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Benzyltriphenylphosphonium glutaconaldehyde

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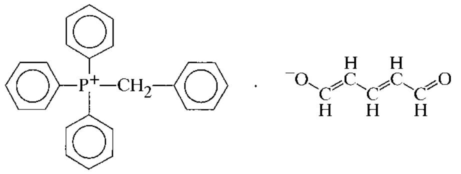
The title compound, $C_{25}H_{22}P^+\cdot C_5H_5O_2^-$, crystallizes in space group $P2_1/c$. The phosphonium cations form zigzag chains with P···P distances of 6.475 (1) and 8.287 (2) Å, and are related by inversion centres. Two types of attractive edge-to-face phenyl interactions exist, resulting in a dominant supramolecular motif. The glutaconaldehyde anions occupy the interchain spacing and hold adjacent chains together *via* multiple C—H···O hydrogen bonds. The bond-length alternation, a parameter which reveals the non-linear optical efficiency at the molecular level, is optimized in the chromophore anion.

Comment

Conjugated polyenes are nonlinear optical chromophores displaying large molecular hyperpolarizabilities. Crystals built up from such chromophores are very rare. We describe here the crystal structure of the title compound, (I), containing a conjugated polyene, the glutaconaldehyde anion, with optimized bond length alternation. This situation is due to the associated cation, the benzyltriphenylphosphonium. Semi-empirical calculations performed on push-pull polyenes have shown that the static quadratic hyperpolarizability can be correlated with the ground state polarization and concomitantly with a structural parameter, the bond length alternation (BLA) (Marder *et al.*, 1994; Meyers *et al.*, 1994). The BLA describes the ground state geometry of the molecule and is defined as the average difference in the lengths between adjacent C—C bonds in the polyenic chain. Calculations indicate that the molecular hyperpolarizability (β) is a maximum when the BLA is ± 0.05 (1) Å (Blanchard-Desce *et al.*, 1997).

The glutaconaldehyde anion is not stable in solution at room temperature and acidic pH and undergoes polymerization. However it is known to be stable in solution at low temperatures and basic pH, and in the solid state only with bulky counterions. In solution, it exists in two similar resonance forms with equal contribution and hence BLA = 0. Computational studies have shown that by modifying the parameters that govern the relative weights of these two resonance forms, it should be possible to optimize the molecular structure so as to maximize the optical nonlinearity in the solid state (Barzoukas *et al.*, 1996). The balance between the two limiting resonance forms of a polyene can be modified by altering the donor–acceptor strengths at the terminals or the nature of the conjugated path with external perturbation. We have attempted to perturb the contribution of the two resonance forms of the glutaconaldehyde anion by external charged centres [metal cations such as sodium (Muthuraman *et al.*, 1999) or bulky organic cations], to optimize the BLA. However, these salts crystallize in centrosymmetric space groups, excluding possible optical nonlinearity at the macroscopic level.



(I)

The unit cell of (I) contains four cation–anion entities. In the crystal lattice, the phosphonium cations form a zigzag chain with P···P distances of 8.287 (2) Å ($-x, -y, 1-z$) and 6.475 (1) Å ($1-x, -y, 1-z$), running parallel with the *a* direction. The cations in the chain are held together by two types of edge-to-face (ef) phenyl interactions (Fig. 2). One type involves four phenyl rings (two per phosphonium cation), resulting in two ef interactions leading to a P···P distance of 8.287 (2) Å, related by an inversion centre. The other type involves two phenyl rings and two benzyl groups (one phenyl and one benzyl per phosphonium cation), having two ef

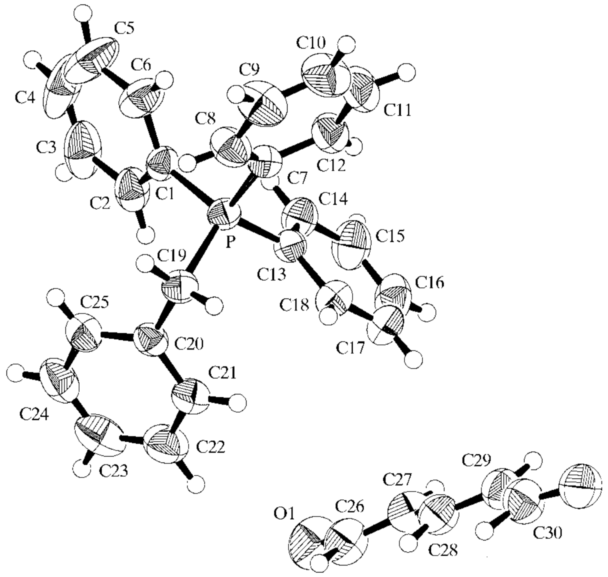


Figure 1
The molecular structure of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level (Johnson, 1976).

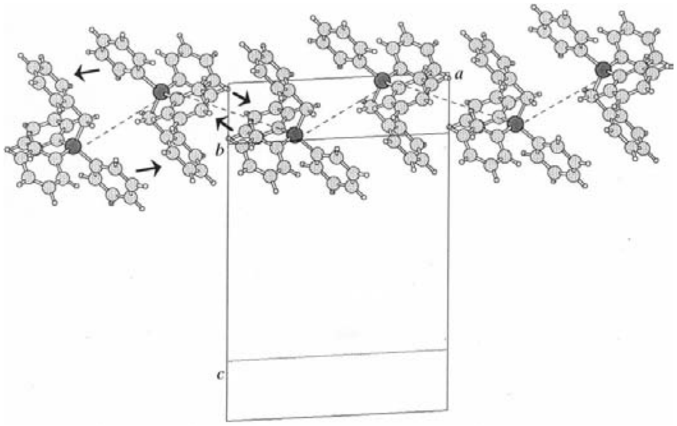


Figure 2
The chain of benzyltriphenylphosphonium cations in (I) formed by ef phenyl–phenyl interactions (Cense, 1990).

interactions leading to a P$\cdots$P distance of 6.475 (1) Å, also related by an inversion centre. The phenylphosphonium cations are known to form supramolecular synthons, the so-called phenyl embraces, through phenyl–phenyl interactions, and Dance *et al.* (Dance & Scudder, 1996; Scudder & Dance, 1998; Hasselgren *et al.*, 1997) have extensively analysed various kinds of multiple attractive phenyl interactions leading to chains and networks, such as those shown in Fig. 2.

The anions in (I) occupy the space between the chains and hold the chains together through multiple C—H$\cdots$O hydrogen bonds (Desiraju, 1996; Steiner & Desiraju, 1998; Desiraju & Steiner, 1999; Table 1). Atom O2($1 - x, 1 - y, 1 - z$) of the glutaconaldehyde anion is closer [4.161 (2) Å] to the P than O1($x, \frac{1}{2} - y, \frac{1}{2} + z$) [4.967 (2) Å] and the values of the C—O distances [C26—O1 = 1.230 (3) and C30—O2 = 1.249 (3) Å] suggest that O2 carries more negative charge and C26—O1 has more double bond character than C30—O2. Such an anion asymmetry due to the counterbalance of charges gives an optimal value for the BLA. There are two C—C single bonds and two C═C double bonds in the anion and a BLA of 0.021 (6) Å is calculated [(1.386 + 1.383)/2 − (1.363 + 1.364)/2].

The crystal structure of (I), as well as that of sodium glutaconaldehyde dihydrate (Muthuraman *et al.*, 1999), establishes that the BLA of polyene entities can reach, in the solid state, the ideal values observed at molecular level with polyenes onto which electron donor and acceptor groups have been grafted. Thus the hyperpolarizability of anion polyenes can be manipulated by the choice of the associated cations in crystalline materials.

Experimental

Compound (I) was prepared by the cation exchange reaction of potassium glutaconaldehyde with benzyltriphenylphosphonium chloride. Benzyltriphenylphosphonium chloride (0.001 mol) was dissolved in water (25 ml) and the pH was adjusted to 12 by adding 0.01 *N* aqueous NaOH. This solution was cooled to 263 K and solid potassium glutaconaldehyde (0.001 mol; Becher, 1988) was added with stirring. After 15 min of stirring, the cooling bath was removed. The solution was extracted immediately with CH_2Cl_2, dried over K_2CO_3 and evaporated to obtain a brown solid. Recrystallization was carried out by dissolution in ethyl acetate and treatment with activated carbon, followed by filtration and slow evaporation to obtain X-ray quality crystals of (I).

Crystal data

$C_{25}H_{22}P^+\cdot C_5H_5O_2^-$
$M_r = 450.52$
Monoclinic, $P2_1/c$
$a = 12.983$ (1) Å
$b = 11.435$ (1) Å
$c = 17.028$ (2) Å
$\beta = 95.35$ (2)°
$V = 2517.0$ (4) Å^3
$Z = 4$

$D_x = 1.189$ Mg m^{-3}
Ag $K\alpha$ radiation
Cell parameters from 5616 reflections
$\theta = 2.05$–$20.95°$
$\mu = 0.077$ mm^{-1}
$T = 296.2$ K
Needle, dark brown
0.29 × 0.16 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Data from $\varphi = 1°$, φ scans
10 920 measured reflections
5616 independent reflections
3489 reflections with $I > 2.6\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 20.95°$
$h = 0 \rightarrow 16$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F
$R = 0.054$
$wR = 0.051$
$S = 2.00$
3489 reflections
298 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00006|F_o|^2]$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.37$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4$^{\rm i}$—H3$^{\rm i}\cdots$O1	0.92	2.35	3.250 (3)	166
C8$^{\rm ii}$—H6$^{\rm ii}\cdots$O2	0.90	2.64	3.533 (3)	177
C11$^{\rm iii}$—H9$^{\rm iii}\cdots$O2	0.95	2.46	3.363 (3)	159
C16$^{\rm iv}$—H13$^{\rm iv}\cdots$O1	0.85	2.79	3.480 (3)	139
C18$^{\rm v}$—H15$^{\rm v}\cdots$O2	0.90	2.72	3.601 (3)	168
C19$^{\rm ii}$—H16$^{\rm ii}\cdots$O2	0.97	2.60	3.568 (3)	177
C19$^{\rm v}$—H17$^{\rm v}\cdots$O2	0.89	2.29	3.162 (2)	167
C23$^{\rm vi}$—H20$^{\rm vi}\cdots$O1	1.01	2.40	3.296 (3)	148

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $-x, 1 - y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

All H atoms were found by difference Fourier analyses and not refined. The C—H distances lie between 0.85 and 1.1 Å and the C—C—H angles close to their ideal value. An average displacement factor $U_{\rm iso} = 0.082$ Å^2 was attributed to each H atom.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *KappaCCD Server Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1084). Services for accessing these data are described at the back of the journal.

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