–CH=NOH group on position 2 of py ring (i) but with the $-CONH_2$ group on either position 3 or 4 of py ring (ii), or to HGG-12 with a benzoyl group on position 3 of ring (ii) (Bregovec, Binenfeld, Maksimović & Bošković, 1984; Bregovec, Maksimović, Deljac, Deljac & Binenfeld, 1986). The efficiency of HS-6, HI-6 as well as of HGG-12 as soman antidote was explained by the structural similarities between the bispyridinium oxime antidotes and nicotine and acetylcholine of nicotinic conformation. The interatomic distances between py N and carbonyl O atoms on ring (ii) of HS-6 is 4·71 Å, the corresponding distances for HI-6 and HGG-12 are 4·91 and 4·61 Å, respectively. The py N atom to oxime O atom distance on ring (i) of HS-6 is 4·62 Å, those for HI-6 and for HGG-12 are 4·62 and 4·64 Å. These distances are close to those of nicotine (4·76 Å) and acetylcholine of nicotinic conformation (4·93 Å). It was suggested that such structural similarities are responsible for the ability of these bispyridinium oximes to act as antagonists of acetylcholine for nicotinic receptors (Su, Tang, Ma, Shih, Liu & Wu, 1983). However, the interatomic distances between py N and oxime O atoms in our symmetrical HS-4 of 4·631 (3) and 4·593 (4) Å for rings (i) and (ii), respectively, are also close to the values found in the structures of the previously mentioned unsymmetrical antidotes. It was also suggested that, for comparison, the bispyridinium-4,4′-dioxime (toxogonin) with the distances between py N and oxime O atoms of 6·28 and 6·29 Å, which do not correspond to a nicotinic receptor, for this reason is not as good antagonist for a nicotinic receptor (Su, Tang, Ma, Shih, Liu & Wu, 1983).

Considering thus all these distances and related antidotal activities it seems premature to form any conclusions on the structure–activity relationship and the mechanism of action of this class of compounds.

The authors thank Professor Z. Binenfeld for suggesting the problem and helpful discussions, Dr V. Deljac for preparing the compound, and the Foundation for Scientific Research of SR Croatia, Zagreb, for financial support.

References

Binenfeld, Z., Deljac, V., Kamenar, B. & Vicković, I. (1984). *Acta Pharm. Jugosl.* **34**, 195–199.

Bošković, B. (1981). *Fundam. Appl. Toxicol.* **1**, 203–213.

Bregovec, I., Binenfeld, Z., Maksimović, M. & Bošković, B. (1984). *Acta Pharm. Jugosl.* **34**, 133–138.

Bregovec, I., Maksimović, M., Deljac, A., Deljac, V. & Binenfeld, Z. (1986). *Acta Pharm. Jugosl.* **36**, 9–13.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kamenar, B., Vicković, I. & Bruvo, M. (1986). *Acta Cryst.* C**42**, 1818–1821.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Su, C.-T., Tang, C.-P., Ma, C., Shih, Y.-S., Liu, C.-Y. & Wu, M.-T. (1983). *Fundam. Appl. Toxicol.* **3**, 271–277.

Acta Cryst. (1987). C**43**, 1576–1579

Substituted Cyclopropanes. 5.* 1-Cyanocyclopropanecarboxylic Acid

By Peter G. Jones

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen,*
Federal Republic of Germany

and Gerd Schrumpf

Institut für Organische Chemie der Universität, Tammannstrasse 2, *D*-3400 *Göttingen,*
Federal Republic of Germany

(*Received* 14 *July* 1986; *accepted* 18 *March* 1987)

Abstract. $C_5H_5NO_2$, $M_r = 111{\cdot}10$, orthorhombic, *Pnma*, $a = 10{\cdot}836\ (4)$, $b = 7{\cdot}164\ (3)$, $c = 6{\cdot}934\ (3)$ Å, $V = 538{\cdot}3\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}37$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}1$ cm^{-1}, $F(000) = 232$, $T = 293$ K, $R = 0{\cdot}065$ for 592 unique observed reflections. C(1) and all substituent atoms lie in crystallographic mirror

---

* Part 4: Schrumpf & Jones (1987*c*).

0108-2701/87/081576-04$01.50 © 1987 International Union of Crystallography

planes. A marked ring bond asymmetry is observed: C(1)—C(2) 1·541, C(2)—C(2^{i}) 1·467 Å (libration-corrected values). Intramolecular hydrogen bonds of the form C(O)OH···NC link the molecules in zigzag strings parallel to the *a* axis.

Introduction. The effects of geminal disubstitution on the geometry of the cyclopropane ring seem to be well understood. On the basis of the Walsh model of bonding in the cyclopropane molecule, it can be shown that substituents that remove electrons *via* σ-inductive effects (*e.g.* halogens) lengthen the bond opposite the substituted C atom and shorten the adjacent ones, while substituents that withdraw π electrons from the ring (*e.g.* carbonyl and cyano groups) induce a ring asymmetry in the opposite sense. These theoretical predictions are borne out convincingly by experiment (Perretta & Laurie, 1975; Hedberg, Hedberg & Boggs, 1982; Meester, Schenk & MacGillavry, 1971; Usha & Venkatesan, 1979).

The geometry of polysubstituted cyclopropanes is of more general interest. It would be very gratifying if the trends in mono- and disubstituted cyclopropanes, which are predictable, could be transferred to the more highly substituted cyclopropanes. By examining many cyclopropane structures, Allen (1980) proposed an additivity scheme for the ring bond asymmetry, which theoretically was suggested by Hoffmann & Stohrer (1971). However, we have recently examined the crystal structures of some polysubstituted cyclopropanes, and our results are clear evidence for a steric effect that is superimposed onto an electronic interaction of the kind proposed by Hoffmann (1970) (Jones & Schrumpf, 1987*a*; Schrumpf & Jones, 1987*a,b,c*).

In an attempt to study more closely the balance of electronic and steric interactions in substituted cyclopropanes, we have begun to study substituents with conformational degrees of freedom. Steric interactions assessed from bond-length and bond-angle variations are ‘magnified’ into conformational changes. In two following reports, we will present our results on two polysubstituted cyclopropanes with ester groups as the substituents (Jones & Schrumpf, 1987*b,c*). One of the problems encountered in these studies is whether unsymmetrical geminal disubstitution without any foreseeable steric interference will induce a bond-angle asymmetry and, in particular, whether the angles of inclination of the two different substituents towards the ring plane will be the same. This question is important for molecules with expected steric interaction between vicinal *cis* substituents, as these bond angles are additional probes for steric repulsion or attraction. Thus, we studied the crystal structure of 1-cyanocyclopropanecarboxylic acid.

Experimental. The title compound was synthesized according to the literature (Singh & Danishefsky, 1975). Single crystals in the form of colourless plates were obtained by slow evaporation of a chloroform solution.

A crystal *ca* 0·6 × 0·4 × 0·1 mm was used to collect two data sets on a Stoe two-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 55°): (i) layers $h0\rightarrow7l$, 2139 reflections, (ii) (remounted) layers $hk0\rightarrow7$, 2540 reflections. Interlayer scale factors were determined by least-squares analysis of common reflections. 705 unique reflections ($R_{\rm int}$ 0·022), 592 with $F > 4\sigma(F)$ used for all calculations [program system *SHELXTL* (Sheldrick, 1978)]. Index ranges after merging $0 \le h \le 14$, $0 \le k \le 9$, $0 \le l \le 8$. Cell constants refined from ω values of 18 axial or near-axial reflections.

Structure solution by routine direct methods. Refinement on F to R 0·065, wR 0·050 with anisotropic C, N and O, isotropic H atoms refined freely, 57 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0001F^2$, $S = 2{\cdot}43$, slope of normal probability plot = 1·82. Max. Δ/σ 0·004, max. and min. features in final $\Delta\rho$ map $\pm$ 0·3 e Å^{-3}. Atomic scattering factors as incorporated in *SHELXTL*.

Discussion. Final atomic coordinates and derived molecular dimensions are presented in Tables 1 and 2.* The bond lengths were corrected for libration by the rigid-body method of Schomaker & Trueblood (1968); $R_{\rm libr} = 0{\cdot}065$. The molecule exhibits crystallographic mirror symmetry (Fig. 1), all atoms except C(2), H(21) and H(22) lying in the plane $y = 0{\cdot}25$.

The ring bond distances exhibit a marked asymmetry of 0·074 Å (corr.). The corresponding uncorrected asymmetry of 0·080 Å is in agreement with the findings in cyclopropane-1,1-dicarboxylic acid (0·073 Å; Meester *et al.*, 1971) and the diamide (0·071 Å; Usha & Venkatesan, 1979), for which unfortunately no libration corrections have been published. The absolute values of the corresponding uncorrected bond lengths in the three molecules are also very close to each other. For 1,1-cyclopropanedicarbonitrile, only the length of the unique bond in the gas phase has been estimated (1·482 Å; Pearson, Choplin, Laurie & Schwartz, 1975), which – in view of the rather large uncertainty of the latter value of 0·010 Å – is in agreement with the solid-state values. Obviously, the cyano and the carboxyl groups have similar π-acceptor strengths, as is well documented by a wealth of chemical data.

For optimal interaction with the appropriate Walsh orbitals, the acid group should adopt a bisected

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43895 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conformation, which is indeed observed (molecular C_s symmetry). The bond angles C(2)C(1)C(12) and C(2)C(1)C(11), which are a measure of the inclination of the respective group towards the ring plane, are practically identical (117·5 and 117·2°). These angles compare well with those of the diacid (116·7°, av.), but are a little larger than those in the diamide (115·3°). These and the intersubstituent angle C(11)C(1)C(12) (117·1° in the title molecule, *cf.* 118·3° in the diacid) should be regarded as the standards for cyano and carbonyl cyclopropanes unaffected by steric interference (Jones & Schrumpf, 1987*d*). The corresponding bond angle in cyclopropanecarbonitrile (119·2°; Kiers, de Boer, Heijdenrijk, Stam & Schenk, 1985) and the amide (117·6°; Long, Maddox & Trueblood, 1969) are somewhat larger (*ca* 2°) than in the disubstituted molecules, which may be due to a small repulsion between the substituents.

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	$U/U_{\rm eq}$
C(1)	4452 (2)	2500	6134 (3)	33 (1)*
C(2)	4391 (1)	3511 (3)	8073 (2)	49 (1)*
C(11)	5625 (2)	2500	5143 (3)	36 (1)*
N(1)	6545 (1)	2500	4370 (3)	52 (1)*
C(12)	3318 (2)	2500	4918 (3)	40 (1)*
O(1)	2300 (1)	2500	5573 (2)	70 (1)*
O(2)	3579 (1)	2500	3055 (2)	54 (1)*
H(21)	3585 (14)	4169 (25)	8301 (25)	59 (5)
H(22)	5148 (17)	4136 (28)	8435 (27)	68 (6)
H(2)	2822 (31)	2500	2281 (46)	95 (11)

* Equivalent isotropic U calculated from anisotropic U:

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

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

		Corrected			Corrected
C(1)—C(2)	1·529 (3)	1·541	C(1)—C(11)	1·445 (4)	1·455
C(2)—C(2$^{\rm i}$)	1·449 (5)	1·467	C(11)—N(1)	1·132 (4)	1·140
C(12)—O(1)	1·193 (3)	1·201	C(12)—O(2)	1·322 (4)	1·331
C(1)—C(12)	1·490 (4)	1·504			

C(2)—C(1)—C(11)	117·2 (2)	C(2)—C(1)—C(12)	117·5 (2)
C(11)—C(1)—C(12)	117·1 (3)	C(2)—C(1)—C(2$^{\rm i}$)	56·6 (3)
C(1)—C(2)—C(2$^{\rm i}$)	61·7 (2)	C(1)—C(11)—N(1)	180·0 (5)
C(1)—C(12)—O(1)	123·2 (3)	C(1)—C(12)—O(2)	112·1 (3)
O(1)—C(12)—O(2)	124·7 (3)		

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

There is a slight lengthening of the CC bond between the ring and the cyano group (1·455 Å) compared with cyclopropanecarbonitrile (1·442 Å; Kiers *et al.*, 1985) and the two isomeric 1,2,3-cyclopropanetricarbonitriles (*cis*: 1·449 Å; Hartmann & Hirshfeld, 1966; *trans*: 1·448 Å, av.; Jones & Schrumpf, 1987*a*). The CC bond between the ring and the acid group (1·490 Å, uncorr.) is also marginally longer than the one between either acid group and the adjacent ring C atom in *trans*-1,2-cyclopropanedicarboxylic acid (1·480 Å, av., uncorr.; Bednowitz, 1969). Both of these small lengthenings in the title molecule relative to the corresponding cyclopropane with only one substituent per ring C atom and the slight exocyclic bond-angle opening might reflect the four-electron repulsive interaction between the O-atom lone pair(s) and the π electrons of the cyano group.

The CN triple-bond length (1·140 Å, corr.) has its usual value as observed in cyclopropanecarbonitrile (1·149 Å; Schenk, 1986), *trans*-cyclopropanetricarbonitrile (1·139 Å; Jones & Schrumpf, 1987*a*) and *cis*-cyclopropanetricarbonitrile (1·144 Å; Hartmann & Hirshfeld, 1966). The cyano group is exactly linear.

The structure of the acid group is expected to be affected by the nature of any hydrogen bonding. In the title compound, the carbonyl O atom eclipses the cyclopropane ring, while the hydroxy group eclipses the cyano group and forms a hydrogen bond to the cyano N atom of a second molecule (see Fig. 2). In

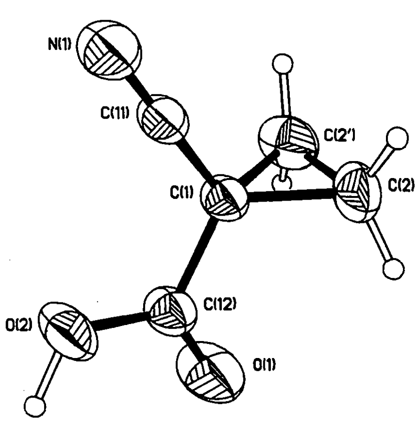

Fig. 1. Thermal-ellipsoid plot of the title molecule (50% level); H atoms as spheres of arbitrary radius.

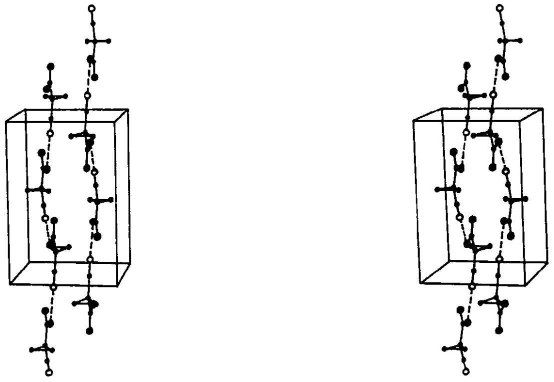

Fig. 2. Stereo packing diagram of the title compound. View direction approximately parallel to the c axis. H atoms omitted for clarity. Hydrogen bonds are indicated by dashes [O(2)···N(1) at $0{\cdot}5+x$, y, $0{\cdot}5-z$ = 2·77 Å].

1,1-cyclopropanedicarboxylic acid, one of the carbonyl O atoms and the hydroxy group of the other acid substituent form an intramolecular hydrogen bond. The second proton and carbonyl O atom are involved in intermolecular hydrogen bonding. The bond lengths and angles of the two acid groups are somewhat different from those of the title molecule, but the geometry of the one forming the intermolecular hydrogen bond is closer to that of the cyano acid, although their conformations are different. Thus, it appears that it is the type of hydrogen bonding which determines the similarity of geometries of the acid groups and not their conformation.

This work was supported by the Fonds der Chemischen Industrie, Frankfurt.

References

ALLEN, F. H. (1980). *Acta Cryst.* **B36**, 81–96.
BEDNOWITZ, A. L. (1969). *Acta Cryst.* **A25**, S129.
HARTMANN, A. & HIRSHFELD, F. L. (1966). *Acta Cryst.* **20**, 80–82.
HEDBERG, L., HEDBERG, K. & BOGGS, J. E. (1982). *J. Chem. Phys.* **77**, 2996–3002.
HOFFMANN, R. (1970). *Tetrahedron Lett.* pp. 2907–2909.
HOFFMANN, R. & STOHRER, W. D. (1971). *J. Am. Chem. Soc.* **93**, 6941–6948.
JONES, P. G. & SCHRUMPF, G. (1987*a*). *Acta Cryst.* **C43**, 1179–1182.
JONES, P. G. & SCHRUMPF, G. (1987*b*). *Acta Cryst.* **C43**, 1579–1582.
JONES, P. G. & SCHRUMPF, G. (1987*c*). *Acta Cryst.* **C43**. In the press.
JONES, P. G. & SCHRUMPF, G. (1987*d*). To be published.
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.
LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst.* **B25**, 2083–2094.
MEESTER, M. A. M., SCHENK, H. & MACGILLAVRY, C. H. (1971). *Acta Cryst.* **B27**, 630–634.
PEARSON, R., CHOPLIN, A., LAURIE, V. W. & SCHWARTZ, J. (1975). *J. Chem. Phys.* **62**, 2949–2951.
PERRETTA, A. T. & LAURIE, V. W. (1975). *J. Chem. Phys.* **62**, 2469–2473.
SCHENK, H. (1986). Private communication.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
SCHRUMPF, G. & JONES, P. G. (1987*a*). *Acta Cryst.* **C43**, 1182–1185.
SCHRUMPF, G. & JONES, P. G. (1987*b*). *Acta Cryst.* **C43**, 1185–1187.
SCHRUMPF, G. & JONES, P. G. (1987*c*). *Acta Cryst.* **C43**, 1188–1192.
SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.
SINGH, R. K. & DANISHEFSKY, S. (1975). *J. Org. Chem.* **40**, 2969–2970.
USHA, R. & VENKATESAN, K. (1979). *Acta Cryst.* **B35**, 2730–2732.

Acta Cryst. (1987). C**43**, 1579–1582

Substituted Cyclopropanes. 6.* *trans*-Triethyl 1,2,3-Tricyano-1,2,3-cyclopropanetricarboxylate

BY PETER G. JONES

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen, Federal Republic of Germany*

AND GERD SCHRUMPF

Institut für Organische Chemie der Universität, Tammannstrasse 2, *D*-3400 *Göttingen, Federal Republic of Germany*

(*Received* 17 *July* 1986; *accepted* 18 *March* 1987)

Abstract. $C_{15}H_{15}N_3O_6$, $M_r = 333{\cdot}31$, monoclinic, $P2_1/c$, $a = 9{\cdot}185\ (2)$, $b = 21{\cdot}797\ (5)$, $c = 8{\cdot}306\ (2)$ Å, $\beta = 91{\cdot}30\ (2)°$, $V = 1663\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}0$ cm^{-1}, $F(000) = 696$, $T = 293$ K, $R = 0{\cdot}071$ for 1535 unique observed reflections. The ring bond lengths show a marked asymmetry. The molecular symmetry is lower than ideal because of conformational differences in the ester groups. The C—C bonds from the ring to the ester groups are long.

Introduction. Polysubstituted cyclopropanes, particularly those with three mutually *cis* vicinal substituents, are excellent models for studying steric crowding. The rigid three-membered ring often forces upon substituents non-bonded contacts well below the sum of the respective van der Waals radii. In previous

---

* Part 5: Jones & Schrumpf (1987*b*).

0108-2701/87/081579-04$01.50
© 1987 International Union of Crystallography