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Bis(guanidinium) cyananilate

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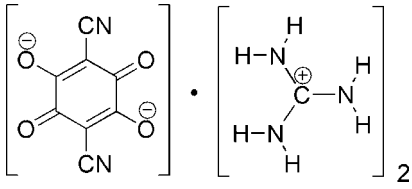
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.131; data-to-parameter ratio = 13.7.

The asymmetric unit of the title compound, $2CH_6N_3^+\cdot C_8N_2O_4^{2-}$, contains one half of a centrosymmetric 2,5-dicyano-3,6-dioxocyclohexa-1,4-diene-1,4-diolate (cyananilate) anion and one guanidinium cation, which are connected by N—H···O and N—H···N hydrogen bonds into a three-dimensional network.

Related literature

For the synthesis and structure of 2,5-dihydroxy-3,6-dicyano-1,4-benzoquinone (cyananilic acid), see: Zaman *et al.* (1996). For related cyananilic acid structures and background references, see: Zaman & Ripmeester (2010).



Experimental

Crystal data

$2CH_6N_3^+\cdot C_8N_2O_4^{2-}$
M_r = 308.28
Monoclinic, $C2/c$
a = 19.4873 (17) Å
b = 3.6611 (3) Å
c = 20.2452 (18) Å
β = 112.887 (2)°
V = 1330.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 173 K
0.35 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.958, T_{max} = 0.976
7261 measured reflections
1704 independent reflections
1379 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.131
S = 1.08
1704 reflections
124 parameters
61 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2^{i}	0.95 (2)	2.20 (2)	3.000 (2)	142 (2)
N2—H2···O1^{i}	0.95 (2)	2.21 (2)	3.020 (2)	143 (2)
N2—H1···O2	0.95 (2)	2.27 (2)	3.062 (2)	140 (2)
N3—H4···N1^{ii}	0.92 (2)	2.14 (2)	3.025 (2)	160 (2)
N3—H3···O2	0.93 (2)	2.02 (2)	2.900 (2)	156 (2)
N4—H6···N1^{ii}	0.92 (2)	2.38 (2)	3.199 (2)	148 (3)
N4—H5···O1^{i}	0.95 (2)	1.95 (2)	2.826 (2)	151 (3)

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

Data collection: *SMART* (Bruker 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2374).

References

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Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zaman, M. B., Morita, Y., Toyoda, J., Yamochi, H., Sekizaki, S. & Nakasuji, K. (1996). *Mol. Cryst. Liq. Cryst.* **287**, 249–257.
Zaman, M. B. & Ripmeester, J. A. (2010). *Supramol. Chem.* **22**, 582–585.

supporting information

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Bis(guanidinium) cyananilate

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S1. Comment

The reaction between cyananilic acid and guanidinium carbonate in methanol leads to the title compound. Since 1997, cyananilic acid (2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone) has been explored due to its valuable physicochemical features. It is an organic acid that has Mott-insulator properties, and organic ferroelectricity (Zaman & Ripmeester, 2010). It forms three dimensional network through N-H···O and N-H···N hydrogen bonds (Fig. 2).

S2. Experimental

Cyananilic acid has been synthesized according to our published method (Zaman *et al.*, 1996) and purified by recrystallization from benzene. Light yellow compound was grown by slow evaporation of a methanol solution containing a 1:1 stoichiometric quantity of guanidinium carbonate (Aldrich, 98%) and cyananilic acid under ambient conditions. Compound decomposes at 593K.

S3. Refinement

N-H distances were restrained to 0.95 (2) Å and all H atoms were refined isotropically. Non- hydrogen atoms were restrained to have the same Uij components with SHELXL97 (Sheldrick, 2008) instruction ′SIMU C1 < N4′.

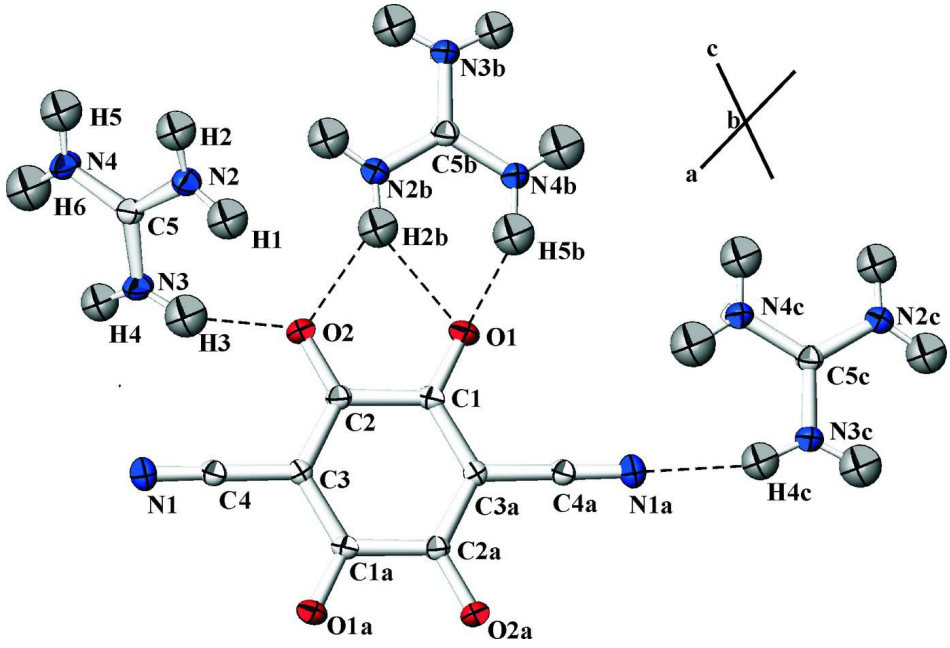

Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Fragments generated by symmetry codes: (*a*) 1/2 - *x*, 1,5 - *y*, 1 - *z*; (*b*) 1/2 - *x*, 1/2 + *y*, 1/2 - *z*; (*c*) 1/2 + *x*, 2.5 - *y*, 1/2 + *z*. Hydrogen bonds are shown with dashed lines.

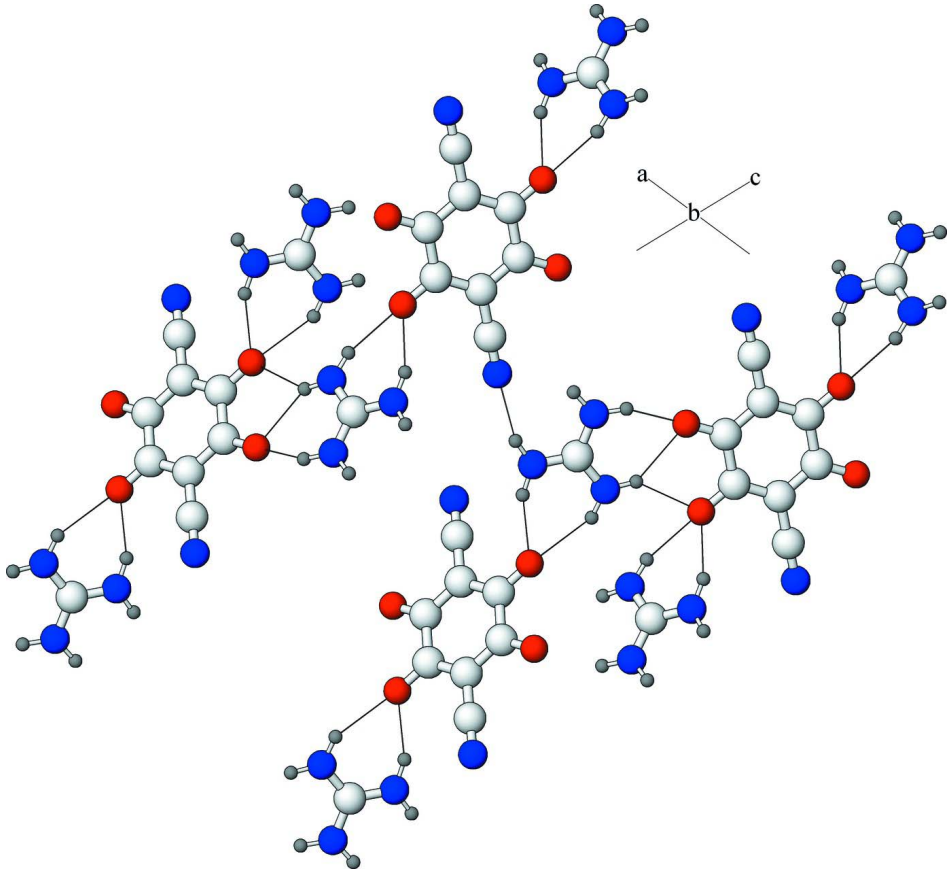

Figure 2

Packing diagram of the hydrogen-bonded framework structure of the title compound viewed down the b axial direction of the unit cell, showing hydrogen-bonding associations as thin lines.

bis(guanidinium) 2,5-dicyano-3,6-dioxocyclohexa-1,4-diene-1,4-diolate

Crystal data

$2CH_6N_3^+ \cdot C_8N_2O_4^{2-}$
M_r = 308.28
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 19.4873 (17) Å
b = 3.6611 (3) Å
c = 20.2452 (18) Å
β = 112.887 (2)°
V = 1330.7 (2) Å^3
Z = 4
F(000) = 640
D_x = 1.539 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71070 Å
Cell parameters from 280 reflections
θ = 5.0–26°
μ = 0.12 mm^{-1}
T = 173 K
Block, colourless
0.35 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.958, T_{max} = 0.976
7261 measured reflections
1704 independent reflections
1379 reflections with $I > 2\sigma(I)$

R_{int} = 0.026
θ_{max} = 28.7°, θ_{min} = 2.2°
h = −26→26
k = −4→4
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.131
S = 1.08
1704 reflections
124 parameters
61 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 0.709P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
C1	0.30409 (9)	0.9359 (5)	0.47852 (9)	0.0199 (4)
C2	0.23212 (9)	0.7966 (5)	0.42334 (8)	0.0194 (4)
C3	0.18096 (9)	0.6179 (5)	0.44716 (9)	0.0193 (4)
C4	0.11214 (10)	0.4852 (5)	0.39572 (9)	0.0213 (4)
C5	0.11254 (10)	0.8997 (5)	0.17992 (9)	0.0221 (4)
O1	0.34792 (8)	1.0991 (4)	0.45742 (7)	0.0288 (4)
O2	0.22010 (7)	0.8452 (4)	0.35861 (7)	0.0254 (3)
N1	0.05680 (9)	0.3773 (5)	0.35458 (9)	0.0297 (4)
N2	0.17845 (9)	0.7347 (5)	0.19774 (8)	0.0255 (4)
H2	0.1912 (16)	0.640 (8)	0.1606 (13)	0.044 (7)*
H1	0.2039 (15)	0.661 (8)	0.2463 (11)	0.046 (7)*
N3	0.08938 (9)	1.0023 (5)	0.23049 (9)	0.0279 (4)
H4	0.0455 (12)	1.133 (7)	0.2154 (13)	0.039 (7)*
H3	0.1219 (15)	0.963 (8)	0.2780 (11)	0.051 (8)*
N4	0.07052 (10)	0.9652 (5)	0.11139 (9)	0.0294 (4)
H6	0.0260 (13)	1.086 (8)	0.1016 (16)	0.057 (9)*
H5	0.0886 (17)	0.897 (8)	0.0757 (14)	0.048 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0204 (8)	0.0214 (9)	0.0206 (8)	−0.0006 (6)	0.0110 (7)	0.0004 (6)

C2	0.0201 (8)	0.0210 (8)	0.0184 (8)	0.0008 (6)	0.0088 (6)	0.0004 (6)
C3	0.0172 (8)	0.0214 (8)	0.0192 (8)	−0.0015 (6)	0.0071 (6)	−0.0006 (6)
C4	0.0209 (8)	0.0229 (9)	0.0218 (8)	−0.0001 (7)	0.0102 (7)	0.0003 (7)
C5	0.0223 (9)	0.0237 (9)	0.0218 (8)	−0.0009 (7)	0.0103 (7)	−0.0002 (6)
O1	0.0267 (7)	0.0376 (8)	0.0259 (7)	−0.0090 (6)	0.0145 (6)	0.0012 (6)
O2	0.0250 (7)	0.0345 (8)	0.0173 (6)	−0.0013 (5)	0.0089 (5)	0.0023 (5)
N1	0.0226 (8)	0.0345 (10)	0.0293 (8)	−0.0045 (7)	0.0072 (7)	−0.0028 (7)
N2	0.0234 (8)	0.0307 (9)	0.0236 (8)	0.0043 (6)	0.0104 (6)	−0.0008 (7)
N3	0.0248 (8)	0.0394 (10)	0.0214 (8)	0.0070 (7)	0.0110 (7)	0.0005 (7)
N4	0.0261 (8)	0.0421 (10)	0.0206 (8)	0.0089 (7)	0.0099 (7)	0.0007 (7)

Geometric parameters (Å, º)

C1—O1	1.246 (2)	C5—N4	1.330 (2)
C1—C3^{i}	1.431 (2)	C5—N2	1.336 (2)
C1—C2	1.502 (2)	N2—H2	0.95 (2)
C2—O2	1.251 (2)	N2—H1	0.95 (2)
C2—C3	1.424 (2)	N3—H4	0.923 (19)
C3—C4	1.426 (2)	N3—H3	0.93 (2)
C4—N1	1.146 (2)	N4—H6	0.92 (2)
C5—N3	1.324 (2)	N4—H5	0.95 (2)
O1—C1—C3^{i}	122.71 (15)	N3—C5—N2	120.05 (17)
O1—C1—C2	118.30 (15)	N4—C5—N2	120.02 (17)
C3^{i}—C1—C2	118.99 (14)	C5—N2—H2	118.3 (18)
O2—C2—C3	123.33 (15)	C5—N2—H1	117.9 (17)
O2—C2—C1	118.10 (15)	H2—N2—H1	122 (2)
C3—C2—C1	118.57 (14)	C5—N3—H4	116.2 (16)
C2—C3—C4	119.52 (15)	C5—N3—H3	117.0 (18)
C2—C3—C1^{i}	122.44 (14)	H4—N3—H3	126 (2)
C4—C3—C1^{i}	118.04 (15)	C5—N4—H6	117.1 (19)
N1—C4—C3	179.7 (2)	C5—N4—H5	119.0 (19)
N3—C5—N4	119.93 (17)	H6—N4—H5	124 (3)

Symmetry code: (i) −*x*+1/2, −*y*+3/2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{ii}	0.95 (2)	2.20 (2)	3.000 (2)	142 (2)
N2—H2···O1^{ii}	0.95 (2)	2.21 (2)	3.020 (2)	143 (2)
N2—H1···O2	0.95 (2)	2.27 (2)	3.062 (2)	140 (2)
N2—H1···N2^{ii}	0.95 (2)	2.64 (3)	3.319 (3)	129 (2)
N3—H4···N1^{iii}	0.92 (2)	2.14 (2)	3.025 (2)	160 (2)
N3—H3···O2	0.93 (2)	2.02 (2)	2.900 (2)	156 (2)
N4—H6···N1^{iii}	0.92 (2)	2.38 (2)	3.199 (2)	148 (3)
N4—H5···O1^{ii}	0.95 (2)	1.95 (2)	2.826 (2)	151 (3)

Symmetry codes: (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) −*x*, *y*+1, −*z*+1/2.