

## Bis(guanidinium) cyananilate

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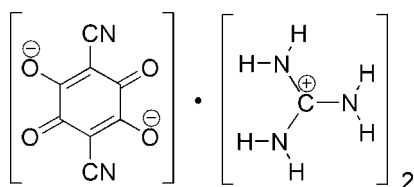
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.131; data-to-parameter ratio = 13.7.

The asymmetric unit of the title compound,  $2\text{CH}_6\text{N}_3^+ \cdot \text{C}_8\text{N}_2\text{O}_4^{2-}$ , 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  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{N}$  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

$2\text{CH}_6\text{N}_3^+ \cdot \text{C}_8\text{N}_2\text{O}_4^{2-}$   
 $M_r = 308.28$   
 Monoclinic,  $C2/c$

$a = 19.4873$  (17) Å  
 $b = 3.6611$  (3) Å  
 $c = 20.2452$  (18) Å

$\beta = 112.887$  (2)°  
 $V = 1330.7$  (2) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

$\mu = 0.12$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.35 \times 0.30 \times 0.20$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

## 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  
 $\Delta\rho_{\text{max}} = 0.44$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.42$  e Å<sup>-3</sup>

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

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

- Bruker (2003). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Dowty, E. (1999). ATOMS. Shape Software, Kingsport, Tennessee, USA.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). Acta Cryst. A64, 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.

**supplementary materials**

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## Bis(guanidinium) cyananilate

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### 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).

### 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.

### 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'.

### Figures

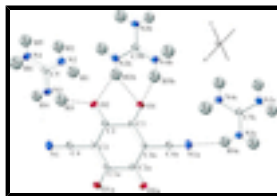


Fig. 1. Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Fragments generated by symmetry codes: (a)  $1/2 - x, 1,5 - y, 1 - z$ ; (b)  $1/2 - x, 1/2 + y, 1/2 - z$ ; (c)  $1/2 + x, 2.5 - y, 1/2 + z$ . Hydrogen bonds are shown with dashed lines.

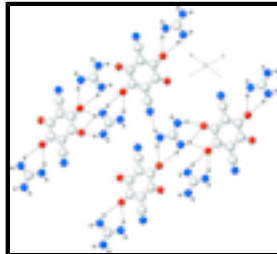
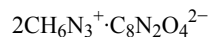


Fig. 2. Packing diagram of the hydrogen-bonded framework structure of the title compound viewed down the b axial direction of the unit cell, showing hydrogen-bonding associations as thin lines.

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

### Crystal data



$M_r = 308.28$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 19.4873\ (17)\ \text{\AA}$

$b = 3.6611\ (3)\ \text{\AA}$

$c = 20.2452\ (18)\ \text{\AA}$

$\beta = 112.887\ (2)^\circ$

$V = 1330.7\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 640$

$D_x = 1.539\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71070\ \text{\AA}$

Cell parameters from 280 reflections

$\theta = 5.0\text{--}26^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Block, colourless

$0.35 \times 0.30 \times 0.20\ \text{mm}$

### Data collection

Bruker SMART 1000 CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\omega$  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  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 28.7^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -26 \rightarrow 26$

$k = -4 \rightarrow 4$

$l = -27 \rightarrow 27$

### 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  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.44\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.42\ \text{e \AA}^{-3}$

### 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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 ( $\text{\AA}$ ,  $^\circ$ )*

C1—O1	1.246 (2)	C5—N4	1.330 (2)
C1—C3 <sup>i</sup>	1.431 (2)	C5—N2	1.336 (2)

## supplementary materials

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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 <sup>i</sup>	122.71 (15)	N3—C5—N2	120.05 (17)
O1—C1—C2	118.30 (15)	N4—C5—N2	120.02 (17)
C3 <sup>i</sup> —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 <sup>i</sup>	122.44 (14)	H4—N3—H3	126 (2)
C4—C3—C1 <sup>i</sup>	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 codes: (i)  $-x+1/2, -y+3/2, -z+1$ .

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 $\cdots$ O2 <sup>ii</sup>	0.95 (2)	2.20 (2)	3.000 (2)	142 (2)
N2—H2 $\cdots$ O1 <sup>ii</sup>	0.95 (2)	2.21 (2)	3.020 (2)	143 (2)
N2—H1 $\cdots$ O2	0.95 (2)	2.27 (2)	3.062 (2)	140 (2)
N2—H1 $\cdots$ N2 <sup>ii</sup>	0.95 (2)	2.64 (3)	3.319 (3)	129 (2)
N3—H4 $\cdots$ N1 <sup>iii</sup>	0.92 (2)	2.14 (2)	3.025 (2)	160 (2)
N3—H3 $\cdots$ O2	0.93 (2)	2.02 (2)	2.900 (2)	156 (2)
N4—H6 $\cdots$ N1 <sup>iii</sup>	0.92 (2)	2.38 (2)	3.199 (2)	148 (3)
N4—H5 $\cdots$ O1 <sup>ii</sup>	0.95 (2)	1.95 (2)	2.826 (2)	151 (3)

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

Fig. 1

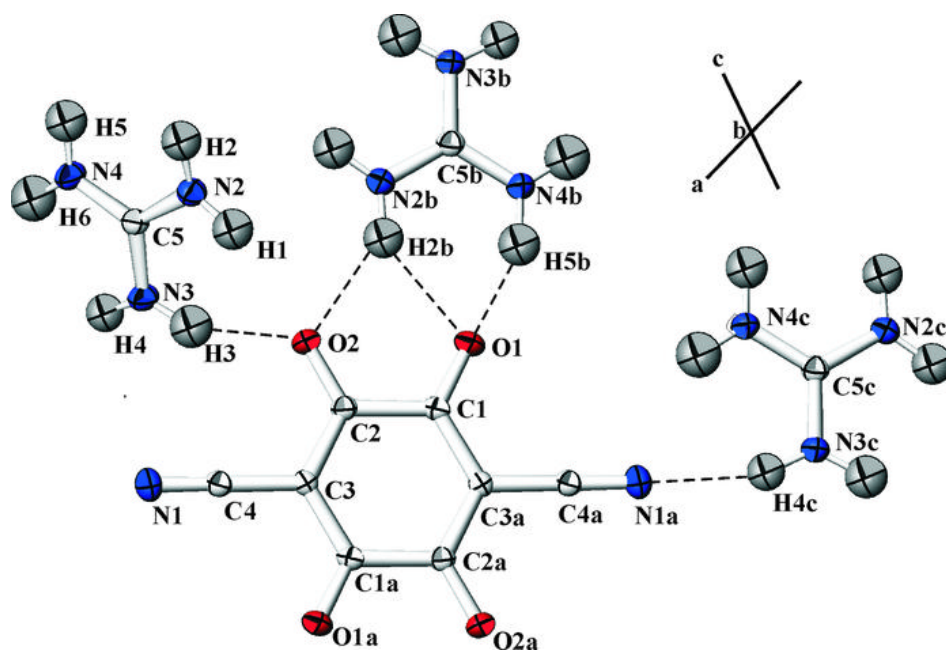


Fig. 2

