Table 3. *Least-squares planes for the molecule*

Distances of atoms from the two planes are given in Å. Atoms not contributing to the plane are marked with an asterisk.

Plane (1): N(1)–0·01 (1), C(2) 0·01 (1), N(3) –0·01 (1), C(4) 0·00 (1), C(5) 0·00 (1), C(6)* 0·01 (1), C(7)* –0·02 (1), C(13)* 0·02 (1), O(14)* –0·02 (1), O(15)* 0·05 (1)

Plane (2): N(1)* –0·02 (1), C(2)* 0·08 (1), C(5)* 0·05 (1), C(6)* –0·02 (1), C(7) –0·01 (1), C(8) 0·00 (1), C(9) 0·00 (1), C(10) 0·00 (1), C(11) –0·01 (1), C(12) 0·02 (1), O(14)* 0·07 (1)

Angle between plane (1) and plane (2): 5·7 (3)°

Plane (1) is that of the imidazolidine ring and (2) that of the benzene ring.

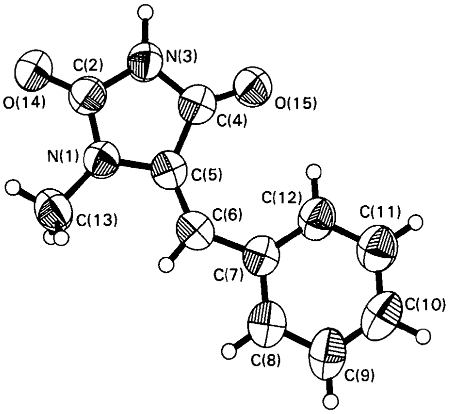

Fig. 1. The structure of (1). Thermal ellipsoids shown as 50% probabilities.

Values of the N(1)—C(5)—C(6) and C(4)—C(5)—C(6) angles in the present *E* isomer are 121·6 (4) and 133·4 (4)° compared to 132·6 (2) and 121·9 (2)° respectively in the *Z* isomer. The sum of these three angles around the C(5) atom is 360·0° to within experimental error in each case.

As is usual with this series of hydantoins, intermolecular hydrogen bonds are observed in the molecule. The N(3)—H(31)···O(14^{i}) and H(31)···O(14^{i}) distances are 2·81 (1) and 1·82 (6) Å respectively while the N(3)—H(31)···O(14^{i}) angle is 165 (5)° [symmetry element: (i) $x, -y, \frac{1}{2}-z$]. Molecules are thus paired by two hydrogen bonds around the twofold axis. It is interesting to note that in the *Z* isomer the hydrogen bond connects N(3) with the O(15) atom of another molecule.

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Substituted Cyclopropanes. 1. *trans*-1,2,3-Tricyanocyclopropane

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Abstract. *trans*-Cyclopropane-1,2,3-tricarbonitrile, $C_6H_3N_3$, $M_r = 117{\cdot}11$, orthorhombic, *Pnma*, $a = 11{\cdot}917$ (3), $b = 8{\cdot}934$ (2), $c = 5{\cdot}456$ (2) Å, $V = 580{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 240$, $T = 293$ K, $R = 0{\cdot}043$ for 403 unique observed reflections. The molecule possesses crystallographic mirror symmetry. The cyclopropane ring is slightly asymmetric, with a longer bond between the *cis* substituents. The effect of the cyano groups on the ring CC bonds is nearly additive.

Introduction. In the last few years, the structural consequences of conjugative interaction between the cyclopropane ring and various substituents have been the subject of numerous investigations. Electron diffraction and microwave spectroscopic studies have furnished reliable gas-phase geometries of a number of substituted cyclopropanes (*e.g.* Taylor, Harmony, Cassada & Staley, 1984; Tamagawa & Hilderbrandt, 1983; Mathur & Harmony, 1978; Hedberg, Hedberg & Boggs, 1982; Gillies, 1976; Schwendeman, Jacobs & Krigas, 1964), which have been interpreted in terms of a simple frontier molecular-orbital model introduced by Hoffmann (1970) to rationalize the data available at that time (Penn & Boggs, 1972) concerning the substituent-induced asymmetry. A large amount of X-ray data has recently been reviewed (Allen, 1980) and strong evidence for the applicability of the Hoffmann model has emerged from those data. The results of a number of *ab initio* calculations on substituted cyclopropanes are in full accord with the experimental findings and the qualitative theoretical predictions.

One of the questions in this context concerns the additivity of the effects of a π-acceptor substituent inducing ring asymmetry (Hoffmann & Stohrer, 1971). One strong π-acceptor substituent is the cyano group; its influence on the geometry of the cyclopropane ring in cyclopropanecarbonitrile has been studied extensively (Pearson, Choplin & Laurie, 1975; Harmony, Nandi, Tietz, Choe, Getty & Staley, 1983; Kiers, de Boer, Heijdenrijk, Stam & Schenk, 1985; Skancke & Boggs, 1979). From the crystal structure of *cis*-cyclopropane-1,2,3-tricarbonitrile (Hartman & Hirshfeld, 1966) it was concluded that there is indeed additivity of induced asymmetry (Allen, 1980). However, from two independent X-ray investigations of cyclopropane-1,1,2,2-tetracarbonitrile, the authors conclude that there is a saturation of the lengthening action of cyano groups (Wang & Stucky, 1973; Lemley, Skarstad & Hughes, 1976).

In the concept developed above and supported both theoretically and experimentally, steric effects have not been considered explicitly. We wanted to study the impact of non-bonded interaction of substituents in *cis* positions in the cyclopropane ring on the induced ring asymmetry and thus needed to compare the structures of two molecules with three vicinal substituents differing only in their relative geometry. We chose *cis*- and *trans*-cyclopropane-1,2,3-tricarbonitrile, the crystal structure of the first having been studied 20 years ago with remarkable precision for that time (Hartman & Hirshfeld, 1966).

Experimental. The title compound was synthesized (Schrumpf, 1987) following in principle the early synthesis (Sadeh & Berger, 1958). The product mixture was separated by column chromatography over alumina with benzene as the eluent. The *trans* isomer was repeatedly recrystallized from ethanol to constant melting point.

Colourless prisms were obtained from ethanol/acetonitrile (2:1). Crystal 0·6 × 0·3 × 0·25 mm. 706 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer using monochromated Mo $K\alpha$ radiation. $2\theta_{\max}$ 50°, octant $+h+k+l$ and some $-h-k-l$ equivalents. Three check reflections, no significant intensity change. No absorption correction. $R_{\rm int}$ 0·016 for 550 unique reflections (index ranges after merging h 0→14, k 0→10, l 0→6), 403 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Cell constants refined from 2θ values of 40 reflections in the range 20–23°.

Structure solution by routine direct methods. Refinement on F to R 0·043, wR 0·044 (all non-H atoms anisotropic, isotropic H refined freely). 53 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00025F^2$, $S = 1{\cdot}63$, slope of normal probability plot 1·43. Max. Δ/σ 0·003. Max. and min. heights in final $\Delta\rho$ map +0·18, −0·24 e Å^{-3}. A libration correction (Schomaker & Trueblood, 1968) indicated that the bond lengths should be increased by 0·003–0·004 Å (see Table 2). Atomic scattering factors those of *SHELXTL*.

Discussion. Final atomic coordinates are given in Table 1 with derived parameters in Table 2.* The molecule possesses crystallographic mirror symmetry, atoms C(1), C(11), N(1) and H(1) lying in the plane $y = 0{\cdot}25$ (see Fig. 1). Cyclopropanecarbonitrile also crystallizes with mirror symmetry in *Pnma* (Kiers *et al.*, 1985), but there is little similarity of cell constants or coordinates. A packing diagram is presented in Fig. 2.

The most interesting result of the current study is the presence of ring bond asymmetry. The bond distance C(2)—C(2$^{\rm i}$) of 1·524 (5) Å between the carbon atoms carrying the *cis* substituents is almost identical to that in the *cis* isomer [1·518 (3) Å; Hartman & Hirshfeld, 1966]. However, the bond C(1)—C(2), between carbon atoms with *trans* substituents, is somewhat (*ca* 2–3σ) shorter. This finding is rather unexpected on the basis of purely electronic reasoning found in the literature to rationalize previous experimental results. It is not easy to deduce the cause of the ring asymmetry observed here. The opinion found occasionally that the average

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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 43713 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond length in molecules substituted by π acceptors is again comparable to that in cyclopropane itself, *i.e.* bond shortening is twice as much as bond lengthening relative to cyclopropane, is supported by the X-ray results on cyclopropanecarbonitrile (at 188 K; m.p. 248 K) with a mean of 1·515 Å (Kiers *et al.*, 1985; Schenk, 1986). The average ring bond length in the title molecule is 1·515 Å, close to the value of 1·519 Å in the *cis* isomer (Hartman & Hirshfeld, 1966).

As to the bond angles between the ring atoms and the cyano carbons in *cis* positions, there is a small wag of about 1°, *i.e.* each cyano group is not in the plane bisecting the respective intraannular ring angle. Consequently, the distance between the two *cis* cyano groups [C(21)···C(21$^{\rm i}$) 2·909 Å] has slightly increased relative to the distance observed in the all-*cis* isomer C(2)···C(2a), related by a crystallographic threefold axis, 2·893 Å; the non-bonded distances quoted here for both substances are also libration-corrected. It is interesting that the angle of inclination of the *cis* cyano groups towards the ring plane is even slightly larger than in cyclopropanecarbonitrile, *i.e.* if there is some sort of repulsion between the *cis* cyano groups, it relaxes by a wagging and not by a rocking motion. The inclination of the third cyano group (*trans* to the other two) is again close to that in cyclopropanecarbonitrile.

The bond distances 1·450 and 1·446 Å between the ring carbons and the respective cyano carbons are about the same for both types of cyano groups within the error limits, and practically the same as the corresponding bond lengths in cyclopropanecarbonitrile (1·442 Å; Kiers *et al.*, 1985) and the *cis* isomer (1·449 Å; Hartman & Hirshfeld, 1966).

Whereas the CN triple bonds have their usual lengths and compare well with those determined in other cyanocyclopropanes (Kiers *et al.*, 1985; Johnson & Schaefer, 1972; Hartman & Hirshfeld, 1966; Wang & Stucky, 1973; Lemley *et al.*, 1976), the CCN angles are found to be slightly non-linear. This is not unusual and the matter has been discussed by Matthews, Swanson, Mueller & Stucky (1971), but it is conspicuous that the degree of non-linearity is greater for the cyano groups in *cis* position than for that in *trans* position. The sign of the observed non-linearity is such that the *cis* N atoms are slightly (2°) tilted away from each other. This is similar to the tilt of the nitrogens in the *cis* isomer which is some 2° away from the C_3 axis.

To summarize, there are several pieces of evidence for an interaction between the *cis* cyano groups, whatever its origin may be. The slight asymmetry of the

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

	x	y	z	$U/U_{\rm eq}$
C(1)	4914 (2)	2500	7309 (5)	33 (1)*
C(11)	5472 (2)	2500	4955 (5)	40 (1)*
N(1)	5917 (2)	2500	3115 (5)	56 (1)*
C(2)	3828 (2)	1649 (2)	7572 (4)	38 (1)*
C(21)	3641 (2)	877 (2)	9855 (4)	38 (1)*
N(2)	3511 (1)	296 (2)	11689 (4)	51 (1)*
H(1)	5398 (20)	2500	8622 (45)	23 (6)
H(2)	3525 (14)	1191 (21)	6158 (38)	35 (5)

* Equivalent isotropic U calculated from anisotropic U:
$U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

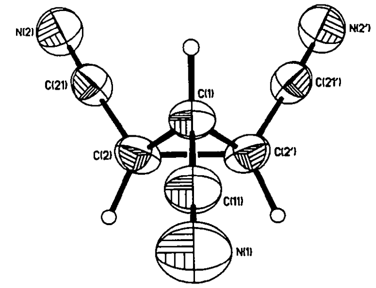

Fig. 1. Thermal-ellipsoid plot (50% level) of the title compound, showing the atom-numbering scheme. H radii are arbitrary. Symmetry-equivalent atoms are indicated by a prime.

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

	Uncorrected	Corrected
C(1)–C(11)	1·446 (5)	1·450
C(1)–C(2)	1·508 (4)	1·511
C(21)–N(2)	1·138 (4)	1·141
C(11)–N(1)	1·136 (5)	1·139
C(2)–C(21)	1·442 (4)	1·446
C(2)–C(2$^{\rm i}$)	1·519 (5)	1·524

C(11)–C(1)–C(2)	118·6 (3)
C(2)–C(1)–C(2$^{\rm i}$)	60·5 (3)
C(1)–C(11)–N(1)	179·5 (4)
C(1)–C(2)–C(21)	117·2 (3)
C(1)–C(2)–C(2$^{\rm i}$)	59·7 (2)
C(21)–C(2)–C(2$^{\rm i}$)	118·6 (2)
C(2)–C(21)–N(2)	178·1 (3)

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

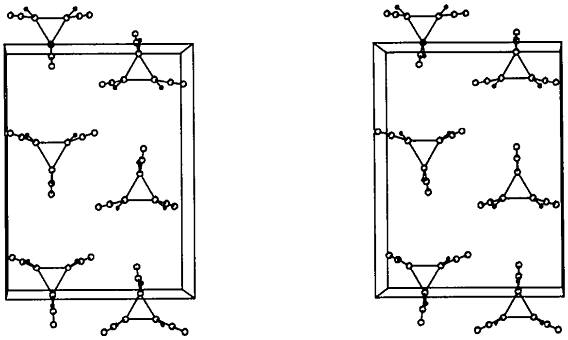

Fig. 2. Stereo packing diagram viewed approximately parallel to the z axis.

ring skeleton, *i.e.* the lengthening of the bond C(2)—C(2^i), can be viewed as contributing to the relaxation of a repulsive interaction between the substituents. In view of the results of cyclopropanecarbonitrile (Kiers *et al.*, 1985), the effects of cyano substituents on the cyclopropane structure are approximately additive, but do not solely depend on topology, but also on the stereochemistry of the individual molecule.

This latter aspect is expected to be even more important for cyclopropanes multiply substituted by carbonyl groups, which additionally introduce several conformational degrees of freedom. We are currently investigating the cumulative effect of halogen substituents on the geometry of the cyclopropane moiety in order to test whether the findings of the present investigation can be transferred to substituents that are not π acceptors.

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Substituted Cyclopropanes. 2.* *cis*-1,2,3-Trichlorocyclopropane

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Abstract. $C_3H_3Cl_3$, $M_r = 145{\cdot}42$, orthorhombic, $Pnma$, $a = 10{\cdot}237$ (3), $b = 8{\cdot}665$ (2), $c = 6{\cdot}220$ (2) Å, $V = 551{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}75$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}15$ mm^{-1}, $F(000) = 288$, $T = 293$ K, $R = 0{\cdot}038$ for 558 unique observed reflections. The molecule displays symmetry close to the ideal C_{3v}; crystallographic mirror symmetry is imposed. The mean ring bond length (corrected for libration) is 1·504 Å; the chlorine substituents thus appear to have little effect on this parameter.

Introduction. In the last few years, there has been considerable progress in understanding the nature of bonding in, and its implication for the geometry of,

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* Part 1: Jones & Schrumpf (1987).

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