The Crystal Structures of 1,1'-Dinitrobicyclopentyl, 1,1'-Dinitrobicyclohexyl and 1,1'-Dinitrobicycloheptyl

Yu Lin Lam,[a] Hsing Hua Huang[*,a] and Trevor W. Hambley[b]
[a] Chemistry Department, National University of Singapore, Singapore 0511
[b] School of Chemistry, University of Sydney, Sydney Australia

The crystal and molecular structures of 1,1'-dinitrobicyclopentyl 1, 1,1'-dinitrobicyclohexyl 2 and 1,1'-dinitrobicycloheptyl 3 have been determined by X-ray diffraction methods. Compound 1 crystallizes in the monoclinic space group, $C2/c$, a = 16.247(2), b = 6.453 5(5), c = 11.161(2) Å, β = 103.36(1)°, Z = 4; compound 2 in the monoclinic space group, $C2/c$, a = 6.461(1), b = 11.012(2), c = 17.978(3) Å, β = 90.73(1)°, Z = 4; and compound 3 in the monoclinic space group, $P2_1/n$, a = 6.430 6(9), b = 11.544(2), c = 19.322(3) Å, β = 90.12(1)°, Z = 4. All three structures adopt *gauche* conformations with the nitro groups in close proximity. As the ring size increases the strain arising from contacts between the nitro groups increases and is reflected in increasing inter-ring and C–N bond lengths.

Previous work [1] on the conformations of 1,1'-dinitrobicyclopentyl, 1,1'-dinitrobicyclohexyl and 1,1'-dinitrobicycloheptyl showed that these compounds exist in carbon tetrachloride solution as *gauche/trans* rotameric mixtures containing, respectively, 83, 42 and 16% of the *gauche* rotamer. Comparison of the IR and Raman spectra of the solids suggested that all three compounds exist in the *gauche* conformation in the solid state. To further add to our understanding of the conformations of these molecules it was thought desirable to determine their crystal and molecular structures. This paper reports the results of such a study by X-ray diffraction methods.

Experimental

The three dinitrobicyclo compounds were prepared as described earlier.[1]

Crystal Structure Determination and Refinements.—Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections measured and refined on an Enraf-Nonius CAD4-F diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.710 69 Å). The data were reduced and Lorentz, polarization and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package (SDP).[2] Details of the data collection and structure refinements are given in Table 1.

All three structures were solved by direct methods using the SHELXS-86 program [3] and were refined by full-matrix least-squares analysis with SHELX-76.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms x, y, z and U_{iso} were refined with the exception of those of structure 3 and those bonded to the disordered atoms in structure 1 which were included at calculated sites (C–H 0.97 Å) with group temperature factors. Scattering factor values used were those supplied by SHELX-76. Drawings were produced using the program ORTEP.[5] Non-hydrogen atom coordinates are listed in Tables 2–4. Bond lengths and angles are given in Tables 5–7 and torsion angles in Tables 8–10. The atomic nomenclature is defined in Figs. 1–3. Listings of hydrogen atom coordinates, thermal parameters and tables of least square planes have been deposited at the Cambridge Crystallographic Data Centre.*
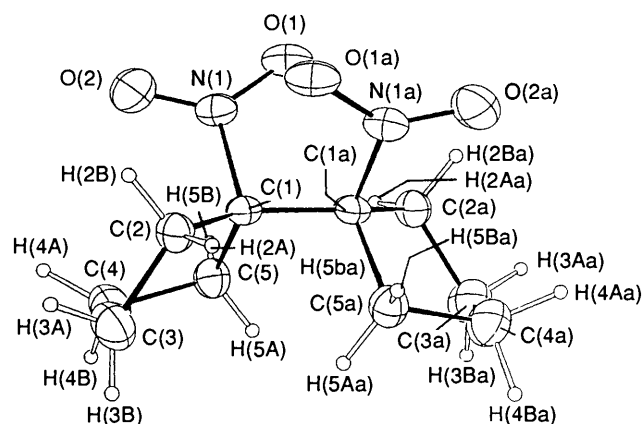

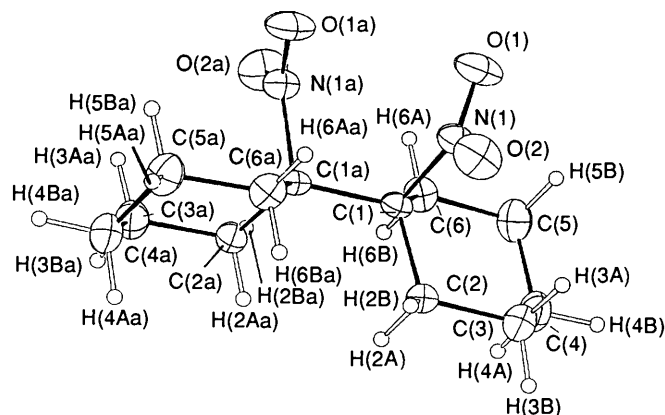**Fig. 1** ORTEP plot of 1,1'-dinitrobicyclopentyl

Fig. 2 ORTEP plot of 1,1'-dinitrobicyclohexyl

Results and Discussion

Crystallographic data for compounds 1–3 are given in Table 1 together with the experimental details.

Crystal Structure of 1,1'-Dinitrobicyclopentyl 1.—Bond lengths, bond angles and torsion angles based on the final atomic positions are given in Tables 5 and 8. The molecules are located on the two fold axis at $\frac{1}{2}$, y, $\frac{3}{4}$ with the centre of the C(1)–C(1a) bond lying on the axis. The molecule is disordered

Table 1 Crystallographic data and experimental details for 1,1'-dinitrobicyclopentyl **1**, 1,1'-dinitrobicyclohexyl **2** and 1,1'-dinitrobicycloheptyl **3**

	1	**2**	**3**
Formula	$C_{10}H_{16}N_2O_4$	$C_{12}H_{20}N_2O_4$	$C_{14}H_{24}N_2O_4$
M	228.25	256.81	284.36
Crystal habit	Colourless plates	Colourless plates	Colourless plates
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$
$a/\text{Å}$	16.247(2)	6.461(1)	6.430 6(9)
$b/\text{Å}$	6.453 5(5)	11.012(1)	11.544((2)
$c/\text{Å}$	11.161(2)	17.978(3)	19.322(3)
$\beta/°$	103.36(1)	90.73(1)	90.12(1)
$U/\text{Å}^3$	1 138.8	1 279.0	1 434.0
Z	4	4	4
$D_c/\text{g cm}^{-3}$	1.331	1.331	1.317
$F(000)$	488	552	616
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	0.65	0.61	0.58
Diffractometer	Enraf-Nonius CAD4-F	Enraf-Nonius CAD4-F	Enraf-Nonius CAD4-F
Monochromator	Graphite	Graphite	Graphite
Data-collection range/°	$1 < \theta < 25$	$1 < \theta < 25$	$1 < \theta < 20$
Scan width/°	$0.80 + 0.34\tan\theta$	$0.80 + 0.34\tan\theta$	$0.80 + 0.34\tan\theta$
Scan mode	$\omega - 1.33\theta$	$\omega - \theta$	$\omega - \theta$
Horizontal counter	$2.70 + 1.05\tan\theta$	$2.70 + 1.05\tan\theta$	$2.70 + 1.05\tan\theta$
Range of hkl	h −19 to 19	h −7 to 7	h −6 to 6
	k 0 to 7	k 0 to 13	k 0 to 11
	l 0 to 13	l 0 to 21	l 0 to 18
Intensity variation (%)	<2	<2	<2
No. of reflections measured	1163	1232	1487
No. of unique reflections	868	1037	1045
No. of reflections used $[I > 2.5\sigma(I)]$	673	870	612
Final number of variables	128	123	194
Merging R values	0.011	0.019	0.013
R_w	0.049	0.041	0.041
R	0.043	0.035	0.041
Weighting constants g,k $[w = g/(\sigma^2 F_o + kF_o^2)]$	$3.89, 5.6 \times 10^{-5}$	$3.03, 1.5 \times 10^{-4}$	$1.72, 4.4 \times 10^{-5}$
Maximum shift/esd	0.012	0.004	0.005
Peaks in final map/e Å^{-3}	±0.15	±0.15	±0.14
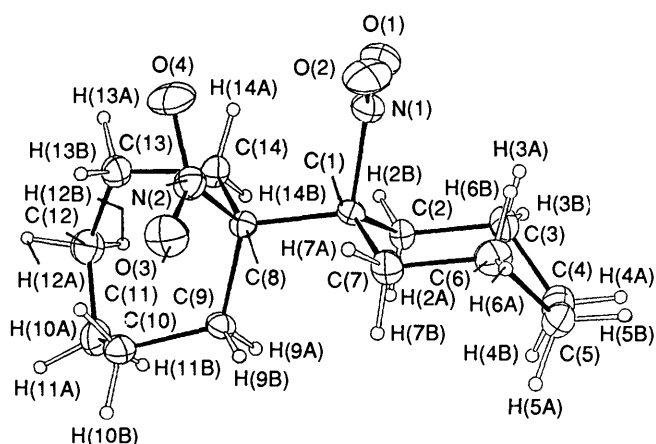
Fig. 3 ORTEP plot of 1,1'-dinitrobicycloheptyl

over two sites with occupancies of 0.516(3):0.484(3). This disorder is due to two enantiomers lying at the one site, the chirality arising from the sense of the rotation about the C(1)–C(1a) axis (*i.e.* the sign of the N–C–C–N torsion angle). An alternative description of the structure with two independent molecules lying on the two-fold axes in the non-centrosymmetric space group *C2* did not resolve this disorder. Analysis of the *E*-statistics and the systematic absences also supported the original choice of the space group. Three carbon atoms [C(1), C(3) and C(4)] and one of the oxygen atoms [O(1)] are only slightly disturbed by the disorder and were

modelled as full occupancy atoms. However, there is a finite movement of these atoms and as a consequence, bond lengths and angles involving them are not physically significant. The five-membered rings adopt skew conformations and the molecule a *gauche* conformation with an apparent N–C–C–N torsion angle of −73.4(2)°. Both NO_2 groups are nearly coplanar with the central C–C bond, the torsion angles C(1a)–C(1)–N(1)–O(1) and C(1)–C(1a)–N(1a)–O(2a) being 2(3)° and −179.9(3)°, respectively. In this conformation, the oxygen atoms, O(2) and O(2a) make close contacts with the methylene groups adjacent to the central carbons [2.925 and 2.776 Å to C(2) and C(5), 2.736 and 2.315 Å to H(2A) and H(5A), respectively]. A least-squares plane through the nitro group shows no significant deviation from planarity. In addition the near equality of the O(1)–N(1)–C and O(2)–N(1)–C bond angles [116.8(3)° and 116.7(3)°] suggests that the repulsion between O(2) and the methylene groups is similar to that between the two O(1) atoms across the two-fold axis. This observed structure shows that the conformation with both NO_2 groups coplanar with the central C–C bond is inherently more stable than a conformation where the NO_2 groups are perpendicular to the central atoms, despite the expectation that the NO_2 groups would tend to avoid each other to the maximum extent. This stability appears to follow from the MO model of Hoffmann and Davidson[6] in which effective overlapping of a degenerate HOMO of the ring with the LUMO of the π-acceptor substituent is observed to occur in the conformation where the π-acceptor substituent assumes a bisected position with respect to the cycloalkane ring.

Crystal Structure of 1,1′-*Dinitrobicyclohexyl* **2.**—The molecules also lie on the two-fold axis at $\frac{1}{2}$, y, $\frac{3}{4}$ but the structure is in no sense isostructural with that of compound **1**. Bond lengths, bond angles and torsion angles are shown in Tables 6 and 9.

After least-squares refinements (final $R = 0.035$), the molecule showed unusually long central C–C and C–N bonds of 1.579(3) and 1.551(2) Å. In the X-ray studies of 1,1′-dinitrobicyclopropyl and 1,1′-dinitrobicyclobutyl,[7] the central C–C and C–N bond lengths were found to be 1.479(2) and 1.508(9) Å and 1.488(2) and 1.520(5) Å, respectively. This lengthening of both the C–N and central C–C bonds with increasing ring size may be attributed to the steric crowding about the C(1)–C(1a) bond. Bond angles about the two central carbon atoms also show evidence of this stress, with values ranging from 106.9(1)–113.5(1)°. The N–C–C bond angles are less than the tetrahedral value [107.6(1) and 106.9(1)°], while the C–C–C bond angles within the cyclohexyl ring are greater. The largest of these C–C–C bond angles is defined by atoms C(5), C(6) and C(1) [113.5(1)°] which is synclinal to the opposite NO_2 group. This angle is slightly larger than the C(3)–C(2)–C(1) angle [112.9(1)°]. In cyclohexane, the C–C–C bond angles have values in the region of 110.4–112.3°.[8] Thus, this widening effect could possibly be due to the steric repulsion between the methylene and the NO_2 groups.

Fig. 2 shows the structure of compound **2**. The cyclohexyl ring adopts a chair conformation characterized by the near coplanarity of the atoms C(2), C(3), C(5) and C(6). Atoms C(1) and C(4) deviate by −0.622 and 0.667 Å, respectively, from this plane. Both nitro groups do not deviate significantly from planarity. The molecule as a whole adopts a *gauche* conformation with an N–C–C–N torsion angle of 58.2(1)°. The resulting structure also shows that both cyclohexyl rings are attached by a bond which is equatorial to both rings with C(1a)–C(1)–C(2)–C(3) and C(1a)–C(1)–C(6)–C(5) torsion angles being 178.5(1) and −176.6(1)°, respectively. By comparison with other possible configurations such a structure would involve the least steric strain.

An interesting feature of this molecule is that unlike its three, four and five-membered ring analogues, both the NO_2 groups in structure **2** adopt a nearly perpendicular conformation with respect to the central C–C bond, the torsion angles C(1a)–C(1)–N(1)–O(1) and C(1)–C(1a)–N(1a)–O(2a) being −93.1(1) and 86.5(1)°. Comparison of this structural analysis with those of 2,3-dinitro-2,3-dimethylbutane[7] shows many similarities. The central C–C bond and the C–N bonds in the latter molecule are 1.575 and 1.550 Å which are approximately equal to the corresponding bonds in structure **2**, 1.579 and 1.551 Å. Likewise, both the NO_2 groups in 2,3-dinitro-2,3-dimethylbutane adopt a perpendicular conformation with respect to the central C–C bond with the O–N–C–C torsion angles being −86 and −99°. Thus as in the open-chain molecule, the degenerate HOMO of the cyclohexane fragment may also be largely localized on the central C–C bond.

Crystal Structure of 1,1′-*Dinitrobicycloheptyl* **3.**—Single crystals, formed as thin plates, were obtained upon recrystallization from chloroform–pentane. Crystallization proved extremely difficult and only very small crystals were obtained. Consequently, the extent of the data was limited and the precision of the structure reduced.

Molecules of compound **3** lie at general sites but approximately adhere to the two-fold symmetry observed in compounds **1** and **2**. Bond lengths, bond angles and torsion angles based on the final atomic positions are shown in Tables 7 and 10. The central C–C bond length, 1.601(9) Å, is greater in this structure than in structure **2**. This is consistent with the increased steric crowding expected on expansion of the ring.

Table 2 Atomic coordinates ($\times 10^4$) with esds in parentheses for 1,1′-dinitrobicyclopentyl[a]

Atom	x	y	z	Occupancy
C(1)	4532(1)	3034(3)	7400(2)	
C(2)	4368(3)	1252(6)	8406(4)	0.516(2)
C(2′)	3938(3)	2810(9)	8121(5)	0.484(2)
C(3)	3430(2)	739(6)	7811(4)	
C(4)	3354(2)	782(7)	6467(4)	
C(5)	3851(3)	2816(7)	6365(4)	0.516(2)
C(5′)	4259(3)	1286(7)	6245(5)	0.484(2)
N(1)	4385(2)	5035(5)	8234(3)	0.516(2)
N(1′)	4291(3)	5056(6)	6459(4)	0.484(2)
O(1)	5058(1)	6069(2)	8779(2)	
O(2)	3662(2)	5438(6)	8255(4)	0.516(2)
O(2′)	3544(3)	5459(7)	6110(4)	0.484(2)

[a] The disorder over two sites gives the unprimed and primed sites for C(2), C(5), N(1) and O(2). The total occupancies of the unprimed and primed sites are constrained to unity.

Table 3 Atomic coordinates ($\times 10^4$) with esds in parentheses for 1,1′-dinitrobicyclohexyl

Atom	x	y	z
C(1)	5076(2)	5669(1)	7939(1)
C(2)	6392(3)	6733(2)	8225(1)
C(3)	6532(3)	6784(2)	9075(1)
C(4)	4411(3)	6814(2)	9419(1)
C(5)	3152(3)	5731(2)	9170(1)
C(6)	2982(3)	5655(2)	8324(1)
N(1)	6236(2)	4488(1)	8160(1)
O(1)	5214(2)	3592(1)	8299(1)
O(2)	8112(2)	4500(1)	8182(1)

Table 4 Atomic coordinates ($\times 10^4$) with esds in parentheses for 1,1′-dinitrobicycloheptyl

Atom	x	y	z
C(1)	256(10)	132(6)	2240(4)
C(2)	1738(11)	1053(7)	1955(4)
C(3)	2095(13)	1051(8)	1170(4)
C(4)	424(14)	1662(9)	738(5)
C(5)	−1623(14)	1059(7)	673(4)
C(6)	1956(13)	−36(8)	1101(4)
C(7)	−1869(12)	132(7)	1882(4)
C(8)	102(11)	243(6)	3065(4)
C(9)	−1199(12)	1309(6)	3246(4)
C(10)	−1536(13)	1541(7)	4028(4)
C(11)	277(15)	2120(8)	4406(5)
C(12)	2206(14)	1392(8)	4544(5)
C(13)	2310(12)	222(8)	4204(4)
C(14)	2243(11)	222(7)	3411(4)
O(1)	3160(10)	−1117(5)	2072(3)
O(2)	142(11)	−1886(5)	2001(3)
O(3)	−2972(10)	−794(5)	3364(3)
O(4)	−77(10)	−1703(5)	3440(3)
N(1)	1260(11)	−1063(6)	2088(3)
N(2)	−1092(12)	−839(7)	3313(3)

The cycloheptyl rings adopt chair-like conformations (Fig. 3) characterized by the near coplanarity of the atoms C(3), C(4), C(5) and C(6) which form the 'back' of the chair and atoms C(2), C(3), C(6) and C(7) which form the 'seat' of the chair. Both nitro groups show small (*ca.* 0.005 Å) but only marginally significant tetrahedral distortions. The molecule adopts a *gauche* conformation with N–C–C–N torsion angle of −54.7(7)°. As in

structure **2**, structural analysis also shows that both bonds attaching the cycloheptyl rings to the central carbon atoms are equatorial. The C(6)–C(7)–C(1)–C(8) and C(10)–C(9)–C(8)–C(1) torsion angles are −176.7(6) and 179.2(6)°. The NO_2 groups are again in a perpendicular conformation with respect to the central C–C bond, the torsion angles O(2)–N(1)–C(1)–C(8) and O(4)–N(2)–C(8)–C(1) being 91.8(7) and 88.1(7)°, respectively.

Although both the central C–C bond length and the N–C–C–N torsion angle in compound **3** are greater than in 2,3-dinitro-2,3-dimethylbutane, the O(2) ··· O(4) distance (*i.e.* the

distance between the eclipsed oxygen atoms in compound **3**) is markedly shorter (2.792 Å). This decrease in the non-bonded distance could be attributed to the steric congestion in the rings which thus forces the NO_2 groups closer to each other. In addition, the six N–C–C bond angles in the molecule are smaller than the tetrahedral value while the C–C–C bond angles involving the central carbon atoms are greater. Comparison of the C–C(1)–C(8) or the C–C(8)–C(1) angles shows that those angles involving the methylene carbons which are synclinal to the opposite NO_2 group are significantly larger: C(8)–C(1)–C(7) is 113.1(6)° while C(8)–C(1)–C(2) is 110.1(6)° and C(1)–C(8)–C(14) is 112.1(6)° while C(1)–C(8)–C(9) is 109.1(6)°. This observed widening is consistent with the existence of steric congestion in the molecule.

Comparison of the Members of Series **1–3**.—Since the structures of 1,1′-dinitrobicyclopropyl and 1,1′-dinitrobicyclobutyl have been reported previously,[7] the structures for

Table 5 Bond lengths/Å and bond angles/° for 1,1′-dinitrobicyclopentyl

C(2)–C(1)	1.671(4)	C(5)–C(1)	1.411(4)
N(1)–C(1)	1.641(4)	C(1)–C(1a)	1.486(4)
C(3)–C(2)	1.552(5)	C(5)–C(4)	1.558(5)
O(2)–N(1)	1.209(4)	C(4)–C(3)	1.477(5)
O(1)–N(1)	1.306(4)	C(3)–C(2′)	1.567(6)
O(1)–N(1′)	1.329(4)	C(2′)–C(1)	1.399(5)
C(5′)–C(1)	1.693(5)	N(1′)–C(1)	1.665(4)
C(5′)–C(4)	1.579(6)	O(2′)–N(1′)	1.215(5)
N(1)–C(1)–C(2)	95.4(2)	N(1)–C(1)–C(5)	110.7(3)
C(3)–C(2)–C(1)	98.7(3)	O(1)–N(1)–C(1)	116.8(3)
O(2)–N(1)–C(1)	116.7(3)	O(2)–N(1)–O(1)	126.5(3)
C(5)–C(1)–C(2)	105.4(3)	C(4)–C(3)–C(2)	105.9(3)
C(5)–C(4)–C(3)	99.6(3)	C(4)–C(5)–C(1)	110.2(3)
N(1′)–C(1)–C(2′)	110.6(3)	C(5′)–C(1)–C(2′)	105.9(3)
N(1′)–C(1)–C(5′)	93.4(2)	C(3)–C(2′)–C(1)	111.0(4)
C(4)–C(3)–C(2′)	97.2(3)	C(5′)–C(4)–C(3)	107.5(3)
C(4)–C(5′)–C(1)	96.2(3)	O(2′)–N(1′)–C(1)	116.2(4)

Table 6 Bond lengths/Å and bond angles/° for 1,1′-dinitrobicyclohexyl

C(2)–C(1)	1.533(2)	N(1)–C(1)	1.551(2)
C(3)–C(2)	1.530(2)	C(5)–C(4)	1.508(3)
O(1)–N(1)	1.214(2)	C(6)–C(1)	1.529(2)
C(1)–C(1a)	1.579(3)	C(4)–C(3)	1.511(3)
C(6)–C(5)	1.525(3)	O(2)–N(1)	1.212(2)
C(6)–C(1)–C(2)	110.2(1)	N(1)–C(1)–C(2)	106.9(1)
N(1)–C(1)–C(6)	107.6(1)	C(3)–C(2)–C(1)	112.9(1)
C(4)–C(3)–C(2)	111.5(2)	C(5)–C(4)–C(3)	110.5(2)
C(6)–C(5)–C(4)	111.7(2)	C(5)–C(6)–C(1)	113.5(1)
O(1)–N(1)–C(1)	118.2(1)	O(2)–N(1)–C(1)	118.6(1)
O(2)–N(1)–O(1)	123.2(1)		

Table 7 Bond lengths/Å and bond angles/° for 1,1′-dinitrobicycloheptyl

C(2)–C(1)	1.531(9)	C(7)–C(1)	1.530(9)
C(8)–C(1)	1.601(9)	N(1)–C(1)	1.551(9)
C(3)–C(2)	1.534(10)	C(4)–C(3)	1.531(10)
C(5)–C(4)	1.494(10)	C(6)–C(5)	1.525(10)
C(7)–C(6)	1.522(10)	C(9)–C(8)	1.529(9)
C(14)–C(8)	1.529(9)	N(2)–C(8)	1.543(9)
C(10)–C(9)	1.549(10)	C(11)–C(10)	1.528(10)
C(12)–C(11)	1.521(11)	C(13)–C(12)	1.503(10)
C(14)–C(13)	1.534(9)	N(1)–O(1)	1.224(7)
N(1)–O(2)	1.204(7)	N(2)–O(3)	1.214(7)
N(2)–O(4)	1.216(8)		
C(7)–C(1)–C(2)	113.2(6)	C(8)–C(1)–C(2)	110.1(6)
C(8)–C(1)–C(7)	113.1(6)	N(1)–C(1)–C(2)	106.8(6)
N(1)–C(1)–C(7)	106.6(6)	N(1)–C(1)–C(8)	106.6(6)
C(3)–C(2)–C(1)	116.7(7)	C(4)–C(3)–C(2)	115.6(7)
C(5)–C(4)–C(3)	116.6(8)	C(6)–C(5)–C(4)	117.7(8)
C(7)–C(6)–C(5)	115.3(8)	C(6)–C(7)–C(1)	118.6(7)
C(9)–C(8)–C(1)	109.1(6)	C(14)–C(8)–C(1)	112.1(6)
C(14)–C(8)–C(9)	113.9(6)	N(2)–C(8)–C(1)	106.1(6)
N(2)–C(8)–C(9)	107.8(6)	N(2)–C(8)–C(14)	107.4(6)
C(10)–C(9)–C(8)	116.1(7)	C(11)–C(10)–C(9)	115.7(7)
C(12)–C(11)–C(10)	117.6(8)	C(13)–C(12)–C(11)	117.1(8)
C(14)–C(13)–C(12)	115.8(8)	C(13)–C(14)–C(8)	117.4(7)
O(1)–N(1)–C(1)	117.8(7)	O(2)–N(1)–C(1)	118.7(7)
O(2)–N(1)–O(1)	123.5(7)	O(3)–N(2)–C(8)	119.2(8)
O(4)–N(2)–C(8)	117.3(7)	O(4)–N(2)–O(3)	123.5(8)

Table 8 Torsion angles/° for 1,1′-dinitrobicyclopentyl

C(5)–C(1)–C(2)–C(3)	−15.1(0.3)	N(1)–C(1)–C(1a)–C(2a)	−171.5(0.2)	C(1a)–C(1)–N(1′)–O(2′)	179.5(0.3)
C(2)–C(1)–C(5)–C(4)	−11.7(0.3)	N(1)–C(1)–C(1a)–C(5a)	61.4(0.3)	C(1a)–C(1)–N(1′)–O(1a)	−3.0(0.3)
N(1)–C(1)–C(2)–C(3)	98.1(0.3)	N(1)–C(1)–C(1a)–N(1a)	−73.4(0.2)	N(1′)–C(1)–C(1a)–C(2′a)	−61.5(0.3)
C(2)–C(1)–N(1)–O(1)	105.8(0.3)	C(2)–C(3)–C(4)–C(5)	−45.2(0.3)	N(1′)–C(1)–C(1a)–C(5′a)	170.0(0.2)
C(2)–C(1)–N(1)–O(2)	−76.1(0.3)	C(2′)–C(1)–C(5′)–C(4)	13.1(0.4)	N(1′)–C(1)–C(1a)–N(1′a)	74.3(0.2)
C(1a)–C(1)–C(2)–C(3)	−159.2(0.3)	N(1′)–C(1)–C(2′)–C(3)	114.9(0.3)	C(1)–C(1a)–C(2′a)–C(3a)	−112.1(0.4)
C(2)–C(1)–C(1a)–C(2a)	90.4(0.2)	C(2′)–C(1)–N(1′)–O(2′)	−31.0(0.4)	C(1)–C(1a)–C(5′a)–C(4a)	159.4(0.2)
C(2)–C(1)–C(1a)–C(5a)	−36.7(0.3)	C(2′)–C(1)–N(1′)–O(1a)	146.6(0.3)	C(1)–C(1a)–N(1′a)–O(1)	−3.0(0.3)
C(2)–C(1)–C(1a)–N(1a)	−171.5(0.2)	C(1a)–C(1)–C(2′)–C(3)	−112.1(0.4)	C(1)–C(1a)–N(1′a)–O(2′a)	179.5(0.3)
C(1)–C(2)–C(3)–C(4)	38.1(0.3)	C(2′)–C(1)–C(1a)–C(2′a)	162.6(0.4)	C(2′)–C(3)–C(4)–C(5′)	47.4(0.4)
N(1)–C(1)–C(5)–C(4)	−113.8(0.3)	C(2′)–C(1)–C(1a)–C(5′a)	34.1(0.4)	O(1)–N(1′a)–C(1a)–C(2′a)	146.6(0.3)
C(5)–C(1)–N(1)–O(1)	−145.5(0.3)	C(2′)–C(1)–C(1a)–N(1′a)	−61.5(0.4)	O(1)–N(1′a)–C(1a)–C(5′a)	−105.0(0.3)
C(5)–C(1)–N(1)–O(2)	32.6(0.4)	C(1)–C(2′)–C(3)–C(4)	−38.6(0.4)	C(1)–C(1a)–C(2a)–C(3a)	−159.2(0.2)
C(1a)–C(1)–C(5)–C(4)	114.3(0.3)	C(5′)–C(1)–N(1′)–O(2′)	77.4(0.4)	C(1)–C(1a)–C(5a)–C(4a)	114.3(0.3)
C(5)–C(1)–C(1a)–C(2a)	−36.7(0.4)	C(5′)–C(1)–N(1′)–O(1a)	−105.0(0.3)	C(1)–C(1a)–N(1a)–O(1a)	2.0(0.3)
C(5)–C(1)–C(1a)–C(5a)	−163.8(0.4)	C(1a)–C(1)–C(5′)–C(4)	159.4(0.2)	C(1)–C(1a)–N(1a)–O(2a)	−179.9(0.3)
C(5)–C(1)–C(1a)–N(1a)	61.4(0.4)	C(5′)–C(1)–C(1a)–C(2′a)	34.1(0.3)	C(5′)–C(1)–C(2′)–C(3)	14.9(0.4)
C(1)–C(5)–C(4)–C(3)	35.5(0.3)	C(5′)–C(1)–C(1a)–C(5′a)	−94.4(0.3)	N(1′)–C(1)–C(5′)–C(4)	−99.4(0.3)
C(1a)–C(1)–N(1)–O(1)	2.0(0.3)	C(5′)–C(1)–C(1a)–N(1′a)	170.0(0.3)		
C(1a)–C(1)–N(1)–O(2)	−179.9(0.3)	C(1)–C(5′)–C(4)–C(3)	−38.8(0.3)		

Table 9 Torsion angles/° for 1,1′-dinitrobicyclohexyl

C(6)–C(1)–C(2)–C(3)	50.9(0.2)	C(2)–C(1)–C(1a)–N(1a)	174.2(0.1)	C(1)–C(6)–C(5)–C(4)	54.2(0.2)
C(2)–C(1)–C(6)–C(5)	−50.5(0.2)	C(1)–C(2)–C(3)–C(4)	−55.1(0.2)	C(1a)–C(1)–N(1)–O(1)	−93.1(0.1)
N(1)–C(1)–C(2)–C(3)	−65.8(0.2)	N(1)–C(1)–C(6)–C(5)	65.8(0.2)	C(1a)–C(1)–N(1)–O(2)	86.5(0.1)
C(2)–C(1)–N(1)–O(1)	147.9(0.1)	C(6)–C(1)–N(1)–O(1)	29.5(0.2)	N(1)–C(1)–C(1a)–N(1a)	58.2(0.1)
C(2)–C(1)–N(1)–O(2)	−32.5(0.2)	C(6)–C(1)–N(1)–O(2)	−150.9(0.1)	C(2)–C(3)–C(4)–C(5)	56.7(0.2)
C(1a)–C(1)–C(2)–C(3)	178.5(0.1)	C(1a)–C(1)–C(6)–C(5)	−176.6(0.1)	C(3)–C(4)–C(5)–C(6)	−56.2(0.2)
C(2)–C(1)–C(1a)–C(2a)	−69.8(0.2)	C(6)–C(1)–C(1a)–C(6a)	−178.7(0.1)		
C(2)–C(1)–C(1a)–C(6a)	55.8(0.2)	C(6)–C(1)–C(1a)–N(1a)	−60.3(0.2)		

Table 10 Torsion angles/° for 1,1′-dinitrobicycloheptyl

C(7)–C(1)–C(2)–C(3)	−53.5(0.8)	C(7)–C(1)–N(1)–O(1)	151.6(0.7)	C(14)–C(8)–C(9)–C(10)	−54.7(0.8)
C(2)–C(1)–C(7)–C(6)	57.3(0.8)	C(7)–C(1)–N(1)–O(2)	−29.3(0.8)	C(9)–C(8)–C(14)–C(13)	60.4(0.8)
C(8)–C(1)–C(2)–C(3)	178.8(0.6)	C(1)–C(7)–C(6)–C(5)	−83.8(0.9)	N(2)–C(8)–C(9)–C(10)	64.4(0.7)
C(2)–C(1)–C(8)–C(9)	73.9(0.7)	N(1)–C(1)–C(8)–C(9)	−170.6(0.6)	C(9)–C(8)–N(2)–O(3)	26.0(0.8)
C(2)–C(1)–C(8)–C(14)	−53.2(0.7)	N(1)–C(1)–C(8)–C(14)	62.3(0.7)	C(9)–C(8)–N(2)–O(4)	−155.0(0.7)
C(2)–C(1)–C(8)–N(2)	−170.2(0.6)	N(1)–C(1)–C(8)–N(2)	−54.7(0.7)	C(8)–C(9)–C(10)–C(11)	79.5(0.8)
N(1)–C(1)–C(2)–C(3)	63.4(0.7)	C(8)–C(1)–N(1)–O(1)	−87.3(0.7)	N(2)–C(8)–C(14)–C(13)	−59.0(0.8)
C(2)–C(1)–N(1)–O(1)	30.4(0.8)	C(8)–C(1)–N(1)–O(2)	91.8(0.7)	C(14)–C(8)–N(2)–O(3)	149.1(0.7)
C(2)–C(1)–N(1)–O(2)	−150.5(0.7)	C(1)–C(8)–C(9)–C(10)	179.2(0.6)	C(14)–C(8)–N(2)–O(4)	−31.9(0.8)
C(1)–C(2)–C(3)–C(4)	81.8(0.8)	C(1)–C(8)–C(14)–C(13)	−175.1(0.6)	C(8)–C(14)–C(13)–C(12)	−85.4(0.8)
C(8)–C(1)–C(7)–C(6)	−176.7(0.6)	C(1)–C(8)–N(2)–O(3)	−90.9(0.7)	C(9)–C(10)–C(11)–C(12)	−72.4(0.9)
C(7)–C(1)–C(8)–C(9)	−53.8(0.8)	C(1)–C(8)–N(2)–O(4)	88.1(0.7)	C(10)–C(11)–C(12)–C(13)	9.1(1.1)
C(7)–C(1)–C(8)–C(14)	179.1(0.6)	C(2)–C(3)–C(4)–C(5)	−72.4(0.9)	C(11)–C(12)–C(13)–C(14)	60.4(1.0)
C(7)–C(1)–C(8)–N(2)	62.2(0.7)	C(3)–C(4)–C(5)–C(6)	6.5(1.0)		
N(1)–C(1)–C(7)–C(6)	−59.8(0.8)	C(4)−C(5)–C(6)–C(7)	62.3(1.0)		

compounds with three to seven-membered rings are available for comparison.

All structures adopt the *gauche* conformation in which the nitro groups are in close contact. The N–C–C–N torsion angle lies in the range 54–70° with the value decreasing as the ring size increases. Furthermore, as the ring size increases, the intra-ring C–C(1)–C angle increases and forces the NO$_2$ groups closer together. This effect is observed in the decrease in the angle between the central C–C bond and the C–N bond from 113.2° in 1,1′-dinitrobicyclopropyl to 106.6° in compound **3**. The effects of the increasing strain with increasing ring size may also be reflected in the rotation of the NO$_2$ groups from a bisected conformation in the three to five-membered analogues to a perpendicular conformation in structures **2** and **3**. Regardless of its orientation with respect to the central C–C bond, the O–N–O and O–N–C bond angles remain unchanged at 123° and 118° for all the structures. This indicates that repulsion between the oxygen and the methylene groups is similar to the repulsion between the two eclipsed oxygens.

Another common feature in these molecules is the widening of the angle between the central C–C bond and the bond containing a central carbon and the methylene group which is synclinal to the NO$_2$ group across the two-fold axis. However, comparison between the members of the series shows that this bond angle decreases with increasing ring size. This could probably again be due to the inter-ring steric congestion. This increased strain is also observed in the steadily increasing C–C and C–N bond lengths. In structure **1**, the values are anomalous as a consequence of the disorder described above.

Acknowledgements

References

1 B. G. Tan, Y. L. Lam, L. H. L. Chia and H. H. Huang, preceding paper.
2 *Structure Determination Package (SDP)*, Enraf-Nonius, Delft, Holland, 1985.
3 G. M. Sheldrick, *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, pp. 175–189.
4 G. M. Sheldrick, SHELX-76, A Program for X-Ray Crystal Structure Determination, University of Cambridge, England, 1976.
5 C. K. Johnson, ORTEP, A Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratories, Oak Ridge, Tennessee, USA, 1965.
6 R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, 1971, **93**, 5699
7 Y. Kai, P. Knochel, S. Kwiatkowski, J. D. Dunitz, J. F. M. Oth, D. Seebach and H-O. Kalinowski, *Helv. Chim. Acta*, 1982, **65**, 137.
8 R. Khan, R. Fourme, D. Andre and M. Renaud, *Acta Crystallogr., Sect. B*, 1973, **29**, 131.