

C3	0.3607 (2)	0.8832 (7)	0.2034 (2)	0.0352 (7)
C5	0.3328 (2)	0.6316 (7)	0.3790 (2)	0.0329 (7)
O6'	-0.01648 (17)	0.6263 (5)	0.33418 (13)	0.0326 (5)
O7'	-0.2245 (2)	0.0626 (6)	0.08408 (15)	0.0396 (5)
O8'	-0.3053 (2)	0.5707 (5)	0.15080 (16)	0.0440 (6)
C1'	0.0827 (3)	0.4305 (7)	0.29228 (19)	0.0311 (7)
C2'	0.0047 (2)	0.2999 (6)	0.1700 (2)	0.0319 (7)
C3'	-0.1496 (3)	0.1831 (6)	0.1992 (2)	0.0311 (7)
C4'	-0.2542 (3)	0.3869 (7)	0.24896 (19)	0.0348 (8)
C5'	-0.1633 (3)	0.5227 (7)	0.3642 (2)	0.0371 (8)

Table 2. Selected geometric parameters (Å, °)

O6—C5	1.226 (3)	O6'—C1'	1.429 (3)
O7—C3	1.209 (3)	O6'—C5'	1.434 (3)
N1—N2	1.419 (3)	O7'—C3'	1.419 (3)
N1—C5	1.369 (3)	O8'—C4'	1.421 (3)
N1—C1'	1.439 (3)	C1'—C2'	1.509 (3)
N2—C3	1.362 (3)	C2'—C3'	1.516 (3)
N4—C3	1.387 (3)	C3'—C4'	1.520 (4)
N4—C5	1.360 (3)	C4'—C5'	1.509 (3)
N2—N1—C5	107.5 (2)	N1—C1'—O6'	107.9 (2)
N2—N1—C1'	118.71 (18)	N1—C1'—C2'	112.7 (2)
C5—N1—C1'	121.17 (17)	O6'—C1'—C2'	111.00 (19)
N1—N2—C3	108.17 (18)	C1'—C2'—C3'	108.73 (17)
C3—N4—C5	111.4 (2)	O7'—C3'—C2'	109.01 (17)
O7—C3—N2	126.8 (2)	O7'—C3'—C4'	111.6 (2)
O7—C3—N4	127.8 (2)	C2'—C3'—C4'	110.3 (2)
N2—C3—N4	105.4 (2)	O8'—C4'—C3'	112.16 (18)
O6—C5—N1	125.7 (2)	O8'—C4'—C5'	108.6 (2)
O6—C5—N4	127.9 (2)	C3'—C4'—C5'	109.1 (2)
N1—C5—N4	106.4 (2)	O6'—C5'—C4'	112.76 (18)
C1'—O6'—C5'	111.1 (2)		

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O7''	0.87 (2)	1.86 (2)	2.727 (4)	173 (3)
N4—H4...O6'''	0.89 (3)	1.91 (2)	2.789 (4)	169 (2)
O7'—H7'...O8''''	0.81 (4)	1.97 (4)	2.771 (5)	170 (2)
O8'—H8'...O7''	0.82 (3)	2.27 (3)	2.949 (4)	140 (3)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *LS* in *TEXSAN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *FINISH* in *TEXSAN*, *PLATON* (Spek, 1990).

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Lists of structure factors, torsion angles, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,1-Diamino-2,2-dicyanoethene

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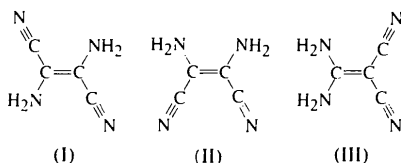
Abstract

The molecule of the title nitrile [1,1-diamino-2,2-ethenedicarbonitrile, C₄H₄N₄] is planar and exhibits a high degree of electron delocalization. It is compared with its two structural isomers of the same formula.

Comment

Although the crystal structures of diaminofumaronitrile, (I) (Yamada, Nagashima, Iwashita, Nakamura & Kumashiro, 1968), and its *cis*-isomer diaminomaleonitrile,

(II) (Penfold & Lipscomb, 1961), have been determined, no comment was made concerning any structural relationships that may exist between the two isomers. Along with the remaining structural isomer, 1,1-diamino-2,2-dicyanoethene, (III), the three compounds form a series in which structural effects attributable to possible electron delocalization can be investigated. Preliminary ^{13}C NMR studies on isomer (III) showed that the chemical environments of the two ethene carbon nuclei are extremely different, having a chemical shift separation of over 132 p.p.m. (Simmonite, 1993).



In order to complete the structural series of compounds of formula $\text{C}_4\text{H}_4\text{N}_4$ and to evaluate crystal suitability for a possible charge-density study of the electronic structure, a single-crystal X-ray structure determination of isomer (III) was undertaken. In marked contrast to the structures of (I) and (II), in which the amino groups adopt both planar and pyramidal geometries, both amino groups in isomer (III) are planar, suggesting a significant resonance contribution to the structure (Fig. 1). The maximum deviation from the plane defined by all the C and N atoms of the molecule is 0.0656 Å for atom H(1), with the mean deviation from the molecular plane being only 0.0175 Å.

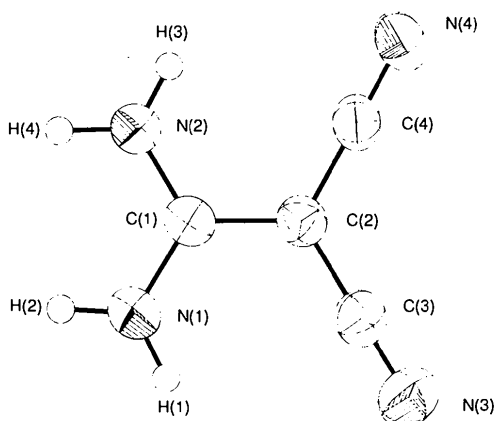


Fig. 1. View of 1,1-diamino-2,2-dicyanoethene, (III), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level; H atoms are depicted as spheres of arbitrary size.

Analysis of the observed bond lengths and angles also supports the proposal of a delocalized structure for (III). The $\text{C}-\text{N}_{\text{amino}}$ bond lengths [1.330 (2) and 1.331 (2) Å] are both in good agreement with the average tabulated value (1.336 Å) found for a $=\text{C}-\text{N}_{\text{vp}}$ bond (Allen

et al., 1987). The different $=\text{C}-\text{N}_{\text{amino}}$ bond lengths found in isomer (I) [1.376 (6) and 1.446 (6) Å] reflect the different geometries of the amino groups. The $=\text{C}-\text{N}_{\text{vp}}$ bond, as expected, has the shorter length, while the pyramidal $\text{C}-\text{N}_{\text{vp}}$ bond is longer. Curiously, this difference is not observed in isomer (II), where the $\text{C}-\text{N}_{\text{amino}}$ bond lengths are 1.398 (8) and 1.387 (7) Å (mean 1.392 Å). If a mean value of 1.411 Å is taken for the $\text{C}-\text{N}_{\text{amino}}$ bond length in isomer (I), it can be seen that there is a stepwise decrease in both the $\text{C}-\text{N}_{\text{amino}}$ and $\text{C}-\text{C}_{\text{nitrile}}$ bond lengths in going from isomers (I) to (II) to (III). This trend is matched by a progressive increase in the $\text{C}=\text{C}$ bond length [1.294 (6), 1.363 (6) and 1.413 (2) Å for (I), (II) and (III), respectively]. Interestingly, the $\text{C}=\text{C}$ bond length in (III) is slightly longer than the $\text{C}-\text{C}_{\text{nitrile}}$ bond.

The title structure forms four notable $\text{H}_{\text{amino}} \cdots \text{N}_{\text{nitrile}}$ hydrogen bonds with distances of 2.03 (2), 2.15 (2), 2.41 (2) and 2.66 (2) Å. When viewed as a projection down *c*, the structure shows a classic herringbone-type packing arrangement.

Experimental

1,1-Diamino-2,2-dicyanoethene was prepared by Dr A. Kröhn, Roche Research Centre, England, and was recrystallized from water.

Crystal data

$\text{C}_4\text{H}_4\text{N}_4$
 $M_r = 108.10$
 Monoclinic
 $P2_1/c$
 $a = 8.444$ (2) Å
 $b = 5.015$ (2) Å
 $c = 12.5573$ (9) Å
 $\beta = 100.345$ (9)°
 $V = 523.1$ (2) Å³
 $Z = 4$
 $D_x = 1.372$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.7107$ Å
 Cell parameters from 25 reflections
 $\theta = 13.1-18.5^\circ$
 $\mu = 0.097$ mm⁻¹
 $T = 290.0$ K
 Plate
 0.40 × 0.38 × 0.11 mm
 Pale pink

Data collection

Rigaku AFC-7R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical
 $T_{\text{min}} = 0.965$, $T_{\text{max}} = 0.990$
 1220 measured reflections
 1145 independent reflections
 899 observed reflections
 $[I > 2.5\sigma(I)]$

$R_{\text{int}} = 0.0096$
 $\theta_{\text{max}} = 27.0^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 6$
 $l = -16 \rightarrow 15$
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.7%

Refinement

Refinement on F
 $R = 0.032$

$\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³

$wR = 0.039$
 $S = 2.59$
 899 reflections
 90 parameters
 All H-atom parameters
 refined
 $w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\max} < 0.0001$

Extinction correction:
 Zachariassen (1967) type
 II, Gaussian isotropic
 Extinction coefficient:
 84.58906
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N(1)	0.1947 (2)	0.5781 (3)	-0.05932 (10)	0.0521 (4)
N(2)	0.3630 (2)	0.2739 (3)	0.0370 (1)	0.0522 (4)
N(3)	0.0368 (2)	0.9761 (3)	0.1368 (1)	0.0664 (5)
N(4)	0.3822 (2)	0.4032 (3)	0.31350 (10)	0.0651 (5)
C(1)	0.2642 (2)	0.4808 (3)	0.03629 (10)	0.0402 (4)
C(2)	0.2355 (2)	0.5932 (3)	0.1342 (1)	0.0425 (4)
C(3)	0.1264 (2)	0.8045 (3)	0.1359 (1)	0.0466 (4)
C(4)	0.3151 (2)	0.4892 (3)	0.2333 (1)	0.0478 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C(1)—C(2)	1.413 (2)	N(4)—C(4)	1.148 (2)
N(1)—C(1)	1.331 (2)	N(1)—H(1)	0.90 (2)
N(2)—C(1)	1.330 (2)	N(1)—H(2)	0.92 (2)
C(2)—C(3)	1.407 (2)	N(2)—H(3)	0.89 (2)
C(2)—C(4)	1.404 (2)	N(2)—H(4)	0.96 (2)
N(3)—C(3)	1.148 (2)		
N(1)—C(1)—N(2)	117.8 (1)	C(1)—C(2)—C(4)	119.6 (1)
N(1)—C(1)—C(2)	121.5 (1)	C(3)—C(2)—C(4)	118.5 (1)
N(2)—C(1)—C(2)	120.7 (1)	N(3)—C(3)—C(2)	179.6 (1)
C(1)—C(2)—C(3)	121.9 (1)	N(4)—C(4)—C(2)	178.9 (1)
N(1)—C(1)—C(2)—C(3)	3.2 (2)	N(2)—C(1)—C(2)—C(3)	-177.2 (1)
N(1)—C(1)—C(2)—C(4)	-178.1 (1)	N(2)—C(1)—C(2)—C(4)	1.5 (2)

The scan width was $(1.26 + 0.35\tan\theta)^\circ$ with an ω scan rate of $8.0^\circ \text{ min}^{-1}$. The weak reflections [$I < 2.5\sigma(I)$] were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Data collection: *MSCI/AF C Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSCI/AF C Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

The author wishes to thank Dr A. Kröhn for the gift of the crystals.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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β -Cyclodextrin (Z)-9-Dodecen-1-ol 2:1 Complex

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Abstract

The structure of the title complex, cycloheptaamylose-(Z)-9-dodecen-1-ol-ethanol-water (1/0.5/0.53/9.6), C₄₂H₇₀O₃₅·0.5C₁₂H₂₄O·0.96H₂O·0.53C₂H₆O, has been determined at 150 K. Two cycloheptaamylose (β -cyclodextrin, β -CD) monomers related by a twofold axis form dimers. The stoichiometry of host:guest is 2:1. Therefore, one guest molecule per dimer is enclosed, disordered over two sites related by the above-mentioned twofold axis. The hydrophobic end of the guest lies in the dimeric interface. The rest of the molecular chain transverses the hydrophobic cavity of either monomer and the extreme hydroxy group is found in the primary hydroxy region.

Comment

This work is part of a series of structure determinations of cyclomaltoheptose or cyclodextrin (CD) complexes, or their methylated derivatives, with linear molecules (Mentzafos, Mavridis & Schenk, 1994) that are components of insect pheromones. There is also an increasing interest in the inclusion of linear molecules inside CDs because of their ability to form composite struc-