

Atomic coordinates are given in Table 1 and bond lengths and angles in Fig. 1.*

Discussion. The $(\text{Bu}_2\text{SiO})_3$ molecule (Bu = *tert*-butyl) has crystallographic 32 (D_3) symmetry (Fig. 1), the molecular centre of mass being the special position $0,0,\frac{3}{4}$. The Si_3O_3 ring is, therefore, strictly planar. In other cyclotrisiloxane structures, deviations from planarity are slight (Bokii, Zakharova & Struchkov, 1972; Shklover, Bokii, Struchkov, Andrianov, Zavin & Svistunov, 1974*a,b*; Shklover, Adaasuren, Kotrelev, Zhdanova, Svistunov & Struchkov, 1980). Bond lengths and angles within this ring are also typical of such structures.

The compound is chemically very stable and yields well formed polyhedral crystals, giving narrow X-ray reflexions of significant intensity well beyond the 2θ limit to which data were collected. Thermal parameters are unusually low in comparison with other organo-silicon-oxygen and -nitrogen compounds studied in our laboratory (Table 1). Presumably the sterically bulky *tert*-butyl groups, which prevent a facile synthesis of $(\text{Bu}_2\text{SiO})_3$, are also responsible for these properties.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a thermal ellipsoid plot have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36613 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1982). **B38**, 1649–1652

Structure of (*E*)-3,4-Bis(*p*-methoxyphenyl)-2,2,5,5-tetramethyl-3-hexene

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(Received 3 December 1981; accepted 22 December 1981)

Abstract. $\text{C}_{24}\text{H}_{32}\text{O}_2$, $M_r = 352.52$, monoclinic, $P2_1/c$, $a = 10.792$ (3), $b = 11.930$ (3), $c = 8.326$ (6) Å, $\beta = 93.97$ (4)°, $Z = 2$, $D_c = 1.095$ Mg m⁻³. The molecule, itself centrosymmetric, lies at a symmetry centre with two statistically disordered orientations. The structure was refined with constraints on both geometrical and thermal parameters to an $R = 0.076$ on 1306 independent reflections classified as observed.

Introduction. In line with our interest in the geometries and conformations of highly strained molecules, we have undertaken the study of the crystal structure of

I thank Dr U. Klingebiel for supplying crystals, and the Verband der Chemischen Industrie for financial support. All computer programs were written by WC and Professor G. M. Sheldrick for a Data General S250 Eclipse mini-computer.

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the title compound (hereinafter DTBDMPE), to confirm experimentally the molecular conformation of (*E*)-2,2,5,5-tetramethyl-3,4-diphenyl-3-hexene (DTBDPE) recently determined by force-field calculations (Favini, Simonetta, Sottocornola & Todeschini, 1981). Colourless crystals were obtained by slow evaporation from saturated methyl ethyl ketone solution. A single crystal, sealed into a glass capillary to prevent sublimation, was mounted on a Syntex P1 diffractometer. The intensity data were collected up to $\theta = 23^\circ$, using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, graphite monochromator). A total of 1483 independent

reflections were measured and 1306 of them having a scan count greater than background were considered observed and used in crystal analysis. Each reflection was assigned a variance $\sigma^2(I) = \sigma^2(I)_{c.s.} + (0.03S)^2$, where S is the scan count. The intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption [$\mu(\text{Mo } K\alpha) = 0.07 \text{ mm}^{-1}$].

The *MULTAN* series of programs (Germain, Main & Woolfson, 1971) gave 14 peaks, of which the numbers 1, 2, 3, 4, 6, 7, 8, 9 were interpreted as the methoxyphenyl group, and the numbers 5, 11, 12, 13 as the *tert*-butyl one.

Peaks 10 and 14 near to the origin might represent the carbon of ethylene. However, neither peak produced a C atom in a reasonable position with respect to both the *tert*-butyl and the phenyl group. These preliminary calculations suggested disorder in the crystal, with two molecules located at the same symmetry centre, but with different orientations, so that the double bonds formed a cross (see Fig. 1; atoms numbered as shown in Fig. 2). This kind of disorder is not unusual, and we have already met two examples, namely (*E*)-3,4-diisopropyl-2,5-dimethyl-3-hexene (Casalone, Pilati & Simonetta, 1980) and salicylideneaniline (Destro, Gavezzotti & Simonetta, 1978).

After isotropic refinement including both *MULTAN* peaks 10 and 14, it was evident that the pair of molecules had local symmetry $2/m$, with the symmetry plane through the *tert*-butyl group. The only exception was the C atom of the methoxy group. Due to packing forces this atom cannot satisfy the requirement for $2/m$ symmetry and in fact the two molecules in each pair must have different conformations.

We then proceeded to anisotropic refinement with constraints, using the *ad hoc* program *CONSTR* (Bianchi, Pilati & Simonetta, 1978). We started with the geometry calculated for DTBDPE after substitution of the phenyl H in a *para* position with an O atom. The C—O bond length was assumed equal to 1.4 Å. From inertial coordinates, crystallographic coordinates for the pair of molecules were generated. A population factor of 0.5 assigned initially to each molecule was kept constant throughout the refinement. These initial

calculations assume local $2/m$ symmetry, provide a packing geometry with no short contacts and assign each *MULTAN* peak to one atom (peaks 10 and 14) or to the average of two atoms, one from each molecule in the pair.

We refined initially a rigid model varying only the orientation angles, a scale factor and the thermal tensors **T** and **L** (Schomaker & Trueblood, 1968). The methyl C was, however, refined as an independent atom with anisotropic thermal parameters. We then kept the orientation angles constant and refined C and O coordinates subject to the following constraints: the

Table 1. Atomic coordinates and equivalent or isotropic thermal parameters

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U (Å ²)
C(12)	0.5150 (3)	0.2837 (3)	0.3227 (5)	0.105 (3)
C(1A)	0.0062 (2)	0.0333 (3)	0.0658 (3)	0.047 (2)
C(2A)	-0.1002 (12)	0.0631 (5)	0.1780 (10)	0.061 (2)
C(3A)	-0.0635 (5)	0.1561 (5)	0.2968 (6)	0.092 (4)
C(4A)	-0.1124 (18)	-0.0376 (8)	0.2927 (14)	0.097 (3)
C(5A)	-0.2240 (5)	0.0945 (5)	0.0914 (6)	0.111 (4)
C(6A)	0.1316 (3)	0.0688 (3)	0.1390 (4)	0.048 (2)
C(7A)	0.1852 (4)	0.1688 (4)	0.0983 (5)	0.058 (2)
C(8A)	0.3003 (5)	0.2017 (5)	0.1650 (7)	0.063 (2)
C(9A)	0.3646 (6)	0.1347 (6)	0.2749 (8)	0.060 (2)
C(10A)	0.3131 (5)	0.0349 (5)	0.3172 (7)	0.070 (2)
C(11A)	0.1980 (4)	0.0027 (4)	0.2497 (5)	0.063 (2)
O(1A)	0.4810 (4)	0.1680 (4)	0.3425 (6)	0.071 (3)
C(1B)	0.0600 (2)	-0.0089 (3)	-0.0153 (3)	0.049 (2)
C(2B)	0.1053 (12)	-0.0612 (5)	-0.1741 (10)	0.061 (2)
C(3B)	0.2429 (5)	-0.0895 (5)	-0.1599 (6)	0.116 (4)
C(4B)	0.1020 (19)	0.0337 (7)	-0.3006 (14)	0.095 (3)
C(5B)	0.0344 (5)	-0.1643 (5)	-0.2361 (6)	0.092 (3)
C(6B)	0.1660 (3)	0.0410 (3)	0.0881 (4)	0.048 (2)
C(7B)	0.2237 (4)	-0.0182 (4)	0.2137 (5)	0.063 (2)
C(8B)	0.3211 (5)	0.0267 (5)	0.3093 (7)	0.071 (2)
C(9B)	0.3630 (6)	0.1328 (6)	0.2809 (8)	0.060 (2)
C(10B)	0.3070 (5)	0.1932 (5)	0.1566 (7)	0.062 (2)
C(11B)	0.2097 (4)	0.1475 (4)	0.0617 (5)	0.057 (2)
O(1B)	0.4617 (4)	0.1784 (4)	0.3770 (6)	0.072 (3)
H(31A)	-0.1360	0.1716	0.3647	0.117
H(32A)	-0.0472	0.2274	0.2390	0.117
H(33A)	0.0081	0.1356	0.3707	0.117
H(41A)	-0.1797	-0.0214	0.3665	0.119
H(42A)	-0.0313	-0.0491	0.3592	0.119
H(43A)	-0.1321	-0.1070	0.2295	0.119
H(51A)	-0.2852	0.1100	0.1746	0.130
H(52A)	-0.2561	0.0306	0.0229	0.130
H(53A)	-0.2147	0.1622	0.0251	0.130
H(7A)	0.1393	0.2194	0.0174	0.082
H(8A)	0.3390	0.2748	0.1342	0.087
H(10A)	0.3619	-0.0120	0.3984	0.095
H(11A)	0.1620	-0.0696	0.2833	0.087
H(31B)	0.2660	-0.1237	-0.2655	0.138
H(32B)	0.2609	-0.1486	-0.0760	0.138
H(33B)	0.2957	-0.0236	-0.1388	0.138
H(41B)	0.1306	0.0033	-0.4039	0.118
H(42B)	0.1597	0.0964	-0.2613	0.118
H(43B)	0.0162	0.0643	-0.3179	0.118
H(51B)	0.0699	-0.1893	-0.3389	0.113
H(52B)	-0.0552	-0.1452	-0.2604	0.113
H(53B)	0.0430	-0.2255	-0.1561	0.113
H(7B)	0.1953	-0.0961	0.2379	0.087
H(8B)	0.3635	-0.0160	0.4020	0.096
H(10B)	0.3389	0.2702	0.1364	0.086
H(11B)	0.1701	0.1920	-0.0299	0.081

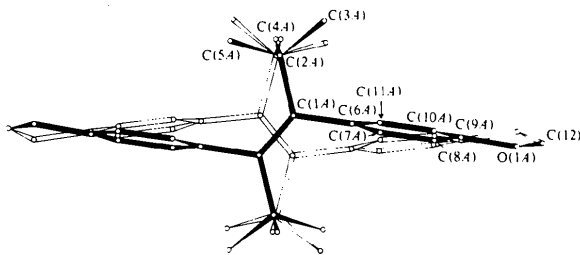


Fig. 1. A view of the statistically disordered molecule, showing the local $2/m$ [excluding C(12)] symmetry.

two molecules must be identical (with the usual exception of the methyl C) and the phenyl group has $mm2$ symmetry with the twofold axis coincident with C(6)–C(9). To allow rotation of the *tert*-butyl and the phenyl groups around the C(1)–C(2) and C(1)–C(6) axis respectively, two independent libration matrices $L_{tert-butyl}$ and L_{phenyl} were refined, though with only one **T** matrix.

At this stage all H atoms, except those of the methyl group, were introduced at calculated positions with isotropic thermal parameters obtained by adding 2 \AA^2 to the equivalent isotropic parameter of the corresponding C atom. The refinement was concluded when displacements of all heavy atoms were below one third of the standard deviation. H atoms were not refined.

Scattering factors from Cromer & Waber (1965) were used for C and O atoms, while those of Stewart, Davidson & Simpson (1965) were used for H. Refinement was based on $\sum w(|F_o| - k|F_c|)^2$ minimization, with weights $w = 4F_o^2/\sigma^2(F_o^2)$ for 1306 observed reflections and $w = 0.0$ otherwise. Final R and R_w were 0.076 and 0.071. The maximum value of the residual density was 0.35 e \AA^{-3} , and it was found in the proximity of C(8B) and C(11A). In Table 1 fractional coordinates and equivalent or isotropic thermal parameters are reported.*

Discussion. Fig. 2 shows the projection of molecule *A* on the plane C(1), C(4), C(6). Bond distances and angles are reported, together with standard deviations. A few values from theoretical DTBDPE geometry are also included. Since the two molecules have been assumed to be identical, small differences between equivalent parameters in molecules *A* and *B* calculated from data in Table 1 are simply due to numerical imprecision. Of course this is not true for the O(1)–C(12) distance, since C(12) has been refined with no constraints; the value in Fig. 2 is the average from the two experimental distances. Table 2 collects some theoretical and experimental parameters. It can be seen from Fig. 2 and Table 2 that the two structures show a strong similarity. No observed bond distance differs from the theoretical one by more than three standard deviations. The maximum values are for C(2)–C(3) [1.520 (12) observed *vs* 1.552 Å calculated] and for C(1)–C(2) [1.570 (10) observed *vs* 1.545 Å calculated]. Significant differences appear for some angles, particularly those involving atoms C(1) and C(2). This implies differences also in related torsional angles. The ethylenic fragment, as defined

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36612 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

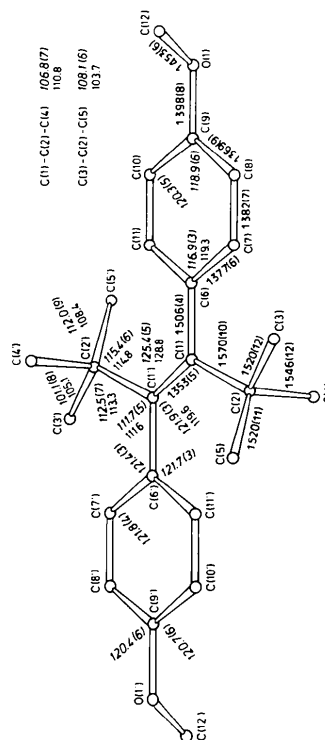


Fig. 2. The projection of the molecule *A* on the plane C(1), C(4), C(6) showing bond distances (Å) and angles ($^{\circ}$). The symbol *A* is omitted; a prime indicates the centrosymmetric part of the molecule. The C(12)–O(1) distance is the average of the values in molecules *A* and *B*. Values without e.s.d.'s refer to theoretical DTBDPE.

Table 2. Comparison of some parameters in DTBDMPE and in DTBDPE

	DTBDMPE	DTBDPE
Torsion angles ($^{\circ}$)		
C(6)–C(1)–C(2)–C(3)	21.7 (6)	20.5
C(6)–C(1)–C(2)–C(4)	–88.3 (9)	–97.5
C(6)–C(1)–C(2)–C(5)	146.5 (4)	139.3
C(6)–C(1)–C(1')–C(2')	–12.4 (6)	–1.8
C(7)–C(6)–C(1)–C(2)	–96.8 (4)	–94.6
Dihedral angle between phenyl and ethylenic groups ($^{\circ}$)		
	86.9 (2)	85.6

through atoms C(1), C(2), C(6) and their equivalents C(1'), C(2') and C(6'), appears to be less planar in the observed than in the theoretical structure (see Table 2). The molecular strain is minimized, both in DTBDPE and DTBDMPE, by appropriate variations in a few geometrical parameters, namely C(1)–C(1'), C(1)–C(2) and C(1)–C(6) bond lengths and bond angles centred on C(1) and C(2). The most important feature is the orthogonality between the phenyl and ethylenic groups.

The authors are grateful to Professor G. Olah for the gift of a sample of the title compound.

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Acta Cryst. (1982). **B38**, 1652–1654

Structure of a New Triterpene Oxide, 3-Filicanone

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(Received 21 October 1981; accepted 22 December 1981)

Abstract. 21-Isopropyl-4 β ,5 β ,9 β ,13 α ,14 β ,17 α -hexamethylperhydrocyclopenta[*a*]chrysen-3-one C₃₀H₅₀O, monoclinic, *P*2₁, *a* = 13.538 (6), *b* = 6.342 (3), *c* = 14.797 (7) Å, β = 96.04 (15)°, *V* = 1263.3 Å³, *D_c* = 1.12 g cm⁻³, *Z* = 2, m.p. = 521–522 K, *F*(000) = 576, *M_r* = 426.7, λ (Mo *K* α) = 0.71069 Å; *R* = 0.09 for 1703 measured reflections (791 observed). The structure has been solved by direct methods and refined by full-matrix least-squares procedures with isotropic *B* values. The molecule has a C(3) oxygen and consists of four six-membered rings and one five-membered ring, all *trans* fused and giving a stretched, long form of the molecule. There are five axial methyl groups in positions 5,9,13,14,17 and one equatorial in position 4. The five-membered ring has an isopropyl substituent at C(21). The name accordingly is 3-filicanone. The interatomic distances and angles are of normal values. Non-bonded interaction between methyl groups in 1,3 positions causes some bending and slight twisting along the major axis of the molecule.

Introduction. The title compound, believed to be a friedelin-type triterpene isolated from the stem bark of *Strychnos dolichothyrsa*, was selected for a three-dimensional X-ray study to elucidate the molecular constitution. The crystals were kindly supplied by Dr R. Verpoorte from Gorleus Laboratories at the State University of Leiden. The molecular formula was established as C₃₀H₅₀O by means of high-resolution mass spectrometry (Verpoorte, 1978). The single-crystal X-ray structure determination shows that the structure of this triterpene is a '3-keto-oxide'.

A well formed, transparent, non-twinned, prismatic *b* crystal was used for data collection on a Picker automatic four-circle diffractometer. Intensities were measured for 1796 reflections ($2\theta_{\max}$ = 45.0°) using

graphite-monochromatized Mo *K* α radiation and the $\omega/2\theta$ scan technique. Twice the normal background counting time was chosen (60 s) to minimize the influence of fluctuations in the background, and hence give as good standard deviations for the weakest reflections as possible. Three reflections were monitored periodically to ensure a common scale, and the intensities varied by less than 2% during the data collection. Reflections with $I < 2\sigma(I)$ were considered unobserved, giving a total of 791 observed reflections after data work-up. The low number of observed reflections is caused by the small size of the crystal (0.3 × 0.12 × 0.08 mm) which had to be selected because of severe twinning in most of the crystals. The intensities of all reflections were placed on an absolute scale, and normalized structure factors were derived. All calculations were performed on a Cyber 74 computer using standard programs (Groth, 1973).

The scattering factors for C and O were taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965). No absorption correction was applied.

Phase angles for the individual E_{hkl} 's were derived from the structure-factor magnitudes by means of a multiresolution tangent-formula approach, *MULTAN* (Germain, Main & Woolfson, 1971). The calculated figures of merit, however, did not make a good discrimination possible. The molecule was initially supposed to consist of five six-membered rings and to be highly symmetrical and the solution was not straightforward. When it was realized that the molecule consisted of four six-membered rings and one substituted five-membered ring and the direction of the longest axis of the molecule in the cell was determined, a solution was eventually found and refined smoothly to a conventional *R* value of 0.11. The positions for all