O1—C11	1.440 (4)	O6—Si30	1.647 (2)
C2—N18	1.430 (4)	N18—C19	1.333 (5)
C2—C3	1.528 (5)	C19—O20	1.226 (5)
C3—O3	1.438 (4)	C19—C21	1.499 (7)
C3—C4	1.504 (5)	C22—O23	1.200 (4)
O3—C22	1.361 (4)	C22—C24	1.475 (5)
C4—N47	1.481 (4)	N47—N48	1.202 (5)
C4—C5	1.524 (5)	N48—N49	1.132 (5)

O1—C1—O5	108.7 (3)	O5—C5—C4	108.6 (3)
O1—C1—C2	109.0 (3)	C6—C5—C4	114.9 (3)
O5—C1—C2	110.9 (3)	C1—O5—C5	111.1 (2)
C1—O1—C11	112.3 (2)	O6—C6—C5	111.1 (3)
N18—C2—C1	111.2 (3)	C6—O6—Si30	118.8 (2)
N18—C2—C3	112.4 (3)	C19—N18—C2	122.3 (3)
C1—C2—C3	105.8 (3)	O20—C19—N18	122.5 (4)
O3—C3—C4	109.7 (3)	O20—C19—C21	122.3 (4)
O3—C3—C2	109.5 (3)	N18—C19—C21	115.2 (4)
C4—C3—C2	110.3 (3)	O23—C22—O3	123.7 (3)
C22—O3—C3	116.7 (3)	O23—C22—C24	124.4 (3)
N47—C4—C3	109.4 (2)	O3—C22—C24	111.9 (3)
N47—C4—C5	108.2 (3)	N48—N47—C4	116.0 (3)
C3—C4—C5	109.0 (3)	N49—N48—N47	173.2 (4)
O5—C5—C6	108.6 (3)		

C3—C4—N47—N48	126.1 (3)	O3—C3—C4—N47	−63.5 (3)
C5—C6—O6—Si30	157.6 (2)	O1—C1—C2—N18	−57.6 (4)
C1—O1—C11—C12	−145.4 (3)	C6—C5—C4—N47	60.8 (4)
C3—O3—C22—O23	−0.0 (5)		

After preliminary photographs, the unit cell was refined and data collected by the SERC Diffractometer Service (Cardiff University). The enantiomer and, thus, the space group were chosen on chemical grounds, and confirmed by the Flack (1983) parameter of −0.09 (15). Crystal decay was monitored by comparing intensities of common or symmetry-related reflections as these occurred on different exposures of the area detector during data collection. No significant decay was observed.

Data collection: *MADNESS* (Enraf–Nonius, 1990). Cell refinement: *MADNESS*. Data reduction: *MADNESS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON*92 (Spek, 1992*a*); *PLATON*92 (Spek, 1992*b*).

The SERC Diffractometer Service are thanked for the collection of X-ray data, and SERC/DTI (in conjunction with Celltech, Glaxo, ICI and The Wellcome Foundation) for support.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Conformational Studies of *trans*-1,4-Substituted Cyclohexanes. I. *trans*-1,4-Cyclohexanedicarbonitrile

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Abstract

The molecules of the title compound ($C_8H_{10}N_2$), which each adopt a chair conformation with the CN substituents equatorially bonded, lie on crystallographic inversion centres and are linked by CN···CN intermolecular interactions to form (101) sheets. The sheets are additionally stabilized by short C—H···N contacts.

Comment

The molecules of *trans*-1,4-cyclohexanedicarboxylic acid and its derivatives exhibit, in solution, a nonvanishing dipole moment (Barón, 1991, and references therein). Similar results observed in other 1,4-disubstituted cyclohexanes, *e.g.* 1,4-cyclohexanedione and 1,4-bis(dicyanomethylene)cyclohexane, have been described in terms of an equilibrium between chair and flexible forms (Le Févre & Le Févre, 1956) or as due to a predominance of a deformed conformation in solution (Aihara, Kitazawa & Iwasaki, 1968; Barón, 1991). Low-temperature X-ray single-crystal data have shown that the molecules of 1,4-

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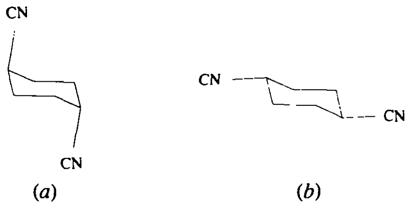
cyclohexanedione present a deformed flexible conformation in the solid state (Mossel & Romers, 1964, and references therein). On the other hand, ^{1}H NMR data of *trans*-1,4-cyclohexanedicarbonitrile, (I), led to the inference that in this compound, in solution, the cyclohexane ring displays a non-inverting chair conformation (Barón, 1988). Therefore, the ring of (I) should be rigid, presenting either conformation (*a*) or (*b*). From IR and Raman measurements in the crystalline state, it has been proposed, assuming the symmetrical geometry $2/m$, that the cyano substituents can only take the diequatorial conformation (*b*) (Ellestad, Klaeboe & Woldbaek, 1982). Quantum-mechanical calculations, using different criteria for molecular optimization, showed that a number of twisted conformations (Gilli, 1992, and references therein) have their energy very close to that of the symmetrical one, thus indicating that the twisted and symmetrical geometries might coexist in solution (Barón, 1988). Taking account of the above results, the present X-ray single-crystal study has been performed to elucidate the correlation between the solution conformation, expected from the electric properties, and the conformation presented by (I) in the crystalline state.



(I)

Fig. 1 shows the molecular geometry. The values of the puckering parameters (Cremer & Pople, 1975), Q = 0.590 (3) Å, $\theta = 0.00\,(5)°$ and φ undefined, indicate that the molecule adopts a chair conformation (Gilli, 1992, and references therein). This is in accordance with the inference from ^{1}H NMR data for (I) in solution. It can be seen from Table 2 that all C—C ring bond lengths and all endocyclic angles do not depart from the mean within experimental error: mean C—C 1.529 (4) Å; mean endocyclic C—C—C 110.5 (1)°. The latter value is smaller than the expected value of 111.1° for the ideal cyclohexane ring (Bucourt & Hainaut, 1965) and even smaller than the mean value of 111.4 (4) ° presented by the parent compound *trans*-1,4-cyclohexanedicarboxylic acid (Dunitz & Strickler, 1966; Von Luger, Plieth & Ruban, 1972). The analysis of the distances between ring atoms related by the inversion centre shows a distortion not described by the puckering parameters. In fact, the C(1)$\cdots$C(1^i) and C(2)$\cdots$C(2^i) distances are equal within experimental error [2.933 (4) and 2.937 (4) Å, respectively], while the C(3)$\cdots$C(3^i) distance [2.955 (4) Å] is larger. This distortion destroys the expected mirror symmetry preserving the inversion centre.

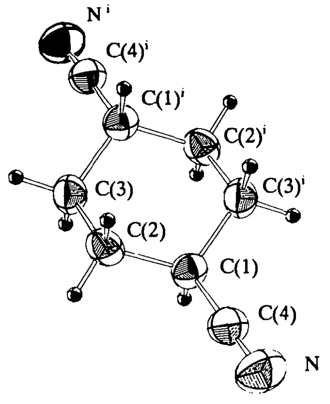


Fig. 1. *ORTEP*II (Johnson, 1976) view of a molecule of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (i) $-x, -y, -z$.

The geometry of the cyano groups matches the geometry described for CN groups bound to cyclic sp^3 C atoms (Donati, Fusi, Ponticelli & Fiorenza, 1989).

In agreement with the conformation proposed by Ellestad *et al.* (1982) from IR data, the CN groups are equatorially bonded to the ring. Fig. 3 shows the Newman projections of the molecule with torsion angles τ_1 = −57.1 (3), τ_2 = 57.1 (3) and τ_3 = −57.5 (3)°. These values are larger than the value assumed for the ideal cyclohexane, τ = 55.8° (Bucourt & Hainaut, 1965). This enlargement is probably due to the necessity of releasing the repulsion induced by the endocyclic angles that are smaller than the ideal.

Fig. 2 shows the molecular packing. It should be noted that the molecular axis is orientated along the $[10\bar{1}]$ direction. This orientation allows the three crystallographic axes to have approximately the same dimensions. The CN dipoles, stacked along chains parallel to the unique b axis, exhibit an approximately antiparallel arrangement; the angle between them is 167.5 (4)°. In addition, the dipoles are approximately perpendicular to the chain axis, making an angle of 83.7 (2)° with that direction. This CN arrangement favours intermolecular interactions *via* dipolar electric forces; the distance between two CN nearest neighbour centres is 3.67 (4) Å. These interactions allow the molecules to be organized in (101) layers. Short C—H$\cdots$N distances within the layers, C(1)—H(1*a*)$\cdots$N = 3.398 (4) and C(2)—H(2*a*)$\cdots$N = 3.669 (4) Å, and between the layers, C(2)—H(2*e*)$\cdots$N^{iii} = 3.686 (4) Å, are observed. These distances suggest the existence of weak electrostatic contributions to the packing forces, mainly within the layers. Interactions of this type have been described as hydrogen bonds by Taylor & Kennard (1982). Recent experimental and theoretical studies of water–benzene complexes by Suzuki *et al.* (1992) and Augspuger, Dykstyra & Zwier (1992) have also shown the significance of the π-electron clouds as hydrogen-bond acceptors.

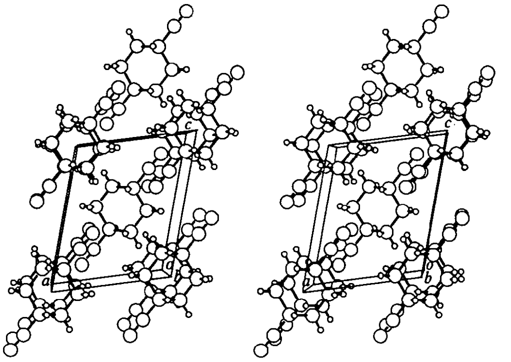


Fig. 2. Stereoscopic view of the unit cell along *b* showing the (101) layers.

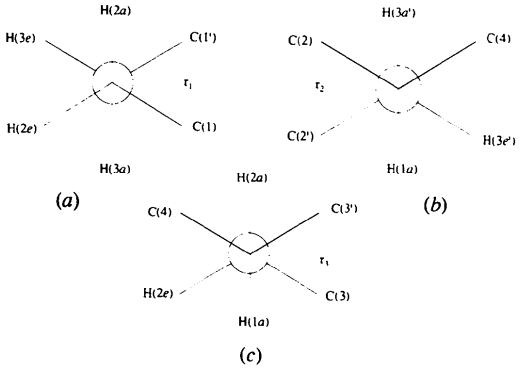


Fig. 3. Newman projections: (*a*) down C(2)—C(3), (*b*) down C(1)—C(3^i) and (*c*) down C(1)—C(2).

The influence of the two different kinds of intermolecular interactions described above might be the cause for the departure of the CN groups from an antiparallel arrangement. This may also induce molecules related by the symmetry operation ($\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$) to be located with their mean plane rotated by 34 (1)°. The deviation of the molecules from the symmetric conformation $2/m$, expected from the spectroscopic data interpretation, might also be explained in terms of the competition between the intermolecular dipolar electric interactions involving the CN groups and the C—H···N electrostatic interactions.

Experimental

The compound was synthesized according to Barón, De Zenobi & Davidson (1975) and crystallized by slow evaporation from acetone.

Crystal data

$C_8H_{10}N_2$
$M_r = 134.18$
Monoclinic
$P2_1/n$
$a = 6.6946$ (2) Å
$b = 7.0268$ (1) Å
$c = 8.3216$ (4) Å
$\beta = 107.21$ (3)°
$V = 373.9$ (2) Å^3
$Z = 2$
$D_x = 1.192$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 2.5$–8.5°
$\mu = 0.069$ mm^{-1}
$T = 295$ K
Irregular
0.3 × 0.2 × 0.125 mm
Colourless

Data collection

CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
785 measured reflections
560 independent reflections
320 observed reflections [$I > 3\sigma(I)$]
$R_{\text{int}} = 0.021$

$\theta_{\text{max}} = 25°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 50 reflections
intensity decay: 4%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.039$
$S = 2.19$
320 reflections
50 parameters
$w = 1.9781/[\sigma^2(F_o) + 0.000095F_o^2]$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.13$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.16$ e Å^{-3}

Extinction correction: $F'_{\text{corr}} = F(1 - CF^2/\sin\theta)$ (Sheldrick, 1976)
Extinction coefficient: $C = 1.6 \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for H atoms; $U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
C(1)	0.0719 (4)	0.0725 (5)	−0.1386 (3)	0.037 (1)
C(2)	−0.1165 (4)	−0.0608 (5)	−0.1709 (3)	0.044 (1)
C(3)	−0.2263 (4)	−0.0367 (5)	−0.0360 (3)	0.044 (1)
C(4)	0.1788 (5)	0.0484 (5)	−0.2684 (3)	0.045 (1)
N	0.2642 (4)	0.0308 (4)	−0.3665 (3)	0.062 (1)
H(1*a*)	0.0149 (4)	0.2157 (5)	−0.1388 (3)	0.044 (7)
H(2*a*)	−0.0629 (4)	−0.1946 (5)	−0.1746 (3)	0.044 (6)
H(2*e*)	−0.2090 (4)	−0.0308 (5)	−0.2766 (3)	0.044 (6)
H(3*a*)	−0.2887 (4)	0.0993 (5)	−0.0402 (3)	0.045 (6)
H(3*e*)	0.3472 (4)	0.1245 (5)	0.0523 (3)	0.045 (6)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.530 (4)	C(1)—C(4)	1.471 (4)
C(2)—C(3)	1.522 (4)	N—C(4)	1.133 (4)
C(3)—C(1^i)	1.534 (4)		
C(2)—C(1)—C(3^i)	110.8 (2)	C(1)—C(2)—C(3)	110.8 (2)
C(3^i)—C(1)—C(4)	109.8 (2)	C(2)—C(3)—C(1^i)	110.1 (2)
C(2)—C(1)—C(4)	110.8 (2)	N—C(4)—C(1)	178.8 (3)
C(4)···C(4^{ii})	3.630(5)	N···C(4^{ii})	3.792(4)
C(4)···N^{ii}	3.556(4)	N···N^{ii}	4.044(4)

D—H···A	H···A	D···A	D—H···A
C(1)—H(1*a*)···N^{iv}	2.656 (4)	3.398 (4)	125.7 (2)
C(2)—H(2*a*)···N^{ii}	2.727 (4)	3.669 (4)	155.3 (2)
C(2)—H(2*e*)···N^{iii}	2.882 (4)	3.686 (4)	144.5 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$; (iii) $-x, -y, -1 - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$.

After an anisotropic refinement of the displacement parameters, the H atoms were stereochemically positioned (C—H = 1.08 Å). Further refinements were performed with the H-atom positions riding on bound C atoms.

Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *MolEN* (Fair, 1990), *PARST* (Nardelli, 1983), *ORTEP*II (Johnson, 1976), *PLUTO* (Motherwell & Clegg). Refinement was by full-matrix least-squares methods.

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Lists of structure factors, anisotropic displacement parameters, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: CR1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Conformational Studies of *trans*-1,4-Substituted Cyclohexanes. II. *trans*-1,4-Dibromo-1,4-cyclohexanedicarbonitrile, $C_8H_8Br_2N_2$

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Abstract

The molecule of the title compound, which has crystallographic symmetry $2/m$, has a chair conformation with the Br and CN substituents located equatorially and axially, respectively. Crystal packing analysis shows that the molecules are organized, *via* CN···CN dipolar interactions, in layers parallel to (001). The layers are linked by CBr···CBr and C—H···Br interactions.

Comment

trans-1,4-Dibromo-1,4-cyclohexanedicarbonitrile, (I), belongs to a series of di- and tetra-substituted cyclohexanes that have a dipole moment in solution (Barón, 1991, and references therein). This has been described in terms of an equilibrium mixture of chair and boat forms in solution (Le Févre & Le Févre, 1956) or as due to the presence of chiral conformers (Aihara, Kitazawa & Iwasaki, 1968; Barón, 1991). To elucidate the relative influence of steric, electronic and packing forces in the molecular geometry in the solid state, and to establish the relationship between solid-state and solution conformations, the molecular structures of several members of the series are currently under study.

In the case of (I), as in *trans*-1,4-cyclohexanedicarbonitrile, (II) (Barón, 1988), ^{1}H NMR data showed that the molecule in solution displays a non-inverting chair conformation of the cyclohexane ring (Barón, 1991). Therefore, the ring should be rigid with the Br atom either diaxially (*a*) or diequatorially (*b*) bonded.

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