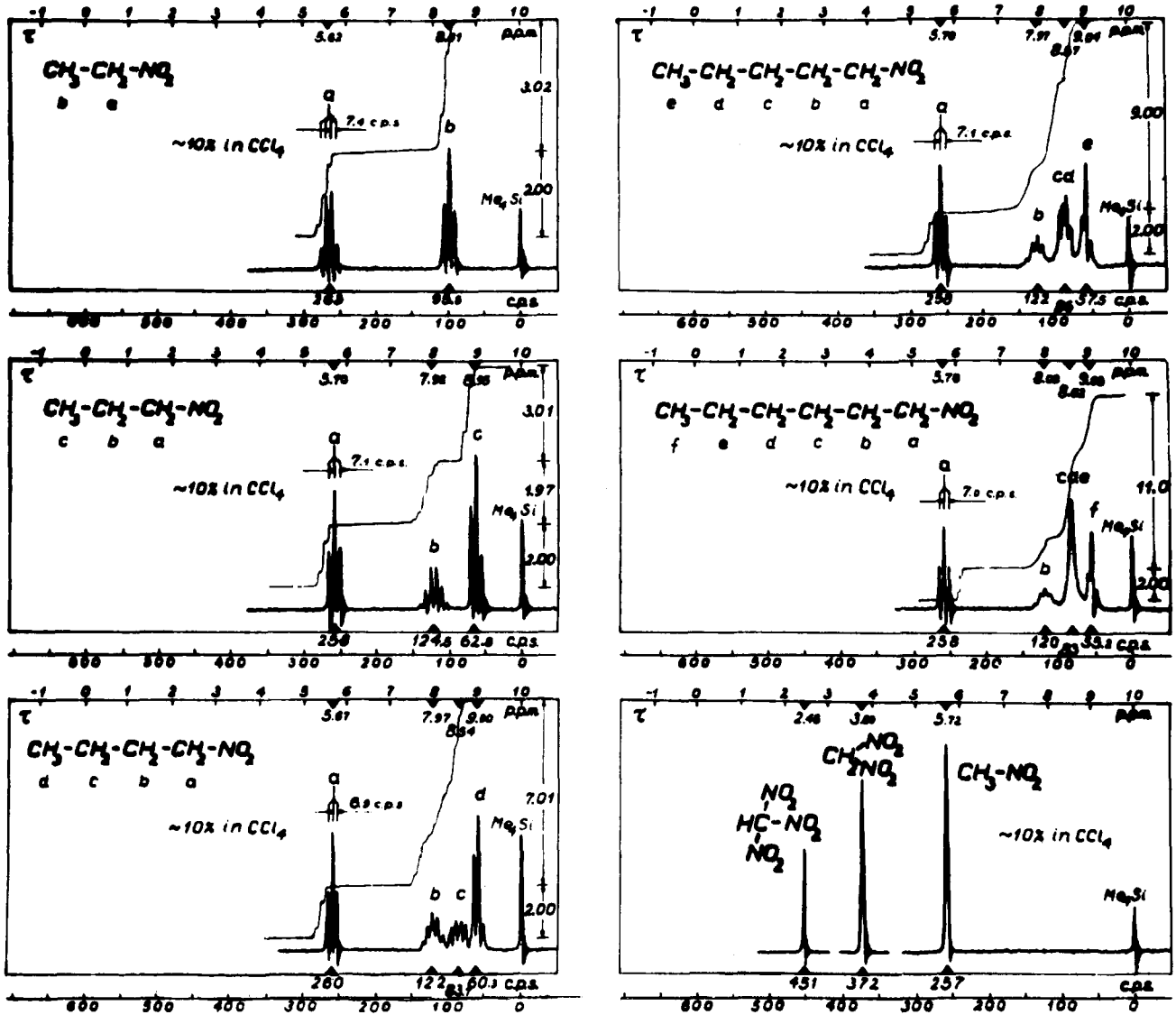


Figure 1.

for 1,1-dinitroalkanes (XII, XIII) fit well into the scheme, being shifted to lower fields as compared with the case of mononitro compounds. Thus, it seems possible to observe the inductive effect of the nitro group along the carbon chain from the terminal methyl shifts if no long-range effect of another nature is effectively operating in the molecule.

The original table of "effective deshielding constants" (σ_i) for the calculation of the position of methylene and methine n.m.r. signals from the equation given by Shoolery[12]

$$\tau = 9.767 - \sum_i \sigma_i \qquad (1)$$

did not include the value for the nitro group. The value of 2.46 p.p.m., calculated by us from the shifts in the series methane → nitromethane → dinitromethane → trinitromethane, did not lead to any reliable results. The lack of additivity of the shifts is evident even from the above series alone (shifts of 4.05, 1.92, and 1.32 p.p.m., respectively). Nevertheless, some assignments may be made from the spectra

CH_3NO_2 or RCH_2NO_2 or $(R)(R')CHNO_2$	5.4–5.7
$CH_2(NO_2)_2$ or $RCH(NO_2)_2$	3.7–3.8
$CH(NO_2)_3$	2.48
$RCH_2CH_2NO_2$ where R = alkyl	7.9–8.0

(12) J. N. Shoolery, *Varian Techn. Inf. Bulletin*, **2**, No. 3 (1959).

Effect of Diamagnetic Anisotropy of C–C Bonds. Conformation of Nitrocyclohexane.—The inductive effect alone does not account for the chemical shifts of the alkyl proton signals in the n.m.r. spectra of nitroalkanes. For example, the CH signal of 2-nitropropane (IX) is shifted to a lower field as compared with the CH_2 signal of nitroethane (II), while an opposite shift should have been expected from the inductive effect. On the other side, the α-hydrogen multiplet of nitrocyclohexane (X) has the same τ-value as the signal of nitromethane (I).

Explanation of those facts was sought for in terms of the average shielding (positive or negative) due to diamagnetic anisotropy of the C–C bonds. We used the approximate equation, derived by McConnell[13]

$$\sigma_{av}(G) = (3\cos^2\theta - 1)(\chi_l - \chi_r)/3r^3 \qquad (2)$$

where $\sigma_{av}(G)$ is the shielding by an axially symmetrical electron cloud G (that of the C–C bond in our instance), r is the distance between the proton and the electrical center of gravity of that cloud, θ is the sharp angle which r makes with the axis of G, and $(\chi_l - \chi_r)$ is the diamagnetic anisotropy of G (the value of -5.5×10^{-30} cm.^{3} was now used for the C–C bond according to Bothner-By and Naar-Colin[14]). The lengths of the C–H and C–C

(13) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(14) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

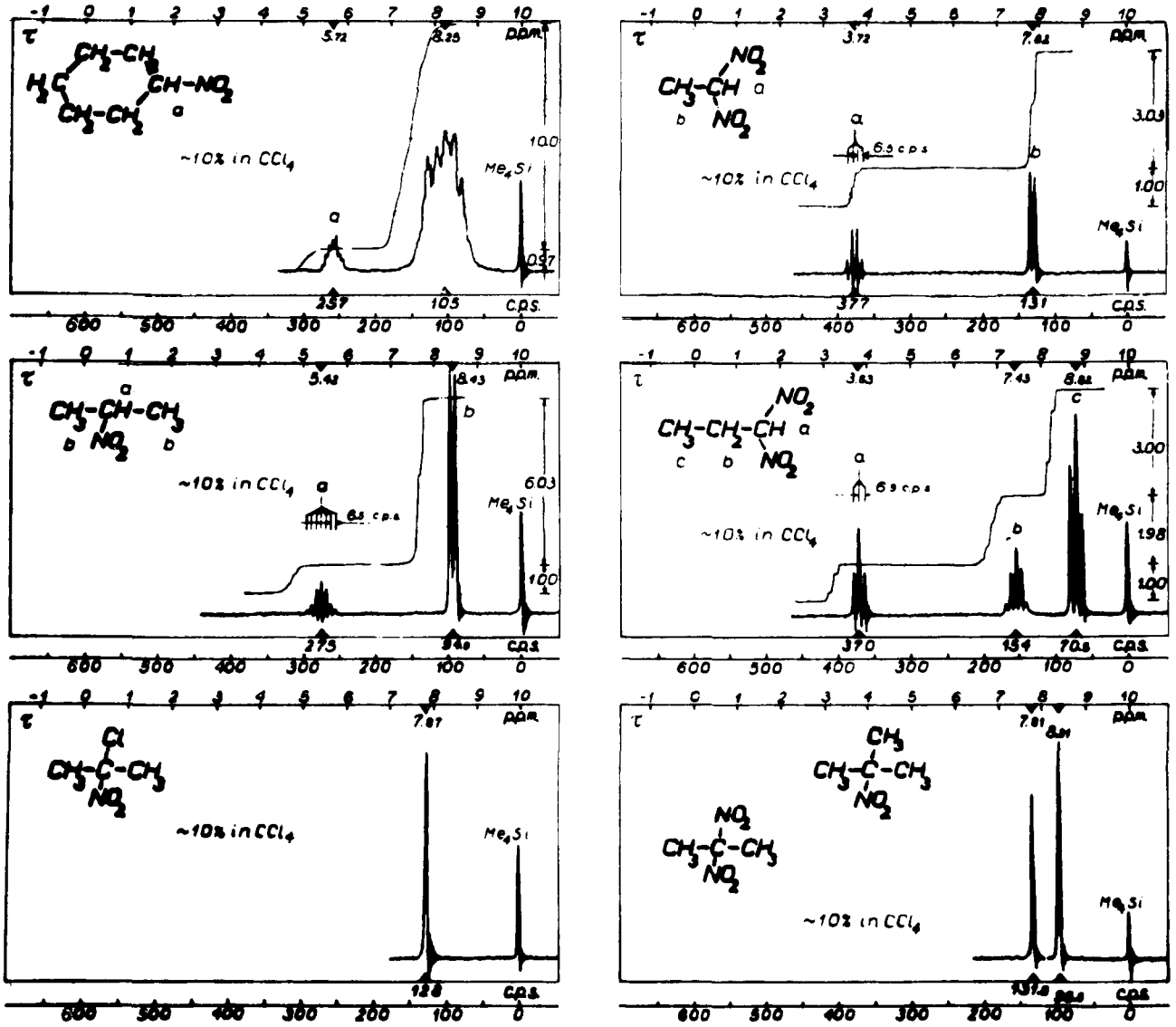


Figure 2.

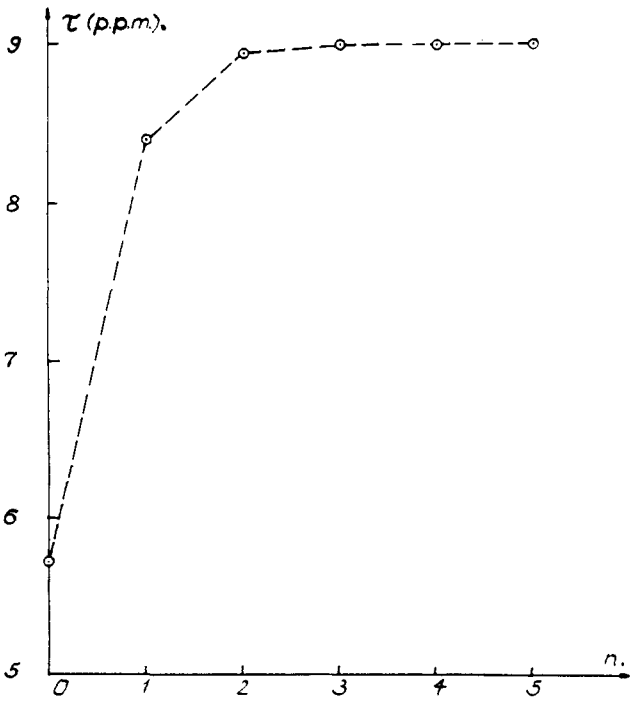


Fig. 3.—Shift of CH_3 signals in CH_3-$(CH_2)_n$-NO_2.

bonds were taken as 1.09 and 1.54 Å., respectively[15]; the tetrahedral angle (109° 28′) between the bonds was assumed.

The diamagnetic anisotropy effect of the C_1–C_2 bond on the hydrogen proton at C_1 (r = 1.53 Å., θ = 42° 12′) in the system

$$\underset{1}{X\text{-}CH_2}\text{-}\underset{2}{C}\text{-}\underset{3}{C}\ldots$$

should result in the resonance signal shift of −0.33 p.p.m. in the τ-scale, as computed from eq. 2, with assumption of the electron center of gravity located at the midpoint of the C_1–C_2 bond. Such values have been actually observed in the spectra of alkanes,[16] but this does not apply in the spectra of nitroalkanes

	CH_3NO_2	$CH_3CH_2NO_2$	$(CH_3)_2CHNO_2$
τ, p.p.m.	5.72	5.62	5.42

where the average apparent effect is −0.13 p.p.m. per C–C bond. We tried to explain this as a result of a shift of the electron center of gravity of the C_1–C_2 bonds towards C_1 due to the inductive effect of the nitro group. Calculation showed that the −0.13 p.p.m. shift would be obtained from eq. 2 if the electron center of gravity

(15) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

(16) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 7.

TABLE I[a]

TRANSITION ENERGIES AND INTENSITIES FOR AB_2C_2 SYSTEM IN NITROCYCLOHEXANE (A TRANSITIONS, $m_A = -1/2 \rightarrow m_A = +1/2$)

m_A	(F_B, m_B)	(F_C, m_C)	First-order energy, c.p.s.	Second-order energy, c.p.s.	Relative intensity
	(1, 1)	(1, 1)	$J_{AB} + J_{AC} = 14$	$1/2B' + 1/2C' = 0.42$	$1 - 2B - 2C = 0.87$
	(1, 1)	(1, 0)	$J_{AB} = 10$	$1/2B' + C' = 0.47$	$1 - 2B = 0.93$
	(1, 1)	(1, −1)	$J_{AB} - J_{AC} = 6$	$1/2B' = 0.34$	$1 - 2B + 2C = 1.00$
	(1, 1)	(0, 0)	$J_{AB} = 10$	$1/2B' + C' = 0.47$	$1 - 2B = 0.93$
	(1, 0)	(1, 1)	$J_{AC} = 4$	$B' + 1/2C' = 0.76$	$1 - 2C = 0.94$
	(1, 0)	(1, 0)	0	$B' + C = 0.81$	1.00
	(1, 0)	(1, −1)	$-J_{AC} = -4$	$B' = 0.68$	$1 + 2C = 1.06$
	(1, 0)	(0, 0)	0	$B' + C' = 0.81$	1.00
1/2	(1, −1)	(1, 1)	$-J_{AB} + J_{AC} = -6$	$1/2C' = 0.07$	$1 + 2B - 2C = 1.00$
	(1, −1)	(1, 0)	$-J_{AB} = -10$	$C' = 0.13$	$1 + 2B = 1.07$
	(1, −1)	(1, −1)	$-J_{AB} - J_{AC} = -14$	0	$1 + 2B + 2C = 1.13$
	(1, −1)	(0, 0)	$-J_{AB} = -10$	$C' = 0.13$	$1 + 2B = 1.07$
	(0, 0)	(1, 1)	$J_{AC} = 4$	$B' + 1/2C' = 0.76$	$1 - 2C = 0.94$
	(0, 0)	(1, 0)	0	$B' + C' = 0.81$	1.00
	(0, 0)	(1, −1)	$-J_{AC} = -4$	$B' = 0.68$	$1 + 2C = 1.06$
	(0, 0)	(0, 0)	0	$B' + C' = 0.81$	1.00

[a] $B' = (J_{AB})^2/\nu_0\delta_{AB} = 0.68$ c.p.s., $C' = (J_{AC})^2/\nu_0\delta_{AC} = 0.13$ c.p.s., $B = J_{AB}/\nu_0\delta_{AB} = 0.0034$, $C = J_{AC}/\nu_0\delta_{AC} = 0.0024$. Transitions designated (F_i, m_i) according to Pople, Bernstein, and Schneider.[19]

was located at a distance of 0.45 Å. from C_1 (translocation by 0.32 Å. from the midpoint of the bond). The corresponding parameters were: $r = 1.31$ Å. and $\theta = 51° 40'$.

A support for this calculation was found in the dipole moment data for nitromethane and nitroethane. The computed shift of the center of gravity of the two-electron negative charge from the neutral point toward C_1

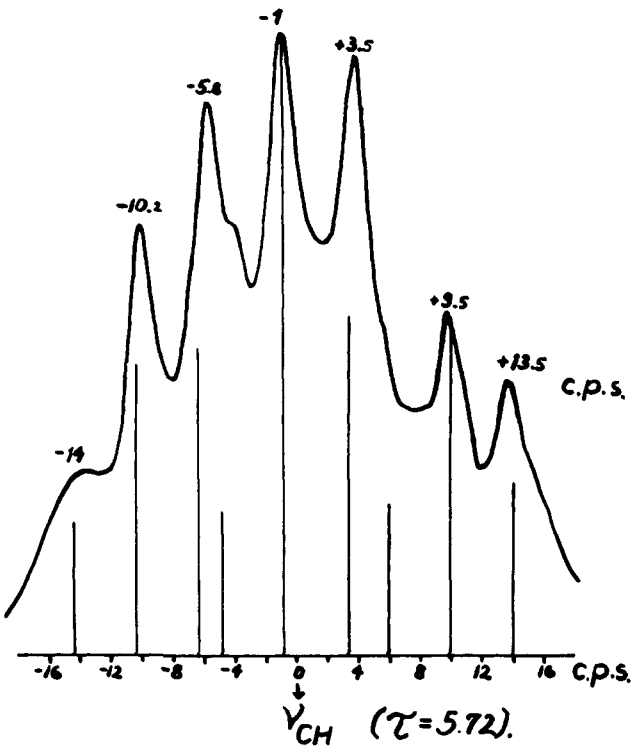


Fig. 4.—Methine multiplet in n.m.r. spectrum of nitrocyclohexane.

should result in the C–C dipole moment of 0.6 D. in nitroethane. The values of dipole moment for gaseous nitromethane[17] and nitroethane[18] are 3.5 and 3.7 D., respectively. Construction of the dipole moment of nitroethane from the moment of nitromethane and that calculated for the C–C bond gave the value of 3.7 D.

The n.m.r. spectrum of nitrocyclohexane (X), particularly the methine multiplet, suggests that in the conditions specified (26°, 10% w./v. soln. in CCl_4) the molecule exists exclusively in the chair conformation with an equatorial nitro group (axial α-hydrogen). If the nitro group were axial and the α-hydrogen equatorial, there should have been a quintet ($J_{ee} \cong J_{ea} \cong 4$ c.p.s.)

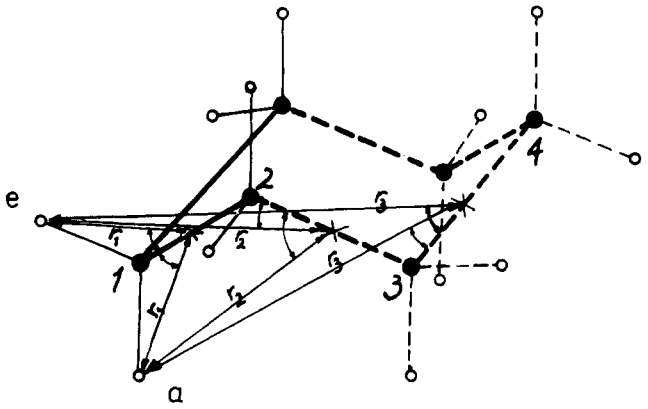


Figure 5.

in the spectrum. The same would have been true if a rapid inversion had occurred ($J_{av} \cong 7$ c.p.s.). Actually, the signal due to the α-hydrogen is a septet with two additional weak peaks (Fig. 4). The appearance of this multiplet may be readily explained in terms of the A_2B_2X system with $J_{AX} \cong 2J_{BX}$, represented approximately by the protons at C_1, C_2, and C_3 in the chair conformation with the α-hydrogen axial (nitro group equatorial).

Using second-order perturbation theory,[19] we computed a theoretical multiplet pattern for the system AB_2C_2, where A is the axial proton at C_1, B and C are axial and equatorial protons at C_2, respectively. The following parameters were assumed

$\nu_A = 5.72$ p.p.m. (from the first moment of the multiplet)

$\nu_B = 8.17$ p.p.m.
$\nu_C = 7.77$ p.p.m.
} approximate values, based on the α-methylene frequency in nitroalkanes (7.97 p.p.m.), assuming that the ring effects shift the axial and equatorial proton signals by 0.2 p.p.m. to higher and lower fields, respectively, so as to give the difference of 0.4 p.p.m., commonly observed for these signals

$J_{AB} = 10$ c.p.s.
$J_{AC} = 4$ c.p.s.
} the values based on literature data on arylnitrocyclohexanes[5]

The calculated transition energies are presented in

(17) L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937).
(18) E. C. Hurdis and C. P. Smyth, *J. Am. Chem. Soc.*, **64**, 2829 (1942)
(19) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution NMR" McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 151–156.

TABLE II

DIAMAGNETIC ANISOTROPY EFFECT IN CYCLOHEXANE RING

	Effect of								
	C_1–C_2			C_2–C_3			C_4–C_5		
Effect on	r_1, Å.	θ_1	σ_{av} (G)	r_2, Å	θ_2	σ_{av} (G)	r_3, Å.	θ_3	σ_{av} (G)
H_a	1.53	42° 12′	−0.33	2.35	66° 54′	+0.08	2.94	88° 55′	+0.07
H_e	1.53	42° 12′	−0.33	2.78	31° 26′	−0.10	3.63	71° 48′	+0.03

TABLE III

Bond	Shift of the electron of gravity from the midpoint to C_1, Å.	Corresponding mean methyl τ-value, p.p.m.
C_1–C_2	0.32	7.0
C_2–C_3	.06	8.7
C_3–C_4	.01	9.0
Limiting case	.00	9.1

TABLE IV

DIAMAGNETIC ANISOTROPY EFFECT IN NITROCYCLOHEXANE RING

	Effect of								
	C_1–C_2			C_2–C_3			C_4–C_5		
Effect on	r_1, Å.	θ_1	σ_{av} (G)	r_2, Å.	θ_2	σ_{av} (G)	r_3, Å.	θ_3	σ_{av} (G)
H_a	1.31	51° 40′	−0.13	2.32	68° 25′	+0.09	2.94	88° 55′	+0.07
H_e	1.31	51° 40′	−0.13	2.73	33° 00′	−0.10	3.63	71° 48′	+0.03

Table I. They are in good agreement with the experimental values, as shown in Fig. 5.

An independent argument in favor of the chair conformation with an equatorial nitro group as the sole species of nitrocyclohexane at 25° is afforded by the consideration of the C–C diamagnetic anisotropy effect in the cyclohexane ring.

The geometrical parameters entering eq. 2 for the cyclohexane ring are shown in Fig. 4 and listed in Table II, together with the corresponding chemical shifts (from the methane signal), calculated on the assumption that the electron centers of gravity fall at the midpoints of the C–C bonds.

Since the effect of the C_1–C_2 bonds are the same in nitrocyclohexane and 2-nitropropane (the latter is represented by full lines in Fig. 3), the difference in the methine proton frequencies between these compounds may be ascribed to an additional effect of the C_2–C_3 and C_4–C_5 bonds in nitrocyclohexane. The effect calculated from Table II, different for axial and equatorial protons is +0.30 p.p.m. for H_a and −0.14 p.p.m. for H_e relative to the methine proton of 2-nitropropane. The actually observed shift is +0.30 p.p.m. which agrees with that of H_a. This, if combined with previous considerations on the methine multiplet in the spectrum of nitrocyclohexane, strongly supports the idea that only the conformer with an equatorial nitro group is present in nitrocyclohexane under the conditions of the experiment.

The calculated effect of the C_1–C_2 bonds (−0.33 p.p.m. per bond), however, is inconsistent with the experimental data (−0.10 to −0.15 p.p.m. per bond), but this deviation was previously explained in terms of a shift of the electron center of gravity, due to the inductive effect of the NO_2 groups, in the example of nitroethane and 2-nitropropane. The position of the center, computed for the latter compounds by adjusting the calculated diamagnetic anisotropy effect to the experimental values, may be applied as well to the C_1–C_2 bonds in nitrocyclohexane. There is, however, a question of how the polarization of further bonds, C_2–C_3 and C_3–C_4, would affect the theoretical difference between the n.m.r. frequencies for axial and equatorial protons (the C_1–C_2 bonds give here no net effect because of their symmetric position in respect to the axial–equatorial pair of protons at C_1).

Estimation of the probable shift of the electron centers of gravity of the C_2–C_3 and C_3–C_4 bonds was based on the assumption that the shift is proportional to the mean value of the methyl frequencies of corresponding carbon atoms, found in the spectra of straight-chain nitroalkanes (Fig. 3). The starting point here was the position of the electron center of gravity of the C_1–C_2 bond, calculated previously from other data. The results are given in Table III.

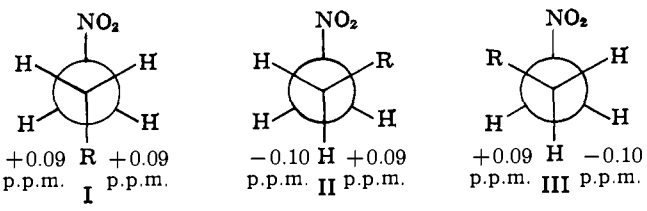
Thus corrected positions of the electron centers of gravity were put into eq. 2 to yield the values presented in Table IV.

Data from Table IV show that the allowance for bond polarization does not affect the difference between axial and equatorial proton frequencies more than within experimental error (*cf.* Table II), but reduces the effect of the C_1–C_2 bonds in nitrocyclohexane to a reasonable value.

Another case in the n.m.r. spectra of nitroalkanes which may be explained in terms of diamagnetic anisotropy shielding is the observation of a small, but evident, dip in the τ-values of the α-proton signals of mono- and 1,1-dinitroethane as compared with the corresponding normal values in the mononitro and 1,1-dinitro series, respectively.

	τ, p.p.m.		τ, p.p.m.
CH_3NO_2	5.72	$CH_2(NO_2)_2$	3.80
$CH_3CH_2NO_2$	*5.62*	$CH_3CH(NO_2)_2$	*3.72*
$CH_3CH_2CH_2NO_2$	5.70	$CH_3CH_2CH(NO_2)_2$	3.83
$CH_3(CH_2)_2CH_2NO_2$	5.67		
$CH_3(CH_2)_3CH_2NO_2$	5.70		
$CH_3(CH_2)_4CH_2NO_2$	5.70		

The effect of deshielding the α-protons when passing from nitromethane to nitroethane was previously explained on the basis of diamagnetic anisotropy of the extra C–C bond. The deshielding is practically cancelled out in the higher members of the homologs. We tried to explain this as a diamagnetic anisotropy effect of the second carbon–carbon bond. Considering the three possible rotational isomers of the system R–CH_2–CH_2–NO_2, where R = alkyl, the following effects of the C_2–C_3 bond were calculated



The calculation shows that if all these conformations are equally populated, the over-all effect will be diamagnetic shielding of the α-protons. This will be even more marked if there is some excess of more energetically favored conformation I ("*trans*").