F1*A*—C1—F1*B*	99.5 (6)	F8*A*—C8—F8*C*	107.2 (4)
F1*A*—C1—F1*C*	115.2 (6)	F8*B*—C8—F8*C*	110.6 (5)
F1*B*—C1—F1*C*	101.8 (5)	F8*D*—C8—F8*E*	99. (1)
F1*D*—C1—F1*E*	114.6 (7)	F8*D*—C8—F8*F*	121. (2)
F1*D*—C1—F1*F*	98.0 (5)	F8*E*—C8—F8*F*	100. (2)
F1*E*—C1—F1*F*	107.6 (7)	C3—C9—C10	119.7 (2)
C1—C2—C3	128.9 (2)	C3—C9—C14	121.1 (2)
C1—C2—F2	109.5 (2)	C10—C9—C14	119.2 (2)
C3—C2—F2	121.6 (2)	C9—C10—C11	120.6 (2)
C2—C3—C4	120.1 (2)	C10—C11—C12	119.6 (2)
C2—C3—C9	123.4 (2)	C11—C12—C13	120.0 (2)
C4—C3—C9	116.5 (2)	C12—C13—C14	120.6 (2)
C3—C4—C5	176.1 (2)	C9—C14—C13	119.9 (2)
C4—C5—C6	176.2 (2)	C6—C15—C16	120.9 (2)
C5—C6—C7	120.0 (2)	C6—C15—C20	120.0 (2)
C5—C6—C15	116.9 (2)	C16—C15—C20	119.2 (2)
C7—C6—C15	123.1 (2)	C15—C16—C17	119.7 (3)
C6—C7—C8	128.8 (2)	C16—C17—C18	120.4 (2)
C6—C7—F7	121.6 (2)	C17—C18—C19	120.4 (2)
C8—C7—F7	109.6 (2)	C18—C19—C20	119.3 (3)
C7—C8—F8*A*	112.8 (3)	C15—C20—C19	121.1 (2)

C1—C2—C3—C4	2.0 (4)	C4—C5—C6—C7	−177 (4)
C1—C2—C3—C9	−178.9 (2)	C4—C5—C6—C15	6 (4)
F2—C2—C3—C4	−175.2 (2)	C5—C6—C7—C8	0.5 (4)
F2—C2—C3—C9	4.0 (4)	C5—C6—C7—F7	−176.3 (2)
C2—C3—C4—C5	169 (4)	C15—C6—C7—C8	177.7 (3)
C9—C3—C4—C5	−10 (4)	C15—C6—C7—F7	0.9 (4)
C2—C3—C9—C10	−144.7 (2)	C5—C6—C15—C16	−144.9 (2)
C2—C3—C9—C14	35.8 (3)	C5—C6—C15—C20	33.9 (3)
C4—C3—C9—C10	34.5 (3)	C7—C6—C15—C16	37.8 (4)
C4—C3—C9—C14	−145.0 (2)	C7—C6—C15—C20	−143.4 (3)
C3—C4—C5—C6	−175 (3)		

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974)

Data collection: *CAD*-4 (Enraf–Nonius, 1977). Cell refinement: *CAD*-4. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods (*MULTAN*; Main *et al.*, 1980). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* (*MolEN*).

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,3,5-Tri-*tert*-butyl-5-(1,3,5-tri-*tert*-butyl-4-oxo-2,5-cyclohexadienyl)methylbicyclo[4.1.0]hept-3-en-2-one, a Highly Hindered Propane

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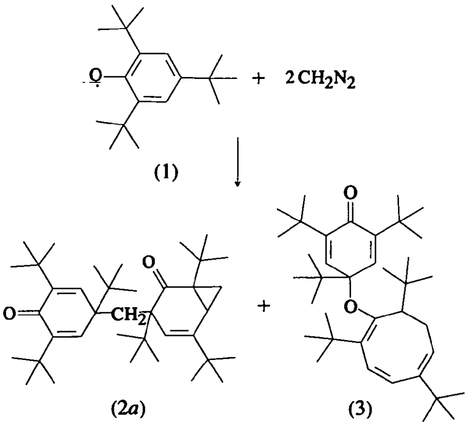
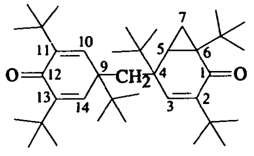
Abstract

The title compound, $C_{38}H_{62}O_2$, is one of the reaction products of diazomethane with two equivalents of 2,4,6-tri-*tert*-butylphenoxyl. In the crystal structure, the cyclopropane ring is almost perpendicular to the basal plane of the boat-configured cyclohexenone ring.

Comment

2,4,6-Tri-*tert*-butylphenoxyl, (1), reacts with diazomethane to give two formal 1:1 addition products, (2) and (3), after elimination of N_2 (Müller, Renner & Rieker, 1968; Rieker, Renner & Müller, 1969). The structures of (2*a*) and (3) were originally derived from chemical reactivity and ^{1}H NMR (60 MHz) also using deuteriated analogues of (2) and (3) obtained from CD_2N_2 or 3,5-dideuterio-2,4,6-tri-*tert*-butylphenoxyl.





(2*b*)

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The ^{1}H-NMR spectra, however, cannot distinguish reliably between structures (*2a*) and (*2b*). Therefore, a crystal structure determination was performed which proved the structure to be (*2b*) .

The conformation of the cyclohexenone ring C1–C6 is characterized by two torsion angles close to 0°, and it is evident that the ring approximates to a boat form (Boeyens, 1978) in which C1 and C4 are the out-of-plane atoms (Fig. 2). This is confirmed by the puckering amplitude Q = 0.458 (2) Å and the parameters θ = 93.5 (3) and φ = 11.4 (3)° (Spek, 1990, 1996). The deviations from the least-squares plane C2,C3,C5,C6 are minor with values of 0.046 (1) (C2), −0.048 (1) (C3), 0.042 (1) (C5) and −0.040 (1) Å (C6). The plane of the three-membered ring (C5,C6,C7) is almost perpendicular to the former one with an interplanar angle of 88.5 (1)°. In the C9–C14 ring, the atoms C10,C11,C13,C14 form a plane with minor deviations of 0.015 (1) (C10), −0.015 (1) (C11), 0.015 (1) (C13) and −0.015 (1) Å (C14). The distances of C9, C12 and O2 to this plane are −0.142 (3), −0.068 (3) and −0.171 (4) Å, respectively. The planes C9,C10,C14 and C11,O2,13 are at angles of 9.8 (1) and 4.9 (1)° to the C10,C11,C13,C14 plane. As a result of the sterical requirements of the *tert*-butyl groups at C4 and C9, the bonds C4—C8 and C8—C9 are lengthened [1.576 (2) and 1.569 (2) Å] and the angle C4—C8—C9 is remarkably large at 127.9 (2)° (*cf*. Winter, Moosmayer & Rieker, 1982).

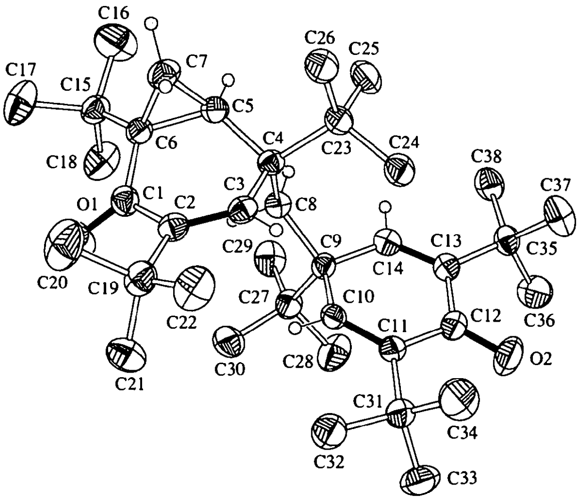

Fig. 1. Structure of (*2b*) showing the atomic labelling. Displacement ellipsoids are drawn at the 50% probability level. H-atom positions of the *tert*-butyl groups are omitted for clarity. Double bonds are shown as filled lines.

A redetermination of the NMR spectrum, using 250 and 400 MHz, agrees well with the X-ray structure determination. The earlier ^{1}H-NMR assignments (Müller *et al*., 1968; Rieker *et al*., 1969) could be confirmed. The protons H8/H8 as well as H10/H14 are magnetically non-equivalent owing to chirality in the bicyclic system. The *tert*-butyl groups were not assigned; however, dynamic NMR experiments show that three of them are rotationally hindered.

The assignments of the ^{13}C NMR are based on chemical shift considerations, 2D, and spin-echo experiments. δ (solvent: $CDCl_3$) = 19.53 (C7), 26.25, 27.47, 27.72, 29.30, 29.39, 29.74 (6 ^{t}Bu), 29.48 (C5), 31.37, 35.07, 35.15, 35.28, 36.83, 39.98, 43.66, 45.87, 48.17 (6 ^{t}Bu, C4, C6, C9), 52.69 (C8), 135.65 (C3), 143.72, 148.11 (C10, C14), 145.61, 147.02, 147.47 (C2, C11, C13), 186.05 (C12), 202.01 (C1).

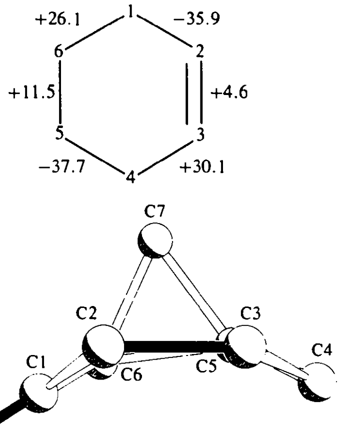

Fig. 2. The cyclohexenone ring with endocyclic torsion angles, and a side view of the cyclohexenone ring.

Experimental

The title compound is one of the products of the reaction of 2,4,6-tri-*tert*-butylphenoxyl with diazomethane (Müller *et al*., 1968; Rieker *et al*., 1969).

Crystal data

$C_{38}H_{62}O_2$
M_r = 550.88
Monoclinic
$P2_1/n$
a = 16.757 (2) Å
b = 11.099 (2) Å
c = 20.165 (2) Å
β = 110.73 (1)°
V = 3507.6 (8) Å^3
Z = 4
D_x = 1.043 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–10°
μ = 0.062 mm^{-1}
T = 211 (2) K
Block
0.50 × 0.45 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
6847 measured reflections
6097 independent reflections
3967 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.0243

θ_{max} = 25°
h = 0 → 19
k = 0 → 13
l = −23 → 22
3 standard reflections monitored every 150 reflections
frequency: 3600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0451$
$wR(F^2) = 0.1137$
$S = 1.011$
6095 reflections
388 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 1.4863P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.0$
$\Delta\rho_{\text{max}} = 0.191$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.167$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.8366 (1)	0.1187 (1)	0.36277 (9)	0.0571 (5)
O2	0.3620 (1)	0.5160 (1)	0.2942 (1)	0.0597 (5)
C1	0.8059 (1)	0.1405 (2)	0.4082 (1)	0.0323 (5)
C2	0.7877 (1)	0.2679 (2)	0.4228 (1)	0.0296 (4)
C3	0.7184 (1)	0.2894 (2)	0.43870 (9)	0.0273 (4)
C4	0.6595 (1)	0.1936 (2)	0.44837 (9)	0.0261 (4)
C5	0.7128 (1)	0.0799 (2)	0.47640 (9)	0.0294 (4)
C6	0.7847 (1)	0.0436 (2)	0.4500 (1)	0.0288 (4)
C7	0.8028 (1)	0.0807 (2)	0.5269 (1)	0.0367 (5)
C8	0.5956 (1)	0.1501 (2)	0.37414 (9)	0.0272 (4)
C9	0.5250 (1)	0.2257 (2)	0.31715 (9)	0.0272 (4)
C10	0.5497 (1)	0.3528 (2)	0.31060 (9)	0.0274 (4)
C11	0.4990 (1)	0.4488 (2)	0.3016 (1)	0.0283 (4)
C12	0.4124 (1)	0.4319 (2)	0.3058 (1)	0.0341 (5)
C13	0.3890 (1)	0.3111 (2)	0.3250 (1)	0.0287 (4)
C14	0.4425 (1)	0.2197 (2)	0.3300 (1)	0.0295 (4)
C15	0.7985 (1)	−0.0878 (2)	0.4323 (1)	0.0351 (5)
C16	0.7722 (2)	−0.1777 (2)	0.4777 (2)	0.0705 (8)
C17	0.8933 (2)	−0.1082 (2)	0.4458 (1)	0.0597 (7)
C18	0.7462 (2)	−0.1155 (2)	0.3549 (1)	0.0521 (6)
C19	0.8476 (1)	0.3657 (2)	0.4142 (1)	0.0379 (5)
C20	0.9409 (1)	0.3258 (2)	0.4511 (2)	0.0626 (7)
C21	0.8299 (2)	0.3871 (2)	0.3351 (1)	0.0527 (6)
C22	0.8359 (1)	0.4839 (2)	0.4485 (1)	0.0502 (6)
C23	0.6189 (1)	0.2367 (2)	0.5044 (1)	0.0317 (5)
C24	0.5706 (1)	0.3563 (2)	0.4844 (1)	0.0358 (5)
C25	0.5565 (1)	0.1423 (2)	0.5133 (1)	0.0444 (6)
C26	0.6893 (1)	0.2557 (2)	0.5771 (1)	0.0446 (6)
C27	0.5091 (1)	0.1625 (2)	0.2407 (1)	0.0362 (5)
C28	0.4288 (2)	0.2156 (2)	0.1841 (1)	0.0589 (7)
C29	0.4950 (2)	0.0264 (2)	0.2437 (1)	0.0473 (6)
C30	0.5844 (2)	0.1846 (2)	0.2162 (1)	0.0483 (6)
C31	0.5246 (1)	0.5754 (2)	0.2862 (1)	0.0336 (5)
C32	0.6159 (1)	0.5781 (2)	0.2869 (1)	0.0487 (6)
C33	0.4664 (2)	0.6151 (2)	0.2115 (1)	0.0547 (6)
C34	0.5184 (2)	0.6660 (2)	0.3414 (1)	0.0567 (7)
C35	0.3046 (1)	0.2964 (2)	0.3383 (1)	0.0327 (5)
C36	0.2286 (1)	0.3252 (2)	0.2707 (1)	0.0546 (7)
C37	0.3043 (2)	0.3789 (2)	0.3988 (1)	0.0519 (6)
C38	0.2929 (1)	0.1673 (2)	0.3591 (1)	0.0433 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.222 (2)	C6—C7	1.527 (3)
O2—C12	1.225 (2)	C6—C15	1.539 (3)
C1—C2	1.497 (3)	C8—C9	1.569 (2)
C1—C6	1.484 (3)	C9—C10	1.490 (3)
C2—C3	1.332 (3)	C9—C14	1.495 (3)
C2—C19	1.530 (3)	C9—C27	1.628 (3)
C3—C4	1.510 (3)	C10—C11	1.334 (3)
C4—C5	1.534 (3)	C11—C12	1.496 (3)
C4—C8	1.576 (2)	C11—C31	1.532 (3)
C4—C23	1.586 (2)	C12—C13	1.486 (3)
C5—C7	1.490 (3)	C13—C14	1.334 (3)
C5—C6	1.533 (3)	C13—C35	1.539 (3)
O1—C1—C2	120.1 (2)	C7—C6—C15	119.9 (2)
O1—C1—C6	122.1 (2)	C5—C7—C6	61.1 (1)
C2—C1—C6	117.8 (2)	C4—C8—C9	127.9 (2)
C1—C2—C3	118.2 (2)	C8—C9—C10	114.2 (2)
C1—C2—C19	117.4 (2)	C8—C9—C14	110.7 (2)
C3—C2—C19	124.3 (2)	C8—C9—C27	106.9 (1)
C2—C3—C4	124.8 (2)	C10—C9—C14	111.2 (2)
C3—C4—C5	107.7 (2)	C10—C9—C27	106.4 (2)
C3—C4—C8	110.4 (1)	C14—C9—C27	107.0 (2)
C3—C4—C23	110.2 (2)	C9—C10—C11	125.7 (2)
C5—C4—C8	102.1 (1)	C10—C11—C12	118.5 (2)
C5—C4—C23	109.1 (1)	C10—C11—C31	123.3 (2)
C8—C4—C23	116.8 (2)	C12—C11—C31	118.2 (2)
C4—C5—C6	121.0 (2)	O2—C12—C11	120.8 (2)
C4—C5—C7	124.3 (2)	O2—C12—C13	120.7 (2)
C6—C5—C7	60.7 (1)	C11—C12—C13	118.6 (2)
C1—C6—C5	112.5 (2)	C12—C13—C14	118.3 (2)
C1—C6—C7	112.3 (2)	C12—C13—C35	119.0 (2)
C1—C6—C15	118.0 (2)	C14—C13—C35	122.7 (2)
C5—C6—C15	122.0 (2)	C9—C14—C13	126.1 (2)
C7—C6—C5	58.3 (1)		

All H atoms were refined using a riding model with *SHELXL*93 (Sheldrick, 1993) defaults. The isotropic U_{H} parameters were set to 1.2 and 1.5 times the equivalent isotropic displacement parameters of the non-H atoms they are attached to.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADSHEL* (Kopf & Rübcke, 1993). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: SK1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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