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Methyl, ethyl, isopropyl and *tert*-butyl 3-oxo-2-(triphenylphosphoranylidene)butyrates, a common pattern for a preferred conformation

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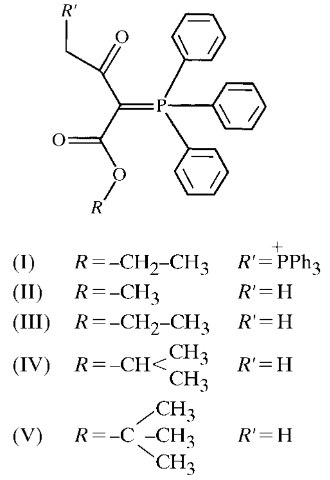
The crystal structures of four alkyl 3-oxo-2-(triphenylphosphoranylidene)butyrates, where the alkyl group is methyl ($C_{23}H_{21}O_3P\cdot0.5C_6H_6$), (II), ethyl ($C_{24}H_{23}O_3P$), (III), isopropyl ($C_{25}H_{25}O_3P$), (IV), or *tert*-butyl ($C_{26}H_{27}O_3P$), (V), show all of them to have the same conformation. They present a tetrahedral P atom and an sp^2 ylidic C atom, with the carbonyl groups adopting *anti* conformations with respect to the keto groups located close to the P atom. P—C—C—O torsion angles, bond lengths and angles indicate an effective electronic delocalization toward the keto groups. In each case, one H atom of the alkoxy group is close to one of the phenyl rings. These preferred conformations are evaluated as the result of attractive and repulsive intramolecular interactions.

Comment

Crystalline (3-carboethoxy-3-triphenylphosphoranylidene-2-oxopropanyl)triphenylphosphonium bromide, (I), has the conformation shown in the scheme below and its ^1H NMR spectrum shows that, in solution, the ethoxylic methyl-H atoms are diamagnetically shielded by a phenyl ring (Barahona *et al.*, 1998). Similar shielding has been observed with other non-ionic ylides, indicating that the preferred conformation of (I) is not dictated by the ionic phosphonium residue (Bachrach & Nitsche, 1994; Bacaloglu *et al.*, 1995; Abell *et al.*, 1982; Abell & Massy-Westropp, 1982). We have therefore examined the crystal structures of four non-ionic ylides with different alkoxy groups, *i.e.* with *R* = CH_3, (II), CH_2CH_3, (III), $CH(CH_3)_2$, (IV), and $C(CH_3)_3$, (V). One of these compounds, (III), has already been described by Abell *et al.* (1989) and is almost isostructural with (IV).

The molecular structures of compounds (II)–(V) are shown in Figs. 1 to 4, respectively, and selected dimensions are given in Tables 1 to 8. Ylides (I) to (V) have a nearly tetrahedral P atom with helically arranged phenyl rings. The Ph*A* phenyl rings bisect the planes formed by the ylidic C atoms and the carbonyl groups, while the Ph*C* phenyl rings present their faces to the alkoxy groups.



(I) $R = -CH_2-CH_3$ $R' = \overset{+}{P}Ph_3$
(II) $R = -CH_3$ $R' = H$
(III) $R = -CH_2-CH_3$ $R' = H$
(IV) $R = -CH(CH_3)_2$ $R' = H$
(V) $R = -C(CH_3)_3$ $R' = H$

The Ph—P=C and Ph—P—Ph angles, which are close to 109°, indicate a slightly distorted tetrahedral environment around the P centres, arguing against dsp^3-P hybridization. The major deviations from normal values are observed for the C1*C*—P1—C1*B* angles in the ethyl [101.2 (1)°], isopropyl [101.0 (2)°] and *tert*-butyl [100.2 (1)°] derivatives, probably as a result of a steric compression between the Ph*C* rings and the alkoxy groups, which pushes Ph*C* toward Ph*B*. The sums of the angles about the ylidic C atom are, in all cases, consistent with a near trigonal planar geometry and sp^2 hybridization.

The P—C1 bond lengths, which are in the range 1.740 (2)–1.757 (3) Å, are between the commonly accepted values for a single (~1.80–1.83 Å; Howells *et al.*, 1973) and a double bond (~1.63–1.73 Å; Howells *et al.*, 1973) as a consequence of

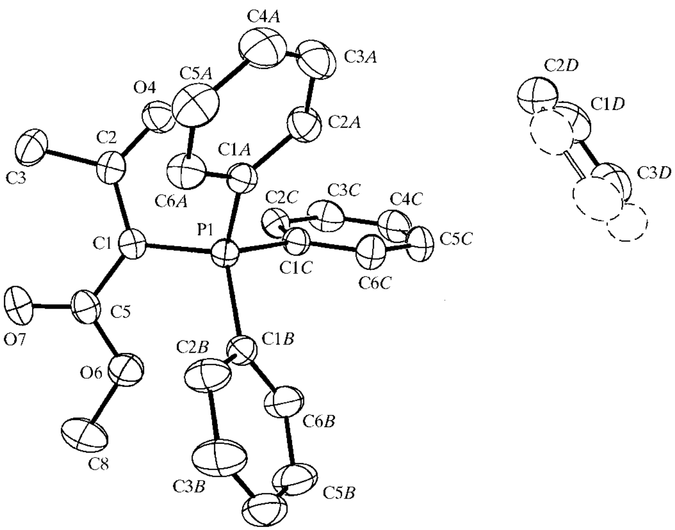


Figure 1
The molecular structure of (II) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

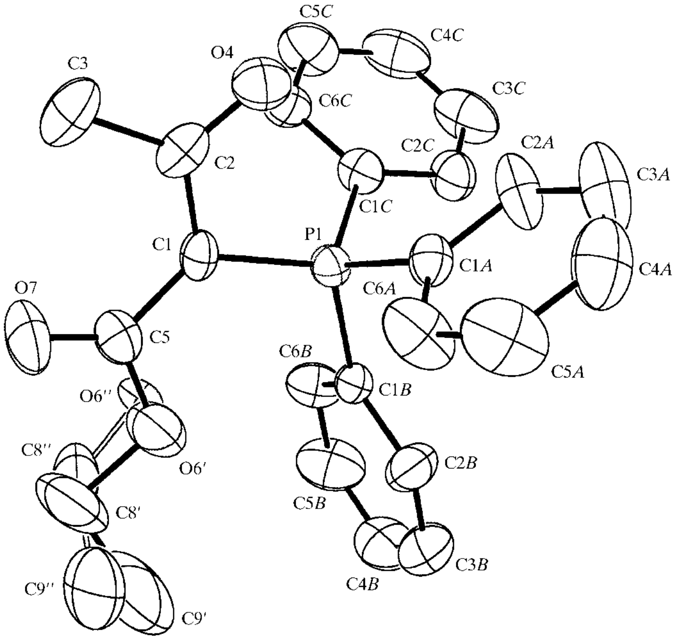


Figure 2
The molecular structure of (III) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

electronic delocalization, which also shortens the C1—C2 and C1—C5 bonds. Consistent with this, the keto C2=O4 bond is longer than in simple ketones. However, in the ester residue, C5=O7 is slightly shorter and C5—O6 slightly longer than in simple ketones and esters.

The P—C—C—O torsion angles are close to zero for the keto group and near to 180° for the ester carbonyl O atom, showing a better delocalization toward the keto group. The carbonyl groups adopt the *anti* conformation to reduce dipole–dipole repulsions and the O4 atoms of the keto groups are within 2.7–2.8 Å of the P atom, *i.e.* within the sum of the van der Waals radii, due to favourable interactions. As a result, the P1—C1—C2 angles are lower than the normal value of 120°. Electronic delocalization has also been seen in crystalline 6-ethoxycarbonyl-6-triphenylphosphoranylidene-5-oxohexanoic acid and 5-ethoxycarbonyl-5-triphenylphosphoranylidene-4-oxopentanoic acid (Abell *et al.*, 1988, 1991), although intramolecular hydrogen bonding could affect the conformations of these compounds.

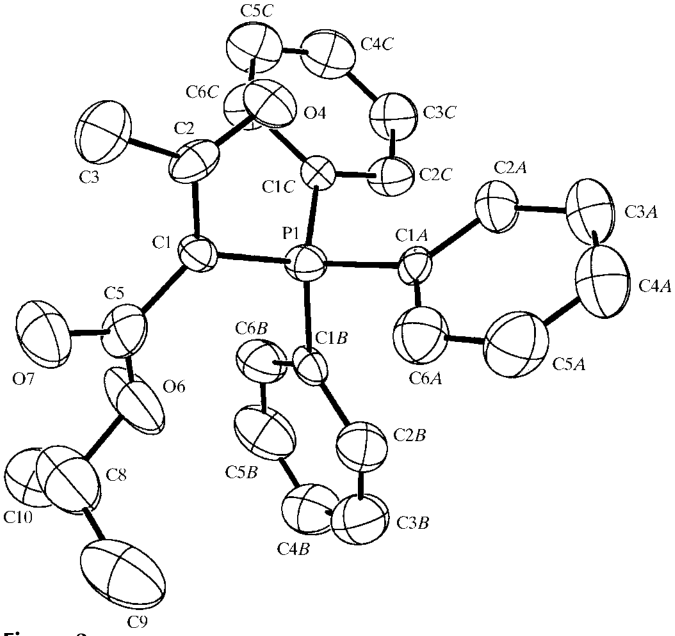


Figure 3
The molecular structure of (IV) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

The P1···O6 distances of *ca* 3 Å are consistent with a favourable interaction which could stabilize a preferred conformation. The crystal structures of (III), (IV) and (V) show a shorter than normal C8—C9 bond for the alkoxy groups [1.486 (11)–1.500 (3) Å, rather than ~1.53 Å (CRC Handbook of Chemistry and Physics, 1992)]. Again, a steric compression caused by neighbouring Ph*C* groups could be important (Seidl *et al.*, 1998). This question will be discussed elsewhere.

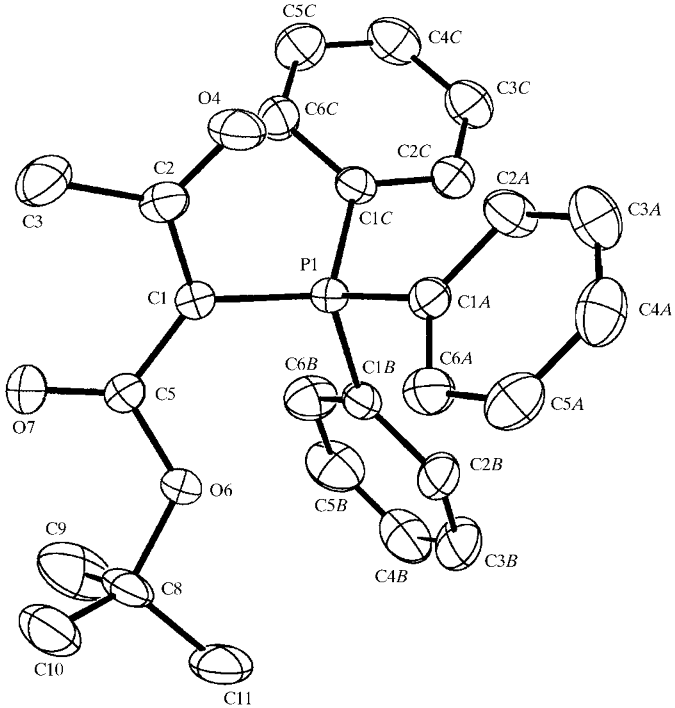


Figure 4
The molecular structure of (V) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

Experimental

The title stabilized ylides were prepared *via* a classical two-step method involving ester ylide C-acylation with acyl halides in order to form a phosphonium salt as the intermediate, followed by an acid–base reaction (transylidation) with a second equivalent of the ester ylide (Cristau & Plúnat, 1994). Thus, compounds (II)–(V) were obtained by the reaction of acetyl chloride with the corresponding carboalkoxymethylenetriphenylphosphorane. The general procedure used for the synthesis of each of the ylides was as follows: a solution of acyl chloride (20 mmol) in dry benzene (5 ml) was added slowly to carboalkoxymethylenetriphenylphosphorane (40 mmol) in dry benzene (100 ml) under a dry atmosphere. The stirred solution was kept at room temperature for 30 min and a white solid separated. After filtration of the carboalkoxymethyltriphenylphosphonium chloride, the solvent was evaporated to give an oil, which was recrystallized from ethyl acetate. Yields were in the range 70–90%.

Compound (II)

Crystal data

$C_{23}H_{21}O_3P\cdot0.5C_6H_6$
$M_r = 415.42$
Monoclinic, $P2_1/n$
$a = 10.698\ (5)$ Å
$b = 8.939\ (4)$ Å
$c = 23.026\ (11)$ Å
$\beta = 91.66\ (4)^\circ$
$V = 2200.9\ (17)$ Å^3
$Z = 4$
$D_x = 1.254$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.149$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.24 × 0.18 × 0.15 mm

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
4102 measured reflections
3892 independent reflections
2766 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\rm max} = 25^\circ$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 27$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.094$
$S = 1.059$
3892 reflections
274 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.721P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (II).

P1—C1	1.747 (2)	C2—O4	1.243 (2)
P1—C1*C*	1.802 (2)	C2—C3	1.510 (3)
P1—C1*A*	1.815 (2)	C5—O7	1.212 (2)
P1—C1*B*	1.819 (2)	C5—O6	1.349 (3)
C1—C2	1.428 (3)	O6—C8	1.435 (3)
C1—C5	1.441 (3)		
C1—P1—C1*C*	115.61 (10)	C1*A*—P1—C1*B*	108.24 (9)
C1—P1—C1*A*	108.97 (10)	C2—C1—C5	123.05 (19)
C1*C*—P1—C1*A*	106.92 (9)	C2—C1—P1	113.18 (15)
C1—P1—C1*B*	111.13 (10)	C5—C1—P1	123.63 (16)
C1*C*—P1—C1*B*	105.66 (10)		
P1—C1—C2—O4	12.0 (3)	P1—C1—C5—O7	162.47 (19)

Table 2
Contact distances (Å) for (II).

P1···O4	2.806 (2)	P1···O6	2.971 (2)

Compound (III)

Crystal data

$C_{24}H_{23}O_3P$
$M_r = 390.39$
Orthorhombic, *Pbca*
$a = 14.815\ (4)$ Å
$b = 16.226\ (5)$ Å
$c = 17.670\ (5)$ Å
$V = 4248\ (2)$ Å^3
$Z = 8$
$D_x = 1.221$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.150$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.27 × 0.20 × 0.16 mm

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
3911 measured reflections
3737 independent reflections
1966 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\rm max} = 25.02^\circ$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 20$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.124$
$S = 0.988$
3737 reflections
284 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.133P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

P1—C1	1.757 (3)	C5—O7	1.197 (4)
P1—C1*A*	1.804 (3)	C5—O6″	1.352 (7)
P1—C1*B*	1.817 (3)	C5—O6′	1.360 (8)
P1—C1*C*	1.821 (3)	O6′—C8′	1.457 (9)
C1—C2	1.434 (4)	C8′—C9′	1.494 (10)
C1—C5	1.444 (4)	O6″—C8″	1.466 (8)
C2—O4	1.248 (4)	C8″—C9″	1.497 (10)
C2—C3	1.507 (4)		
C1—P1—C1*A*	109.67 (14)	C1*B*—P1—C1*C*	101.19 (14)
C1—P1—C1*B*	113.78 (14)	C2—C1—C5	123.5 (3)
C1*A*—P1—C1*B*	107.20 (15)	C2—C1—P1	109.9 (2)
C1—P1—C1*C*	114.37 (15)	C5—C1—P1	126.4 (3)
C1*A*—P1—C1*C*	110.18 (15)		
P1—C1—C2—O4	1.7 (4)	P1—C1—C5—O7	170.7 (3)

Table 4
Contact distances (Å) for (III).

P1···O4	2.699 (4)	P1···O6″	3.026 (7)
P1···O6′	3.014 (8)		

Compound (IV)

Crystal data

$C_{25}H_{25}O_3P$
$M_r = 404.42$
Orthorhombic, *Pbca*
$a = 14.932\ (7)$ Å
$b = 16.343\ (6)$ Å
$c = 17.780\ (7)$ Å
$V = 4339\ (3)$ Å^3
$Z = 8$
$D_x = 1.238$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.149$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.22 × 0.19 × 0.16 mm

Data collection

Siemens $R3m$ diffractometer
$\omega/2\theta$ scans
4441 measured reflections
3824 independent reflections
1801 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.096$
$\theta_{\rm max} = 24.99°$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 21$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.160$
$S = 1.026$
3824 reflections
266 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 5.363]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (IV).

P1—C1	1.753 (5)	C2—C3	1.483 (7)
P1—C1*A*	1.795 (4)	C5—O7	1.221 (6)
P1—C1*B*	1.796 (5)	C5—O6	1.341 (6)
P1—C1*C*	1.818 (5)	O6—C8	1.436 (8)
C1—C5	1.429 (7)	C8—C10	1.469 (11)
C1—C2	1.443 (6)	C8—C9	1.486 (11)
C2—O4	1.244 (6)		
C1—P1—C1*A*	109.1 (2)	C1*B*—P1—C1*C*	101.0 (2)
C1—P1—C1*B*	114.0 (2)	C5—C1—C2	122.5 (5)
C1*A*—P1—C1*B*	107.5 (2)	C5—C1—P1	124.8 (4)
C1—P1—C1*C*	115.1 (2)	C2—C1—P1	112.2 (4)
C1*A*—P1—C1*C*	109.7 (2)		
P1—C1—C2—O4	0.9 (6)	P1—C1—C5—O7	174.7 (5)

Table 6
Contact distances (Å) for (IV).

P1···O4	2.703 (16)	P1···O6	3.023 (16)

Compound (V)

Crystal data

$C_{26}H_{27}O_3P$
$M_r = 418.45$
Monoclinic, $P2_1/n$
$a = 9.668$ (6) Å
$b = 13.975$ (8) Å
$c = 16.625$ (11) Å
$\beta = 94.69$ (5)°
$V = 2239$ (2) Å^3
$Z = 4$

$D_x = 1.241$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.147$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.30 × 0.20 × 0.18 mm

Data collection

Siemens $R3m$ diffractometer
$\omega/2\theta$ scans
4193 measured reflections
3945 independent reflections
3025 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\rm max} = 25°$

$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 19$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.101$
$S = 1.013$
3945 reflections
276 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.987P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 7
Selected geometric parameters (Å, °) for (V).

P1—C1	1.7400 (19)	C2—C3	1.504 (3)
P1—C1*A*	1.8058 (19)	C5—O7	1.206 (2)
P1—C1*C*	1.809 (2)	C5—O6	1.348 (2)
P1—C1*B*	1.812 (2)	O6—C8	1.472 (2)
C1—C2	1.429 (3)	C8—C9	1.500 (3)
C1—C5	1.449 (3)	C8—C11	1.507 (3)
C2—O4	1.243 (2)	C8—C10	1.522 (3)
C1—P1—C1*A*	112.87 (10)	C1*C*—P1—C1*B*	100.18 (9)
C1—P1—C1*C*	113.23 (9)	C2—C1—C5	123.22 (16)
C1*A*—P1—C1*C*	109.56 (8)	C2—C1—P1	110.90 (13)
C1—P1—C1*B*	112.60 (9)	C5—C1—P1	125.35 (13)
C1*A*—P1—C1*B*	107.57 (9)		
P1—C1—C2—O4	−2.7 (2)	P1—C1—C5—O7	−159.49 (18)

Table 8
Contact distances (Å) for (V).

P1···O4	2.707 (2)	P1···O6	3.012 (2)

Some problems were found in structure (III), which displayed a splitting of the non-aromatic ligand into two almost equally populated halves (Fig. 2). Because of the uneven quality of the diffraction data, and in order to systematize the refinement procedures used, the phenyl rings were refined under the assumption of a flat geometry and equal bond lengths. The only solvated structure was that of (II), with half a benzene molecule per formula unit. H atoms were included at idealized positions (C—H = 0.96 Å) and refined using a riding model for both coordinates and displacement parameters. The terminal methyl groups were, in addition, allowed to rotate as fixed bodies around the corresponding O—C or C—C axis.

For all compounds, data collection: *P3/P4-PC* (Siemens, 1993); cell refinement: *P3/P4-PC*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC*; software used to prepare material for publication: *PARST* (Nardelli, 1983) and the Cambridge Structural Database (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1566). Services for accessing these data are described at the back of the journal.

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