refluxed about 10 min. and cooled. The white solid material remaining was extracted for several hours with toluene in a Soxhlet extractor and then was washed with acetone, chloroform, and finally toluene again. The solvents from the washings were evaporated and the residue saved for recovery of the paracyclonaphthane VI (see below). The polymeric material remaining was slightly grayish white and did not soften or melt at 310°.

Poly-p-xylylene (II) was prepared by treatment of α-bromoxylene in a manner analogous to that of the preparation of I, with the exception that the quaternary amine was treated directly by hot concentrated sodium hydroxide overnight.[10] The polymer was obtained after cooling the hot solution and diluting it with water, followed by filtration of the solid. The crude polymer was triturated many times with hot toluene and acetone and was dried to a white lumpy powder. No attempt was made to recover any paracyclophane.

Poly-o-xylylene (III) was obtained as a generous gift of Dr. L. A. Errede, Central Research Laboratories, 3M Co., St. Paul, Minn.

Polystyrene (IV) was whittled from a large mass of polystyrene. Freshly distilled styrene was allowed to polymerize slowly for several years to form this mass.

Polyphenyl (V) was provided in liberal quantity by Dr. Peter Kovacic, Case Institute of Technology, Cleveland, Ohio.

[2.2]Paracyclonaphthane (VI).—The extraction residue from the preparation of polybenzo-p-xylylene (see above) was recrystallized from a mixture of nitrobenzene–acetic acid solvent thinned with a little benzene and water; this crude material melted at 292–297°. The crude crystals were sublimed under vacuum (210° (0.05 mm.)) and 0.14 g. (45%) of white needles was obtained, m.p. 292–297°. The needles were sublimed thrice more, m.p. 291–293° (Cram, m.p. 299–301°). Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.17; H, 6.77.

Sample Preparation.—All polymer reductions were carried out under as nearly identical conditions as possible. The initial polymer suspensions were allowed to stand over the potassium mirrors at −70° for about 0.5 hr. before a full e.p.r. signal was obtained. This is somewhat longer than the time required for the simpler aromatic hydrocarbons; however, the difficulty of

(10) This procedure was suggested by Dr. L. A. Errede in a private communication.

reduction was no doubt due to the polymer chain size and insolubility. Sample sizes were about 5–10 mg. in about 2 ml. of solvent.

A sample of polyphenyl in DME (no potassium) was examined for an e.p.r. signal, since its method of preparation[11] might have involved the inclusion of magnetic impurities. No paramagnetism was observed in the sample.

In the investigation of the electron "storage" of polymer I, the solvent containing the polymer solution was frozen with liquid nitrogen and the tube containing the potassium mirror (C, Fig. 1) was subsequently removed so as not to provide a continuing reducing source. The colored polymeric solution was melted, but the entire sample tube was kept bathed in a cold viscous isopropyl alcohol–Dry Ice mixture, whereupon the biphenyl compartment was broken open to the solution and the solution was filtered into this section (G) of the tube. The polymer and all of the colored material were retained upon the filter and a clear solution was brought into section G, indicating that no potential electron-donor material had been introduced. The colorless DME–biphenyl solution was then filtered back through the sintered glass, at which time the solution assumed the characteristic dark blue-green of biphenyl negative ion and produced the strong biphenyl negative ion e.p.r. spectrum. Since the system had been thoroughly degassed and flamed out prior to introduction of the samples, it is unlikely that the decolorization of the solution resulted from reaction of the radical with a radical-scavenging material adsorbed upon the filter. To be sure, the polymeric material upon the filter retained its characteristic dark color and subsequently discharged its supply of electrons to the biphenyl solution when the latter was brought into the tube section D.

(11) P. Kovacic and F. W. Koch, J. Org. Chem., 28, 1864 (1963).

Nitrogen-14 Nuclear Magnetic Resonance in Nitro Compounds

By M. Witanowski, T. Urbański, and L. Stefaniak

Received February 6, 1964

Nonaromatic nitro groups were shown to give rather narrow N^{14} n.m.r. peaks. Their chemical shifts are characterized by a very regular dependence on the electronegativity of the rest of the molecule. Spectral identification of nitramines and primary, secondary, and tertiary nitroalkanes is possible. Nitromethane is suggested as an internal standard for calibration of N^{14} n.m.r. spectra.

N^{14} magnetic resonance spectra are characterized by very low sensitivity and broadness of the signals. This is probably the main reason why relatively little work has so far been done[1,2] in this field in spite of the fact that the first nuclear magnetic resonance spectrum to be observed was the N^{14} spectrum of ammonium nitrate.[3] Applicability of N^{14} spectra to chemical structure determination was even questioned.[2]

Results of our investigation of the N^{14} n.m.r. spectra of aliphatic nitro compounds seem to be promising as far as identification and localization of nitro groups in saturated systems are concerned. The resonance peaks

(1) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, pp. 313–315; see also B. M. Schmidt, L. C. Brown, and D. Williams, J. Mol. Spectry., 2, 539 (1958); ibid., 3, 30 (1959); B. Holder and M. P. Klein, J. Chem. Phys., 23, 1956 (1955).

(2) P. C. Lauterbur, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, pp. 506–509.

(3) W. G. Proctor and F. C. Yu, Phys. Rev., 81, 20 (1951).

of aliphatic NO_2 groups are narrow and show regular changes of chemical shifts with structural changes in the remaining part of the molecule.

The N^{14} n.m.r. shifts (at 4.3 Mc.) of fifteen aliphatic nitro compounds and also of nitrobenzene are presented in Table I. Sample spectra are shown in Fig. 1.

The observed range of the chemical shifts is 344 c.p.s. (78 p.p.m.) and the average half-width of the peaks is about 40 c.p.s. so that the N^{14} signals of different types of nitro groups may be easily resolved.

Thus far saturated aqueous ammonium nitrate solution has been used as an external reference for calibrating N^{14} n.m.r. spectra.[1,2] It has serious drawbacks as a standard for accurate work with narrow signals because of relatively low concentration per volume of nitrogen nuclei and disturbances in the n.m.r. probe characteristic of every external standard, resulting in decreased effective sensitivity, increased base line drift, and inaccuracy of measured shifts. We suggest nitromethane
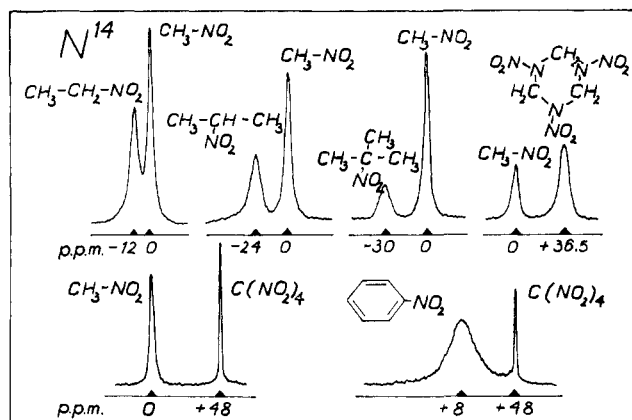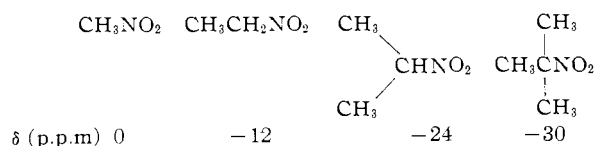
Figure 1.

as an internal reference for N^{14} spectra. Its narrow peak (half-width of 24 c.p.s.) may be detected even at small concentrations (5–10% v./v.). Nitromethane is a good solvent for most organic substances and may be used both as a solvent and an internal reference that is particularly convenient for the examination of organic solids. The reliability of the chemical shifts measured from the nitromethane peak was tested by varying the proportion of nitromethane and the substance examined and by dilution studies.

All shifts reported in Table I were shown to be concentration independent. Dilution of the samples with CCl_4 and acetone up to about 10% of the solute did not lead to any changes other than within the experimental error (± 2 c.p.s., 0.5 p.p.m.). In the case of N^{14} peaks lying very close to that of nitromethane (e.g., III–VI, XI, XVI), tetranitromethane may be used as a convenient secondary internal standard. Its very narrow resonance has a chemical shift of $+48$ p.p.m. from nitromethane.

The N^{14} chemical shift of the aliphatic nitro group shows evident dependence on the electron-withdrawing or electron-donating effects of the rest of the molecule. Increasing positive inductive effect $(+I)$ moves the NO_2 signal to lower fields as seen in the series

$$CH_3NO_2 \quad CH_3CH_2NO_2 \quad \begin{array}{c} CH_3 \\ \diagdown \\ CHNO_2 \\ \diagup \\ CH_3 \end{array} \quad \begin{array}{c} CH_3 \\ | \\ CH_3CNO_2 \\ | \\ CH_3 \end{array}$$

δ (p.p.m)   0 -12 -24 -30

Increasing negative inductive effect $(-I)$ results in an opposite shift

$$CH_3NO_2 \qquad CH(NO_2)_3 \qquad C(NO_2)_4$$
δ (p.p.m.)   0 $+35.5$ $+48$
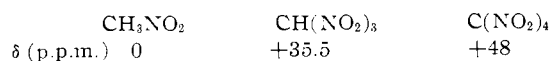
Other cases also fit well into the scheme; e.g., the chlorine atom in 2-chloro-2-nitropropane (IX) induces an upfield shift from the value for 2-nitropropane (VII). If the nitro group is bonded with a more electronegative atom than carbon, as in nitramines XIV and XV, the N^{14} signal is shifted to higher fields.

On the basis of the data from Table I it is possible to distinguish spectrally between primary nitroalkanes

No.	Compound	Nitro group resonance peaks Chemical shift ref. CH_3NO_2		Half-width c.p.s. ± 2
		c.p.s. ± 2	p.p.m. ± 0.5	
I	CH_3NO_2	0	0	24
II	$CH_3CH_2NO_2$	-49	-12	30
III	$CH_3(CH_2)_2NO_2$	-41	-10	35
IV	$CH_3(CH_2)_3NO_2$	-41	-10	40
V	$CH_3(CH_2)_4NO_2$	-40	-10	56
VI	$CH_3(CH_2)_5NO_2$	-42	-10	57
VII	$(CH_3)_2CHNO_2$	-96	-24	38
VIII	Nitrocyclohexane	-80	-20	92
IX	$(CH_3)_2(Cl)CNO_2$	-53	-13	35
X	$(CH_3)_3CNO_2$	-128	-30	43
XI	$(C_6H_5)CH_2NO_2$	-32	-7.5	163
XII	$CH(NO_2)_3$	$+152$	$+35.5$	11
XIII	$C(NO_2)_4$	$+206$	$+48$	10
XIV (RDX)	$O_2NN \begin{array}{c} CH_2N^{NO_2} \\ \diagdown \\ \diagup CH_2 \\ CH_2N \diagdown_{NO_2} \end{array}$	$+158$	$+36.5$	35
XV (DPT)	$O_2NN \begin{array}{c} CH_2N{-}CH_2 \\ | \quad | \\ CH_2 \quad NNO_2 \\ | \\ CH_2N{-}CH_2 \end{array}$	$+116$	$+27$	30
XVI	$(C_6H_5)NO_2$	$+34$	$+8$	110

($\delta \cong -10$ p.p.m.), secondary nitroalkanes ($\delta \cong -20$ p.p.m.), tertiary nitroalkanes ($\delta \cong -30$ p.p.m.), and nitramines ($\delta \cong +30$ p.p.m.).

There is no adequate theory of N^{14} chemical shifts, but it has been suggested that the dominant factor is the local paramagnetic term (resulting in deshielding the N^{14} nucleus) which should be proportional to the electronegativity of the atoms or groups attached to the nitrogen atom.[1] This is just opposite to the results of our observations of the changes in the N^{14} chemical shifts for aliphatic nitro groups (Table I).

Experimental

(4) F. D. Chattaway and J. M. Harrison, J. Chem. Soc., 109, 171 (1916).
(5) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, and L. B. Scott, J. Am. Chem. Soc., 73, 2769 (1951).