# 4- and 5-nitroindane

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Mononitration of indane produces a mixture of 4- and 5- nitroindanes. Crystallization from mixtures occurs after distillation improves composition of a major component to above 80%. 4-Nitroindane: triclinic, space group  $P\overline{1}$  (#2), a = 7.332(4) Å, b = 8.304(4) Å, c = 8.358(4) Å,  $\alpha = 61.43(4)^{\circ}$ ,  $\beta = 67.60(4)^{\circ}$ ,  $\gamma = 70.15(4)^{\circ}$ , V = 405.4(4) Å<sup>3</sup>, Z = 2. Non-H-atoms are nearly planar, aliphatic H's are eclipsed. 5-Nitroindane: monoclinic, space group  $P2_1/c$  (#14), a = 10.946(8) Å, b = 15.643(10) Å, c = 9.415(6) Å,  $\beta = 92.34(5)^{\circ}$ , V = 1611(2) Å<sup>3</sup>, Z = 8. Non-H-atoms in the two molecules differ in torsion of the nitro group with respect to indane and fold of the nonbenzylic methylene group. Semiempirical calculations (PM3) suggest that distorsion from planarity may be associated with the two lowest energy vibrational modes. Uv, ir, ms, proton, and <sup>13</sup>C-nmr spectra are correlated with the solid state structures.

**KEY WORDS:** Structure; indane; indane derivatives; nitroindanes; crystallography; nmr; infrared; ultraviolet.

## Introduction

Subsequent nitration of nitroaromatics is sufficiently slower than the initial nitration under electrophilic aromatic substitution conditions, that the principal kinetic products are commonly isolable. A case in point is the nitration of indane, which produces nearly equal amounts of the two isomeric aryl mononitroindanes. As part of a synthetic sequence which required 5-nitroindane, we have separated and characterized 4-nitroindane (4-NI) and 5-nitroindane (5-NI). The synthetic method employed was a modification of that used by Lindner and Bruhin.<sup>1</sup> These compounds are among the simpler nitroaromatic compounds for which chromatographic separation and detection methods have been reported.<sup>2-5</sup>

## Experimental

Substances and solvents were of reagent grade (typically >98% purity). The following instrumenta-

tion was used in the characterizations: melting points (Shimadzu DSC-5), ft-ir (Perkin Emer 1600 spectrometer), uv (Varian DMS-100S spectrometer), proton and <sup>13</sup>C-nmr (Bruker 300 spectrometer), gas chromatography (Varian 3400, He carrier, 175°C, packed OV-101 [2 m × 5 mm], thermal conductivity detector). Gc-ms (Hewlett-Packard 5890/5971), helium carrier, 30 m × 0.325 mm capillary DB-5 5  $\mu$ m, 150°C; crystallography (see Table 1).

#### Nitroindanes

To 7.69 mL (11.82 g, 100 mmol) indane and 5.0 mL concentrated  $H_2SO_4$  at 0°C (ice/water bath) was added a similarly cooled mixture of 10 mL concentrated nitric and 10 mL concentrated sulfuric acid, and the mixture was stirred rapidly. The colorless mixture became dark red. After 5 min, the whole was poured quickly into a mixture of 500 mL water and 250 g ice. After the ice melted, the mixture was extracted with ether (2× or until clear) and the combined ether extracts were washed with 5% NaHCO<sub>3</sub> solution and then with brine. After removing the ether, the dark brown oil was distilled at 500 mtorr. A first fraction,

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	Table 1.	Crystal	data and	summary	of intensity	collection	and refinement
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Compound	4-Nitroindane, 4-NI	5-Nitroindane, 5-NI		
Formula	CoHoNO2	C <sub>a</sub> H <sub>a</sub> NO <sub>2</sub>		
Formula weight	163.24	163.24		
Space group	P1(#2)	$P2_1/c(#14)$		
Temp., °C	21	21		
Cell constants				
<i>a</i> , Å	7.332(4)	10.946(8)		
b, Å	8.304(4)	15.643(10)		
c, Å	8.358(4)	9.415(6)		
α, deg.	61.43(4)	_ ,,,		
β, deg.	67.60(4)	92.34(5)		
y, deg.	70.15(4)	_ ``		
Cell volume, Å <sup>3</sup>	405.4(4)	1611(2)		
Formula units/unit cell	2	8		
<i>F</i> (000)	172	688		
$D_{\text{cale}}$ g-cm <sup>-3</sup>	1.337	1.346		
$\mu_{calc}$ cm <sup>-1</sup>	0.96	0.96		
Diffractometer, scan	Siemens R3m/y, omega scans			
Radiation, graphite monochromator	ation, graphite monochromator $M_0K_{\alpha}(\lambda = 1)$			
Max. crystal dimensions, mm	$0.5 \times 0.5 \times 0.3$	$0.5 \times 0.4 \times 0.3$		
Scan width, deg	2.6	2.4		
Standard reflections	11.2;2.0.6;0.6.0	4.0.0;0.8.0;0.0.4		
Decay of standards	none	none		
Reflections measured	2183	2842		
20 range, deg.	3.555.0	3.5-45.0		
Range of h, k, l	$-9 \rightarrow 9, -10 \rightarrow 9, -9 \rightarrow 10$	$-11 \rightarrow 11, -16 \rightarrow 0, 0 \rightarrow 10$		
Reflections observed $[(F_o^2 > 4\sigma(F_o^2)]$	1136	883		
Independent refl, R(merge)	1859, 0.0453	2109, 0.0607		
Computer programs	SHEL	XS. <sup>16</sup> SHELXL <sup>17</sup>		
No. of parameters/restraints	109/0	218/0		
Extinction	$F_c = (F_c)(\text{scale})[1 + 0.0]$			
x	None	$1.8(7) \times 10^{-3}$		
Weights	$1/[\sigma^2(F_0^2) + (aP)^2]$ , P	$P = \frac{1}{3} [\max(0 \text{ or } F_{2}^{2})] + \frac{2}{3} (F_{2}^{2})$		
a	0.11	0.07		
GOF	1.035	0.748		
$R = \sum   F_0  -  F_c   / \sum  F_0 , \text{ (all refl.)}$	0.0707	0.1215		
R (on observed refl.)	0.0552	0.0525		
$R_{\rm w}$ (all refl.)	0.1857	0.1382		
Difference map features, e/Å <sup>3</sup>	+0.20, -0.15	+0.18, -0.22		

<sup>a</sup> Structure factors Reference 18.

which emerged below 60°C, was unreacted indane. The broad fraction from 60-125°C contained the two nitroindanes. [NOTE: If the distillation is carried above 145°C, the dark material in the distillation flask may explode. The distillation is always safe, in our experience, provided that the process is terminated at 125°C. On two early occasions, distillations carried to above 145°C led to explosions from the small amount of material remaining in the distillation flask which deposited finely divided carbon over the interior of the distillation apparatus and forced a separation in the vacuum connection.] Nitroindanes fractions were analyzed by gc (He carrier, stationary phase DB-5 capillary or OV-101 packed, 150-175°C); 4-NI had a lower retention time than 5-NI. The combined nitroindanes were fractionated at 300 mtorr. 4-NI distilled beginning at 72°C as a nearly colorless liquid, amounting to about the first 5% of the total distillate volume. The second, broad fraction (85% of the distillate) emerged from 74-81°C and consisted of mixtures of the two isomers (4- and 5-NI) with compositions ranging from 60/40 to 20/80, respectively. Above 81°C, yellow 5-NI began crystallizing in the condenser. About the last 10% of the distillate was collected with a heated condenser as nearly pure 5-NI. Redistillation of both enriched fractions gave the isomers with >98%purity (gc).

Characterization: 4-Nitroindane, mp 44°C (lit.,<sup>1</sup> 44-44.5°C; lit.,<sup>4</sup> 42.5°C; lit.,<sup>5</sup> 43-44°C]; uv (CH<sub>3</sub>CN)  $\epsilon \times 10^3$  ( $\lambda$ /nm): 0(405), 3.2 (310 sh), 8.8 (267 max), 4.8 (238 min), 19.0 (208 max). Mass spectrum, EI, -70v (mass, abundance): 163 (M, base), 146(22), 117(40), 116(65), 115(M-NO<sub>2</sub>, 95), 91 (23), 63 (31); [lit.,<sup>5</sup> 163(M+), 115(100), 116(67), 146, 91, 117]. 5-Nitroindane, mp 41°C (lit.,<sup>1</sup> 40-40.5°C, lit.,<sup>4</sup> 40°C; lit.,<sup>5</sup> 39-40°C); uv (CH<sub>3</sub>CN)  $\epsilon \times 10^3$  ( $\lambda$ /nm): 0(415), 10.6 (281 max), 2.6 (240 min), 10.9 (223 max), 10.1 (218 min), 17.6 (205 max). Mass spectrum, EI, -70v, (mass, abundance): 163 (M, 55), 146(10), 117(40), 116(65), 115(M-NO<sub>2</sub>, base), 91(55), 51(21); [lit.,<sup>5</sup> 163(100), 115(75), 146(35); lit.,<sup>6</sup> 163(M+), 115(100), 116(67), 146, 91, 117].

Infrared spectra were measured on samples 2% in anhydrous KBr as pellets, and the chief features are given in Table 2. Proton and <sup>13</sup>C-nmr (300 MHz, CDCl<sub>3</sub>, ref. TMS, 25°C), see Tables 3 and 4. Low resolution proton (60 MHz) spectra have been reported:<sup>5</sup> 4-NI (CDCl<sub>3</sub>)  $\delta 2.15$ , 2H, m, J = 7 Hz;  $\delta 3.0$ , 2H, t, J = 7 Hz;  $\delta 3.42$ , 2H, t, J = 7 Hz;  $\delta 7.1-8.1$ , 3H; 5-NI (CDCl<sub>3</sub>)  $\delta 2.18$ , 2H, t, J = 7 Hz;  $\delta 3.0$ , 4H, overlapping t's, J = 7 Hz;  $\delta 7.9$ , 1H, s;  $\delta 7.5$ , 2H, dd.

	ane-
5-NI	Assignment
3103	ν C-H arvl
3072	ν C-H aryl
3050	ν C-H arvl
2955	ν C-H alkyl
2843	ν C-H alkyl
1611	ν Ph
1588 sh	ν Ph
1515 s	v، NO <sub>2</sub>
1479	· a - · - 2
1468	
1462	
1453	δ CH <sub>2</sub>
1434	δ CH <sub>2</sub>
1422	5 CH2
1345 s	V NO-
1309 sh	w CH
1276	ω CH <sub>2</sub>
12/0	w Ch <sub>2</sub>

τ CH<sub>2</sub>

νCN

δ NO<sub>2</sub>

γ CH

νСΗ

γ Ph(4)

**Table 2.** Infrared band energies  $(cm^{-1})$  for 4- and 5-nitroindane<sup>*a*</sup>

4-NI ·

3107

3093 3063

2959

2845

1613

1592

1454

1434 1427

1350 s

1275

1214

1197

1174

975

939

913

876

776

737 s

826 m

800 m

1067 m

1331 sh

1522 s 1478

<sup>a</sup> Bands are weak unless otherwise indicated: s = strong, m = moderate; sh(oulder).

1211

1156

1115

1103

1035

901 m

834 m

813 m

805 sh

741 s

919

875

1069 m

#### Crystallography

Crystals of 4-NI and 5-NI were grown from the melt as large prisms; the former were nearly colorless and the latter yellow. Specimens were cut, mounted and sealed in capillaries. For 4-NI, a second irregular crystal was included in the capillary which was not near the X-ray beam path. Details of the data collections and refinements are given in Table 1. The data were corrected for Lorentz and polarization effects but not for absorption. After development of the model, it was refined by full-matrix least-squares minimizing the differences in  $F^2$ . The final unrestrained refinement included all non-H-atoms with attendant anisotropic vibrational amplitudes. H-atoms were placed in calculated positions; they were assigned isotropic vibrational factors which exceeded the equivalent isotropic

4-Nitroindane						
Shieldings(δ, ppm) Couplings (J, Hz) H1a,b H2a,b H3a b	3.004 H1a,b —	2.134 H2a,b 7.5 —	3.364 H3a,b  7.5	7.933 H5	7.276 H6	7.496 H7
H5 H6 H7				_	7.7 —	<1 7.7 —
5-Nitroindane						
Shieldings(ð, ppm) Couplings (J, Hz) H1a,b H2a,b H3a b	2.955 H1a,b 	2.155 H2a,b 7.5 —	2.980 H3a,b 7.5	7.971 H4	7.968 H6	7.290 H7
H4 H6 H7			_	_	1.4 —	0.7 7.4

 Table 3. Proton nuclear magnetic resonance shieldings and couplings<sup>a</sup>

<b>Table 5.</b> Atomic coordinates( $\times 10^4$ ) and equivalent isotropy	opic
displacement parameters ( $Å^2 \times 10^3$ ) for 4-nitroindance	a

Atom	<i>x</i>	у	z	U(eq)
N(1)	886(2)	10701(2)	7321(2)	65(1)
O(1)	-668(3)	11347(2)	8233(3)	95(1)
O(2)	2392(2)	11374(2)	6614(2)	95(1)
C(1)	-2428(4)	5913(3)	8501(4)	90(1)
C(2)	-3843(4)	7200(4)	9436(4)	104(1)
C(3)	-2732(3)	8595(3)	9135(3)	74(1)
C(3A)	-703(2)	8202(2)	7874(2)	53(1)
C(4)	948(2)	9065(2)	7044(2)	53(1)
C(5)	2689(3)	8468(2)	5894(3)	65(1)
C(6)	2802(3)	6972(3)	5539(3)	82(1)
C(7)	1205(3)	6076(3)	6341(4)	82(1)
C(7A)	-531(3)	6680(2)	7499(3)	64(1)

<sup>*a*</sup> U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>a</sup> First order and non-first-order fit by RACCOON;<sup>12</sup> standard tetramethylsilane, 25°C.

vibrational factor of the attached atom by 20%. Positions of the non-H-atoms are given in Tables 5 and 6. Bond lengths and interbond angles, anisotropic vibrational parameters for the non-H-atoms and the H-atom positions, and selected least-squares planes in 4-NI and 5-NI have been deposited as Supplementary Materials.

In each structure, the magnitudes of the vibrations for the nitro oxygen atoms and for the nonbenzylic methylene carbon were larger than the other non-Hatoms. These regions of the structures are especially subject to low energy conformation distortion (see

 
 Table 4. Carbon-13 nmr shieldings (ppm\*)<sup>a</sup> for 4-nitroindane and 5-nitroindane

Assignment	4-NI	5-NI
C1	32.817	32.619?
C2	24.771	25.574
C3	33.988	32.974?
C3A	140.600	145.926
C3B	145.768	152.285
C4	148.184	121.894
C5	121.850	147.070
C6	127.247	119.368
C7	130.029	124.642

<sup>a</sup> Standard tetramethylsilane, 25°C.

below). Somewhat elongated ellipsoids could not be resolved into contributing positions for these atoms probably because the conformational distortions populate a range of nearby locations rather than an energetically favorable subset. The generally "thermal" nature of the structures may be ascribed in part to the relatively small difference in the X-ray experimental temperature and the melting temperatures of 4-NI and 5-NI. The general accuracy of the structures suffer from this as indicated, for example, by the poorer agreement factors.

### Semi-empirical calculations

Using HYPERCHEM<sup>7</sup> Release 4.0, models for 4-NI and 5-NI were constructed and geometries opti-

C(5)

0(2)



Fig. 1. Thermal ellipsoid plot (50%) of the molecular structure of 4-nitroindane.

		· · · · · · · · · · · · · · · · · · ·	·	
Atom	x`	<u>y</u>	Z	U(eq)
N(1A)	7365(3)	5485(3)	430(4)	68(1)
O(1A)	7584(3)	6249(2)	393(4)	95(1)
O(2A)	7984(3)	4953(2)	-166(4)	89(1)
C(1A)	3429(4)	4221(3)	3556(5)	80(2)
C(2A)	3748(4)	3288(3)	3469(5)	97(2)
C(3A)	4599(4)	3190(2)	2247(5)	66(1)
C(3AA)	5096(4)	4071(2)	2039(4)	52(1)
C(4A)	6070(3)	4334(2)	1266(4)	54(1)
C(5A)	6332(3)	5192(3)	1244(4)	53(1)
C(6A)	5682(4)	5789(3)	1966(5)	70(1)
C(7A)	4721(4)	5521(3)	2736(5)	71(1)
C(7AA)	4428(4)	4665(3)	2786(5)	58(1)
N(1B)	7440(3)	3185(3)	4410(4)	70(1)
O(1B)	7359(3)	3950(2)	4641(4)	93(1)
O(2B)	6795(3)	2658(2)	5005(4)	94(1)
C(1B)	11106(3)	1888(2)	943(5)	67(1)
C(2B)	10826(4)	949(3)	1099(5)	79(1)
C(3B)	9880(4)	847(2)	2207(5)	69(1)
C(3BA)	9464(4)	1750(2)	2496(4)	50(1)
C(4B)	8551(3)	2021(2)	3362(4)	54(1)
C(5B)	8363(4)	2882(3)	3462(4)	52(1)
C(6B)	9013(4)	3477(2)	2715(4)	60(1)
C(7B)	9914(4)	3192(2)	1868(4)	61(1)
C(7BA)	10150(3)	2334(3)	1760(4)	52(1)

**Table 6.** Atomic coordinates  $(\times 10^4)$  and equivalent isotropic displacement parameters  $(\mathring{A}^2 \times 10^3)$  for 5-nitroindane<sup>a</sup>

<sup>a</sup> U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

mized first with an empirical MM+ force field.<sup>8</sup> Beginning with these models, ground state structures were calculated using the PM3 method<sup>9</sup> with an energy state convergence criterion of 0.001 kcal/mol. Ground state energies calculated were -2235.844 kcal/mol (4-NI) and -2237.693 kcal/mole (5-NI). Vibrational spectra with claims of increased correlation with experiment were calculated based on the converged PM3 structures.<sup>10</sup>

### Discussion

A comparison of the physical and spectroscopic properties for 4-NI and 5-NI shows a combination of similarities and differences. In the uv, the tail of the strong, second lowest energy electronic transition for 4-NI (267 nm) barely touches the visible range resulting in a very pale yellow color. In 5-NI, the transition maximum is intensified by 20% and shifted to 281 nm, and the tail extends about 10 nm further into the visible, enough to produce a decidedly yellow color. This is consistent with a bathochromic and hyperchromic effect of the p-nitro substitution in 5-NI compared to 4-NI. By ei-ms, the isomers show essentially indistinguishable spectra displaying mostly the prominent parents (m/e 163) and M-H<sub>2</sub>, NO<sub>2</sub> (m/e 115) daughters. The infrared spectra (Table 2) are quite similar with the distinguishing features chiefly in the substitution dependent region of the out-of-plane ring bending modes ( $\gamma$ Ph and  $\gamma$ CH, 700–1000 cm<sup>-1</sup>). Since the in-plane NO<sub>2</sub> deformation may be expected in the vicinity of 800 cm<sup>-1</sup>, definitive assignment of bands for each isomer is somewhat problematic.

Figure 1 shows a plot of the solid state structure of 4-NI. Non-H-atoms of 4-NI are nearly planar; the mean deviation from the plane for the 12 atoms is 0.026 Å. The nitro group is in the mean molecular plane and the adjacent benzylic H's are essentially equidistant from the plane and the alkyl H's are eclipsed viewed along the C-C bonds. Nonplanar conformational isomers are possible involving rotation of the nitro group or folding of the five-membered ring by movement of C2 out of the molecular plane. Semiempirical (PM3) calculations on 4-NI suggest that the energy difference between planar and nonplanar isomers is low and virtually without barrier. The conformation in which the carbons lie in a plane and the nitro group is twisted by 24° about the C-N bond is the calculated lowest energy structure, but it is only very slightly lower in energy than a fully planar form (difference +0.008 kcal/mole). If the solid state structure, which is planar, is near the low energy conformation or a time-averaged structure then the nitro torsional motion ought to be a fairly low energy vibration. Based on the SCF model, the second lowest vibrational mode (about 76 cm<sup>-1</sup>) is an out-of-plane CH<sub>2</sub> deformation of C2 relative to the rest of the molecule. The lowest vibrational mode calculated is the C-NO<sub>2</sub> torsional vibration (about  $22 \text{ cm}^{-1}$ ) which is qualitatively similar to the experimentally observed 60–70  $\rm cm^{-1}$  for arylnitro groups.<sup>11</sup>

Figure 2 presents a view of the two molecules (a and b) comprising the asymmetric unit in the structure of 5-NI. In 5-NIa, the C-atoms C1, C3-C7aa may be fit to a plane with mean deviation of 0.004 Å, but C2 is decidedly out of that mean plane by 0.32 Å. The equivalent carbon in 5-NIb is -0.14 Å out of the mean C-atom plane for which the mean deviation is 0.013 Å. This suggests that like 4-NI, torsional deformation of the saturated ring in 5-NI is a low energy motion. The nitro group in 5-NIb is rotated by 8.4° relative to the indane plane compared with 2.9° in 5-NIa and 3.9°



Fig. 2. Thermal ellipsoid plot (50%) of the two 5-nitroindane molecules.

in 4-NI. The differences between the inequivalent 5-NI molecular structures agree with the kinds and magnitudes of lower energy vibrations expected based on a semi-empirical PM3 calculation of the structure of 5-NI. The calculation arrives at an essentially planar structure with the largest non-H-atom torsion less than  $0.12^{\circ}$ . The two lowest energy vibrations, like 4-NI, are for the nitro torsion (21 cm<sup>-1</sup>) and the out-of-plane C2 deformation (67 cm<sup>-1</sup>).

A first-order calculation of the proton chemical shifts in 4-NI suggests that all six kinds of H's ought to be well separated at 300 MHz.<sup>12</sup> The spectrum is tabulated in Table 3 which shows this to be the case. At C2,  $H_{2a}$  and  $H_{2b}$  are equivalent, the highest field resonance at  $\delta 2.134$ , and the coupling with H's at C3 and C1 are equal producing a pentet  $(J_{1,2} = J_{2,3} = 7.5)$ Hz). The proton nmr signals for the H's at C1 and C3 are triplets. Nevertheless, these may represent averaged environments since the rate of conformational interconversion at room temperature for 4-NI is undoubtedly fast. The downfield triplet and pairs of doublets are consistent with the aryl substitution structure. For 5-NI, first-order calculation suggests that the protons at C1 an C3 are overlapped and those at C4 and C6 might be strongly coupled. The spectrum shows the H's at C1 and C3 as a pair of overlapping triplets near  $\delta 2.95 - 3.00$ . Upfield at  $\delta 2.155$ , H's on C2 are equivalent and vicinal coupling  $(J_{1,2} = J_{2,3} = 7.5 \text{ Hz})$ produces a pentet. In the aromatic region, H's on C4 and C6 are overlapped and strongly coupled with  $\Delta \nu /$ J = 0.50. The upfield H on C7 is isolated at  $\delta 7.29$ and coupled to both other aryl H's.

Carbon-13 nmr spectra are partly assignable based on nominal substituent effects on the shieldings.<sup>13</sup> For 4-NI, the benzylic carbons have nearly equivalent shieldings ( $\delta$ 32.817 and 33.988) with the latter likely the benzylic C3 next adjacent to the C4-nitro group. For 5-NI, the benzylic carbons are very nearly equivalent ( $\delta$ 32.619 and 32.974) while the balance of the carbons have typical shieldings (Table 3).

As mentioned above, the conformations of each nitroindane are probably equilibrium averages of a group of torsionally dissimilar relatives, which conformations are energetically accessible within the constraints imposed by the packing. Principally, these conformations involve rotation of the nitro group and deformation of C2 from the mean indane plane. Bond lengths and interbond angles are within the normal ranges for these typical organic compounds.<sup>14</sup> By way of comparison, the structure of one other mononitroindane has been reported, that of 1,1,3,3,5-pentamethyl-6-nitroindane.<sup>15</sup> This recent study of musk compounds also includes several other low-melting 5-methyl-4,6dinitroindanes. Indane rings are distorted from planarity principally at the non-benzylic methylene (C2), which carbons show the same librational excesses as found in 4-NI, 5-NIa and 5-NIb. Nitro groups in the musks are adjacent to aryl methyls and thus the oxygens are not in the mean plane of the aryl ring atoms. In 4-NI and 5-NI, the nitro groups are more nearly in the aromatic ring plane. In 4-NI, this angle (between nitro and aromatic ring) has a value which is in the lower portion of the range observed in an extensive study of o-nitroaromatics.<sup>19</sup>

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Supplementary material. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5060 (for 4-NI) and CCDC-1003/5088 (for 5-NI). Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0) 1223-336033 or e-mail: teched@chemcrys.cam.ac.uk).

#### 4- and 5-nitroindane

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