(a)

(b)

Fig. 2. The picrate ion showing (a) the plane of the major libration with the axis marked ● close to C(22), and (b) the plane of the second major libration with the axis marked ●.

& Hamor, 1980), 2,2',4,4',6,6'-hexachlorobiphenyl shows 87.3° (Singh & McKinney, 1979), and biphenyl-2,2'-bicarboxlic acid shows 71.3° (Fronczek, Davis, Gehring & Gandour, 1987). These values are in qualitative agreement with earlier predictions (Branch, Bryson, Gray, Ibbotson & Worral, 1964).

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Structures of 1,1'-Dicyanobicyclopentyl, 1,1'-Dicyanobicyclohexyl and 1,1'-Dicyanobicycloheptyl

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Abstract. 1,1'-Bicyclopentane-1,1'-dicarbonitrile, $C_{12}H_{16}N_2$, (1), $M_r = 188.3$, orthorhombic, $Cmca$, $a = 9.711 (2)$, $b = 6.885 (1)$, $c = 16.258 (2)$ Å, $V = 1087.0 (3)$ Å³, $Z = 4$, $D_x = 1.150$ Mg m⁻³, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.064$ mm⁻¹, $F(000) = 408$, $T = 297$ K, $R = 0.042$ for 355 observed reflections. 1,1'-Bicyclohexane-1,1'-dicarbonitrile, $C_{14}H_{20}N_2$, (2), $M_r = 216.3$, monoclinic, $P2_1/n$, $a = 5.944 (3)$, $b =$

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Table 1. *Experimental data and experimental details for* 1,1'-*dicyanobicyclopentyl* (1),
1,1'-*dicyanobicyclohexyl* (2) *and* 1,1'-*dicyanobicycloheptyl* (3)

	(1)	(2)	(3)
Crystal size (mm)	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.25
Diffractometer	Siemens $R3m/V$	Siemens $R3m/V$	Siemens $R3m/V$
Monochromator	Graphite	Graphite	Graphite
Data-collection range (°)	$3.0 < 2\theta < 48$	$3.0 < 2\theta < 50$	$3.0 < 2\theta < 50$
Scan width (°)	2.00	2.00	2.00
Scan mode	ω	ω	ω
Range of h	0 to 11	0 to 6	0 to 11
k	0 to 8	0 to 20	0 to 8
l	−19 to 0	−6 to 6	−22 to 0
Absorption correction	None	None	None
Standard reflections	313, 2$\bar{2}$4	$\bar{2}$01, $\bar{1}$32	028, 203
Intensity variation (%)	±1.5	±1.5	±1.5
No. of reflections measured	1152	1079	1912
No. of unique reflections	509	941	582
No. of reflections used $[I > 2.5\sigma(I)]$	355	573	423
Final No. of variables	54	74	47
R_{int} (%)	–	6.74	–
wR (%)	4.58	10.6	6.50
R (%)	4.23	9.59	5.78
Weighting constants g, k $[w = g/(\sigma^2 F_o + kF_o^2)]$	1, 5×10^{-4}	1, 19×10^{-4}	1, 2×10^{-4}
Maximum shift/e.s.d.	0.183	0.009	0.001
Peaks in final difference map (e $Å^{-3}$)	0.17, −0.12	0.33, −0.23	0.19, −0.21
S	1.46	2.32	2.97

17.919 (9), $c = 6.028$ (3) Å, $\beta = 108.81$ (4)°, $V = 607.7$ (5) $Å^3$, $Z = 2$, $D_x = 1.182$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.065$ mm^{-1}, $F(000) = 236$, $T = 297$ K, $R = 0.096$ for 573 observed reflections. 1,1'-Bicycloheptane-1,1'-dicarbonitrile, $C_{16}H_{24}N_2$, (3), $M_r = 244.4$, orthorhombic, $Cmca$, $a = 9.971$ (2), $b = 7.24$ (1), $c = 19.334$ (4) Å, $V = 1395.1$ (4) $Å^3$, $Z = 4$, $D_x = 1.163$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.064$ mm^{-1}, $F(000) = 536$, $T = 297$ K, $R = 0.058$ for 423 observed reflections. All three compounds adopt *trans* conformations with the cyclopentyl rings in the 'envelope' form and the cyclohexyl and cycloheptyl rings in the chair form. As the ring size increases, the strain arising from steric interactions is reflected in an increasing central inter-ring C(1)—C(1') bond length, which varies from 1.537 (5) Å in (1) to 1.591 (6) Å in (3).

Introduction. Previous work (Chong, Chia & Huang, 1985) on the conformations of 1,1'-dicyanobicyclopentyl, 1,1'-dicyanobicyclohexyl and 1,1'-dicyanobicycloheptyl showed that these compounds exist in carbon tetrachloride solution as *gauche/trans* rotameric mixtures containing, respectively, 4.5, 11 and 38% of the *gauche* rotamer at 298 K. This is in striking contrast to the corresponding ratios for the dinitro analogues of these compounds: 83, 42 and 16% for 1,1'-dinitrobicyclopentyl, 1,1'-dinitrobicyclohexyl and 1,1'-dinitrobicycloheptyl in the same solvent at 298 K (Lam, Tan, Huang & Chia, 1990). The dinitro compounds have also been shown to exist in the *gauche* conformation in the solid state with the nitro groups in close proximity and with the cyclopentyl rings adopting a skewed conformation

and the cyclohexyl and cycloheptyl rings adopting chair-like conformations (Lam, Huang & Hambley, 1990). A comparison of the crystal structures of the title compounds and their dinitro analogues would be of interest. This paper reports the results of such a study by X-ray diffraction methods.

Experimental. The three dicyanobicyclo compounds were prepared as described previously (Chong, Chia & Huang, 1985).

Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections ($7 < 2\theta < 28°$). Details of the data collection and structure refinements are given in Table 1. Compound (2) did not yield good quality crystals. The data were collected from the best crystal available.

All three structures were solved by direct methods using the *SHELXS*86 program (Sheldrick, 1985) and were refined by full-matrix least-squares analysis (on F) with the *XLS* program, which is based on *SHELX*76 (Sheldrick, 1976). The data were reduced and Lorentz and polarization corrections were applied using the above programs. The function minimized was $\sum w(F_o - F_c)^2$. All non-H atoms were refined anisotropically. H atoms in (1) were located from a difference map and refined with fixed isotropic thermal parameters. H atoms in (2) and (3) were placed at calculated positions with fixed isotropic thermal parameters. Scattering-factor values used were those supplied by *SHELX*76. Drawings were produced using the *XP* program (Siemens Analytical X-ray Instruments, Inc., 1989). Non-H atomic coordinates are listed in Tables 2–4. The atomic

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$) *for 1,1'-dicyanobicyclopentyl* (1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	5000	-33 (4)	4528 (2)	47 (1)
C(2)	6228 (2)	-1093 (3)	4137 (1)	62 (1)
C(3)	5774 (3)	-1595 (4)	3270 (2)	84 (1)
C(1N)	5000	1997 (4)	4225 (2)	56 (1)
N(1)	5000	3547 (4)	3974 (2)	85 (1)

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$) *for 1,1'-dicyanobicyclohexyl* (2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	4837 (8)	437 (3)	5045 (9)	32 (2)
C(2)	7009 (11)	863 (3)	4798 (11)	48 (2)
C(3)	6727 (12)	1715 (3)	4974 (12)	57 (3)
C(4)	6261 (14)	1941 (4)	7167 (13)	69 (3)
C(5)	4148 (12)	1532 (3)	7454 (11)	56 (3)
C(6)	4384 (11)	698 (3)	7312 (10)	47 (2)
C(1N)	2725 (10)	632 (3)	3046 (9)	35 (2)
N(1)	1107 (10)	823 (3)	1534 (9)	61 (2)

Table 4. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$) *for 1,1'-dicyanobicycloheptyl* (3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	5000	3523 (6)	5755 (2)	78 (2)
C(1N)	5000	2022 (7)	5598 (2)	51 (2)
C(1)	5000	40 (6)	5413 (2)	43 (1)
C(2)	6278 (3)	-834 (4)	5711 (1)	63 (1)
C(3)	6484 (4)	-729 (5)	6491 (1)	69 (1)
C(4)	5713 (4)	-2038 (6)	6925 (2)	96 (2)

nomenclature is defined in Figs. 1–3. Listings of selected bond lengths, bond angles and torsion angles are given in Table 5.*

Discussion. Crystallographic data for the title compounds are given in Table 1 together with experimental details.

Crystal structure of 1,1'-*dicyanobicyclopentyl* (1). The molecule as a whole adopts a *trans* conformation with C_{2h} symmetry, the midpoint of the central C(1)—C(1') bond lying on the centre of symmetry (Fig. 1). This is different from 1,1'-dinitrobicyclopentyl which exists in the *gauche* conformation in the

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* Lists of structure factors, anisotropic thermal parameters, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55089 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

solid state. In the *trans* conformation of (1), a σ_h plane passes through the central C(1)—C(1') bond as well as both cyano groups although N(1)—C(1N)—C(1) is slightly bent at 178.5°. This plane bisects the cyclopentyl rings. In this orientation, the possibility of enhanced stability arising from overlapping between the highest occupied orbital of the cyclopentyl ring and the low-lying unoccupied orbitals of the π system in the cyano group is increased (Hoffmann & Davidson, 1971). Both rings adopt an 'envelope' form with C_s symmetry, the four atoms C(2), C(3), C(4) and C(5), or their counterparts in the second ring, being coplanar. Atom C(1) deviates by 0.56 Å
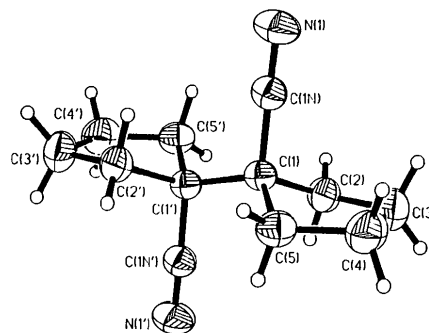

Fig. 1. Thermal ellipsoid plot of 1,1'-dicyanobicyclopentyl (1) showing atomic numbering. C(2) and C(5), C(3) and C(4), are related by mirror symmetry. C(1) and C(1'), *etc.* are related by twofold rotational symmetry.
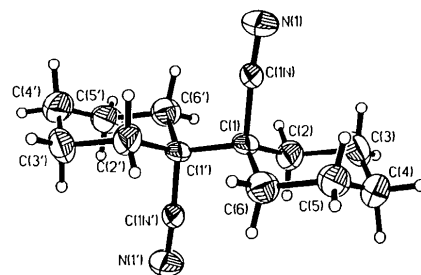

Fig. 2. Thermal ellipsoid plot of 1,1'-dicyanobicyclohexyl (2) showing atomic numbering. C(1) and C(1'), *etc.* are symmetry related pairs.
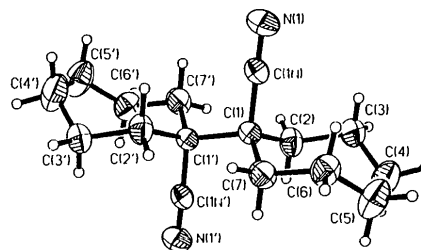

Fig. 3. Thermal ellipsoid plot of 1,1'-dicyanobicycloheptyl (3) showing atomic numbering. C(1) and C(1'), *etc.* are related by twofold rotational symmetry.

Table 5. *Selected bond lengths (Å), bond angles (°), torsion angles (°) and angles between planes (°) for 1,1'-dicyanobicyclopentyl (1), 1,1'-dicyanobicyclohexyl (2) and 1,1'-dicyanobicycloheptyl (3)*

	(1)	(2)	(3)
C(1N)—N(1)	1.142 (4)	1.143 (7)	1.128 (6)
C(1N)—C(1)	1.482 (4)	1.475 (6)	1.481 (6)
C(1)—C(1')	1.537 (5)	1.582 (10)	1.591 (6)
C(1)—C(2)	1.535 (3)	1.547 (8)	1.542 (4)
C(2)—C(3)	1.516 (4)	1.544 (8)	1.516 (4)
C(3)—C(4)	1.503 (6)	1.491 (12)	1.483 (5)
C(4)—C(5)	1.516 (4)	1.511 (11)	1.416 (7)
C(5)—C(6)	–	1.507 (9)	1.483 (5)
C(6)—C(7)	–	–	1.516 (4)
C(7)—C(1)	–	–	1.542 (4)
C(6)—C(1)	–	1.548 (9)	–
C(5)—C(1)	1.535 (3)	–	–
N(1)—C(1N)—C(1)	178.5 (3)	176.3 (6)	178.3 (4)
C(1N)—C(1)—C(1')	107.7 (3)	106.7 (4)	106.3 (4)
C(2)—C(1)—C(1')	115.3 (2)	111.7 (5)	111.5 (2)
C(6)—C(1)—C(1')	–	112.8 (6)	–
C(2)—C(1)—C(5)	101.9 (2)	–	–
C(2)—C(1)—C(6)	–	108.9 (4)	–
C(2)—C(1)—C(7)	–	–	111.4 (3)
C(1N)—C(1)—C(2)—C(3)	78.9 (3)	65.2 (6)	58.5 (3)
C(1N)—C(1)—C(6)—C(5)	–	64.0 (6)	–
C(1N)—C(1)—C(1')—C(2')	59.2 (3)	62.2 (6)	62.6 (4)
C(1N)—C(1)—C(1')—C(6')	–	62.3 (6)	–

Angles between planes

(1)	C(1)—C(2)—C(5)/C(2)—C(3)—C(4)—C(5)	35.2 (5)
(2)	C(1N)—C(1)—C(1')/C(1)—C(2)—C(6)	88.2 (10)
	C(1)—C(2)—C(6)/C(2)—C(3)—C(5)—C(6)	47.2 (10)
	C(2)—C(3)—C(5)—C(6)/C(3)—C(4)—C(5)	49.0 (10)
(3)	C(1)—C(2)—C(7)/C(2)—C(3)—C(6)—C(7)	50.8 (5)
	C(2)—C(3)—C(6)—C(7)/C(3)—C(4)—C(5)—C(6)	54.1 (5)

from the tetraatomic plane. The fact that the 'envelope' form has been adopted in preference to the skewed form found in the more congested 1,1'-dinitrobicyclopentyl, is consistent with the former structure being less strained. The resulting molecular structure also shows that both cyclopentyl rings are joined by a bond which is equatorial to both rings. Such a structure would appear to involve the least steric strain compared with those involving axial/axial or axial/equatorial linkages.

The central C(1)—C(1') bond length of 1.537 Å is surprisingly shorter than that in *meso*-2,3-dicyano-2,3-dicyclopentylbutane (1.597 Å) (Lam, Chong, Koh & Huang, 1991) and 2,3-dicyano-2,3-dimethylbutane (1.561 Å) (Gleason & Britton, 1982), in view of the comparable steric crowding expected about the central C(1)—C(1') bond. However, bond angles about the two central C atoms do show some evidence of steric stress with values in the range 107.7–115.3°.

Crystal structure of 1,1'-dicyanobicyclohexyl (2). The molecules of (2) also adopt a *trans* conformation with the N(1)—C(1N)—C(1) angle at 176.3° (Fig. 2). The two cyclohexyl rings are in the chair form, and are attached equatorially to each other by the central

C(1)—C(1') bond. Such a *trans* structure would belong to the C_{2h} point group. However, the observed space group is $P2_1/n$, not *Cmca*, as in the case of (1), because of some distortion in the cyclohexyl rings resulting in slight deviations from the basic C_{2h} symmetry. Consequently, the plane passing through the central C(1)—C(1') bond and containing the CN groups does not strictly bisect the cyclohexyl rings. Instead of being perpendicular to this plane, structural analysis shows that the rings are twisted by 2° from the perpendicular orientation. With this distortion, (2) sacrifices a small degree of symmetry for more efficient crystal packing as shown by the higher density of the crystal and lower thermal motions. The chair conformation is characterized by the near coplanarity of the atoms C(2), C(3), C(5) and C(6). C(1) and C(4) deviate by −0.66 and 0.66 Å, respectively, from this plane.

This molecule also shows an unusually long central C(1)—C(1') bond (1.582 Å) which is longer than that in compound (1) and is comparable to that in 1,1'-dinitrobicyclohexyl (1.579 Å) (Lam, Huang & Hambley, 1990). This lengthening of the bond with increasing ring size may be attributed to steric crowding about the C(1)—C(1') bond. Bond angles around the two central C atoms reveal evidence of this stress with values in the range 106.7–112.8°. Two of the C—C—C bond angles around C(1) exterior to the ring are smaller than the tetrahedral value [106.7 and 107.8°] while five of the C—C—C bond angles within the cyclohexyl ring are greater. The largest of these, defined by the atoms C(5), C(6) and C(1) (113.3°), is synclinal to the opposite CN group. This angle is slightly larger than the C(3)—C(2)—C(1) angle (111.7°). In cyclohexane the C—C—C bond angles have values in the range 110.4–112.3°. This widening effect was also found in 1,1'-dinitrobicyclohexyl (Lam, Huang & Hambley, 1990), and could be a result of steric repulsion between the methylene and the CN groups.

Crystal structure of 1,1'-dicyanobicycloheptyl (3). Molecules of (3) exist in a *trans* conformation with C_{2h} symmetry (Fig. 3). The cyano group is essentially collinear with C(1), the N(1)—C(1N)—C(1) angle being 178.3°. The cycloheptyl rings adopt chair-like conformations in which atoms C(3), C(4), C(5) and C(6), which form the 'back' of the chair, are essentially coplanar, as are atoms C(2), C(3), C(6) and C(7) which form the 'seat' of the chair. As in compounds (1) and (2), structural analysis shows that the central C(1)—C(1') bond is equatorial to both rings. There is also a σ_h plane passing through the CN groups and the central C(1)—C(1') bond. This plane bisects the cycloheptyl rings whose structure is of C_s symmetry. C(1) is 0.625 Å from the plane C(2), C(3), C(6) and C(7); and C(4) −1.02 Å, from the same plane.

The central C(1)—C(1') bond length, 1.591 Å, is slightly longer in this structure than in compound (2). This is not unexpected as the ring size is now larger. The greater steric congestion is also clearly reflected in the values of the bond angles around the two central C atoms. The six C—C—C bond angles within the molecule are smaller than the tetrahedral value while the C—C—C bond angles involving the central C atoms are greater. These deviations are consistent with the existence of steric congestion in the molecule.

Comparison with the dinitro analogues of compounds (1)–(3). All the compounds (1)–(3) are in the *trans* conformation with the N(1)—C(1N)—C(1) bond angle lying in the range 176.3–178.5°. The cyclopentyl ring adopts the 'envelope' structure while the cyclohexyl and cycloheptyl rings are in the chair conformation. The structures of (1) and (3) belong to the C_{2h} point group while that of (2) is of approximate C_{2h} symmetry. The central C(1)—C(1') bond length increases with ring size as a result of increasing steric congestion.

On the other hand, the shape of the polar substituent in the dinitro analogues is angular rather than cylindrical. As expected, this causes greater steric congestion. These dinitro bicycloalkanes 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. The cyclopentyl ring adopts a skewed structure rather than the 'envelope' form. The cyclohexyl and cycloheptyl rings adopt chair conformations, as in compounds (2) and (3), but are of lower symmetry.

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Structure of *N-tert*-Butyloxycarbonyl-α-aminoisobutyryl-DL-pipecolyl-α-aminoisobutyric Acid Methyl Ester*

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Abstract. $C_{20}H_{35}N_3O_6$ (Boc-Aib-DL-Pip-Aib-OMe, Boc = *tert*-butyloxycarbonyl, Aib = α-aminoisobutyric acid, Pip = pipecolic acid, OMe = methoxy), M_r = 413.5, monoclinic, $P2_1/c$, a = 18.055 (3), b = 15.048 (3), c = 17.173 (3) Å, β = 91.7 (1)°, V = 4663.8 (9) Å^3, Z = 8, D_m = 1.16, D_x = 1.178 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.081 mm^{-1}, F(000) = 1792, T = 297 K. The final R value for 4925 [$I \geq 3\sigma(I)$] reflections is 0.065 (wR = 0.067). The peptide backbone of the two independent molecules in the asymmetric unit is folded at the -Aib-Pip- sequence to form a type-I (I') β-bend stabilized by a 1←4 intramolecular N—H⋯O=C hydrogen bond between the Aib(3) peptide N—H and Boc urethane C=O groups.

Introduction. Pipecolic acid, also referred to as homoproline or piperidine-2-carboxylic acid, is one

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