X-Ray Crystallographic Evidence for Intermolecular Hydrogen Bonding, including a Bifurcated Hydrogen Bond, between Nitro and Hydroxy Groups in Two 3-Chloro-6-nitrobicyclo[2.2.1]heptan-2-ols

Jan C. A. Boeyens, Louis Denner, and Joseph P. Michael*
Department of Chemistry, University of the Witwatersrand, Jan Smuts Avenue, Johannesburg, South Africa 2001

The structures of 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*exo*-ol (**7**) and 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*endo*-ol (**8**), prepared in moderate yields by oxidation of 5-*endo*-nitrobicyclo[2.2.1]hept-2-ene (**3**) with chromyl chloride followed by reduction of the crude chloroketone mixture with sodium borohydride, were determined by *X*-ray crystallography. In compound (**7**), linear hydrogen bonds occur intermolecularly between the hydroxy and nitro groups, while in compound (**8**), the intermolecular hydrogen bonds between these groups are unsymmetrically bifurcated.

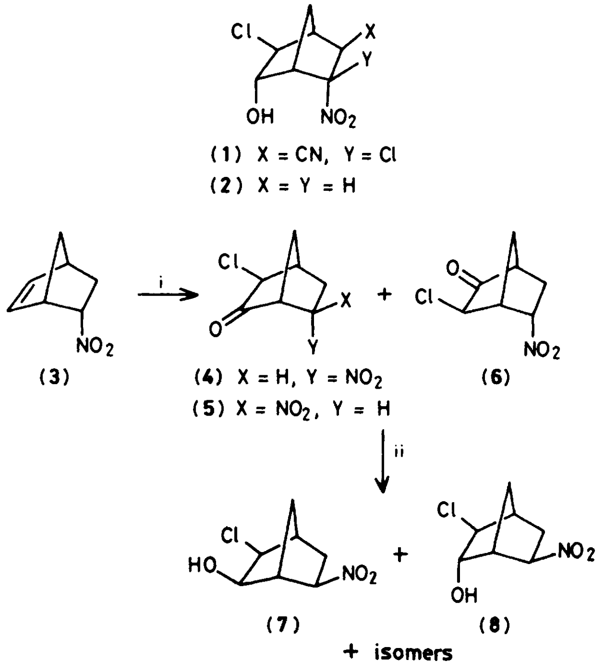
We have previously reported the existence of an intramolecular hydrogen bond between the hydroxy and nitro groups in the norbornanol (**1**).[1] As part of a continuing crystallographic search for hydrogen bonds in nitronorbornanols, we attempted to prepare the less substituted analogue (**2**), the idea being to trim away polar functional groups which might themselves influence the packing of molecules within the crystal lattice. The proposed route (see Scheme) involved the addition of chromyl chloride to 5-*endo*-nitrobicyclo[2.2.1]hept-2-ene[2] (**3**) (the Sharpless procedure[3]), followed by hydride reduction of the appropriate chloroketone (**4**) from the expected mixture of compounds (**4**) and (**6**).

In the event, the crude product mixture from the chromyl chloride reaction (58%) could not be quantitatively separated into its components; only small amounts of the pure isomer (**4**) and its stereoisomer (**5**), merely sufficient for characterisation, could be separated by column chromatography. Consequently, the reduction of the keto group was carried out on the crude adduct mixture using sodium borohydride in methanol. The product mixture from this reaction was far more complex than expected, but the two most abundant products, (**7**) (17%) and (**8**) (31%), were separated and characterised.

The surprising feature of both these products was that the nitro group had isomerised to the *exo*-position; their n.m.r. spectra show that the protons α to the nitro groups are not coupled to the C(1) bridgehead hydrogen atoms, a characteristic feature of *endo*-protons.[4] This was a tiresome, but not unprecedented, result: Grob[5] has reported the failure to obtain 6-*endo*-nitrobicyclo[2.2.1]heptan-2-*endo*-ol by reduction of the corresponding ketone, a very ready isomerisation of the nitro group also occurring under his reaction conditions. Although the chloroalcohols (**7**) and (**8**) were not the desired ones, their crystal and molecular structures nonetheless proved very interesting. Figures 1 and 4 show the crystal structures of the two compounds, and Figures 2, 3, and 5 the packing diagrams. Tables 1 and 2 list the fractional atomic co-ordinates and selected temperature factors for both compounds, Table 3 contains bond lengths and selected non-bonded distances, and Table 4 contains selected bond and torsion angles. Full Tables of temperature factors and bond angles are available in Supplementary Publication No. SUP. 23998 (13 pp.).*

The most significant feature about compound (**7**) is the short intermolecular contact, 2.10 Å, between the hydroxylic hydrogen atom of one molecule and O(2) of the nitro group of the neighbouring molecule at symmetry position (x, $1 + y$, z). In comparison, the H ··· O (3) separation is 2.92 Å. If one uses the criterion that hydrogen bonding occurs at H ··· O distances shorter than *ca.* 2.4 Å,[6] then the former value provides good grounds for proposing intermolecular hydrogen bonding in (**7**). Furthermore, the hydrogen bond is nearly linear [O(1)-H ··· O(2) = 174°], a desirable, but not always attainable, situation for a strong hydrogen bond.[7] As is apparent from Figure 3, molecules of (**7**) of a single enantiomeric series are linked by intermolecular hydrogen bonds in infinite chains along the *b* axis, and each of the four molecules within the unit cell participates in a hydrogen-bonded assembly only with molecules occupying the same relative symmetry position in neighbouring unit cells. The existence of hydrogen bonding in the solid state for (**7**) is supported by the O–H stretch in the i.r. spectrum (Nujol mull) as a broad band centred at 3 465 cm^{-1}.

The H ··· O(2) and H ··· O(3) intermolecular contacts in the isomeric compound (**8**) are 2.26 and 2.42 Å, respectively,



Scheme. *Reagents:* i, CrO_2Cl_2, acetone, −78°; ii, $NaBH_4$, MeOH

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* For details of Supplementary Publications see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

Table 1. Fractional atomic co-ordinates (Å × 10^4) and equivalent thermal vibrational parameters (× 10^3/Å^2) of non-hydrogen atoms for compounds (**7**) and (**8**)

	exo-Alcohol (**7**)				*endo*-Alcohol (**8**)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Cl	1 104(1)	−3 676(1)	4 096(1)	66(1)	3 090(1)	4 275(1)	708(1)	58(1)
N	3 658(2)	3 129(3)	3 825(3)	40(2)	−2 713(4)	3 442(3)	4 085(2)	43(2)
O(1)	3 501(2)	−2 738(3)	5 425(2)	44(1)	−849(4)	1 713(3)	1 278(2)	64(2)
O(2)	3 655(2)	3 594(3)	4 974(2)	52(2)	−4 413(3)	3 121(3)	3 910(2)	61(2)
O(3)	3 874(3)	4 115(3)	2 930(2)	65(2)	−2 198(4)	4 116(3)	4 878(2)	66(2)
C(1)	3 274(3)	162(4)	4 708(3)	30(2)	−1 498(5)	3 806(3)	2 225(3)	42(2)
C(2)	3 343(3)	−1 737(4)	4 268(3)	34(2)	−355(4)	3 098(3)	1 332(3)	43(2)
C(3)	2 048(3)	−1 970(4)	3 456(3)	41(1)	1 783(4)	3 353(3)	1 728(3)	41(2)
C(4)	1 406(3)	−220(4)	3 605(3)	42(2)	1 599(4)	4 252(3)	2 785(3)	39(2)
C(5)	2 085(3)	1 080(5)	2 742(3)	46(2)	850(4)	3 178(4)	3 652(3)	42(2)
C(6)	3 399(3)	1 266(4)	3 492(3)	35(2)	−1 283(4)	2 956(3)	3 267(2)	37(2)
C(7)	1 867(3)	341(4)	4 987(3)	40(2)	−191(5)	5 009(3)	2 506(3)	45(2)

Table 2. Fractional atomic co-ordinates (Å × 10^3) and isotropic thermal vibrational parameters (× 10^3/Å^2) of hydrogen atoms for compounds (**7**) and (**8**)[a]

	exo-Alcohol (**7**)				*endo*-Alcohol (**8**)			
	x	y	z	U_{iso}	x	y	z	U_{iso}
H(1)	384(2)	41(3)	543(3)	22(7)	−264(5)	402(3)	204(2)	42(9)
H(2)	405(3)	−192(4)	369(3)	35(8)	−55(4)	351(3)	55(3)	54(9)
H(3)	217(3)	−225(4)	253(3)	38(8)	242(4)	251(3)	182(2)	37(8)
H(4)	50(3)	−20(4)	342(3)	44(8)	271(4)	460(3)	299(2)	34(8)
H(5-*exo*)	169(3)	221(5)	271(3)	61(11)	83(4)	361(3)	440(3)	52(9)
H(5-*endo*)	217(3)	64(4)	182(3)	52(9)	157(5)	230(4)	364(3)	54(10)
H(6)	412(3)	94(4)	293(3)	29(7)	−168(4)	202(3)	313(2)	41(8)
H(7-*syn*)	163(3)	−47(2)	569(3)	45(9)	1(4)	559(3)	186(3)	48(9)
H(7-*anti*)	160(3)	154(4)	522(3)	41(8)	71(4)	552(3)	315(3)	52(9)
H(O)	354(4)	−373(5)	524(4)	71(14)	−24(6)	149(4)	67(3)	85(14)

[a] The hydrogen atoms have been given the same numbers as the carbon atoms to which they are attached. The designations *syn* and *anti* are in relation to the OH group.

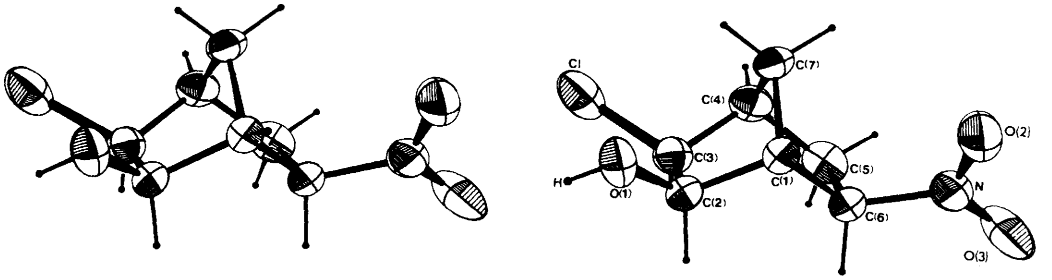

Figure 1. ORTEP-generated stereoscopic view of a molecule of 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*exo*-ol (7) showing the numbering scheme used for non-hydrogen atoms. Thermal ellipsoids are at 50% probability

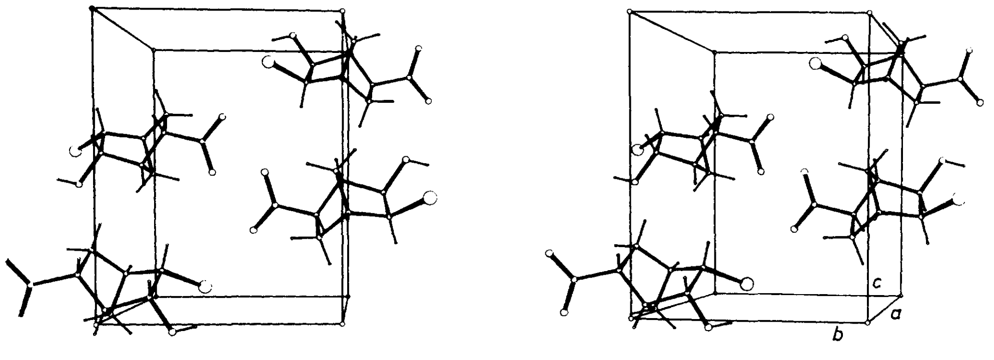

Figure 2. Stereoscopic view of the contents of the unit cell for 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*exo*-ol (7)

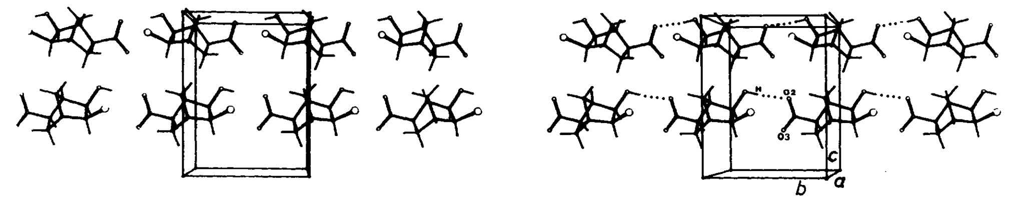

Figure 3. Stereoscopic view of the intermolecular hydrogen bonding in 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*exo*-ol (**7**). Molecules at symmetry positions $(-x, -y, -z)$ and $(0.5 - x, y, 0.5 - z)$ have been omitted for clarity

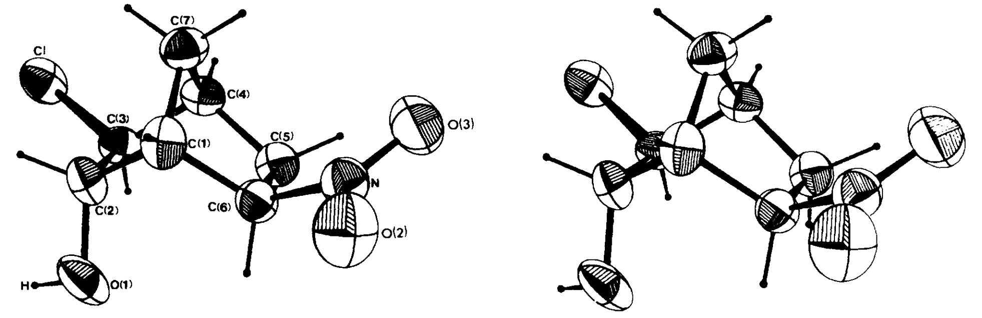

Figure 4. ORTEP-generated stereoscopic view of a molecule of 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*endo*-ol (**8**) showing the numbering scheme used for non-hydrogen atoms. Thermal ellipsoids are at 50% probability

Table 3. Bond lengths and selected non-bonded distances (Å) for compounds (**7**) and (**8**)

	Compound (**7**)	Compound (**8**)
Cl–C(3)	1.800(3)	1.810(3)
N–C(6)	1.507(4)	1.508(4)
O(1)–C(2)	1.412(4)	1.423(4)
O(2)–N	1.222(3)	1.227(3)
O(3)–N	1.220(3)	1.214(3)
C(1)–C(2)	1.542(4)	1.537(4)
C(1)–C(6)	1.516(4)	1.523(4)
C(1)–C(7)	1.535(4)	1.531(5)
C(2)–C(3)	1.571(4)	1.555(4)
C(3)–C(4)	1.529(5)	1.517(4)
C(4)–C(5)	1.540(5)	1.537(4)
C(4)–C(7)	1.527(4)	1.529(4)
C(5)–C(6)	1.556(4)	1.543(4)
O(1) ··· O(2)[a]	2.888(3)	3.078(4)
O(1) ··· O(3)[a]	3.557(3)	3.205(4)
H(1)–C(1)	0.94(3)	0.84(3)
H(2)–C(2)	0.99(3)	1.04(3)
H(3)–C(3)	0.98(3)	0.95(3)
H(4)–C(4)	0.96(3)	0.92(3)
H(5-*exo*)–C(5)	0.97(4)	1.01(3)
H(5-*endo*)–C(5)	1.01(3)	1.01(3)
H(6)–C(6)	1.01(3)	0.99(3)
H(7-*syn*)–C(7)	0.99(3)	0.99(3)
H(7-*anti*)–C(7)	1.00(3)	1.01(3)
H–O(1)	0.79(4)	0.90(4)
O(1)–H ··· O(2)[a]	2.10(4)	2.26(4)
O(1)–H ··· O(3)[a]	2.92(4)	2.42(5)
O(1)–H ··· N[a]	2.84(4)	2.64(4)

[a] For compound (**7**), O(2), O(3) and N are at $(x, 1 + y, z)$; for compound (**8**), they are at $(0.5 + x, 0.5 - y, 0.5 + z)$.

Table 4. Selected bond and torsion angles (°) for compounds (**7**) and (**8**)

	Compound (**7**)	Compound (**8**)
Cl–C(3)–C(2)	112.3(2)	111.5(2)
Cl–C(3)–C(4)	111.1(2)	111.7(2)
N–C(6)–C(1)	112.4(2)	108.8(2)
N–C(6)–C(5)	110.3(3)	113.5(3)
O(1)–C(2)–C(1)	106.8(2)	110.4(3)
O(1)–C(2)–C(3)	115.8(2)	113.3(3)
O(2)–N–O(3)	122.6(3)	121.9(3)
O(2)–N–C(6)	119.2(2)	116.8(3)
O(3)–N–C(6)	118.2(3)	121.3(3)
C(1)–C(2)–C(3)	102.1(2)	102.5(2)
C(1)–C(6)–C(5)	103.5(2)	103.3(2)
C(1)–C(7)–C(4)	94.0(2)	94.4(3)
C(2)–C(1)–C(6)	107.2(2)	107.0(3)
C(2)–C(1)–C(7)	101.6(2)	101.6(3)
C(2)–C(3)–C(4)	103.0(2)	103.6(2)
C(3)–C(4)–C(5)	107.6(3)	106.7(3)
C(3)–C(4)–C(7)	102.9(3)	101.7(3)
C(4)–C(5)–C(6)	102.2(2)	103.2(2)
C(5)–C(4)–C(7)	101.7(3)	102.2(3)
C(6)–C(1)–C(7)	103.1(2)	102.4(3)
C(2)–O(1)–H	110(3)	99(3)
O(1)–H ··· O(2)[a]	174(4)	152(4)
O(1)–H ··· O(3)[a]	139(4)	147(4)
O(2)–N–C(6)–C(5)	110.0(4)	−169.5(3)
O(3)–N–C(6)–C(5)	−70.6(5)	10.4(5)
Cl–C(3)–C(2)–O(1)	−6.6(5)	121.1(3)
C(1)–C(2)–O(1)–H	179.7(3)	171.0(3)

[a] For compound (**7**), O(2) and O(3) are at $(x, 1 + y, z)$; for compound (**8**), they are at $(0.5 + x, 0.5 - y, 0.5 + z)$.

sufficiently close to one another and to the cut-off value of 2.4 Å to make the suggestion of a highly unusual intermolecular three-centre (bifurcated) hydrogen bond between the hydroxy and nitro groups (Figure 5) worthy of serious consideration. In this structure, the hydroxylic proton is shared between two enantiomeric molecules related by a two-fold screw axis. In contrast to compound (**7**), only two hydrogen-bonded chains of molecules per unit cell are propagated through the crystal lattice along the *c* axis of the unit cell. Support for hydrogen bonding in the solid state comes from the i.r. spectrum (Nujol mull), in which the O–H stretching absorption is at 3 470 cm^{-1}

The conformations of the nitro groups in (**7**) and (**8**) are

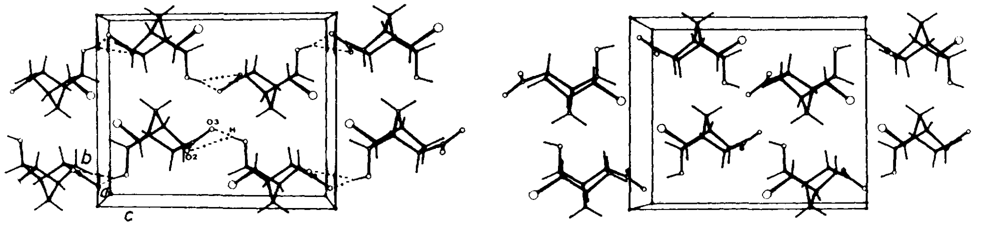

Figure 5. Stereoscopic view of the contents of the unit cell and the intermolecular hydrogen bonding in 3-*exo*-chloro-6-*exo*-nitrobicyclo[2.2.1]heptan-2-*endo*-ol (**8**)

remarkably different (Figures 1 and 4, Table 4). Some molecular mechanics calculations we have performed on 2-*exo*-nitronorbornane show that the preferred conformation of the nitro group is one in which it lies very nearly in the same plane as the C(2)–C(3) bond, the O(*endo*)–N–C(2)–C(3) dihedral angle being −1.8°.[8] This value is much closer to that (10.4°) for (**8**) than to that (−70.6°) for (**7**), leading one to suspect that the latter compound may be the unusual one. With both the chloro and hydroxy substituents in (**7**) being *exo*, the nitro group cannot adopt the theoretically preferred conformation without at the same time suffering severe steric and electrostatic interactions with the chlorine atom in the adjacent unit cell. In consequence, the nitro group cannot become properly orientated for three-centre hydrogen bonding to the nearby hydroxy group. These problems apparently do not exist in (**8**). Whether nitro group conformation and hydrogen-bonding type are necessarily interdependent is, however, by no means certain, and the existence of the unexpected bifurcated hydrogen bond in (**8**) may be nothing more than a fascinating coincidence.

Experimental

N.m.r. spectra were recorded on a Bruker WP-80 or Varian EM-360A instrument. Chemical shifts are reported relative to tetramethylsilane. Extensive decoupling experiments allowed the unambiguous assignment of signals. I.r. spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer using the potassium bromide dispersion technique for solid samples. Mass spectra were obtained on a Varian-MAT CH-7 instrument. Thin-layer chromatograms were run on Merck DC-Fertigplatten Kieselgel F-254 plates.

Addition of Chromyl Chloride to 5-endo-*Nitrobicyclo*[2.2.1]-*hept*-2-*ene* (**3**).—The Sharpless procedure[3] was used in this reaction. Chromyl chloride[9] (8.68 g, 48.06 mmol) was added dropwise over 30 min to a vigorously stirred solution of the *endo*-nitro compound (**3**)[2] (3.80 g, 27.31 mmol) in acetone (60 ml) at −78 °C such that the internal temperature never exceeded −70 °C. After a further 65 min at −78 °C, the mixture was stirred at room temperature for 6 h, after which it was poured into an ice-cold aqueous solution of sodium metabisulphite (10M, 30 ml). After being stirred for 45 min at 0 °C, the acetone was removed under reduced pressure, and the green residue was extracted with ether (3 × 25 ml). From these extracts was obtained a viscous oil (3.00 g, 58% isolated yield) containing a mixture of chloroketones which was used without separation in the following reaction. Attempts to separate the mixture into its components by chromatography on silica gel using hexane–ethyl acetate mixtures were largely unsuccessful, but on one occasion small quantities of two products were obtained sufficiently pure for characterisation. These structures were assigned as 3-exo-*chloro*-6-exo-*nitrobicyclo*[2.2.1]*heptan*-2-*one* (**5**), m.p. 78—79 °C (from di-isopropyl ether–ethyl acetate) (Found: C, 44.1; H, 4.1; N, 7.4. $C_7H_8ClNO_3$ requires C, 44.4; H, 4.25; N, 7.4%); R_F (hexane–ethyl acetate 1 : 1 v/v) 0.86; $\nu_{max.}$(KBr) 1 762 (C=O), 1 550 and 1 367 cm^{-1} (NO_2); δ($CDCl_3$) 4.66 (1 H, dd, *J ca.* 3.9 Hz, H-6), 3.76 (1 H, d, *J* 2.7 Hz, H-3), 3.39 (1 H, br s, H-1), 2.86 (1 H, m, H-4), 2.90—2.60 (2 H, m, H-5), 2.31 (1 H, d with further fine coupling, *J* 11 Hz, H-7-*anti*), and 2.00 (1 H, d with further fine coupling, *J* 11 Hz, H-7-*syn*); *m/z* 189/191 (6/2%, M^+), 142/144 (6/2, $M^+ - NO_2$), 115 (6), 107 (8), 80 (11), 79 (100), and 77 (39); and 3-exo-*chloro*-6-endo-*nitrobicyclo*[2.2.1]*heptan*-2-*one* (**4**), m.p. 86—87 °C (from ethyl acetate) (Found, C, 44.3; H, 4.1; N, 7.3. $C_7H_8ClNO_3$ requires C, 44.4; 4.25; N, 7.4%); R_F (hexane–ethyl acetate 1 : 1 v/v) 0.57; $\nu_{max.}$(KBr) 1 762 (C=O), 1 550 and 1 368 cm^{-1} (NO_2); δ($CDCl_3$) 5.09 (1 H, 5-line m, *J* 4.5 Hz, H-6), 4.15 (1 H, d, *J* 3.4 Hz, H-3), 3.25 (1 H, m, H-1), 2.92 (1 H, m, H-4), 2.75—1.95 (3 H, m, H-5-*exo*, H-5-*endo*, and H-7-*anti*), and 1.79 (1 H, d with further fine coupling, *J* 12 Hz, H-7-*syn*); *m/z* 189/191 (0.9/0.6%, M^+), 143/145 (2/0.8, $M^+ - NO_2$), 115 (7), 80 (34), 79 (100), and 77 (98).

3-exo-*Chloro*-6-exo-*nitrobicyclo*[2.2.1]*heptan*-2-endo-*ol* (**8**) *and* 3-exo-*Chloro*-6-exo-*nitrobicyclo*[2.2.1]*heptan*-2-exo-*ol* (**7**).—Sodium borohydride (188 mg, 4.97 mmol) was added to a solution of the unseparated chloroketones (1.41 g, 7.42 mmol) in dry methanol (25 ml), and the mixture was stirred at room temperature for 6.5 h. Excess of hydride was destroyed with water followed by 2M-hydrochloric acid solution. After a further 2 h, the methanol was removed under reduced pressure and the residue was extracted with ether (3 × 25 ml). After removal of the solvent, the crude product (1.21 g) was separated by column chromatography on silica gel using hexane–ethyl acetate mixtures as eluant, into 3-exo-*chloro*-6-exo-*nitrobicyclo*[2.2.1]-*heptan*-2-endo-*ol* (**8**) (412 mg, 31%), 3-exo-*chloro*-6-exo-*nitrobicyclo*[2.2.1.]*heptan*-2-exo-*ol* (**7**) (227 mg, 17%), and various fractions containing unseparated chloronitronorbornanols (485 mg, 36%). The former compound, (**8**), was obtained as prisms, m.p. 117—119 °C (from di-isopropyl ether) (Found: C, 44.1; H, 5.3; N, 7.5. $C_7H_{10}ClNO_3$ requires C, 43.9; H, 5.3; N, 7.3%); R_F (hexane–ethyl acetate 1 : 1 v/v) 0.52; $\nu_{max.}$(KBr) 3 480 (br, OH), 1 533 and 1 370 (NO_2), and 1 060 cm^{-1} (C–O); δ([$^2H_6$]acetone) 5.00 (1 H, dd, *J ca.* 4.2 Hz, H-6), 4.31 (1 H, m, H-2), 3.53 (1 H, dd, *J* 2.3 and 2.1 Hz, H-3), 2.96 (1 H, m, H-1), 2.78 (1 H, br s, OH, exchanges with D_2O), 2.58—2.03 (3 H, m, H-5 and H-4), 1.93 (1 H, d with further fine coupling, *J* 11 Hz, H-7-*syn*), and 1.65 (1 H, d with further fine coupling, *J* 11 Hz, H-7-*anti*); *m/z* 145 (4%, $M^+ - NO_2$), 108 (27), 90 (19), 80 (46), 78 (54), 76 (19), and 66 (100). The latter compound, (**7**), was obtained as prisms, m.p. 94—95 °C (from di-isopropyl ether) (Found: C, 44.2; H, 5.3; N, 7.3. $C_7H_{10}ClNO_3$ requires C, 43.9; H, 5.3; N, 7.3%); R_F (hexane–ethyl acetate 1 : 1 v/v) 0.37; $\nu_{max.}$(KBr) 3 490 (br, OH), 1 540 and 1 386 (NO_2), and 1 099 cm^{-1} (C–O); δ([$^2H_6$]acetone) 4.56 (1 H, dd, *J ca.* 4.2 Hz, H-6), 4.08 (1 H, dd, *J* 5.6 and 3.0 Hz, H-3), 4.00 (1 H, m, H-2), 2.78 (1 H, br s, OH, exchanges with D_2O), 2.46 (1 H, m, H-1), 2.30—2.05 (3 H, m, H-4 and H-5), 1.90 (1 H, d with further fine coupling, *J* 11.4 Hz, H-7-*syn*), and 1.50 (1 H, d with further fine coupling, *J* 11.4 Hz, H-7-*anti*); *m*/*z* 145 (2%, $M^+ - NO_2$), 144 (23), 108 (30), 90 (15), 80 (45), 78 (49), 76 (17), and 66 (100).

Crystallographic Analyses of (**7**) *and* (**8**).—(a) Compound (**7**), $C_7H_{10}ClNO_3$, $M = 191.61$. Monoclinic, $a = 10.57(1)$, $b = 7.76(1)$, $c = 10.17(1)$ Å, $\beta = 93.03(5)°$, $V = 832.9$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,7$ Å), D_m (flotation) = 1.51, $Z = 4$, $D_x = 1.53$ g cm^{-3}, $F(000) = 400$, space group $P2_1/c$. Colourless prisms (by diffusion of hexane vapour into a solution of the compound in tetrachloromethane), 0.1 × 0.2 × 0.2 mm, μ(Mo-K_a) = 3.67 cm^{-1}.

Data collection and processing: Philips PW1100 four-circle diffractometer, scan mode $\omega/2\theta$, scan width 1.60 θ, scan speed 0.053 θ s^{-1}, graphite-monochromated Mo-K_α radiation; 1 244 unique reflections measured ($3 < \theta < 23$, $\pm h,k,l$), 1.079 with F(obs) > σ F. Stability of standard reflections 0.73%. The data were corrected for Lorentz and polarisation effects, but not for absorption.

(b) Compound (**8**), $C_7H_{10}ClNO_3$, $M = 191.61$. Monoclinic, $a = 6.91(1)$, $b = 9.97(1)$, $c = 12.11(1)$ Å, $\beta = 92.36(5)°$, $V = 833.30$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,7$ Å), D_m (flotation) = 1.54, $Z = 4$, $D_x = 1.53$ g cm^{-3}, $F(000) = 400$, space group $P2_1/n$. Colourless prisms (by diffusion of hexane vapour into a solution of the compound in tetrachloromethane), 0.3 × 0.2 × 0.3 mm, μ(Mo-K_α) = 3.67 cm^{-1}.

Data collection and processing: Philips PW1100 four-circle diffractometer, scan mode $\omega/2\theta$, scan width 1.20θ, scan speed 0.040 θ s^{-1}, graphite-monochromated Mo-K_α radiation; 1 229 unique reflections measured ($3 < \theta < 23$, $\pm h,k,l$), 1 083 with F (obs) > σ F. Stability of standard reflections 1.04%. The data were corrected for Lorentz and polarisation effects, but not for absorption.

Structure analysis and refinement of both compounds: The structures were solved with the centrosymmetric direct-methods option of the program SHELX.[10] Four *E*-maps were calculated for each structure from reflections with $E > 1.2$, and all non-hydrogen atoms could be located in this way. The co-ordinates were then refined by full-matrix least-squares refinement, and difference Fourier maps revealed all hydrogen atoms. Subsequent refinement using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms converged at a conventional *R* of 0.0420 for (**7**), and 0.0440 for (**8**). Unit weights were used throughout. The computations were carried out on a CDC Cyber 750 computer.

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