

Intramolecular Hydrogen Bonding between Nitro and Hydroxy Groups in a Norbornyl System : a Crystallographic and Spectroscopic Investigation

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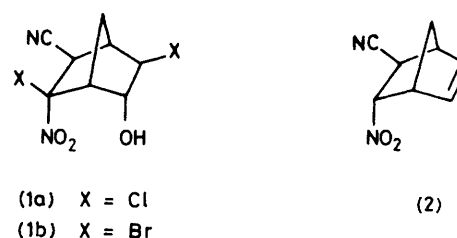
The structure of 3-*exo*,6-*exo*-dichloro-5-*endo*-hydroxy-3-*endo*-nitrobicyclo[2.2.1]heptane-2-*exo*-carbonitrile (1a), prepared from 3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile (2) and *N*-chlorosuccinimide, was elucidated by X-ray crystallography. The compound possesses an intramolecular hydrogen bond between the *endo*-nitro and hydroxy groups, further evidence for which was obtained from i.r. and n.m.r. spectra.

Intramolecular hydrogen bonding in compounds containing nitro and hydroxy groups attached to vicinal carbon atoms occurs if a six-membered ring can result from the interaction between the two functional groups.¹ The hydrogen bond in *o*-nitrophenols is rather strong, as evinced, for example, by infrared shifts to lower wavenumber of between 300 and 500 cm⁻¹ for the O-H stretching absorption relative to that of 'free' phenols;² but for acyclic saturated 2-nitroalcohols, shifts of only 10–30 cm⁻¹ for the O-H stretch have been found.³ Spectroscopic evidence for intramolecular hydrogen bonding in the latter systems is nonetheless substantial,^{1,3–5} and the phenomenon is now accepted as genuine, even if not entirely general.⁶

Intramolecular hydrogen bonding in 3-nitroalcohols, by contrast, remains almost entirely unexplored. To our knowledge, the sole example is due to Baitinger *et al.*, who have shown that 3-nitropropanol is unlikely to possess even weak intramolecular hydrogen bonds.³ In this compound, and also in the general case, it is probable that the preferred molecular conformation will be one in which the functional groups are too remote for interaction. Hydrogen bonding should become observable, however, if one could boost the population of a conformer in which the nitro and hydroxy groups are in close proximity. In this paper we present evidence that hydrogen bonding does indeed occur in the compound 3-*exo*,6-*exo*-dichloro-5-*endo*-hydroxy-3-*endo*-nitronorbornane-2-*exo*-carbonitrile (3-*exo*,6-*exo*-dichloro-5-*endo*-hydroxy-3-*endo*-nitrobicyclo[2.2.1]heptane-2-*exo*-carbonitrile) (1a), a compound in which the nitro and hydroxy groups are effectively constrained into near-neighbourhood by virtue of their location on the norbornyl skeleton.

Results and Discussion

In an earlier publication⁷ we described the preparation and X-ray crystallographic structure determination of the dibromo compound (1b). The intramolecular O...O separations between the hydroxy oxygen atom and both oxygen atoms of the nitro group, *ca.* 3 Å, were sufficiently small⁸ to make the existence of an intramolecular hydrogen bond between the two *endo* functional groups, perhaps even a bifurcated one, an attractive possibility. Owing to the presence of the two heavy bromine atoms, however, hydrogen atoms could not be located. We felt that the substitution of chlorine for bromine would probably allow the problem of locating hydrogen atoms crystallographically to be overcome. Accordingly, compound (1a) was prepared in 68.5% yield by chlorination of 3-*endo*-nitronorbornene-2-*exo*-carbonitrile (3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile) (2) with *N*-chlorosuccin-



imide in methanol, an unusual reaction which, we suspect, involves neighbouring-group participation by the nitro group after halogenation at the *exo*-face of the norbornenyl double bond.⁷ Compounds (1a) and (1b) were found to be isostructural, and the hydrogen atoms in the former could indeed be located crystallographically.

The results of the crystal structure analysis are shown in Figure 1 (crystal structure), Figure 2 (molecular structure), Tables 1 and 2 (atom positions and components of vibration tensors), and Tables 3–5 (molecular geometry). Structure factors and additional bond and torsional angles are listed in Supplementary Publication No. SUP 23830 (6 pp.).† From the positioning of individual molecules within the unit cell (Figure 1), it is clear that the O-H group cannot be involved in intermolecular hydrogen bonding, at least in the solid state; the closest intermolecular contact of the hydroxy hydrogen atom, to Cl(1) (3.17 Å), is too great for hydrogen bonding.⁹ Within each molecule, however, the same hydrogen atom is positioned such that its interaction with the nitro group, as expected, is highly probable (Figure 2).

Whether this interaction is genuinely a hydrogen bonding one is a matter for speculation. In (1a), the O(1)...O(2) and O(1)...O(3) distances, 3.00 and 3.08 Å, respectively, are probably short enough to support the idea of hydrogen bonding⁸ if one bears in mind that the putative hydrogen bond is intramolecular. More important is the H...O separation, which should be shorter than about 2.4 Å if hydrogen bonding is to operate.¹⁰ It can be seen from Table 5 that the O(1)-H...O(2) distance (2.04 Å) is entirely compatible with an intramolecular hydrogen bond, while the significantly greater O(1)-H...O(3) distance (2.66 Å) is not. Therefore, if a hydrogen bond exists in (1a) [and probably in (1b)], it cannot be bifurcated. A point of added interest arises

† For details of the Supplementary Publication Scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

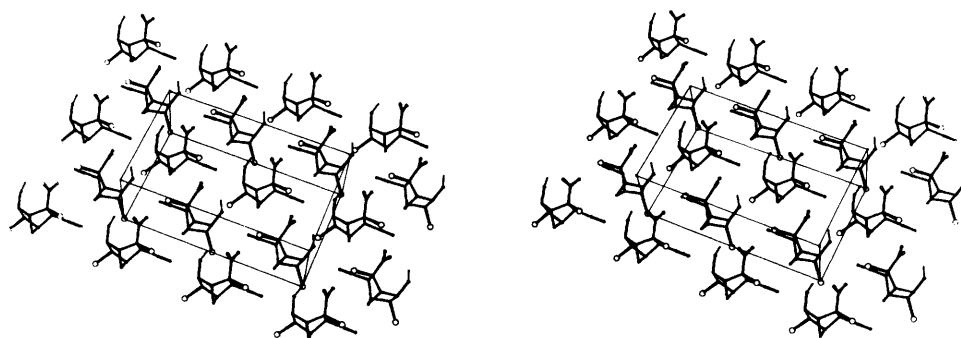


Figure 1. ORTEP-generated stereo-packing diagram for (1a). Hydrogen atoms other than that of the hydroxy group have been omitted for clarity

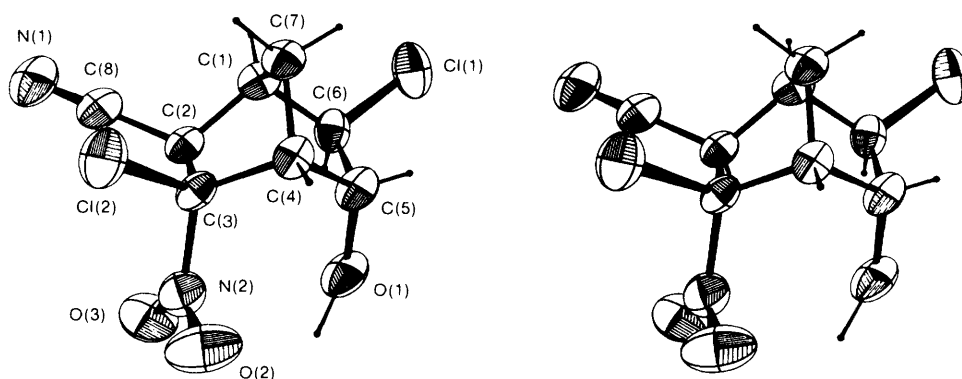


Figure 2. ORTEP-generated stereoscopic view of a molecule of (1a)

Table 1. Fractional atomic co-ordinates ($\text{\AA} \times 10^4$) and equivalent thermal vibration parameters ($U_{eq} \times 10^3/\text{\AA}^2$) of non-hydrogen atoms^a

	x/a	y/b	z/c	U_{eq}
Cl(1)	0	-119(2)	5 000	71(2)
Cl(2)	6 046(5)	2 713(1)	6 133(4)	54(1)
O(1)	4 662(12)	37(4)	7 395(7)	56(4)
O(2)	7 940(11)	1 325(5)	7 793(8)	70(5)
O(3)	5 459(12)	1 642(5)	9 066(7)	63(4)
N(1)	1 514(13)	3 445(5)	7 314(8)	61(5)
N(2)	6 181(12)	1 544(4)	7 962(8)	49(5)
C(1)	1 484(14)	1 435(5)	5 771(9)	39(5)
C(2)	2 609(12)	1 890(5)	6 997(8)	35(4)
C(3)	4 894(12)	1 770(4)	6 695(8)	34(4)
C(4)	4 779(13)	1 111(5)	5 563(8)	35(4)
C(5)	3 850(14)	284(5)	6 104(9)	43(5)
C(6)	1 569(13)	507(5)	6 149(11)	44(5)
C(7)	3 064(14)	1 469(6)	4 663(9)	40(5)
C(8)	2 001(14)	2 771(5)	7 160(8)	44(5)

^a The numbering scheme adopted is shown in Figure 2.

from the pronounced elongation of the thermal ellipsoids for O(1) and O(2) towards the hydroxylic hydrogen atom (Figure 2), thereby lending further credence to an intramolecular hydrogen bond.

In conformational terms, the orientations of both the nitro and the hydroxy groups are rather surprising. The torsional angles in Table 5 show that the C(3)-C(2) bond lies nearly in the plane of the nitro group; similarly, the dihedral angle between the O(1)-H and C(5)-C(4) bonds is unexpectedly small. With both functional groups adopting what would

Table 2. Fractional atomic co-ordinates ($\text{\AA} \times 10^3$) and isotropic thermal vibration parameters ($U_{iso} \times 10^3/\text{\AA}^2$) of the hydrogen atoms^a

	x/a	y/b	z/c	U_{iso}
H(1)	20(13)	162(5)	546(7)	38(22)
H(2)	252(10)	153(5)	781(8)	30(19)
H(4)	615(14)	105(5)	528(8)	54(26)
H(5)	372(13)	-12(5)	553(8)	48(26)
H(6)	145(12)	35(5)	697(9)	51(26)
H(7)- <i>syn</i>	329(10)	205(5)	426(7)	28(18)
H(7)- <i>anti</i>	268(12)	112(5)	390(9)	43(23)
H(hydroxy)	635(25)	23(13)	781(20)	339(107)

^a Hydrogen atoms bonded to carbon have been given the same numbers as the carbon atoms to which they are attached. The designations *syn* and *anti* are defined relative to the nitrile group.

appear to be intrinsically high energy conformations, an overriding energy-lowering attractive interaction between them seems an inescapable conclusion.* Although the geometrical arrangement of the interacting groups in (1a) is not the most favourable for strong hydrogen bonding [the angle formed at O(2) by the $\text{H} \cdots \text{O}(2)$ vector and the plane of the nitro group is about 76°], a weak interaction of the hydrogen atom with a π orbital of the nitro group is certainly not precluded.⁶

Spectroscopic evidence for the persistence of hydrogen

* The hypothesis that the observed conformational preferences are intrinsically unfavourable may, of course, be erroneous; to clarify this point, the conformational analysis of this and similar systems using empirical force-field methods is under investigation.

Table 3. Bond lengths (Å)

Cl(1)-C(6)	1.801(9)	C(3)-C(4)	1.534(10)
Cl(2)-C(3)	1.787(7)	C(4)-C(5)	1.561(11)
O(1)-C(5)	1.416(11)	C(4)-C(7)	1.517(11)
O(2)-N(2)	1.234(9)	C(5)-C(6)	1.553(11)
O(3)-N(2)	1.225(9)	H(1)-C(1)	0.94(8)
N(1)-C(8)	1.134(10)	H(2)-C(2)	0.99(8)
N(2)-C(3)	1.523(10)	H(4)-C(4)	0.97(9)
C(1)-C(2)	1.568(12)	H(5)-C(5)	0.86(8)
C(1)-C(6)	1.527(12)	H(6)-C(6)	0.86(9)
C(1)-C(7)	1.554(10)	H(7)- <i>syn</i> -C(7)	1.02(7)
C(2)-C(3)	1.568(9)	H(7)- <i>anti</i> -C(7)	0.97(9)
C(2)-C(8)	1.472(11)	O(1)-H(hydroxy)	1.21(15)

Table 4. Selected bond angles (°)

Cl(1)-C(6)-C(1)	111.7(7)	C(1)-C(6)-C(5)	103.8(6)
Cl(1)-C(6)-C(5)	112.6(6)	C(1)-C(7)-C(4)	94.7(6)
Cl(2)-C(3)-N(2)	103.0(5)	C(2)-C(1)-C(6)	104.4(7)
Cl(2)-C(3)-C(2)	112.8(5)	C(2)-C(1)-C(7)	102.7(6)
Cl(2)-C(3)-C(4)	110.8(5)	C(2)-C(3)-C(4)	102.2(6)
O(1)-C(5)-C(4)	114.0(8)	C(3)-C(2)-C(8)	114.2(7)
O(1)-C(5)-C(6)	111.2(7)	C(3)-C(4)-C(5)	109.5(6)
O(2)-N(2)-O(3)	124.8(7)	C(3)-C(4)-C(7)	100.3(6)
O(2)-N(2)-C(3)	116.5(7)	C(4)-C(5)-C(6)	102.5(6)
O(3)-N(2)-C(3)	118.5(7)	C(5)-C(4)-C(7)	102.9(7)
N(1)-C(8)-C(2)	178.4(9)	C(6)-C(1)-C(7)	100.9(6)
N(2)-C(3)-C(2)	112.1(6)	H-O(1)-C(5)	122(10)
N(2)-C(3)-C(4)	116.4(6)	O(1)-H...O(2)	133(14)
C(1)-C(2)-C(3)	102.7(6)	H...O(2)-N(2)	76(6)
C(1)-C(2)-C(8)	113.9(7)		

bonding in solutions of (1a) is reasonable. However, the applicability of i.r. spectroscopy in the present study was limited by the poor solubility of (1a) in non-polar solvents. In chloroform, for instance, the maximum solubility of (1a) was about 0.1% w/v (about 0.004M). Nonetheless, the O-H stretching frequency was discernible as a weak but apparently symmetrical band at 3 605 cm⁻¹; not surprisingly, no band ascribable to O-H...O-H intermolecular hydrogen bonding was apparent. In the accessible concentration range 0.03–0.1% w/v, the position of the band was concentration-independent. By comparison, borneol, the *endo*-hydroxy group of which is in a similar steric environment, absorbs at 3 620 cm⁻¹ at comparable concentrations; and 3-nitropropanol absorbs³ at 3 639 cm⁻¹. The magnitude of the O-H absorption shift for (1a) relative to these two model systems is thus at least as great as that shown by 2-nitroalcohols,¹ and is not incompatible with weak hydrogen bonding.

The more important spectroscopic evidence for the persistence of hydrogen bonding in solutions of (1a) comes from its ¹H n.m.r. spectra (Table 6). The concentration-independence of the chemical shift of the OH signal is a hallmark of intramolecular hydrogen bonds, indicating the unimportance of solute-solute and solute-solvent intermolecular hydrogen bonding. More arresting, however, is the appearance of the OH signal as a doublet coupled to the hydrogen atom on C(5). The coupling constant of this doublet, but not its chemical shift, is virtually independent of solvent and of temperature. In itself, the observation of spin-spin coupling for a proton which under normal circumstances would be expected to be involved in rapid exchange need not necessarily imply the sort of conformational immobility associated with intramolecular hydrogen bonding. More convincingly, exchange in a fairly concentrated solution (10% in deuteriated acetone) containing an equivalent of water is very slow; only after four weeks at

Table 5. Selected non-bonded distances (Å) and torsional angles (°)^a

O(1)...O(2)	3.00(1)
O(1)...O(3)	3.08(1)
O(1)...N(2)	2.65(1)
O(1)-H...O(2)	2.04(18)
O(1)-H...O(3)	2.66(20)
O(1)-H...N(2)	2.11(20)
O(1)-H...Cl(1) (intermolecular) ^b	3.17
O(2)-N(2)-C(3)-C(2)	170.3(3)
O(3)-N(2)-C(3)-C(2)	-14.3(5)
C(4)-C(5)-O(1)-H	-26.8(6)
H(5)-C(5)-O(1)-H	109.1(4)

^a Torsional angles are presented in the range -180 to +180°; the angle a-b-c-d is positive when the sense of rotation from a to d is clockwise as viewed along the b-c bond. ^b Cl(1) at x, 1-y, z-0.5.

Table 6. Chemical shifts and coupling constants for the hydroxy group of (1a)

Solvent	Temperature (K)	Concentration (%)	Chemical shift, δ	³ J/Hz
CDCl ₃	Ambient	ca. 0.1 (w/v)	2.08 ^a	4.2
[² H ₆]Acetone	Ambient	0.5–20	5.30 ^a	4.6
[² H ₆]Benzene	Ambient	1	0.80	4.6
[² H ₈]Dioxane	Ambient	1, 10	4.77 ^a	4.4
CD ₃ CN	Ambient	1	4.00 ^a	4.6
[² H ₆]DMSO	Ambient	1, 10	6.22 ^a	4.6
[² H ₆]Acetone	303	1	5.48 ^b	4.6
[² H ₆]Acetone	273	1	5.68 ^b	4.6
[² H ₆]Acetone	243	1	5.89 ^b	4.6
[² H ₆]Acetone	213	1	6.17 ^b	4.6

^a At 80 MHz. ^b At 500 MHz.

room temperature had the hydroxy doublet vanished completely.

Owing to the likelihood of rotational averaging, the observed coupling constant may not be a reliable guide to the conformation of the OH group. However, since *J* does not vary with temperature, rotational averaging is unlikely, and coupling would appear to be a genuine result of conformational locking arising from an intramolecular hydrogen bond. In terms of the modified Karplus relationship introduced by Fraser *et al.* for H-C-O-H systems,¹¹ the observed ³J value of 4.6 Hz corresponds to a dihedral angle for H-C(5)-O(1)-H of 125°, which correlates reasonably well with the 109° angle determined crystallographically. While one must take cognisance of the dangers of reading too much into a Karplus-type relationship, if the 125° angle is at all meaningful, then the intriguing implication is that, unless the conformation of the nitro group is also substantially altered (and in this regard, it is known that the rotational barrier about C-NO₂ bonds is very small indeed¹²), the hydrogen bond in (1a) may well be bifurcated in solution, in contrast with the situation in the solid state.

The nearly linear downfield displacement (in acetone) of the OH chemical shift with decreasing temperature (Table 6) is a well known phenomenon in hydrogen-bonded systems, and has usually been ascribed to shifts in association equilibria favouring a smaller fraction of broken hydrogen bonds with decreasing temperature.¹³ The downfield displacement of the OH chemical shift with increased solvent polarity is also

precedented, and is probably due largely to specific solute-solvent interactions,¹⁴ since the solvents employed in this study are mostly ones in which local ordering around polar centres of solute molecules is highly likely. The range of solvents explored in this study was not large enough for a reliable correlation between chemical shift and solvent parameters to be established, but within the limits of the experiment, no linear relationship between chemical shift and various solvent polarity or basicity parameters¹⁵ seems to exist.

In conclusion, it is quite possible that the single most important factor favouring the formation of the hydrogen bond in (1a) is just the unavoidable proximity of the two interacting functional groups resulting from their positioning on the norbornyl skeleton. Indeed, intramolecular hydrogen bonding exists, or has been postulated, when functional groups as varied as phenyl,¹⁶ sulphoxide,¹⁷ or alkenyl¹⁸ rather than nitro occupy the 6-*endo* position of 2-*endo*-norbornanols. Electrostatic and steric factors must, of course, be reckoned with, too; but that hydrogen bonding occurs at all in these systems may well be primarily a reflection of exceedingly favourable geometry.

Experimental

Spectroscopy.—N.m.r. spectra were recorded on a Bruker WP-80 instrument, or for variable-temperature work, on a Bruker WM-500 spectrometer. Me₄Si was the internal standard with all solvents used, which were dried when necessary with activated 4 Å molecular sieves. I.r. spectra were recorded on a Pye Unicam SP3-300 or a Perkin-Elmer 580B spectrometer as solutions in dry chloroform using solution cells (0.1 mm path-length) fitted with sodium chloride windows. Mass spectra were obtained on a Varian CH-7 instrument.

Synthesis of (1a).—(Experiment by Mr. N. F. Blom.) 3-*Endo*-Nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile⁷ (2) (0.362 g, 2.205 mmol), *N*-chlorosuccinimide (0.648 g, 4.85 mmol), and ammonium hexafluorophosphate (2.5 mg) were stirred together in dry methanol (10 ml) at room temperature for 12 h, followed by heating under reflux for 5.5 h. The solvent was removed *in vacuo*, water (10 ml) was added, and the solution was extracted with ether (3 × 10 ml). Drying (MgSO₄) and evaporation of the extracts yielded 3-*exo*,6-*exo*-dichloro-5-*endo*-hydroxy-3-*endo*-nitrobicyclo[2.2.1]heptane-2-*exo*-carbonitrile (1a), recrystallised from methanol as prisms (0.380 g, 68.5%), m.p. 194–195 °C (Found: C, 38.1; H, 3.2; N, 11.1. C₈H₈Cl₂N₂O₃ requires C, 38.3; H, 3.2; N, 11.2%). ν_{max} (KBr) 3 415 (OH), 2 265 (CN), 1 570 (NO₂), and 1 352 cm⁻¹ (NO₂); δ ([²H₆]acetone) 5.30 (1 H, d, *J* 4.64 Hz, H-O), 4.57 (2 H, m, 5-H and 2-H), 4.02 (1 H, m, 6-H), 3.40 (1 H, m, 4-H), 2.96 (1 H, m, 1-H), 2.40 (2 H, t with further small coupling, *J* 1.3 Hz, 7-*syn*-H and 7-*anti*-H); *m/z* 204 (5%, *M* - NO₂), 141 (58), 138 (48), 126 (56), 113 (46), 102 (60), 90 (36), and 77 (100).

Crystallographic Analysis of (1a).—C₈H₈Cl₂N₂O₃, *M* = 251.07. Monoclinic, *a* = 6.62(1), *b* = 15.95(1), *c* = 9.90(1) Å, β = 92.94(1)°, *U* = 1042.4 Å³, *D_m* (flotation) = 1.60 g cm⁻³, *Z* = 4, *D_c* = 1.59 g cm⁻³, *F*(000) = 512, space group *Cc* (No. 9), graphite-monochromated Mo-*K*_α radiation, μ (Mo-*K*_α) = 5.45 cm⁻¹, λ = 0.7107 Å.

Crystals of (1a) (0.2 × 0.2 × 0.5 mm) were grown from methanol solution. Intensities of 747 reflections [715 with *F*_{obs} > σ (*F*)] were collected on an automated Philips PW1100 four-circle diffractometer (scan mode, ω - 2 θ ; scan width, 1.2°; scan speed 0.04° s⁻¹; range of reflections, 3 < θ < 27). Intensity measurements were performed at room temperature.

The data were corrected for Lorentz-polarisation effects. The positions of the chlorine atoms were determined from a Patterson map; subsequent difference Fourier maps and cycles of full-matrix least-squares refinement revealed the positions of the rest of the atoms. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were refined independently, with isotropic thermal parameters. At the termination of refinement, *R* was found to be 0.0378 for 714 reflections. The program SHELX¹⁹ was used on a CDC cyber 174 machine for all crystallographic computations.

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