

## Tetrabutylammonium $\alpha$ -acetyl- $\gamma$ -butyrolactonate containing a three-dimensional hydrogen-bonded network

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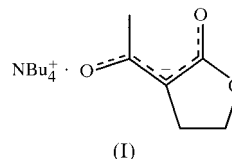
The title compound,  $C_{16}H_{36}N^+ \cdot C_6H_7O_3^-$ , crystallizes with two independent anions and two independent cations in the asymmetric unit. Each anion adopts an *s-trans* conformation and forms  $O \cdots H-C$  hydrogen bonds to the  $\alpha$ -methylene groups of four neighbouring tetrabutylammonium cations, to create a three-dimensional hydrogen-bonded network.

### Comment

The anions of tetrabutylammonium salts of CH-acidic and NH-acidic compounds are initiators for the metal-free anionic polymerization of acrylates, methacrylates and acrylonitrile (Reetz *et al.*, 1995a). Moreover, they are intermediates in phase-transfer catalyzed reactions (Dehmlow & Dehmlow, 1993). Structural information on these compounds shows that most are not real carbanions, as previously suggested (March, 1992), but that they form dimers or higher aggregates *via*  $O \cdots H-C$  or  $N \cdots H-C$  hydrogen bonds, originating from the interaction of the anions with the tetrabutylammonium cations (Reetz, Hütte, Herzog & Goddard, 1996). In all known cases, the major hydrogen-bonding interactions are with the  $\alpha$ -methylene groups of the *n*-butyl chains of the tetrabutylammonium cations, which are relatively CH acidic. Indeed, *ab initio* calculations on the parent tetramethylammonium cation indicate that the positive charge does not reside on the N atom but is delocalized on the four methyl groups (Reetz *et al.*, 1999a). The actual structure adopted by the salts depends, however, on the number and location of the donor atoms (hydrogen-bond acceptors) in the anion. Anions with two donor atoms, such as malonates, tend to form centrosymmetric dimers, in which the enolate takes up a U-shaped conformation and the donor atoms are simultaneously bonded to adjacent  $\alpha$ -methylene groups of two neighbouring tetrabutylammonium cations (Reetz, Hütte & Goddard, 1993). The result is a cage-like structure. Cryoscopic investigations on tetrabutylammonium malonates in benzene show that these

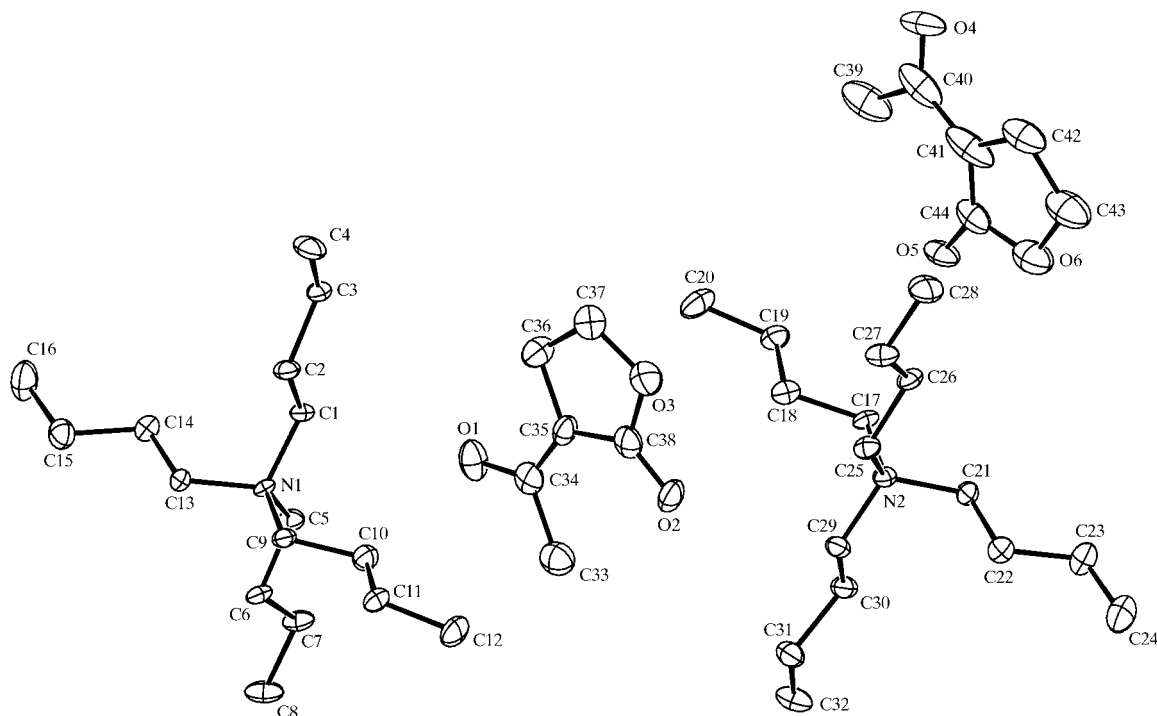
dimers are also maintained in solution (Reetz *et al.*, 1999b). In contrast, carbazolide or dibenzoazapinide anions containing only one donor result in the formation of infinite chains (Reetz, Hütte, Goddard & Minet, 1995), while the salts of 9-ethylfluorenone and cyclopentadienide anions, where suitable donor atoms are absent, exhibit weak hydrogen bonding or none at all, hence the interaction is non-directional (Reetz *et al.*, 1995b). If one side of the anion is sterically shielded, then the anion can bond to only one side of the cation to give chiral ion pairs (Reetz, Hütte, Goddard & Robyr, 1996; Reetz, Hütte & Goddard, 1999a).

The title compound, (I), is an initiator for the polymerization of *n*-butyl acrylate. The exothermic polymerization reaction occurs, however, only after a significant induction time, indicative of a low basicity. Methyl methacrylate cannot be polymerized using (I). Presumably, it is too weak a Michael acceptor to undergo a reaction with the weak nucleophile. The  $\alpha$ -acetyl- $\gamma$ -butyrolactonate anion contains two donor atoms available for forming hydrogen bonds, but the anion can adopt two possible conformations, *s-cis* (U-shape) as well as *s-trans*. A structure determination was undertaken in order to establish the conformation of the  $\alpha$ -acetyl- $\gamma$ -butyrolactonate anion in the solid and determine how the anion interacts with the tetrabutylammonium cation, so as to better understand the properties of the salt.



Compound (I) crystallizes with two independent cations and two independent anions in the asymmetric unit (Fig. 1). Apart from a significant difference in the C34–C35 and C40–C41 bond lengths, comparable distances and angles in the independent ions differ by less than three standard uncertainties, so average geometries will be discussed. (The difference remains even after correction for libration, and therefore may be statistical in nature or the result of unresolved disorder.) Bond distances in the anions are in accord with extensive delocalization of the negative charges from the carbanion centres (C35, C41) to the carbonyl O atoms (O1, O2, O4 and O5). Thus, the C–C distances are shortened to 1.405 (9) Å (mean) and the C=O distances are lengthened to 1.240 (7) Å. The enolate adopts the *s-trans* conformation, and the anions are planar (mean r.m.s. deviation 0.035 Å). This geometry corresponds to the most stable conformation found for  $\beta$ -ketoesterenolates in solution, as demonstrated by  $^1H$  NMR spectroscopy (Cambillau & Guibe, 1982). This contrasts with most malonates, which adopt the *s-cis* conformation (U-shape) in the solid state and in solution. To our knowledge, it is only in the hexamethylguanidinium salt of dimethyl 2-ethylmalonate that this is not the case (Reetz, Bingel & Harms, 1993).

The *n*-butyl chains in the tetrabutylammonium cations adopt the commonly observed all-*trans* conformation,

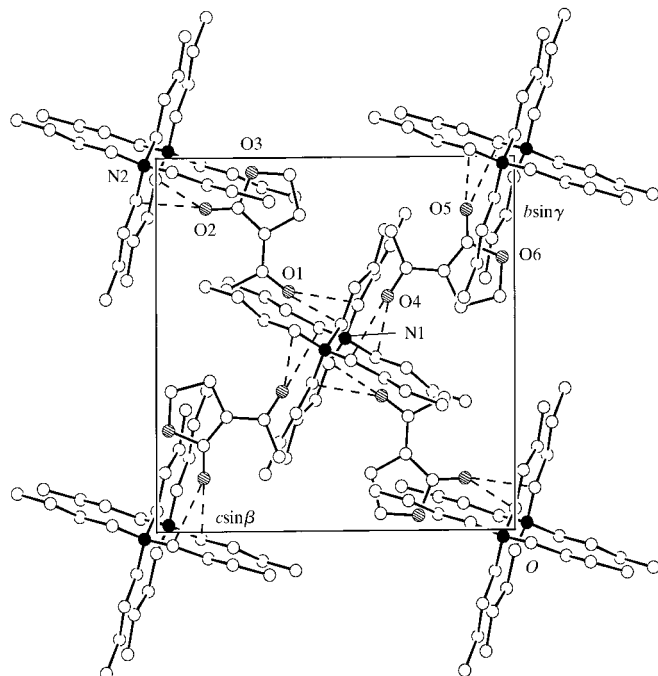


**Figure 1**

Molecular structure showing the labelling of the non-H atoms. Atomic displacement ellipsoids shown at the 50% probability level.

although there are structures where exceptions to this rule exist (e.g. in cyclopentadienyltetrabutylammonium; Reetz *et al.*, 1995*b*). The coordination about the N atoms is not ideally tetrahedral but flattened, with significantly smaller C–N–C angles in the planes of the *n*-butyl groups. Thus, the two C–N–C angles [mean 105.1 (3)°] in the planes of the alkane

chains (e.g. C1–N1–C5 and C9–N1–C13) are significantly smaller than the other four C–N–C angles around each N atom [mean 111.7 (2)°]. Angles along the alkane chain alternate, with the N–C–C angle at the  $\alpha$ -C atom [mean 116.0 (3)°] larger than the C–C–C angle at the  $\beta$ -C atom [109.2 (5)°], which in turn is smaller than the C–C–C angle at the  $\gamma$ -C atom [mean 112.4 (3)°].



**Figure 2**

Packing of the ions in the unit cell viewed down *a*, showing the pseudo 4<sub>2</sub> axis of symmetry. O...H–C interactions are shown as dashed lines.

Fig. 2 shows the packing of the molecules viewed along the *a* axis of the triclinic cell. The arrangement of the anions and cations approximates to the tetragonal space group  $P4_2$ . In fact, the (*okl*) reflections show approximate fourfold symmetry and (*h00*) reflections with  $h = 2n$  ( $n = 1, 2, 3, \dots$ ) are systematically strong. The packing is characterized by alternating sheets of anions and cations. Although not required by symmetry, the two independent acetilbutyrolactonate anions are almost coplanar (r.m.s. deviation 0.119 Å). The mean planes of the anions lie between close-packed layers of the tetrabutylammonium cations, 3.057 Å from the N atoms. Particularly worthy of note is the arrangement of the anions with respect to the cations. Each carbonyl group of the anions forms a short intermolecular interaction with one  $\alpha$ -C–H of a tetrabutylammonium ion in the neighbouring layer. Thus, O1 is 3.316 (3) Å from C5(1 + *x*, *y* – 1, *z*) and 3.331 (3) Å from C1(–*x*, –*y*, –1 – *z*), while O2 is 3.222 (3) Å from C25(*x*, *y*, *z* – 1) and 3.305 (3) Å from C29(1 – *x*, –*y*, 1 – *z*). Similarly, O4 is 3.256 (3) Å from C9(*x*, *y* – 1, 1 + *z*) and 3.415 (3) Å from C13(–*x*, –*y*, –*z*), while O5 is 3.286 (3) Å from C17(*x*, *y*, *z* – 1) and 3.311 (3) Å from C21(–*x*, –*y*, 1 – *z*) (Fig. 2). Extended Hückel molecular orbital calculations (Hoffmann, 1963) on the anion show that most of the negative charge is delocalized on the O atoms of these carbonyl groups.

In summary, the crystal structure reveals that the title compound adopts an *s-trans* conformation in the solid. As a result, the anions do not form discrete dimers with the cations, as in the case of malonates, but rather adopt a three-dimensional hydrogen-bonding network. Such an association in the liquid, *inter alia*, may explain the poor nucleophilicity of the anion towards methyl methacrylate and the long initiation times observed in the polymerization of *n*-butylacrylate.

## Experimental

The title compound was synthesized in 88% yield by deprotonation of  $\alpha$ -acetyl- $\gamma$ -butyrolactone by HONBu<sub>4</sub> at room temperature using toluene to remove the water azeotropically (Reetz *et al.*, 1988; Reetz, Hütte & Goddard, 1993; Raj *et al.*, 1992). The residue was dissolved in warm dimethyl sulfoxide at 353 K and slowly cooled to room temperature to give acicular crystals. The solvent was removed and the crystals were washed in diethyl ether, and a suitable crystal was mounted in a glass capillary under argon.

### Crystal data

C <sub>16</sub> H <sub>36</sub> N <sup>+</sup> ·C <sub>6</sub> H <sub>7</sub> O <sub>3</sub> <sup>-</sup>	Z = 4
M <sub>r</sub> = 369.57	D <sub>x</sub> = 1.080 Mg m <sup>-3</sup>
Triclinic, P $\bar{1}$	Mo K $\alpha$ radiation
a = 12.309 (4) Å	Cell parameters from 25 reflections
b = 13.659 (3) Å	$\theta$ = 12.7–20.1°
c = 13.6110 (10) Å	$\mu$ = 0.070 mm <sup>-1</sup>
$\alpha$ = 89.920 (10)°	T = 100 K
$\beta$ = 94.100 (10)°	Needle, colourless
$\gamma$ = 95.01 (2)°	0.63 × 0.39 × 0.18 mm
V = 2273.8 (9) Å <sup>3</sup>	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\max}$ = 27.44°
$\omega$ –2 $\theta$ scans	$h$ = –15 → 15
11 019 measured reflections	$k$ = –17 → 17
10 330 independent reflections	$l$ = 0 → 17
7010 reflections with $I > 2\sigma(I)$	3 standard reflections
R <sub>int</sub> = 0.038	frequency: 30 min
	intensity decay: 4.7%

### Refinement

Refinement on F <sup>2</sup>	H-atom parameters constrained
R(F) = 0.074	$w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 2.206P]$
wR(F <sup>2</sup> ) = 0.219	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.041	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
10 330 reflections	$\Delta\rho_{\max} = 0.53 \text{ e } \text{Å}^{-3}$
471 parameters	$\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$

The methyl groups, C33 and C39, were refined as rigid rotating groups. The relatively high R value of 0.074 is possibly due to unresolved disorder associated with the atoms C34, C35, C41 and C42 (see *Comment*).

**Table 1**

Selected bond lengths (Å).

O1–C34	1.256 (3)	O5–C44	1.216 (3)
O2–C38	1.236 (3)	C34–C35	1.387 (4)
O3–C38	1.391 (3)	C35–C38	1.403 (4)
O3–C37	1.434 (3)	C40–C41	1.422 (4)
O4–C40	1.253 (3)	C41–C44	1.394 (4)

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1995); cell refinement: CAD-4 EXPRESS; data reduction: DATAP (Coppens *et al.*, 1965); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1402). Services for accessing these data are described at the back of the journal.

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