Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N,*N*-Bis(cyanomethyl)nitrous amide

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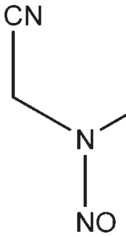
Received 6 May 2010; accepted 11 May 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.050; wR factor = 0.162; data-to-parameter ratio = 17.0.

In the title compound, $C_4H_4N_4O$, both H atoms bonded to one methylene C atom are involved in C—H⋯N hydrogen-bonding interactions; one of the interactions results in dimers of the title molecule lying about inversion centers in $R_2^2(12)$ motifs and the other forms chains of molecules lying along the c axis.

Related literature

For background to ferroelectric compounds, see: Haertling (1999); Homes *et al.* (2001). For related structures, see: Adolf *et al.* (1996); Kaida *et al.* (1990). For graph-set notation, see: Bernstein *et al.* (1994).



Experimental

Crystal data

$C_4H_4N_4O$
M_r = 124.11
Monoclinic, $P2_1/c$
a = 6.5622 (13) Å
b = 8.9765 (18) Å
c = 11.008 (4) Å
β = 108.55 (3)°
V = 614.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.742, T_{max} = 1.000
6154 measured reflections
1408 independent reflections
1094 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.162
S = 1.05
1408 reflections
83 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3B⋯N2^{i}	0.97	2.50	3.450 (2)	165
C3—H3C⋯N1^{ii}	0.97	2.62	3.183 (2)	117

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2279).

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supporting information

Acta Cryst. (2010). E**66**, o1362   [https://doi.org/10.1107/S1600536810017265]

N,*N*-Bis(cyanomethyl)nitrous amide

Yuan Zhang and Meng Ting Han

S1. Comment

At present, much attention in the field of ferroelectric materials is focused on developing ferroelectric organic or inorganic compounds (Haertling *et al.*, 1999; Homes *et al.*, 2001). It has been reported that *N*,*N*-bis(cyanomethyl)-nitramide crystallizes in space group (C 2) at room temperature (Adolf *et al.*, 1996), a noncentrosymmetric space group is required for ferroelectric behavior. Its ferroelectric property still needs to be further confirmed by many experiments, such as dielectric measurements and DSC to varify the permittivity anomaly, phase transition, etc. For this reason, we have synthesized the title compound to investigate its physical properties. The dielectric constant of the title compound as a function of temperature indicates that the permittivity is basically temperature-independent (dielectric constant = 3.2 to 5.6), suggesting that this compound should not be a real ferroelectric or there may be no distinct phase transition within the measured temperature range. Similarly, below the melting point (308 K) of the compound, the dielectric constant as a function of temperature also goes smoothly, and there is no dielectric anomaly observed. Herein, we report the synthesis and crystal structure of the title compound.

The bond distances and bond angles in the title compound agree very well with the corresponding distances and angles reported for a closely related compound (Kaida *et al.*, 1990); both cyanic groups are linear (Fig. 1). It is interesting to note that both H-atoms bonded to only one methylene carbon (C3) are involved in hydrogen bonding interactions of the type C—H···N, C3—H3B···N2 hydrogen bonds result in dimers of the title molecule lying about inversion centers in $R_2^2(12)$ motifs in graph set notation (Bernstein *et al.*, 1994) while C3—H3C···N1 interactions result in chains of molecules lying along the *c*-axis (Tab. 1, Fig. 2). Dipole–dipole and van der Waals interactions are effective in the molecular packing.

S2. Experimental

A solution of sodium nitrite (2.3 g, 33 mmoles) in water (10 ml) was added at 291–293 K to a solution of 2,2′-azanediyldiacetonitrile hydrochloride (1.7 g, 28 mmoles) in water (30 ml). The mixture was heated for 1.5 h at 313–323 K and allowed to stand for 12 h at 293 K. The title compound as nitroso derivative, was extracted with ether, the ether solution was evaporated. Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of an ethyl acetate solution of the title compound.

S3. Refinement

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

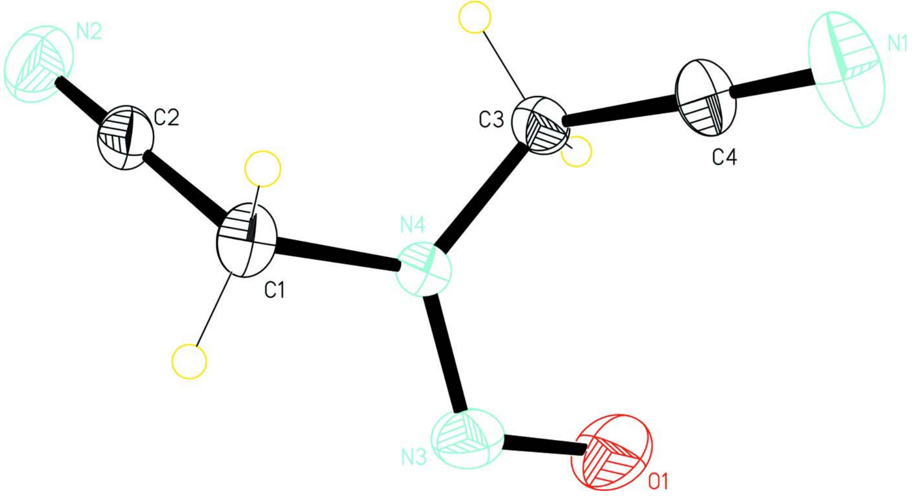

Figure 1

Perspective drawing of the title compound with displacement ellipsoids drawn at the 30% probability level.

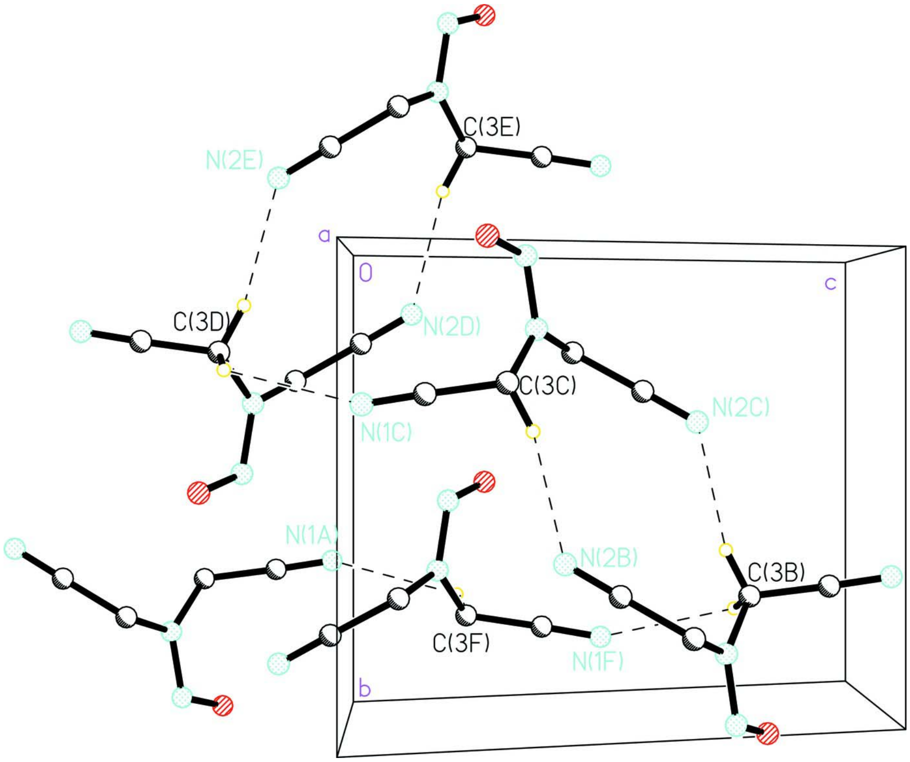

Figure 2

The crystal packing of the title compound viewed along the *a*-axis showing H-bondings interactions; the H atoms not involved in H-bonds have been ommitted for clarity.

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Crystal data

$C_4H_4N_4O$	Monoclinic, $P2_1/c$
$M_r = 124.11$	Hall symbol: -P 2ybc

a = 6.5622 (13) Å
b = 8.9765 (18) Å
c = 11.008 (4) Å
β = 108.55 (3)°
V = 614.7 (3) Å^3
Z = 4
F(000) = 256
D_x = 1.341 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1409 reflections
θ = 2.3–27.5°
μ = 0.10 mm^{-1}
T = 293 K
Prism, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
CCD_Profile_fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{\min}$ = 0.742, $T_{\max}$ = 1.000

6154 measured reflections
1408 independent reflections
1094 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059
$\theta_{\max}$ = 27.5°, $\theta_{\min}$ = 3.0°
h = −8→8
k = −11→11
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.162
S = 1.05
1408 reflections
83 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.20 e Å^{-3}
$\Delta\rho_{\min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.15 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.1721 (2)	−0.00421 (14)	0.24979 (14)	0.0738 (5)
N1	0.1213 (3)	0.3227 (2)	0.03826 (14)	0.0730 (6)
N2	0.6354 (3)	0.36079 (17)	0.61699 (14)	0.0593 (5)
N3	0.3553 (2)	0.02971 (15)	0.31634 (14)	0.0537 (5)
N4	0.38510 (18)	0.17474 (12)	0.33544 (10)	0.0345 (4)
C2	0.6201 (2)	0.29919 (17)	0.52436 (14)	0.0411 (4)
C1	0.6039 (2)	0.22069 (18)	0.40327 (13)	0.0419 (4)

H1A	0.6543	0.2860	0.3487	0.050*
H1B	0.6962	0.1336	0.4222	0.050*
C4	0.1609 (2)	0.30241 (19)	0.14509 (15)	0.0439 (4)
C3	0.2111 (2)	0.28025 (16)	0.28328 (13)	0.0405 (4)
H3B	0.2504	0.3752	0.3264	0.049*
H3C	0.0835	0.2446	0.3006	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0564 (9)	0.0523 (9)	0.0991 (11)	−0.0192 (6)	0.0056 (7)	−0.0124 (6)
N1	0.0569 (11)	0.1157 (16)	0.0448 (9)	0.0196 (9)	0.0140 (7)	0.0171 (8)
N2	0.0655 (11)	0.0593 (10)	0.0484 (8)	−0.0107 (8)	0.0113 (7)	−0.0105 (7)
N3	0.0509 (9)	0.0336 (8)	0.0697 (10)	−0.0029 (6)	0.0094 (7)	−0.0008 (6)
N4	0.0342 (7)	0.0298 (7)	0.0356 (7)	0.0010 (5)	0.0056 (5)	0.0001 (4)
C2	0.0369 (8)	0.0392 (8)	0.0407 (8)	−0.0047 (6)	0.0032 (6)	0.0029 (6)
C1	0.0357 (9)	0.0485 (9)	0.0387 (8)	−0.0044 (7)	0.0076 (6)	−0.0030 (6)
C4	0.0339 (8)	0.0545 (9)	0.0390 (9)	0.0035 (7)	0.0058 (6)	0.0048 (6)
C3	0.0449 (9)	0.0372 (8)	0.0352 (8)	0.0099 (6)	0.0067 (6)	−0.0017 (6)

Geometric parameters (Å, º)

O1—N3	1.2305 (18)	C2—C1	1.481 (2)
N1—C4	1.135 (2)	C1—H1A	0.9700
N2—C2	1.136 (2)	C1—H1B	0.9700
N3—N4	1.3233 (18)	C4—C3	1.464 (2)
N4—C1	1.4516 (18)	C3—H3B	0.9700
N4—C3	1.4539 (17)	C3—H3C	0.9700
O1—N3—N4	113.89 (13)	C2—C1—H1B	109.2
N3—N4—C1	115.67 (12)	H1A—C1—H1B	107.9
N3—N4—C3	121.36 (12)	N1—C4—C3	178.53 (19)
C1—N4—C3	122.83 (12)	N4—C3—C4	112.80 (12)
N2—C2—C1	178.83 (17)	N4—C3—H3B	109.0
N4—C1—C2	111.97 (13)	C4—C3—H3B	109.0
N4—C1—H1A	109.2	N4—C3—H3C	109.0
C2—C1—H1A	109.2	C4—C3—H3C	109.0
N4—C1—H1B	109.2	H3B—C3—H3C	107.8

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*B*···N2$^{\mathrm{i}}$	0.97	2.50	3.450 (2)	165
C3—H3*C*···N1$^{\mathrm{ii}}$	0.97	2.62	3.183 (2)	117

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+1/2, z+1/2$.