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.

References

Aihara, A., Kitazawa, C. & Iwasaki, F. (1968). *Bull. Chem. Soc. Jpn,* **41**, 1034.

Augspuger, J. D., Dykstyra, C. E. & Zwier, T. S. (1992). *J. Phys. Chem.* **96**, 7252–7257.

Barón, M. (1988). *J. Mol. Struct.* **172**, 355–367.

Barón, M. (1991). *J. Mol. Struct.* **248**, 275–280.

Barón, M., De Zenobi, E. L. & Davidson, M. (1975). *J. Mol. Struct.* **24**, 432–438.

Bucourt, R. & Hainaut, D. (1965). *Soc. Chim.* **5**, 1366–1378.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **95**, 1354–1358.

Donati, D., Fusi, S., Ponticelli, F. & Fiorenza, M. (1989). *Acta Cryst.* **C45**, 317–319.

Dunitz, J. D. & Strickler, P. (1966). *Helv. Chim. Acta,* **8**, 290–291.

Ellestad, O. H., Klaeboe, P. & Woldbaek, T. (1982). *J. Mol. Struct.* **95**, 117–129.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Gilli, G. (1992). *Fundamentals of Crystallography,* edited by C. Giacovazzo, pp. 465–534. Oxford Univ. Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Le Févre, C. G. & Le Févre, R. J. W. (1956). *J. Chem. Soc.* pp. 3549–3563.

Mossel, A. & Romers, C. (1964). *Acta Cryst.* **17**, 1217–1223.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Suzuki, S., Green, P. G., Bumgarner, R. E., Dasgupta, S., Goddard, W. A. III & Balke, G. A. (1992). *Science,* **257**, 942–945.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Von Luger, P., Plieth, K. & Ruban, G. (1972). *Acta Cryst.* **B28**, 706–710.

Conformational Studies of *trans*-1,4-Substituted Cyclohexanes. II. *trans*-1,4-Dibromo-1,4-cyclohexanedicarbonitrile, C8H8Br2N2

G. Echeverria,* G. Punte† ‡ and B. E. Rivero§

Departamento de Física, Facultad de Ciencias Exactas, UNLP, CC 67, 1900 La Plata, Argentina

M. Barón‡

Departamento de Física, Facultad de Ciencias Exactas y Naturales, UBA, Pabellón 1, Ciudad Universitaria, 1428 Buenos Aires, Argentina

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-cyclohexane-dicarbonitrile, (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.

* CONICET fellowship.

† Also with Facultad de Ingeniería, UNLP, Argentina.

‡ Member of Carrera del Investigador Científico, CONICET, Argentina.

§ Member of Carrera del Investigador Científico, CICPBA, Argentina.

Since the other substituent, CN, is bulkier than the Br atom, an equatorial cyano and an axial Br substituent would be expected, in agreement with previous results for related compounds (Kozima & Yoshimo, 1953). The main purpose of the X-ray single-crystal study reported here was to determine the ring conformation and the location of the substituents in (I).

(I)

(a)   (b)
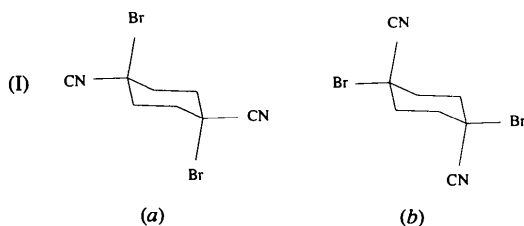
An *ORTEP*II (Johnson, 1976) drawing of the molecule is displayed in Fig. 1. The mean C—C ring bond length and mean C—C—C endocyclic angle are 1.520 (8) Å and 111.5 (5)°, respectively. From Table 2 it can be seen that the C—C ring bond lengths and C—C—C endocyclic angles do not depart from the mean values within experimental error, and are in agreement with the ideal values (Bucourt & Hainaut, 1965). Therefore, the endocyclic angles are larger than those in (II), the mean C—C—C intervalency angle in (II) being 110.5 (1)° (Echeverría, Punte, Rivero & Barón, 1995). Contrary to expectations, the CN groups and Br atoms, which lie on the mirror plane of the molecule, are axially and equatorially bonded to the ring, respectively. The angle between the two substituents, 105.2 (6)°, is smaller than the ideal tetrahedral angle. The CN substituent geometry compares well with the geometry reported for CN groups bound to a cyclic sp^3 C atom (Donati, Fusi, Ponticelli & Fiorenza, 1989). The dihedral angle between the planes of the chair, α = 130.1 (5)°,

is larger than in (II) [128.0 (2)°]. Fig. 3 shows Newman projections of the molecule with torsion angles τ_1 = −55.1 (7), τ_2 = 55.1 (7) and τ_3 = −54.8 (7)°. These values, smaller than those in (II) [τ_1 = −57.1 (3), τ_2 = 57.1 (3) and τ_3 = −57.5 (3)°, respectively (Echeverría *et al.*, 1995)], are close to the ideal cyclohexane value. All the conformational features described above seem to indicate that the inclusion of the Br substituent induces the enlargement of the endocyclic angles, allows ring flattening, relative to (II), and helps towards the stabilization of a geometry closer to that shown by the ideal unsubstituted cyclohexane.

Fig. 2(*a*) shows the molecular organization in the crystal. The molecules with their 'ring plane' approximately perpendicular [91.4 (3)°] to the *a* axis are disposed on layers parallel to the (001) plane. These layers are centred at 0. The CN substituents, arranged in an antiparallel fashion, are stacked along *b* forming endless chains. The nearest-neighbour distance between CN moiety centres is 3.806 (7) Å. This array favours CN···CN dipolar interactions within the layers (CN sheets). In the previous paper we reported that a similar layered structure, built up mainly from CN dipolar electric interactions, is present in (II) (Echeverría *et al.*, 1995). This can be seen in Fig. 2(*b*), where, for comparison, the molecular packing of (II) has been referred to a unit cell different from the one previously reported. The unit-cell transformation is ($\overline{1}01/0\overline{1}0/100$); the space group associated with the new cell is $P2_1/a$. With this cell, it can be seen that in going from (II) to (I) the distance between the CN sheets (d_{001}) and the β
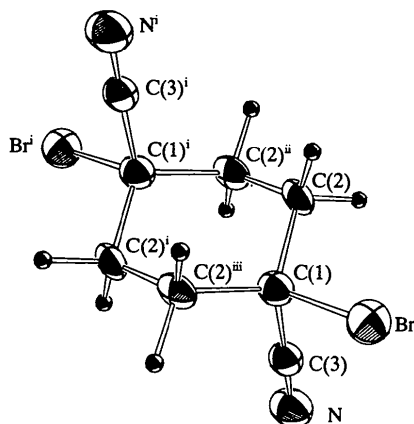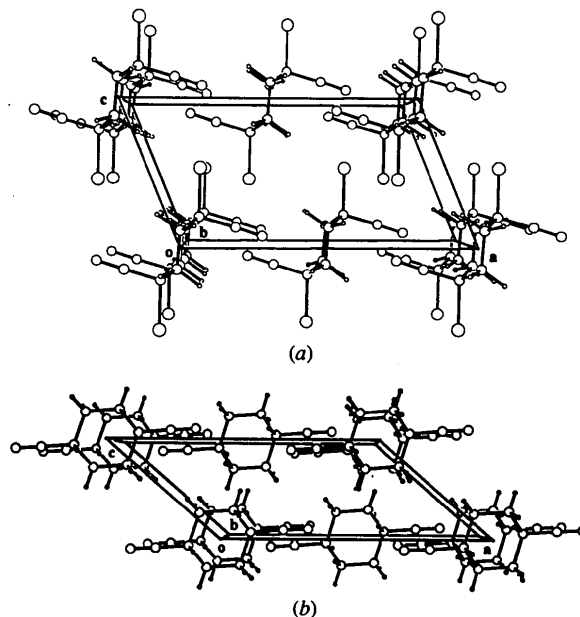
Fig. 1. *ORTEP*II (Johnson, 1976) view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability. Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) *x*, −*y*, *z*; (iii) −*x*, *y*, −*z*.

Fig. 2. View of the unit cell along *b* showing the (001) layers: (*a*) *trans*-1,4-dibromo-1,4-cyclohexanedicarbonitrile, (I); (*b*) *trans*-1,4-cyclohexanedicarbonitrile, (II).

angle exhibit large variations, while the a, b and c values show small differences.

Further analysis of the molecular packing of (I) shows that the polar C—Br bonds, belonging to adjacent CN sheets, are in an antiparallel array similar to that of the CN substituents. The distance between two nearest-neighbour Br atoms is 3.981 (5) Å. In addition, short C—H$\cdots$Br intermolecular contacts are observed between layers (Table 2). As a result of H$\cdots$Br distances and C—H$\cdots$Br directionality [3.043 (8) Å and 146.3 (3)° for equatorially bonded H, and 3.07 (1) Å and 150.2 (5)° for axially bonded H], these interactions are likely to be attractive and can be described as hydrogen bonds according to Taylor & Kennard (1982). This interpretation is supported by recent experimental and theoretical studies of water–benzene complexes by Suzuki, Green, Bumgarner, Dasgupta, Goddard & Balke (1992) and Augspuger, Dykstyra & Zwier (1992). These authors have shown the significance of π-electron clouds as hydrogen-bond acceptors.

A model to explain the structure of (I) from the structure of (II) can be proposed taking into account that the crystals of (II) are formed by CN sheets stabilized by CN$\cdots$CN dipolar interactions and that contiguous sheets only interact via weak electrostatic and van der Waals forces (Echeverria et al., 1995). If it is assumed that the inclusion of Br substituents does not provide intermolecular interactions strong enough to overcome the CN$\cdots$CN dipolar electric interactions, the Br atoms should be located between the CN sheets. This Br location induces a rotation of the 'ring plane' relative to the CN sheets and favours the observed short CBr$\cdots$CBr and C—H$\cdots$Br contacts that stabilize the three-dimensional structure (see Fig. 2). With respect to (II), the equatorial location of the Br atom causes a shrinking of the longest non-bonded intramolecular atom–atom distance. In addition, the inclusion of the Br substituent between CN sheets causes a relative displacement of the contiguous CN sheets, decreasing the β angle and inducing the C2/m space group.
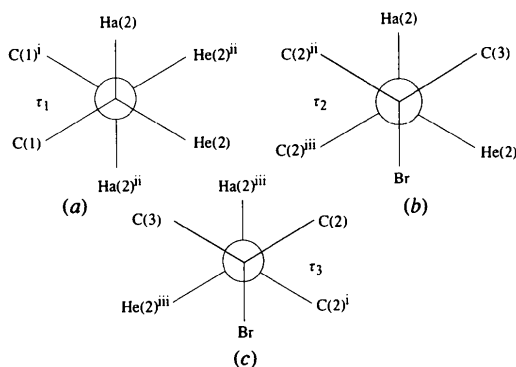
The molecular organization of the title compound, as compared with (II), implies an enhancement of the interaction between contiguous CN sheets that raises the melting point from 419 to 479 K (Barón, De Zenobi & Davidson, 1975).

Experimental

The compound was synthesized according to Barón et al. (1975) and crystallized by slow evaporation from acetone.

Crystal data

$C_8H_8Br_2N_2$	Mo $K\alpha$ radiation
$M_r = 291.98$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$C2/m$	reflections
$a = 11.920 (8)$ Å	$\theta = 2.5$–$8.5°$
$b = 6.885 (5)$ Å	$\mu = 8.1$ mm^{-1}
$c = 6.457 (3)$ Å	$T = 295$ K
$\beta = 112.14 (5)°$	Irregular
$V = 490.8 (5)$ Å^3	0.25 × 0.15 × 0.075 mm
$Z = 2$	Colourless
$D_x = 1.976$ Mg m^{-3}	

Data collection

CAD-4 diffractometer	$R_{int} = 0.028$
θ–2θ scans	$\theta_{max} = 25°$
Absorption correction:	$h = -14 \rightarrow 14$
refined from ΔF	$k = 0 \rightarrow 8$
(DIFABS; Walker &	$l = 0 \rightarrow 7$
Stuart, 1983)	3 standard reflections
440 measured reflections	monitored every 30
370 independent reflections	reflections
306 observed reflections	intensity decay: 4%
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.037$	$\Delta\rho_{max} = 0.68$ e Å^{-3}
$wR = 0.037$	$\Delta\rho_{min} = -0.56$ e Å^{-3}
$S = 1.39$	Extinction correction: none
306 reflections	Atomic scattering factors
35 parameters	from International Tables
$w = 0.9642/[\sigma^2(F_o) +$	for X-ray Crystallography
$0.00037F_o^2]$	(1974, Vol. IV, Table 2.2B)

Fig. 3. Newman projections: (a) down C(2)—C(2^{ii}), (b) down C(1)—C(2), (c) down C(1)—C(2^{iii}).

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

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

	x	y	z	U_{iso}/U_{eq}
Br	0.1761 (1)	0	0.5381 (2)	0.0399 (4)
C(1)	0.1062 (8)	0	0.210 (2)	0.029 (4)
C(2)	0.0307 (6)	0.1835 (9)	0.126 (1)	0.029 (2)
C(3)	0.2125 (9)	0	0.140 (2)	0.029 (4)
N	0.2908 (8)	0	0.081 (2)	0.044 (4)
H(2a)	-0.0223 (6)	0.1934 (9)	0.231 (1)	0.025 (1)
H(2e)	0.0865 (6)	0.3136 (9)	0.163 (1)	0.025 (1)

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

Br—C(1)	1.96 (1)	C(3)—N	1.13 (2)
C(1)—C(2)	1.527 (8)	C(2)—C(2''')	1.514 (9)
C(1)—C(3)	1.50 (2)		
Br—C(1)—C(2)	109.6 (2)	C(1)—C(3)—N	178 (1)
Br—C(1)—C(3)	105.2 (7)	C(1)—C(2)—C(2''')	111.2 (5)
C(2)—C(1)—C(3)	110.2 (3)	C(2)—C(1)—C(2'')	111.7 (4)

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C(2)—H(2a)$\cdots$Br^{iv}	3.07 (1)	4.049 (8)	150.2 (5)
C(2)—H(2e)$\cdots$Br^{v}	3.043 (8)	3.994 (6)	146.3 (3)

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

After an anistropic refinement of the displacement parameters, the H-atom positions were obtained from a Fourier synthesis. Further refinements were performed with the H atoms 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).

References

Aihara, A., Kitazawa, C. & Iwasaki, F. (1968). *Bull. Chem. Soc. Jpn,* **41**, 1034.

Augspuger, J. D., Dykstyra, C. E. & Zwier, T. S. (1992). *J. Phys. Chem.* **96**, 7252–7257.

Barón, M. (1988). *J. Mol. Struct.* **172**, 355–367.

Barón, M. (1991). *J. Mol. Struct.* **248**, 275–280.

Barón, M., De Zenobi, E. L. & Davidson, M. (1975). *J. Mol. Struct.* **24**, 432–438.

Bucourt, R. & Hainaut, D. (1965). *Soc. Chim.* **5**, 1366–1378.

Donati, D., Fusi, S., Ponticelli, F. & Fiorenza, M. (1989). *Acta Cryst.* **C45**, 317–319.

Echeverria, G., Punte, G., Rivero, B. E. & Barón, M. (1995). *Acta Cryst.* **C51**, 1020–1023.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kozima, K. & Yoshimo, T. (1953). *J. Am. Chem. Soc.* **75**, 166–171.

Le Févre, C. G. & Le Févre, R. J. W. (1956). *J. Chem. Soc.* pp. 3549–3563.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Suzuki, S., Green, P. G., Bumgarner, R. E., Dasgupta, S., Goddard, W. A. III & Balke, G. A. (1992). *Science,* **257**, 942–945.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

5-(Isopropylamino)-8-methyl-2-quinolone

L. Sudha, K. Subramanian* and J. Sivaraman

Department of Physics, Anna University, Madras 25, India

V. T. Ramakrishnan

Department of Organic Chemistry, University of Madras, Madras 25, India

Th. Steiner and G. Koellner

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14159 Berlin, Germany

Abstract

The title compound, $C_{13}H_{16}N_2O$, is a new laser dye. The quinolone ring system is essentially planar. The methyl and the amino groups at C(5) and C(8) are in equatorial positions with respect to the ring. The isopropyl group is inclined from the plane of the aromatic ring. N—H$\cdots$O and weak C—H$\cdots$O hydrogen bonds are formed.

Comment

This study was undertaken as part of our program on the structural aspects of quinolone laser dyes. The laser performance of the title compound, (I), is yet to be studied, but the laser emission of similar compounds is around $\lambda = 410$ nm (Hammond, Fletcher, Henry & Atkins, 1975; Hammond *et al.*, 1976).

(I)
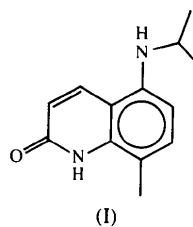
Bond lengths and valence angles in the quinolone ring are normal (Chinnakali, Sivakumar, Natarajan, McGuire & Clearfield, 1991); the C(3)—C(4) bond length of 1.350 (6) Å is indicative of a localized double bond. The angles C(4)—C(10)—C(5) and C(3)—C(2)—O(2) are greater than 120°, while C(3)—C(2)—N(1) is less than 120°, as is commonly found in quinolone derivatives (Kido, Nakagawa, Fujiwara & Tomita, 1981). The C(2)—O(2) bond length is 1.259 (5) Å, indicative of a double bond, which is a unique value in quinolone derivatives (Chinnakali *et al.*, 1991). The C(8)—C(8')