

Fig. 2. Stereo plot of the unit cell viewed down the a axis with b horizontal and c vertical.

this plane. The phenyl-group C atoms are coplanar to within 0.006 (3) Å and the attached C atoms lie within 0.018 (3) Å of this plane. The butyl group is less planar, as expected since there are no chemical factors disposing it toward planarity, but the C atoms lie within 0.034 (3) Å of the least-squares plane through them. The butyl group lies at 13.4 (4)° to the phenyl group and there is an angle of 40.8 (4)° between the tetrafluorophenyl and phenyl groups. This latter angle is substantially smaller than the 57.9° in 2,3,5,6-tetrafluorobiphenyl (TFB) (Goodhand & Hamor, 1978) and the 52.9° in 2,3,4,

5,6-pentafluorobiphenyl (PFB) (Brock, Naae, Goodhand & Hamor, 1978) but is similar to the 40.5° in 4'-*n*-butylbiphenyl-4-carbonitrile (Vani, 1983). These results suggest that the inter-ring torsion angle depends at least as much upon crystal-packing effects as upon intramolecular interactions. The inter-ring C—C bond length, 1.477 (4) Å, is shorter than those in TFB and PFB, 1.492 and 1.493 (3) Å, possibly as a consequence of the lower inter-ring torsion angle.

The C—C bonds in the tetrafluorophenyl ring range from 1.373 (4) to 1.398 (4) Å and in the phenyl group from 1.379 (4) to 1.403 (4) Å. In each case, the two shortest bonds are C(2)—C(3) and C(5)—C(6) though the differences are of marginal significance. The C—F bond lengths, average 1.339 Å, are similar to those in the aforementioned compounds.

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Structure of (*E*)-1,2-Dimesitylvinyne Bis(mesitylenecarboxylate)

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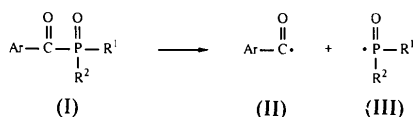
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Abstract. C₄₀H₄₄O₄, $M_r = 588.79$, triclinic, $P\bar{1}$, $a = 7.9092$ (5), $b = 10.9149$ (8), $c = 11.654$ (1) Å, $\alpha = 115.100$ (7), $\beta = 90.182$ (6), $\gamma = 108.597$ (5)°, $V = 852$ (4) Å³, $Z = 1$, $D_x = 1.147$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 5.4$ cm⁻¹, $F(000) = 316$, $T = 295$ K,

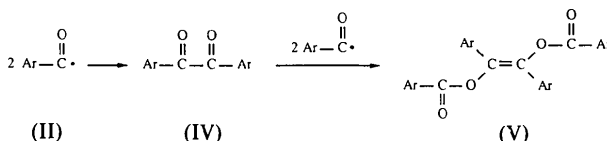
$R = 0.048$ for 2308 unique reflections with $I \geq 2.5\sigma(I)$. Owing to steric hindrance the dihedral angles between the trimethylphenyl groups and the planes of the bonds to the adjacent sp^2 C atoms are larger than usual. The central ethene fragment is twisted by 7.7 (3)°. The *para*-methyl groups are disordered, while the *ortho* groups are well localized.

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Introduction. Fairly recently, acylphosphine oxides (I) were introduced as effective free-radical-generating photoinitiators (Lechtken, Bueth & Hesse, 1980; Lechtken, Bueth, Jacobi & Trimborn, 1980; Heine, Rosenkranz & Rudolph, 1980). Meanwhile their photochemical behaviour has been studied extensively (Hageman, 1989). It has been established that these compounds undergo photo-induced α cleavage into acyl and phosphinoyl radicals as shown below.



On irradiation of 2,4,6-trimethylbenzoyldiphenylphosphine oxide [(I), Ar = mesityl = 2,4,6-trimethylphenyl; $\text{R}^1 = \text{R}^2 = \text{phenyl}$] in ethanol, with daylight, white crystals were formed, m.p. 592–593 K (from $\text{CH}_2\text{Cl}_2/\text{hexane}$). NMR and mass spectrometry indicated this compound to be a stilbene derivative formed presumably by the reaction sequence shown below, as proposed by Jacobi, Henne & Böttcher (1986).



Our spectroscopic data indicate compound (V) must be assigned the *E* configuration. Also, its melting point is considerably higher than that of an isomeric compound (509–512 K) obtained by reaction of 2,4,6-trimethylbenzoyl chloride with lithium (Horner & Dickerhof, 1983). The postulated structure was confirmed by the X-ray analysis described below.

Experimental. X-ray data for a bar-shaped transparent colourless crystal ($0.25 \times 0.10 \times 0.10$ mm), glued on top of a glass fibre, were collected on an Enraf-Nonius CAD-4F diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Lattice parameters and their e.s.d.'s were derived from the setting angles of 25 reflections with $7 < \theta < 25^\circ$. The space group was determined from the probability distribution of the normalized structure factors as $P\bar{1}$ ($\langle ||E|^2 - 1| \rangle = 1.029$). 6334 reflections [$\theta < 70^\circ$; $\omega/2\theta$ scan; $\Delta\omega = (0.60 + 0.15\tan\theta)^\circ$; $-9 \leq h \leq 8$, $-13 \leq k \leq 12$, $0 \leq l \leq 14$] were scanned, of which 3175 were unique ($R_{\text{int}} = 0.017$). Three reference reflections (032, $\bar{1}20$, $\bar{1}01$) showed a drift of 5% during the 94 h of exposure time, with occasional fluctuations of up to 12%. The intensities were corrected for Lp and the drift, but not for absorption. Variance $\sigma^2(I)$ was calculated

based on counting statistics plus a term $(PI)^2$, where $P (= 0.036)$ is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). The 2308 reflections with $I \geq 2.5\sigma(I)$ were used in the subsequent analysis. The structure was solved by direct methods (SHELXS86; Sheldrick, 1986) and refined on F by weighted full-matrix least-squares techniques with SHELX76 (Sheldrick, 1976) on a MicroVAX II. All non-H atoms were refined with anisotropic thermal parameters. The H atoms were located from a difference Fourier map at chemically reasonable positions, except for the two *para*-methyl groups C(9) and C(19) where more than three maxima appeared. Accordingly we assumed disorder in these two groups, and refined them as rigid groups with two possible positions each. The other H atoms were refined individually; the (isotropic) temperature factors for chemically equivalent H atoms were taken to be equal. Convergence was reached at $R = 0.048$ [$wR = 0.056$, $w = 1/\sigma^2(F)$, 267 parameters, $S = 0.32$, $(\Delta/\sigma)_{\text{ave}} = 0.02$, $(\Delta/\sigma)_{\text{max}} = 0.4$]. The final difference Fourier map did not show features outside the range -0.17 – 0.23 e \AA^{-3} . Fig. 1 shows the molecule with adopted numbering. Atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1.* Data on the geometry are assembled in Table 2. Scattering factors of Cromer & Mann (1968) were used. Geometrical calculations and illustrations were made with the programs PLATON and PLUTON of the EUCLID package (Spek, 1982).

* Lists of anisotropic thermal parameters, H-atom parameters, torsion angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53357 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

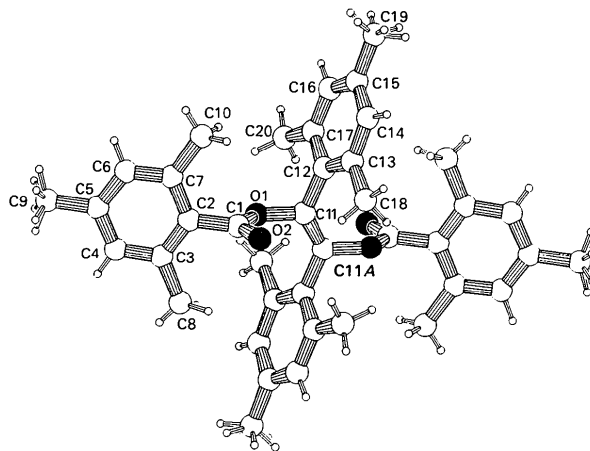


Fig. 1. View of the molecule, shown with both disordered methyl groups, with adopted numbering.

Table 1. Final coordinates and equivalent isotropic thermal parameters (\AA^2) of the non-H atoms with *e.s.d.'s* in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(1)	0.2090 (2)	0.5875 (1)	0.4577 (1)	0.0543 (5)
O(2)	0.1011 (2)	0.7411 (2)	0.4317 (2)	0.1045 (9)
C(1)	0.2156 (3)	0.6891 (2)	0.4187 (2)	0.0585 (7)
C(2)	0.3785 (3)	0.7214 (2)	0.3595 (2)	0.0535 (7)
C(3)	0.3667 (3)	0.6573 (2)	0.2267 (2)	0.0636 (8)
C(4)	0.5228 (4)	0.6911 (3)	0.1757 (3)	0.077 (1)
C(5)	0.6869 (4)	0.7857 (3)	0.2514 (3)	0.079 (1)
C(6)	0.6943 (3)	0.8486 (3)	0.3829 (3)	0.0718 (9)
C(7)	0.5432 (3)	0.8181 (2)	0.4394 (2)	0.0579 (7)
C(8)	0.1882 (5)	0.5540 (4)	0.1405 (3)	0.100 (1)
C(9)	0.8556 (4)	0.8210 (4)	0.1932 (4)	0.126 (2)
C(10)	0.5568 (4)	0.8883 (3)	0.5833 (2)	0.079 (1)
C(11)	0.0737 (2)	0.5553 (2)	0.5316 (2)	0.0539 (7)
C(12)	0.1284 (3)	0.6429 (2)	0.6736 (2)	0.0517 (6)
C(13)	0.0446 (3)	0.7404 (2)	0.7456 (2)	0.0587 (7)
C(14)	0.1080 (3)	0.8240 (2)	0.8759 (2)	0.0659 (8)
C(15)	0.2506 (3)	0.8164 (2)	0.9374 (2)	0.0645 (7)
C(16)	0.3295 (3)	0.7180 (2)	0.8644 (2)	0.0620 (8)
C(17)	0.2725 (3)	0.6312 (2)	0.7339 (2)	0.0541 (7)
C(18)	-0.1125 (4)	0.7546 (3)	0.6852 (3)	0.081 (1)
C(19)	0.3168 (4)	0.9106 (3)	1.0787 (2)	0.088 (1)
C(20)	0.3609 (4)	0.5239 (3)	0.6603 (2)	0.0704 (9)

Table 2. Bond distances (\AA) and angles ($^\circ$)

O(1)—C(1)	1.353 (3)	C(7)—C(10)	1.505 (3)
O(1)—C(11)	1.426 (2)	C(11)—C(11A)*	1.304 (3)
O(2)—C(1)	1.192 (3)	C(11)—C(12)	1.493 (3)
C(1)—C(2)	1.477 (3)	C(12)—C(13)	1.404 (3)
C(2)—C(3)	1.390 (3)	C(12)—C(17)	1.404 (3)
C(2)—C(7)	1.400 (3)	C(13)—C(14)	1.385 (3)
C(3)—C(4)	1.383 (4)	C(13)—C(18)	1.508 (4)
C(3)—C(8)	1.513 (5)	C(14)—C(15)	1.378 (3)
C(4)—C(5)	1.376 (5)	C(15)—C(16)	1.387 (3)
C(5)—C(6)	1.380 (4)	C(15)—C(19)	1.502 (3)
C(5)—C(9)	1.513 (5)	C(16)—C(17)	1.384 (3)
C(6)—C(7)	1.382 (4)	C(17)—C(20)	1.507 (4)
C(1)—O(1)—C(11)	118.7 (2)	O(1)—C(11)—C(11A)*	116.4 (2)
O(1)—C(1)—O(2)	122.3 (2)	O(1)—C(11)—C(12)	115.1 (2)
O(1)—C(1)—C(2)	110.6 (2)	C(11A)—C(11)—C(12)*	128.1 (2)
O(2)—C(1)—C(2)	127.1 (2)	C(11)—C(12)—C(13)	121.3 (2)
C(1)—C(2)—C(3)	120.2 (2)	C(11)—C(12)—C(17)	118.5 (2)
C(1)—C(2)—C(7)	118.8 (2)	C(13)—C(12)—C(17)	120.1 (2)
C(3)—C(2)—C(7)	121.0 (2)	C(12)—C(13)—C(14)	118.5 (2)
C(2)—C(3)—C(4)	118.1 (2)	C(12)—C(13)—C(18)	121.8 (2)
C(2)—C(3)—C(8)	120.9 (2)	C(14)—C(13)—C(18)	119.7 (2)
C(4)—C(3)—C(8)	121.0 (2)	C(13)—C(14)—C(15)	122.8 (2)
C(3)—C(4)—C(5)	122.4 (3)	C(14)—C(15)—C(16)	117.6 (2)
C(4)—C(5)—C(6)	118.2 (3)	C(14)—C(15)—C(19)	121.1 (2)
C(4)—C(5)—C(9)	121.4 (3)	C(16)—C(15)—C(19)	121.4 (2)
C(6)—C(5)—C(9)	120.4 (3)	C(15)—C(16)—C(17)	122.5 (2)
C(5)—C(6)—C(7)	121.9 (3)	C(12)—C(17)—C(16)	118.5 (2)
C(2)—C(7)—C(6)	118.3 (2)	C(12)—C(17)—C(20)	121.4 (2)
C(2)—C(7)—C(10)	121.3 (2)	C(16)—C(17)—C(20)	120.0 (2)
C(6)—C(7)—C(10)	120.4 (2)		

* The symmetry code for the A site is $-x, 1-y, 1-z$.

Discussion. Several dihedral angles between least-squares planes are of interest. Owing to the *ortho*-methyl groups, the phenyl rings cannot assume a planar configuration with the adjacent double bonds. The dihedral angle between the central butene fragment and the 2,4,6-trimethylphenyl ring attached to

it is $71.5 (2)^\circ$. In the Cambridge Structural Database (CSD), nine structures containing this complete fragment were found; the mean angle between the two planes was $60 (7)^\circ$. In the structure described here, the dihedral angle between the C(2)—C(1)—O(1)—O(2) plane and the 2,4,6-trimethylphenyl ring attached to it in the trimethylbenzoyloxy fragment is $81.4 (1)^\circ$. In the CSD this complete fragment was found in three structures; the mean angle between the two planes is $55 (9)^\circ$. Finally the central torsion angle around the double bond O(1)—C(11)—C(11A)—C(12A) is $-7.7 (3)^\circ$. These findings indicate some steric hindrance between the two trimethylphenyl rings. Other dihedral angles of interest are those between the C(2)—C(1)—O(1)—O(2) plane and the O(1)—C(11)—C(11A)—O(1A) plane $88.1 (2)^\circ$; between the trimethylphenyl ring in the trimethylbenzoyloxy group and the O(1)—C(11)—C(11A)—O(1A) plane $13.4 (2)^\circ$; and between the two non-equivalent trimethylphenyl rings $55.7 (1)^\circ$.

The occurrence of disorder in the two *para*-methyl groups is readily understood, as the local molecular environment has twofold symmetry. In our crude model this disorder was described by doubling both methyl groups into two components; each was found to have an occupancy factor of essentially 0.5 and a position more or less eclipsed to one of the adjacent *meta*-C atoms. On the other hand, the four *ortho*-methyl groups are well localized. Each group has one H atom eclipsed to the *meta*-C atom, the dihedral angles being 1, 12, 4 and 1° for C(4), C(6), C(14) and C(16), respectively.

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