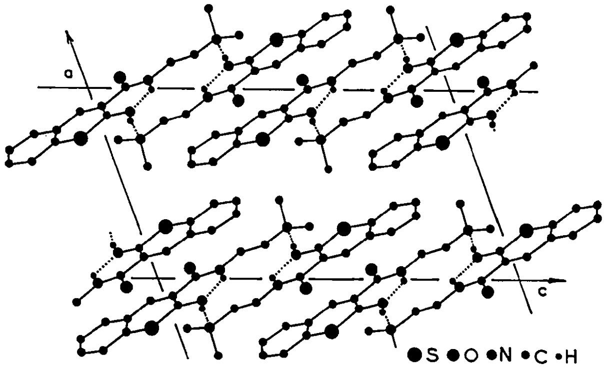

Fig. 2. Vue de la structure parallèlement à l'axe *b*. Les traits en pointillé représentent les liaisons hydrogène.

La Fig. 2 montre que les molécules forment des couches dont les positions moyennes sont les plans (100). Dans une même couche, elles sont associées deux par deux par deux liaisons hydrogène N(16)—H(16)···N(13^{i}) [3,047 (2) Å, 171 (2)°] [(i): $2-x$, $\frac{1}{2}-y$, $\frac{3}{2}+z$].

Références

B. A. Frenz & Associates Inc. (1982). *Structure Determination Package*. College Station, Texas, E.-U. et Enraf/Nonius, Delft, Pays-Bas.

Banerjee, A., Brown, C. J. & Jain, P. C. (1985). *Acta Cryst.* C**41**, 1505–1507.

Darocha, B. F., Titus, D. D., Sandman, D. J. & Warner, D. E. (1982). *Acta Cryst.* B**38**, 2267–2269.

Elahmad, Y. (1986). Thèse Doctorat ès Sciences Pharmaceutiques, Univ. de Paris-Sud, France.

Gazengel, J.-M. (1986). Thèse Doctorat ès Sciences Pharmaceutiques, Univ. de Caen, France.

International Tables for X-ray Crystallography (1974). Tome IV, pp. 99 et 149. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht, Pays-Bas.)

Johnson, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee, E.-U.

Luss, H. R. & Smith, D. L. (1980). *Acta Cryst.* B**36**, 986–989.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et Louvain, Belgique.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3^{e} éd., pp. 224 et 228. Cornell Univ. Press.

Rodier, N., Uzan, L., Reynaud, P. & Brion, J.-D. (1984). *Bull. Soc. Chim. Fr.* I, pp. 317–320.

Acta Cryst. (1987). C**43**, 1594–1597

Conformation and Structure of 1,1′-Bicyclopropyl-1,1′-dicarbonitrile

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Abstract. $C_8H_8O_2$, $M_r = 136{\cdot}15$, orthorhombic, *Pbcn*, $a = 8{\cdot}5605$ (10), $b = 6{\cdot}8946$ (16), $c = 12{\cdot}9144$ (18) Å, $U = 762{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 0{\cdot}4$ cm^{-1}, $F(000) = 280$, $T = 293$ K, $R = 0{\cdot}063$ for 558 unique observed reflections. The molecule possesses crystallographic twofold symmetry. The molecules display a *gauche* conformation with a dihedral angle of 58°. The central bond length C(1)—C(1^{i}) (1·508 Å, libration corrected) is not shortened, in contrast to crystalline 1,1′-bicyclopropyl. The cyclopropane rings are asymmetric. The overall asymmetry of the cyclopropane rings is determined by the cyano substituents, but the individual CC bond distances reflect some additional effect probably originating from steric interactions.

Introduction. We have recently investigated the structure and conformational equilibrium of 1,2-diisocyanoethane (Schrumpf & Martin, 1982; Trætteberg, Almenningen, Schrumpf & Martin, 1987) and isocyanoethyl cyanide (Schrumpf & Martin, 1983) because of the unusual properties of these isocyanides. The structure of the diisocyanide is very similar to that of 1,2-dicyanoethane (succinonitrile) (Fernholt & Kveseth, 1979; Fujiyama, Tokumaru & Shimanouchi, 1964), and the rotational equilibria of the diisocyanide, isocyanocyanide and dicyanide are essentially the same. All three molecules are different from most of the other 1,2-disubstituted ethanes in that the *anti* conformer is the most stable in the vapour phase, but a mixture of *anti* and *gauche* conformers of similar energy is present

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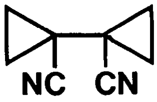
in the liquid. There is a plastic phase just below the melting point, which at lower temperatures undergoes a transition to a crystalline phase containing only the *gauche* conformation. It appears that in the condensed phases, the greater molecular stability of the *anti* rotamer is outweighed by the more favourable intermolecular interactions in polar media. The trend towards a smaller energy difference between the *gauche* and the *anti* conformers on going from the free molecule to the liquid phase is also observed in the 1,2-dihalogenoethanes (Tanabe, 1972, 1974).

Surprisingly, in 1,1,2,2-tetramethylsuccinonitrile, the *anti* conformer is present in the crystal (Gleason & Britton, 1982). In solution, the *anti* form is still the more abundant (Chia, Huang & Lim, 1969; Chia, Huang & Sheppard, 1970). Whether the enhanced stability of the *anti* conformer in the tetramethyl derivative compared to succinonitrile originates from the smaller dipole moment of the *gauche* form (arising from a larger dihedral angle) or whether the dipolar contributions to the lattice energy are smaller because of the higher lipophilicity (brought about by the four additional methyl groups) is uncertain. In order to test the latter hypothesis, we decided to investigate the conformation of a molecule similar to the tetramethyl derivative. We chose 1,1′-bicyclopropyl-1,1′-dicarbonitrile as a model, where two methyl H atoms are substituted by a C—C bond between the geminal C atoms. We have already studied this molecule by vibrational spectroscopy and found evidence for the presence of a C_2 conformation in the solid state (Schrumpf, 1987). Here we present the crystal structure of the title compound.



(I)

Experimental. The title molecule was synthesized according to the literature (Cobb, Vives & Mahan, 1978). Suitable crystals were grown from ether–petrol ether.

Colourless plate, 0·65 × 0·35 × 0·1 mm. Stoe–Siemens four-circle diffractometer, monochromated Mo *Kα* radiation, profile-fitting mode (Clegg, 1981). 1567 intensities to $2\theta_{\max}$ 55°, 874 unique reflections (R_{int} 0·029), 558 with $F > 4\sigma(F)$ used for all calculations (program *SHELX*76; Sheldrick, 1976). Three check reflections, no significant intensity change. Index ranges after merging $h \leq 10$, $k \leq 8$, $l \leq 16$. Cell constants refined from 2θ values of 66 reflections in the range 19–23°.

Structure solution by routine direct methods. Full-matrix refinement on F to R 0·063, wR 0·056 [H atoms refined freely, 62 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0002F^2$, $S = 2{\cdot}18$]. Max. Δ/σ 0·1, max. and min. features in final $\Delta\rho$ map 0·14, $-0{\cdot}16$ e Å^{-3}. Atomic scattering factors as incorporated in *SHELX*.

Discussion. Final atomic coordinates and derived molecular parameters are presented in Tables 1 and 2.* The bond lengths were corrected for libration by the rigid-body method of Schomaker & Trueblood (1968); $R_{\text{lib}} = 0{\cdot}0524$. Fig. 1 shows the atom-numbering scheme.

Table 1. *Atomic coordinates* (× 10^4) *and isotropic displacement factors* (Å^2 × 10^3)

	x	y	z	U
C(1)	5116 (2)	6893 (3)	3076 (1)	47 (1)*
C(2)	6609 (3)	7683 (4)	3542 (2)	67 (1)*
H(21)	7040 (24)	6992 (34)	4171 (18)	80 (7)
H(22)	7323 (27)	8166 (30)	3046 (17)	66 (6)
C(3)	5125 (4)	8728 (4)	3701 (2)	75 (1)*
H(31)	4882 (24)	9850 (34)	3330 (16)	66 (6)
H(32)	4581 (32)	8600 (37)	4375 (26)	116 (10)
C(4)	4455 (2)	5200 (3)	3571 (1)	56 (1)*
N	3938 (3)	3836 (3)	3927 (2)	88 (1)*

* Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

		Corrected			Corrected
C(1)—C(2)	1·514 (4)	1·526	C(1)—C(1$^{\text{i}}$)	1·501 (4)	1·508
C(1)—C(3)	1·501 (4)	1·515	C(2)—C(3)	1·475 (5)	1·489
C(1)—C(4)	1·446 (4)	1·461	C(4)—N	1·136 (3)	1·148

C(3)—C(1)—C(2)	58·6 (2)	C(4)—C(1)—C(1$^{\text{i}}$)	112·7 (3)
C(4)—C(1)—C(2)	116·4 (3)	C(3)—C(2)—C(1)	60·3 (2)
C(4)—C(1)—C(3)	116·4 (3)	C(2)—C(3)—C(1)	61·1 (2)
C(2)—C(1)—C(1$^{\text{i}}$)	120·4 (3)	C(1)—C(4)—N	177·6 (3)
C(3)—C(1)—C(1$^{\text{i}}$)	122·3 (3)		

Symmetry operator: (i) $1-x, y, 0{\cdot}5-z$.

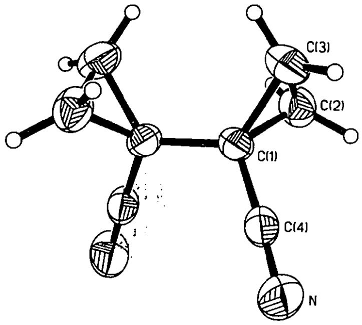


Fig. 1. Thermal-ellipsoid plot (50% level) of the title compound, showing the labelling scheme of the asymmetric unit. H atoms as spheres of arbitrary radius.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43929 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Lengths of the central bond in* 1,1′-*bicyclopropyls* (*BCP's*)

	Compound	r (Å, uncorrected)	r (Å, corrected)	Ref.
(1)	BCP	1·487 (4)	1·490†	(*a*)
(2)	*anti-cis,cis*-2,2′-Dibromo-BCP	1·49 (2)		(*b*)
(3)	Dimethyl 1,1′-dimethyl-BCP-2,2′-dicarboxylate	1·51*		(*c*)
(4)	1,1′-Dinitro-BCP	1·476 (3)	1·479	(*d*)
(5)	1-Nitro-1′-nitroso-BCP	1·473 (5)		(*d*)
(6)	BCP-1,1′-dicarbonitrile	1·501 (4)	1·508	(*e*)

References: (*a*) Eraker & Rømming (1967); (*b*) Schrumpf & Süsse (1972); (*c*) Jongsma & van der Meer (1971); (*d*) Kai, Knochel, Kwiatkowski, Dunitz, Oth, Seebach & Kalinowski (1982); (*e*) this work.

* E.s.d. not given.
† Based on published *B* values.

The molecules, which display crystallographic twofold symmetry, are present in the *gauche* conformation with a dihedral angle of 57·9° between the cyano substituents. This contrasts with the structurally related 1,2-dicyano-1,1,2,2-tetramethylethane, which occurs as the *anti* rotamer in the crystalline phase (Gleason & Britton, 1982). The hydrocarbon 1,1′-bicyclopropyl also crystallizes in the *anti* form (Eraker & Rømming, 1967), which may explain the differences in the central C—C bond lengths (see below).

In the vapour phase, the *gauche* angle of succinonitrile is 75° (Fernholt & Kveseth, 1979). In the tetramethyl derivative, this angle is 85° in CCl_4 solution (Chia *et al.*, 1969). The latter observation might have steric causes. In the title molecule, the terminal CH_2 groups are smaller than the CH_3 groups in the tetramethyl analogue. In addition to differences in dihedral orientation, the geminal methyl groups are more spread out than the CH_2 groups in the title molecule, because the intra-annular angle in each cyclopropane ring is only 60° in comparison to 108° for the angle between the geminal methyl groups in the aliphatic analogue. According to molecular models, this allows a smaller *gauche* angle, which is opposed by repulsive non-bonded HH interactions, in the bicyclopropyl than in the tetramethyl compound.

The central bond length C(1)—C(1^{i}) is 1·508 Å (1·501 Å uncorrected). In the hydrocarbon, 1,1′-bicyclopropyl, this bond distance is only 1·490 Å (1·487 Å uncorrected) (Eraker & Rømming, 1967). A few other structures of substituted bicyclopropyls have been reported (Table 3). The length of the central C—C bond varies in a manner which appears not to be correlated simply with a single parameter such as *anti* or *gauche* conformation or substitution at C(1) and C(1^{i}) by electron donors or acceptors. It must therefore be concluded that the C(1)—C(1^{i}) bond distance is influenced by several factors, *e.g.* conjugation between the two cyclopropane moieties (which depends on the conformation), steric factors, and electronic effects from the substituents at C(1) and C(1^{i}), which affect the strength of the central bond (as is observed in simple ethyl derivatives). The main obstacles to a rationalization of these effects are the limited amount of data on substituted bicyclopropyls, the varying accuracies of the structure determinations [Table 3, compounds (2) and (3)], the unsystematic choice of the substitution loci [compounds (2) and (3)], the nature of the substituents (NO and NO_2 have additional degrees of rotational freedom) and multiple substitution [compound (3)], which render the molecules of Table 3 largely uncomparable. We intend to pursue these problems in our laboratories by studying more appropriate model molecules.

The cyclopropane rings are asymmetric. This is to be expected because of the cyano substituents, which shorten C(2)—C(3), the bond opposite, to 1·489 Å (corrected) and lengthen the adjacent bonds (1·515 and 1·526 Å, respectively) relative to cyclopropane. The difference between the latter bonds of about 3σ is unexpected. The cyano group lies in the plane bisecting the angle C(2)C(1)C(3) [*i.e.* ∠C(4)C(1)C(2) = ∠C(4)-C(1)C(3)], and thus its electronic influence on C(1)—C(2) and C(1)—C(3) should be the same. However, there is a difference between C(1^{i})C(1)C(2) (120·4°) and C(1^{i})C(1)C(3) (122·3°) of 2°. This might originate from a repulsive interaction between the H atoms at C(3) and C(3^{i}), which come quite close to each other in this conformation with H(31)···H(31^{i}) 2·15 Å. Apart from this supposition, we have no convincing explanation for C(1)—C(3) being shorter than C(1)—C(2). This asymmetry is also observed in the other bicyclopropyl derivatives with *gauche* conformations.

The bond lengths of the cyano group are normal compared to other simple cyano-substituted cyclopropanes (Kiers, de Boer, Heijdenrijk, Stam & Schenk, 1985; Hartman & Hirshfeld, 1966; Jones & Schrumpf, 1987*a,b,c*).

Fig. 2 shows the molecular packing. There are no unusually short intermolecular contacts.

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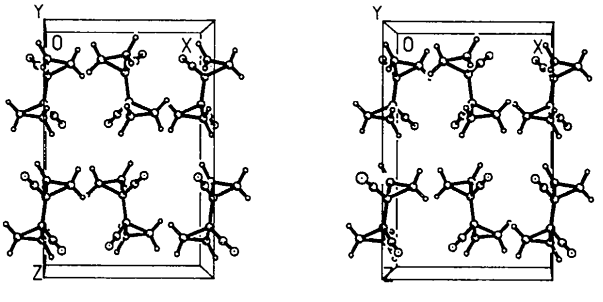

Fig. 2. Stereo packing diagram; view direction parallel to the y axis.

References

CHIA, L. H. L., HUANG, H. H. & LIM, P. K. K. (1969). *J. Chem. Soc. B*, pp. 608–612.

CHIA, L. H. L., HUANG, H. H. & SHEPPARD, N. (1970). *J. Chem. Soc. B*, pp. 359–362.

CLEGG, W. (1981). *Acta Cryst.* A**37**, 22–28.

COBB, R. L., VIVES, V. C. & MAHAN, J. E. (1978). *J. Org. Chem.* **43**, 931–936.

ERAKER, J. & RØMMING, C. (1967). *Acta Chem. Scand.* **21**, 2721–2726.

FERNHOLT, L. & KVESETH, K. (1979). *Acta Chem. Scand. Ser. A*, **33**, 334–341.

FUJIYAMA, T., TOKUMARU, K. & SHIMANOUCHI, T. (1964). *Spectrochim. Acta*, **20**, 415–428.

GLEASON, W. B. & BRITTON, D. (1982). *Cryst. Struct. Commun.* **11**, 1159–1162.

HARTMAN, A. & HIRSHFELD, F. L. (1966). *Acta Cryst.* **20**, 80–82.

JONES, P. G. & SCHRUMPF, G. (1987*a*). *Acta Cryst.* C**43**, 1179–1182.

JONES, P. G. & SCHRUMPF, G. (1987*b*). *Acta Cryst.* C**43**, 1576–1579.

JONES, P. G. & SCHRUMPF, G. (1987*c*). *Acta Cryst.* C**43**, 1579–1582.

JONGSMA, C. & VAN DER MEER, H. (1971). *Recl Trav. Chim. Pays-Bas*, **90**, 33–38.

KAI, Y., KNOCHEL, P., KWIATKOWSKI, S., DUNITZ, J. D., OTH, J. F. M., SEEBACH, D. & KALINOWSKI, H.-O. (1982). *Helv. Chim. Acta*, **65**, 137–162.

KIERS, C. T., DE BOER, J. S. A. M., HEIJDENRIJK, D., STAM, C. H. & SCHENK, H. (1985). *Recl Trav. Chim. Pays-Bas*, **104**, 7–9.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

SCHRUMPF, G. (1987). In preparation.

SCHRUMPF, G. & MARTIN, S. (1982). *J. Mol. Struct.* **81**, 155–165.

SCHRUMPF, G. & MARTIN, S. (1983). *J. Mol. Struct.* **101**, 57–67.

SCHRUMPF, G. & SÜSSE, P. (1972). *Chem. Ber.* **105**, 3041–3049.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

TANABE, K. (1972). *Spectrochim. Acta Part A*, **28**, 407–424.

TANABE, K. (1974). *Spectrochim. Acta Part A*, **30**, 1901–1914.

TRÆTTEBERG, M., ALMENNINGEN, A., SCHRUMPF, G. & MARTIN, S. (1987). *J. Mol. Struct.* Submitted.

Acta Cryst. (1987). C**43**, 1597–1599

Studies in Nonlinear Optical Materials: Structure of Methyl 2-(4-Ethyl-5-methyl-2-thioxo-2,3-dihydro-1,3-thiazol-3-yl)propionate

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Abstract. $C_{10}H_{15}NO_2S_2$, $M_r = 245\cdot0$, orthorhombic, $P2_12_12_1$, $a = 6\cdot639\,(2)$, $b = 8\cdot205\,(2)$, $c = 22\cdot528\,(6)$ Å, $V = 1227\cdot2\,(6)$ Å^3, $Z = 4$, $D_m = 1\cdot315$, $D_x = 1\cdot326$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 3\cdot63$ cm^{-1}, $F(000) = 520$, $T = 293$ K, $R = 0\cdot037$ for 1115 significant reflections. The second-harmonic-generation (SHG) efficiency of this compound is only 1/10th of the urea standard. The observed low second-order nonlinear response may be attributed to the unfavourable packing of the molecules in the crystal lattice.

Introduction. As part of a long-range research programme on developing organic compounds exhibiting good nonlinear optical properties, the molecular packing of the title compound was investigated. Although the present molecule is not one with a well defined charge-transfer axis such as nitroanilines (Levine, Bethea, Thurmond, Lynch & Bernstein, 1979; Lipscomb, Garito & Narang, 1981) and push–pull ethylenes (Kanagapushpam, Padmanabhan & Venkatesan, 1987), it was considered worth investigating in view of its large ground-state dipole moment ($\sim 30\cdot7 \times 10^{-30}$ Cm) and also because it crystallizes in a non-centrosymmetric space group.

Experimental. Single crystals of the title compound obtained from methanol by slow evaporation, approximate dimensions 0·05 × 0·45 × 0·40 mm. D_m by flotation. Preliminary oscillation and Weissenberg photographs indicated that the crystals were orthorhombic. Lattice parameters refined by a least-squares fit to settings for 25 accurately centred reflections. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1}, $\theta \leq 25°$. During data collection two standard reflections (219 and 124) showed only statistical fluctuations within ±2%. 1365 reflections collected, *hkl* range *h*: 0 to 7, *k*: 0 to 9, *l*: 0 to 26, 1115 significant, $|F_o| \geq 3\sigma|F_o|$. Data not corrected for absorption. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters for non-H atoms and positional and isotropic thermal parameters for H atoms (all located from difference map) converged to $R = 0\cdot037$, $wR = 0\cdot046$, $S = 1\cdot2$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1\cdot1467/[\sigma^2(F) + 0\cdot001\,127\,|F_o|^2]$. In the final cycles of refinement, Δ/σ for non-H atoms is about 0·02,

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