40 ml/min. The retention times of the various starting materials and photoproducts under these conditions follow: phenol (**4**), 3 min; methyl phenoxyacetate (**14**), 7 min; methyl 2-hydroxyphenylacetate (**12**), 10 min; methyl 4-hydroxyphenylacetate (**13**), 13 min; methyl 4-chlorophenoxyacetate (**10**), 16 min; methyl 2-chlorophenoxyacetate (**11**), 16 min; and methyl 2,4-dichlorophenoxyacetate (**9**), 25 min. Each photoproduct was identified by comparison of its nmr and ir spectra with those of an independently obtained sample. The product yields are given in Table I and are determined using only the starting material reacted for calculation. The yields were obtained from integrated recorder curves after response to each compound had been measured and corrections made for varying responses.

Specific Irradiations. The general procedures described in the previous section were followed in each case. The essential information is given in Table I.

Ultraviolet Spectra of Methyl Phenoxyacetates and Transmission Curves for Light Filters. The uv spectra shown in Figure 1 were determined on 0.0022 *M* solutions of the three methyl phenoxyacetates in methanol using a Cary 14 uv spectrometer. The transmission curves for the three light filters shown in Figure 1 were determined on the actual filters used in irradiations by a Beckman Dk 2a uv spectrometer.

Registry No. 9, 1928-38-7; **10**, 4841-22-9; **11**, 6956-85-0; **14**, 2065-23-8.

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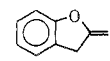

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(8) In the Vycor-filtered reactions even at low conversions color developed in the reaction mixtures and a significant amount of the incident radiation was not being absorbed by the starting material. This situation prevented reliable quantum yield determinations.

(9) A somewhat similar observation has been made by E. A. Caress and I. E. Rosenberg, *J. Org. Chem.*, **36**, 769 (1971).

(10) (a) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963). (b) For a recent review, see D. Bellus, *Advan. Photochem.*, **8**, 109 (1971). (c) This similarity has been noted previously by Pinhey, *et al.*, in their complete paper on aromatic ether photochemistry: D. P. Kelly, J. T. Pinhey, and R. D. G. Rigby, *Aust. J. Chem.*, **22**, 977 (1969).

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(12) Aldrich Chemical Co., Milwaukee, Wis.

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The Molecular Geometry of β-Pinene as Deduced from the Crystal and Molecular Structure of *cis*-Pinocarvyl *p*-Nitrobenzoate†

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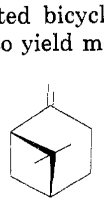
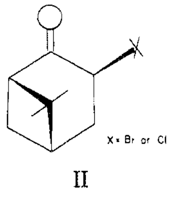
The crystal structure of *cis*-pinocarvyl *p*-nitrobenzoate (abbreviated name, *cis*-PNB), a derivative of β-pinene, has been determined from three-dimensional X-ray data obtained near the temperature of liquid nitrogen. The unit cell was monoclinic with the following dimensions: at approximately −193°, $a = 10.583 \pm 0.006$ Å, $b = 6.740 \pm 0.003$ Å, $c = 10.443 \pm 0.009$ Å, $\beta = 90.46 \pm 0.15°$; at approximately 22°, $a = 10.904 \pm 0.012$ Å, $b = 6.778 \pm 0.006$ Å, $c = 10.906 \pm 0.009$ Å, $\beta = 91.77 \pm 0.27°$. Systematic absences occurred for $0k0$ when k was odd, indicating space group $P2_1$. The *p*-nitrobenzoate geometry is similar to that found in other *p*-nitrobenzene derivatives. The cyclobutane ring in the *cis*-pinocarvyl portion of the molecule is normal (internal dihedral angle 141°), leading to severe steric interactions between C-3 and C-7. These interactions are minimized in *cis*-PNB through a decreased puckering in the C-2,C-3,C-4 end of the molecule. The observed C-3···C-7 distance is 2.72 Å. Since the same interactions exist in β-pinene, it is postulated that the *cis*-pinocarvyl grouping and β-pinene have very similar molecular geometries. *cis*-PNB exhibits pseudo-mirror molecular symmetry, C-10 being the only nonhydrogen atom not related to another atom by the mirror plane.

β-Pinene (I) and related bicyclic terpenes undergo cyclobutane ring opening to yield monocyclic or acyclic molecules and cyclobutane ring expansion to form bornane or fenchane compounds.[1-3] Such rearrangements dominate β-pinene chemistry, suggesting that the original bicyclic ring system is relatively unstable.



I

It has been postulated that the rigid cyclobutane ring leads to severe distortions in the rest of the bicyclic system. Support for this idea is found in the reported crystal structures of chloro-3-nopinone and bromo-3-nopinone (II).[4] In these structures the cyclobutane ring is normal, but the angle between plane C-2,C-3,C-4 and the best



II

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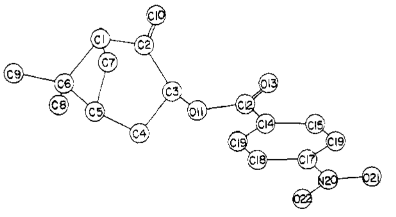
† From theses submitted by R. A. M., J. A. H., and W. E. S. in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis.

plane through C-1, C-2, C-4, and C-5 is only 30°, compared with the 50-60° observed in cyclohexane rings (see Table III). The structural details are not precisely known because the halogen atoms reduced the certainty with which the positions of the other atoms could be determined.

The crystal structure analysis of *cis*-pinocarvyl *p*-nitrobenzoate (abbreviated name, *cis*-PNB) (III) was carried out in order to determine the precise geometry of a β-pinene derivative. *cis*-PNB was suitable for this purpose because the carbon, nitrogen, and oxygen atoms all have approximately equal electron densities. Consequently, it was possible to determine their positions with much higher precision than for the halogenated compounds.



III

Experimental Section

X-Ray Data. Crystals of *cis*-pinocarvyl *p*-nitrobenzoate (mp 103.0-103.6°, $[\alpha]^{26}\text{D}$ −96.0°) suitable for X-ray diffraction analysis were kindly provided by Dr. James Farrand. The unit cell was found to be monoclinic with the following dimensions: at approximately −193°, a = 10.583 ± 0.006 Å, b = 6.740 ± 0.003 Å, c = 10.443 ± 0.009 Å, β = 90.46 ± 0.15°: at approximately 22°, a = 10.904 ± 0.012 Å, b = 6.778 ± 0.006 Å, c = 10.906 ± 0.009 Å, β = 91.77 ± 0.27°. The unit cell parameters were determined by the back-reflection Weissenberg technique. Systematic absences occurred for $0k0$ when k was odd indicating space group $P2_1$. Comparison of measured and calculated crystal densities indicated two molecules of *cis*-PNB per unit cell.

Three-dimensional X-ray data were obtained at approximately −193° using the multiple film equiinclination Weissenberg method and a liquid nitrogen gas flow cryostat.[5] Two crystals were used to obtain layers $0kl$ to $7kl$ and $h0l$ to $h4l$. The reflection intensities were estimated visually by comparison with a calibrated intensity scale. Lorentz and polarization, but no absorption, corrections were made. The data from the two crystal settings were scaled together by the method of Rollett and Sparks.[6] A total of 1361 unique, observed reflections was obtained. An additional 120 reflections were either unobserved or too weak to be measured with confidence. The relative intensities were converted to normalized structure factors, $|E_{hkl}|$, by the K-curve method of Karle and Hauptmann.[7,8]

Structure Determination and Refinement. The unit cell positions of atoms O-11, C-12, O-13, C-14, C-15, C-16, C-17, C-18, C-19, and N-20 were determined by the Patterson search methods of Braun, Hornstra, and Leenhouts.[9-11] Phases calculated from this fragment were used to start the tangent formula refinement procedure.[12] Two cycles were required to determine the positions of the remainder of the nonhydrogen atoms in the molecule. The structure was refined by block-diagonal least-squares methods to an R index[13] of 0.10 using unit weights and anisotropic temperature factors. A three-dimensional difference electron-density map was computed at this point, revealing the positions of all the hydrogen atoms. The least-squares refinement was continued with the hydrogen atoms included. The final R index for all observed reflections was 0.085. Each hydrogen atom was assigned an isotropic temperature factor equal to the final isotropic temperature factor of the atom to which it was bonded, and all hydrogen parameters were held constant during the least-squares refinement.[14] Table I shows the final atomic coordinates and their estimated standard deviations. The anisotropic temperature factors were normal for a structure determined near liquid nitrogen temperature.[15]

Results and Discussion

Figure 1 shows the bond lengths and bond angles in *cis*-PNB.

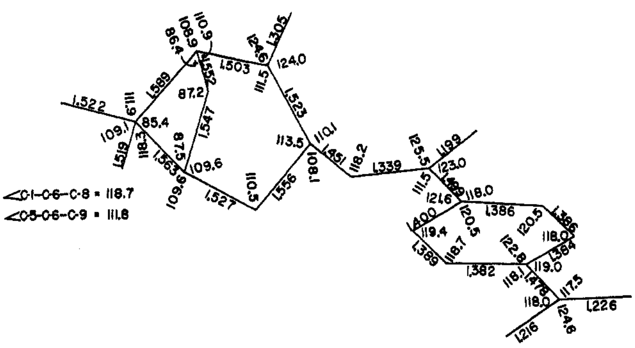


Figure 1. Bond lengths and bond angles in *cis*-PNB. The estimated standard deviation for C–C and C–N bonds is 0.008 Å; for C–O bonds, 0.007 Å; and for the C–N bond, 0.006 Å. The molecule is shown in orthogonal projection in the 010 plane.

Table I
Atomic Parameters

Atom	Fractional coordinates X^a	Y	Z
C-1	0.4411 (6)	0.5260 (9)	−0.2737 (5)
C-2	0.4160 (5)	0.3974 (9)	−0.1591 (5)
C-3	0.2922 (5)	0.4530 (9)	−0.0951 (5)
C-4	0.1910 (5)	0.5352 (9)	−0.1901 (5)
C-5	0.2543 (6)	0.6389 (9)	−0.3027 (5)
C-6	0.3350 (5)	0.4856 (9)	−0.3791 (5)
C-7	0.3801 (6)	0.7338 (10)	−0.2575 (5)
C-8	0.2842 (6)	0.2761 (10)	−0.3945 (5)
C-9	0.3723 (6)	0.5654 (11)	−0.5098 (6)
C-10	0.4893 (6)	0.2533 (10)	−0.1204 (6)
O-11	0.2392 (4)	0.2817 (6)	−0.0309 (3)
C-12	0.2486 (5)	0.2723 (9)	0.0969 (5)
O-13	0.2961 (4)	0.3959 (7)	0.1645 (4)
C-14	0.1933 (5)	0.0834 (9)	0.1476 (5)
C-15	0.1828 (6)	0.0629 (9)	0.2792 (5)
C-16	0.1327 (5)	−0.1085 (9)	0.3316 (5)
C-17	0.0929 (5)	−0.2566 (9)	0.2487 (5)
C-18	0.1001 (5)	−0.2393 (9)	0.1171 (5)
C-19	0.1514 (6)	−0.0675 (10)	0.0655 (5)
N-20	0.0360 (4)	−0.4386 (8)	0.3022 (4)
O-21	0.0375 (4)	−0.4579 (7)	0.4189 (4)
O-22	−0.0077 (4)	−0.5599 (7)	0.2275 (4)
H-1 (C-1)[b]	0.516	0.519	−0.322
H-1 (C-3)	0.316	0.545	−0.030
H-1 (C-4)	0.135	0.426	−0.219
H-2 (C-4)	0.150	0.628	−0.136
H-1 (C-5)	0.200	0.740	−0.340
H-1 (C-7)	0.404	0.821	−0.332
H-2 (C-7)	0.364	0.795	−0.176
H-1 (C-8)	0.200	0.276	−0.445
H-2 (C-8)	0.268	0.246	−0.309
H-3 (C-8)	0.354	0.191	−0.434
H-1 (C-9)	0.315	0.497	−0.550
H-2 (C-9)	0.426	0.461	−0.530
H-3 (C-9)	0.429	0.679	−0.505
H-1 (C-10)	0.468	0.162	−0.057
H-2 (C-10)	0.550	0.197	−0.170
H-1 (C-15)	0.210	0.171	0.330
H-1 (C-16)	0.118	−0.092	0.412
H-1 (C-18)	0.076	−0.368	0.075
H-1 (C-19)	0.176	−0.066	−0.020

[a] Estimated standard deviation times 10^4 in parentheses. [b] H-j (n-k) refers to the jth hydrogen atom bonded to the kth atom of type n.

***p*-Nitrobenzoate Grouping.** The geometry of the *p*-nitrobenzoate portion of *cis*-PNB is similar to that reported for a number of other *p*-nitrobenzene derivatives.[11,23-26] The average C–C bond length within the benzene ring is 1.386 Å and, within experimental error, all the benzene C–C bonds are equivalent. The average distance of the six benzene carbons from the least-squares plane through the ring was 0.004 Å, with the greatest distance being 0.006 Å. The average bond angle within the benzene ring is 120.0°.

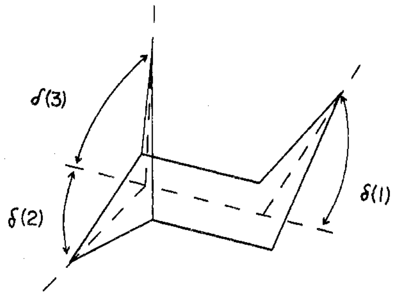


Figure 2. Interplanar angles δ(1), δ(2), and δ(3) formed by the boat and chair conformations of the pinane bicyclic ring system.

Angle C-15–C-16–C-17 is significantly smaller, and angle C-16–C-17–C-18 is significantly larger than the average. The angle between the plane of the nitro group and the best plane through the six benzene carbons is 5°, and the angle between the carboxylate plane and the benzene plane is 7°.

β-Pinene Grouping. The bond lengths and bond angles in the four-membered ring composed of C-1, C-5, C-6, and C-7 agree closely with the values reported for other cyclobutane derivatives.[27-30] The angle between plane C-1,C-7,C-5 and plane C-1,C-6,C-5 is 141°. Values of 149–180° have been reported for other cyclobutane rings. It is likely that the increased pucker aids in relieving severe steric interactions between C-3 and C-7 in *cis*-PNB. Contrary to expectations, bonds C-1–C-2 and C-2–C-3 are not significantly shorter than C-3–C-4 or C-4–C-5, even though the first two bonds involve the trigonal C-2. All four bonds have values close to the normal value of 1.530 Å. The double bond between C-2 and C-10 is shorter than in ethylene (1.334 Å), but close to the length of the exocyclic double bond in *trans*-2,8-dihydroxy-1(7)-*p*-menthene (1.314 Å).[31,32] The (noncyclobutane) ring bond angles at atoms C-1, C-2, C-3, C-4, and C-5 all have values within the range (109–114°) observed in other cyclohexane structures.

Table II contains the values found for the conformation angles within the *cis*-PNB bicyclic ring system.

Ideal cyclohexane boat and chair conformations have conformation angles of 0 and ±60°. The values in Table II indicate that the *cis*-PNB molecule is flatter at the C-3 end and more puckered at the C-6 and C-7 ends than an ideal boat or chair cyclohexane conformation. The greater deviation from ideality exhibited by *cis*-PNB and chloro-3-nopinone compared with some reported cyclohexane derivatives is shown in Table III and Figure 2. Increased ring distortion in β-pinene bicyclic structures appears to be necessary in order to minimize the steric repulsions between C-3 and C-7. For example, in *cis*-PNB a small amount of relief is gained through puckering of the cyclobutane ring, as mentioned earlier. However, the major relief arises from the movement of C-3 toward the C-1,C-2,C-4,C-5 plane and away from C-7, leading to small δ(1) values (*i.e.*, a "flattened" ring). The C-3⋯C-7 distance observed in *cis*-PNB is 2.72 Å, which is considerably smaller than the sum of the van der Waals radii (3.2 Å).

The ring strain in the molecule could have been partially decreased if the bond angle C-1–C-2–C-3 were near 120°. However, the observed value is 111.5°. The tendency for ring bond angles at carbons involved in exocyclic double bonds to be close to 110° (rather than 120°) has been found previously.[32,33]

In summary, the β-pinene portion of *cis*-PNB lies between a classical bridged chair and a Y-shaped molecule. Previous nmr studies on isopinocampheol[34] and nopinone[35] have been interpreted in terms of the same kind of conformation. Since the ring distortion arises from the need to minimize repulsion between C-3 and C-7, it is very likely that β-pinene itself will closely resemble the β-pinene portion of *cis*-PNB.

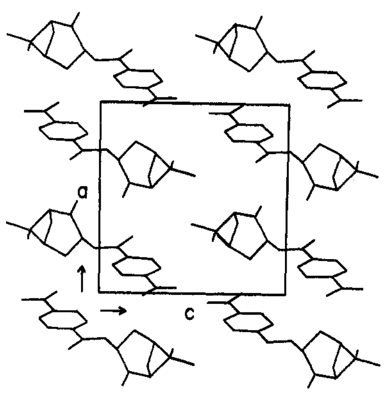


Figure 3. *cis*-PNB crystal packing shown in orthogonal projection in the 010 plane.

Table II
Ring Conformation Angles in the β-Pinene Portion of *cis*-PNB

Atoms $i-1, i, j, j+1$	τ_{ij},[a] deg	Atoms $i-1, i, j, j+1$	τ_{ij},[a] deg
C-6, C-1, C-2, C-3	−64.4	C-7, C-5, C-6, C-1	27.3
C-7, C-1, C-2, C-3	28.7	C-4, C-5, C-7, C-1	83.4
C-1, C-2, C-3, C-4	30.0	C-6, C-5, C-7, C-1	−27.7
C-2, C-3, C-4, C-5	−27.9	C-2, C-1, C-6, C-5	83.7
C-3, C-4, C-5, C-6	61.9	C-7, C-1, C-6, C-5	−26.9
C-3, C-4, C-5, C-7	−33.6	C-2, C-1, C-7, C-5	−81.6
C-4, C-5, C-6, C-1	−82.9	C-6, C-1, C-7, C-5	27.1

[a] Looking down bond $[i–j]$, τ_{ij} is defined as the clockwise angle between bond $[(i-1)-i]$ and bond $[j-(j+1)]$.

Table III[a]
Interplanar Angles δ(1), δ(2), and δ(3) in *cis*-PNB, Chloro-3-nopinone, and Various Cyclohexane Compounds

Compd	δ(1), deg	δ(2), deg	δ(3), deg	Ref
Cyclohexane[b]	60.0	60.0		*d*
Cyclohexane[c]	54.6	54.6		*d*
Cyclohexylammonium chloride	50.0	49.0		*e*
Bicyclohexylidene	49.4	51.1		*f*
cis-PNB	28.2	71.5	69.8	
Chloro-3-nopinone	30.0	75.0	70.0	*g*

[a] See Figure 2. [b] Ideal model. [c] Electron diffraction. [d] R. A. Wohl, *Chimia*, **18**, 219 (1964). [e] S. T. Rao and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **25**, 2509 (1969). [f] K. Sasvari and M. Low, *Acta Crystallogr.*, **19**, 840 (1965). [g] Reference 4.

Molecular Symmetry. The conformation of the benzoate linkage allows a pseudo-mirror plane to be constructed through C-3, C-6, C-7, C-8, C-9, and the nitrobenzoate group. Atoms C-1 and C-2 are approximately related to atoms C-5 and C-4, respectively, by this mirror plane. Of the nonhydrogen atoms, only C-10 is not related by pseudo-mirror symmetry to another atom in the molecule.

Crystal Packing. Figure 3 shows a projection of the unit cell down the *b* axis. The *p*-nitrobenzoate grouping is oriented perpendicular to the 001 plane. Most of the intermolecular distances are much larger than normal van der Waals distances, only 11 distances involving C, N, or O being less than 3.4 Å. The strongest intermolecular interactions occur along the *b* axis, where the molecules are packed so that O-13, C-12, C-14, and C-15 of each molecule lie near O-22, N-20, C-17, and C-18 of another molecule one *b*-axis translation away. In the *c*-axis direction, the closest intermolecular distances occur between each nitro oxygen and either C-16 or C-17 of another *cis*-PNB molecule. In the *a* axis direction the packing involved alternating C-10-O-13′ and C-4-O-22″ interactions.

Registry No. β-Pinene, 127-91-3; *cis*-pinocarvyl *p*-nitrobenzoate, 42540-80-7

Supplementary Material Available. A listing of anisotropic temperature factors, observed and calculated structure factors, and distances of atoms in *cis*-PNB from the least-squares plane through the molecule will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 photocopy or $2.00 for microfiche, referring to code number JOC-74-86.

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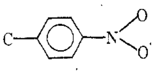
(10) The molecular fragment used for the Patterson search procedures was i. The detailed geometry was taken from the published structure of *p*-nitrobenzoic acid.[11]



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(12) J. Karle, *Acta Crystallogr., Sect. B*, **24**, 182 (1968).

(13) The crystallographic *R* index is simply defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(14) The atomic scattering factors for carbon, nitrogen, and oxygen were taken from Hanson, *et al.*,[16] and the hydrogen scattering factors were those of Stewart, *et al.*[17] The scaling and intensity data corrections were carried out with programs supplied by The Crystallography Laboratory, University of Pittsburgh.[18,19] The three-dimensional Fourier synthesis, tangent formula, and least-squares refinement programs were provided by F. R. Ahmed.[20] Weights were assigned during the final refinement cycles according to the equation $w = [(c_1|F_o|^2 + c_2|F_o| + c_3)(c_4 \sin^2 \theta + c_5 \sin \theta + c_6)]^{-1}$, where the least-squares constants $c_1 = 1.38$, $c_2 = -0.20$, $c_3 = 0.014$, $c_4 = 2.30$, $c_5 = -5.76$, and $c_6 = 5.24$ were evaluated by the method suggested by Cruickshank.[21,22]

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Acidities of Nitroalkanes in Ammonia. A Warning Concerning the Use of Nuclear Magnetic Resonance as a Method of Analysis

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The deprotonation of nitromethane and of nitroethane by ammonia is readily studied by nmr; the carbon acids and their conjugate bases each show separate signals. At a constant temperature the per cent deprotonation of each acid increases as the concentration of the sample increases. The deprotonation of nitromethane at −33° increases linearly from 34 to 80% as the total concentration of acid plus conjugate base increases from 0.18 to 2.18 *M*. Over this concentration range the chemical shift of the nitromethide ion decreases by 13 Hz. Both carbon acids undergo more deprotonation with decreasing temperature. Significant deprotonation is achieved below −10° for nitromethane and below 5° for nitroethane, the stronger acid. Attempts to express the results at a constant temperature in terms of equilibrium constants were unsuccessful, perhaps because changes in ion aggregation and in solvent polarity accompany variations in sample concentration.

An acidity scale for acids in liquid ammonia solvent is just beginning to be developed. A few pK_a values are available for very weak acids which require amide ion to bring about deprotonation as well as for considerably stronger acids which undergo deprotonation by ammonia itself.[1] For dilute solutions results generally have been obtained by means of potentiometric titration[2] and by using ultraviolet absorption spectroscopy to analyze reaction mixtures.[3] For more concentrated mixtures, nmr has been employed.[4,5]

Nmr is an especially attractive method of analyzing liquid ammonia reaction mixtures. Experimental techniques are relatively simple. Separate signals may be observed for both an acid and its conjugate base, greatly facilitating analysis of mixtures.

We decided to study the deprotonation of nitromethane (I) and nitroethane (II) in ammonia by an nmr method.

CH_3NO_2
I

$CH_3CH_2NO_2$
II