

## 4-(Dimethylamino)pyridinium 2-butoxy-3-dicyanomethylene-4-oxocyclobut-1-en-1-olate

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## Key indicators

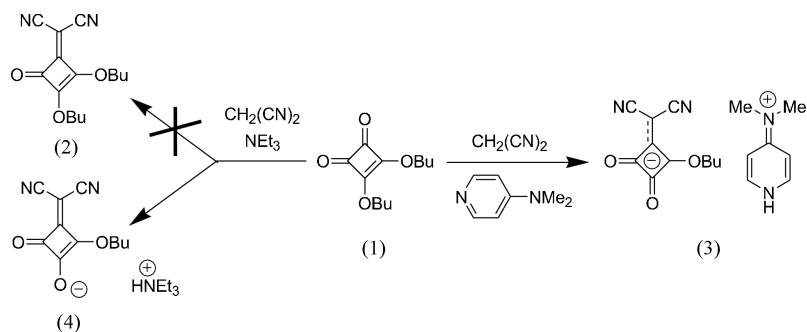
Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
Disorder in main residue  
R factor = 0.040  
wR factor = 0.101  
Data-to-parameter ratio = 12.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the crystal structure of the title compound,  $\text{C}_7\text{H}_{11}\text{N}_2^+\cdot\text{C}_{11}\text{H}_9\text{N}_2\text{O}_3^-$ , both the cation and the anion lie on a mirror plane. Three C atoms of the butyl group are disordered over two positions related by this plane. The bond-length analysis shows that the surplus negative charge of the anion is delocalized between the cyclobutene ring and the dicyanomethylene group. The 4-dimethylaminopyridinium cation has an intermediate aromatic-quinoid structure.

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## Comment

According to Oswald (2000), 3,4-dibutoxy-3-cyclobutene-1,2-dione, (1), when reacted with malononitrile in the presence of a tertiary amine, particularly triethylamine (TEA), yields 2-(2,3-dibutoxy-4-oxo-2-cyclobutenylidene)malononitrile, (2). This product is an important intermediate for the synthesis of squarylium dyes, which are of interest for use as red and near infrared (NIR) fluorescent labels and probes for biological and biomedical assays (Oswald, 2000; Oswald *et al.*, 1999; Terpetschnig *et al.*, 1993; Terpetschnig & Lakowicz, 1993; Hamilton *et al.*, 2000), as well as colouring agents for photoelectric conversion elements and photoelectrochemical batteries (Hiroo & Masaki, 2000). One can also think of other potential applications of these compounds, which may take advantage of their long-wave absorption and emission. In this paper, we report that, in the presence of 4-dimethylaminopyridine instead of TEA, the reaction proceeds with elimination of a butyl group to give the title salt, (3) (Fig. 1).



Taking into account the above data, we have revised Oswald's assumption (Oswald, 2000) with respect to the structure of (2). Indeed, our  $^1\text{H}$  NMR, IR, and elemental analysis data confirm that the reaction of (1) with malononitrile and TEA leads to product (4) rather than (2), as suggested by Oswald (2000). The  $^1\text{H}$  NMR spectrum of (4) shows the H-atom signals of the butoxy and triethylamino groups, and an NH singlet peak. The integrations of the triplet at 4.59 p.p.m. ( $\text{OCH}_2$ ), the quartet at 3.07 p.p.m. ( $\text{NCH}_2$ ), and the singlet at 9.78 p.p.m. (NH) yielded the ratio of 2:6:1,

indicating one butoxy group per triethylammonium cation. These data are in good agreement with the  $^1\text{H}$  NMR spectrum of (3).

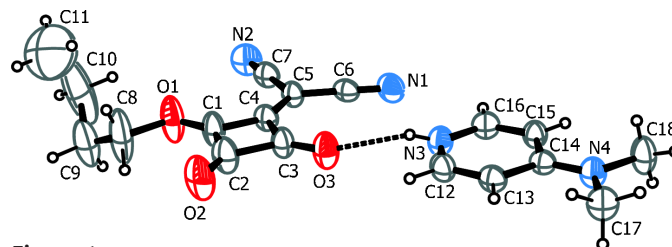
In the crystal structure of (3), both the cation and the anion occupy special positions on a mirror plane, so that all non-H atoms, except for the disordered butyl group, lie on this plane. Atoms C9, C10 and C11 are disordered over two positions related by the mirror plane. The C1–O1–C8–C9–C10–C11 fragment has the  $-ap,-sc,-sc$  conformation (Table 1) (and consequently  $+ap,+sc,+sc$  for the symmetry-related disordered component) The C2=O2 and C3=O3 bond lengths [1.215 (2) and 1.207 (2) Å respectively] are in accord with the mean value for carbonyl groups (1.21 Å; Bürgi & Dunitz, 1994). A remarkably uniform bond-length distribution is observed within the cyclobutene ring, as compared to the unsubstituted and uncharged semisquaric acid (Semmingsen & Groth, 1988). The C1–C4 and C4–C5 bonds have virtually the same lengths [1.395 (3) and 1.391 (2) Å]; those are intermediate between the mean values (Bürgi & Dunitz, 1994) for single and double C–C bonds (1.46 and 1.32 Å, respectively). Shortening of the  $Csp^2-Csp^1$  and elongation of the  $Csp-N$  bonds occur in the dicyanomethylene group. This bond-length distribution suggests that the surplus negative charge of the anion is delocalized between two fragments with strong electron-accepting properties, namely the cyclobutene ring and the dicyanomethylene group.

The cation has a distinctly quinoidal structure with nearly double N4=C14 [1.313 (2) Å] and shortened C12–C13 and C15–C16 bonds [1.360 (3) and 1.334 (3) Å, respectively; the mean values for double N=C and aromatic C=C bonds are 1.28 and 1.38 Å, Bürgi & Dunitz, 1994]. In spite of this, the average value for the N3–C12 and N3–C16 bonds is equal to the mean value for the  $C_{ar}=N$  bonds in the pyridinium ring (1.335 Å). Therefore, we can also assume that the surplus of positive charge is delocalized mainly in the region between the two N atoms of the cation.

In the crystal structure, cations and anions are linked into ion pairs *via* N–H...O hydrogen bonds (Table 2).

## Experimental

For the preparation of (3), malononitrile (330 mg, 5.00 mmol) was dissolved in benzene (20 ml). 3,4-Dibutoxy-3-cyclobutene-1,2-dione [(1); 1.1 ml, 5.09 mmol] was added dropwise with stirring. 4-Dimethylaminopyridine (600 mg, 4.91 mmol) was then added slowly. The mixture was stirred at room temperature for 10 min and left overnight to crystallize at room temperature. The resulting crystalline product was filtered off, washed with benzene and diethyl ether to give crude product (3) (1.45 g, 85%). One of the crystals obtained was selected for the X-ray structural study. Analysis found: C 63.67, H 6.02, N 16.73%; calculated for  $C_{18}H_{20}N_4O_3$ : C 63.52, H 5.92, N 16.46%.  $\delta_H$  (200 MHz, DMSO- $d_6$ ): 13.52–12.96 (1H, broad s,  $NH^+$ ), 8.21 (2H, *m*, aromatic H), 6.98 (2H, *m*, aromatic H), 4.59 (2H, *t*, 6.5 Hz,  $OCH_2$ ), 3.18 [6H, *s*,  $N(CH_3)_2$ ], 1.78–1.57 (2H, *m*,  $CH_2$ ), 1.48–1.24 (2H, *m*,  $CH_2$ ), 0.90 (3H, *t*, 7.4 Hz,  $CH_3$ ); *m/z* (FAB–MS, glycerol): 123 (DMAP  $H^+$ ), 463 (*M* + DMAP  $H^+$ ). IR  $\nu$  ( $cm^{-1}$ ): 3280, 3144, 3100, 2964, 2932, 2880, 2228 (CN), 2208 (CN), 1788 (CO), 1684, 1652, 1580, 1556, 1464, 1420, 1372, 1360, 1340, 1252, 1228, 1020. UV:  $\lambda_{max}$  (abs): 283, 335 nm (water). Compound (4) was prepared in an



**Figure 1**  
View of the components of (3) (30% probability displacement ellipsoids). The symmetry-equivalent alternative disorder component of the butyl group is not shown. The dashed line indicates a hydrogen bond.

analogous way. Analysis found: C 63.80, H 7.90, N 12.96%; calculated for  $C_{17}H_{25}N_3O_3$ : C 63.93, H 7.89, N 13.16%;  $\delta_H$  (200 MHz, DMSO- $d_6$ ): 10.15–9.55 (1H, broad s,  $NH^+$ ), 4.59 (2H, *t*, 6.7 Hz,  $OCH_2$ ), 3.07 [6H, *q*, 7.4, 14.5 Hz,  $N(CH_2CH_3)_3$ ], 1.77–1.58 (2H, *m*,  $CH_2$ ), 1.48–1.26 (2H, *m*,  $CH_2$ ), 1.18 [9H, *t*, 7.3 Hz,  $N(CH_2CH_3)_3$ ], 0.90 (3H, *t*, 7.4 Hz,  $CH_3$ ). IR  $\nu$  ( $cm^{-1}$ ): 3516, 2976, 2940, 2744, 2684, 2636, 2512, 2264 (CN), 2240 (CN), 1784, 1672, 1544, 1472, 1428, 1352, 1252, 1080, 1060. UV:  $\lambda_{max}$  (abs): 335 nm (water).

### Crystal data

$C_7H_{11}N_2^+ \cdot C_{11}H_9N_2O_3^-$   
 $M_r = 340.38$   
Monoclinic,  $P2_1/m$   
 $a = 11.513$  (3) Å  
 $b = 6.7830$  (17) Å  
 $c = 12.176$  (3) Å  
 $\beta = 102.94$  (2)°  
 $V = 926.7$  (4) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.22$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 24 reflections  
 $\theta = 11$ –13°  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Needle, yellow  
0.4 × 0.1 × 0.1 mm

### Data collection

Siemens P3/PC diffractometer  
 $\theta$ – $2\theta$  scans  
Absorption correction: none  
2053 measured reflections  
1962 independent reflections  
916 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.097$

$\theta_{max} = 26.1^\circ$   
 $h = -14 \rightarrow 13$   
 $k = 0 \rightarrow 8$   
 $l = 0 \rightarrow 15$   
2 standard reflections every 98 reflections  
intensity decay: 3%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.101$   
 $S = 0.82$   
1962 reflections  
163 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.004$   
 $\Delta\rho_{max} = 0.11$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.09$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1–C1	1.293 (3)	C1–C4	1.395 (3)
O1–C8	1.468 (3)	C2–C3	1.493 (3)
O2–C2	1.215 (2)	C3–C4	1.450 (3)
O3–C3	1.207 (2)	C4–C5	1.391 (2)
N1–C6	1.160 (3)	C5–C6	1.396 (3)
N3–C12	1.324 (3)	C5–C7	1.414 (3)
N3–C16	1.346 (3)	C8–C9	1.515 (4)
N4–C14	1.313 (2)	C12–C13	1.360 (3)
N4–C17	1.479 (3)	C13–C14	1.410 (3)
N4–C18	1.461 (3)	C14–C15	1.418 (3)
C1–C2	1.448 (3)	C15–C16	1.334 (3)
C1–O1–C8–C9	–155.3 (3)	C8–C9–C10–C11	–62.2 (7)
O1–C8–C9–C10	–64.9 (5)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3N $\cdots$ O3	0.86	2.16	2.834 (2)	135

The C—C bond lengths within the disordered butyl group were restrained to 1.520 (5) Å. All H atoms were placed in calculated positions and included in the refinement in the riding-model approximation with  $U_{iso} = nU_{eq}(\text{parent atom})$  ( $n = 1.5$  for the methyl groups and  $n = 1.2$  for the remaining H atoms). All of the methyl groups were free to rotate around the C—C bond, thus the H atoms at C17 and C18 are disordered over the symmetry plane.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* routine *CIF UPDATE* (Farrugia, 1999).

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