CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Tome IV. Birmingham: Kynoch Press. (Distributeur actuel Kluwer Academic Publishers, Dordrecht.)
DELAGE, C., H'NAÏFI, A. & GOURSOLLE, M. (1986). *C.R. Acad. Sci. Sér* II, **303**, 1645–1650.
DELAGE, C., H'NAÏFI, A., GOURSOLLE, M. & CARPY, A. (1986). *C.R. Acad. Sci. Sér* II, **302**, 219–222.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. de York, Angleterre, et de Louvain, Belgique.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1988). C**44**, 2189–2191

Structure of *syn*-1-*tert*-Butyl-4-(4-*tert*-butylcyclohexylidene)cyclohexane

BY R. MARIEZCURRENA*

Laboratorio de Cristalografía, Facultad de Química, Gral. Flores 2124, *Montevideo, Uruguay*

AND L. FORNARO

Cátedra de Física, Facultad de Química, Gral. Flores 2124, *Montevideo, Uruguay*

(*Received* 9 *December* 1987; *accepted* 24 *June* 1988)

Abstract. $C_{20}H_{36}$, $M_r = 276\cdot3$, triclinic, $P\bar{1}$, $a = 6\cdot212\,(3)$, $b = 11\cdot39\,(4)$, $c = 15\cdot17\,(3)$ Å, $\alpha = 117\cdot5\,(8)$, $\beta = 72\cdot56\,(2)$, $\gamma = 102\cdot2\,(6)°$, $V = 905\,(8)$ Å^3, $Z = 2$, $D_x = 1\cdot23$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot276$ mm^{-1}, $F(000) = 312$, $T = 294$ K, $R = 0\cdot044$ for 1534 reflections. The two cyclohexane rings adopt differently distorted chair conformations. All bond distances and angles within the molecule are normal. The crystal packing is mainly stabilized by van der Waals forces.

Introduction. An X-ray structural investigation of the title compound has been carried out in order to elucidate the influence of the *tert*-butyl groups on the geometry of the bicyclohexylidene. The structure of the present compound is of interest because it forms part of the mechanism studies of 'ene' reactions of alkenes with singlet oxygen (Asveld & Kellogg, 1982).

Experimental. Preliminary precession and Weissenberg photographs of colorless acicular crystals, $0\cdot15 \times 0\cdot30 \times 0\cdot40$ mm, indicate crystals to be triclinic, $P\bar{1}$. Lattice constants were determined from the photographic data and confirmed by diffractometer measurements. A Picker computer-controlled four-circle diffractometer with graphite monochromator ($\lambda = 0\cdot71096$ Å) was used for measurements of unit-cell constants and for data collection. Scan parameters: θ–2θ scan, scan width $(1\cdot0 + 0\cdot692\tan\theta)°$, background estimated by stationary counting at $\pm0\cdot8°2\theta$ from the peak maxima; speed 1° min^{-1}; h 0 to 6, k -12 to 11, l -15 to 16; no significant variation of three standard reflections; Lorentz and polarization corrections; neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with considerable difficulty. The E maps obtained from the better sets did not reveal atom positions with chemical sense. One set exhibited 'double peaks' in almost all positions. All these 'double peaks' had equal shifts with a vector $\Delta s = 0\cdot077\mathbf{a} + 0\cdot038\mathbf{b} + 0\cdot040\mathbf{c}$. This vector was used to locate most of the C-atom positions. Subsequent $\Delta\rho$ maps completed the structure. Full-matrix least-squares refinement on $|F|$ with *SHELX*76 (Sheldrick, 1976) with C atoms anisotropic and an isotropic thermal parameter for H atoms converged to $R = 0\cdot044$, $wR = 0\cdot048$ for 1650 observed reflections $[I > 3\sigma(I)]$ and 326 parameters. Max. Δ/σ in last least-squares cycle $<0\cdot002$. Min. and max. $\Delta\rho$ $-0\cdot10$ and $+0\cdot12$ e Å^{-3}.

Discussion. Final atomic parameters for non-H atoms are given in Table 1.† The structure of the molecule is shown in Fig. 1. The bond lengths and angles are listed in Table 2. The molecule consists of two *tert*-butyl-substituted cyclohexane rings, linked by a double bond. The cyclohexane rings show the chair conformation.

---

* To whom correspondence should be addressed.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51187 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/88/122189-03$03.00

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors for non*-H *atoms with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
C1	3750 (3)	2143 (2)	6791 (1)	3·92 (10)
C2	5159 (4)	1240 (2)	6825 (2)	4·77 (12)
C3	3788 (4)	67 (2)	7016 (2)	4·80 (13)
C4	2306 (3)	9253 (2)	6252 (2)	3·90 (10)
C5	720 (4)	197 (2)	6371 (2)	4·36 (11)
C6	1982 (4)	1387 (2)	6178 (2)	4·43 (12)
C7	1126 (4)	7934 (2)	6289 (2)	4·97 (12)
C8	2902 (5)	7067 (3)	6137 (3)	7·40 (19)
C9	−604 (6)	8153 (4)	7292 (3)	7·80 (20)
C10	−67 (6)	7171 (3)	5411 (3)	7·31 (19)
C11	4183 (3)	3466 (2)	7171 (2)	4·23 (11)
C12	2935 (4)	4390 (2)	7088 (2)	4·78 (12)
C13	1963 (4)	5473 (2)	8131 (2)	4·31 (12)
C14	3781 (3)	6277 (2)	8725 (2)	4·15 (11)
C15	5062 (4)	5320 (2)	8784 (2)	4·90 (12)
C16	6017 (4)	4243 (2)	7736 (2)	5·05 (12)
C17	2876 (4)	7432 (2)	9767 (2)	4·63 (11)
C18	1836 (6)	8384 (3)	9602 (3)	6·95 (18)
C19	4853 (6)	8210 (3)	274 (3)	6·97 (17)
C20	1112 (6)	6931 (3)	487 (2)	6·78 (17)

Table 2. *Bond distances* (Å) *and bond angles* (°)

C1—C2	1·512 (3)	C1—C11	1·339 (3)
C2—C3	1·523 (3)	C11—C12	1·500 (3)
C3—C4	1·528 (3)	C12—C13	1·527 (3)
C4—C5	1·525 (3)	C13—C14	1·528 (3)
C5—C6	1·521 (3)	C14—C15	1·526 (3)
C6—C1	1·512 (3)	C15—C16	1·526 (3)
C4—C7	1·543 (3)	C16—C11	1·508 (3)
C7—C8	1·531 (3)	C14—C17	1·552 (3)
C7—C9	1·523 (4)	C17—C18	1·516 (4)
C7—C10	1·526 (3)	C17—C19	1·537 (3)
		C17—C20	1·522 (4)
C1—C2—C3	114·0 (2)	C11—C12—C13	112·1 (2)
C2—C3—C4	112·4 (2)	C12—C13—C14	112·3 (2)
C3—C4—C5	106·5 (2)	C13—C14—C15	108·7 (2)
C4—C5—C6	112·8 (2)	C14—C15—C16	112·6 (2)
C5—C6—C1	114·6 (2)	C15—C16—C11	111·5 (2)
C6—C1—C2	112·8 (2)	C16—C11—C12	110·0 (2)
C3—C4—C7	115·8 (2)	C13—C14—C17	113·8 (2)
C5—C4—C7	114·9 (2)	C15—C14—C17	114·7 (2)
C4—C7—C8	109·6 (2)	C14—C17—C18	109·9 (2)
C4—C7—C9	112·3 (2)	C14—C17—C19	109·4 (2)
C4—C7—C10	109·4 (2)	C14—C17—C20	111·9 (2)
C8—C7—C9	109·2 (3)	C18—C17—C19	107·7 (2)
C8—C7—C10	107·3 (2)	C18—C17—C20	109·1 (3)
C9—C7—C10	108·9 (3)	C19—C17—C20	108·8 (3)
C2—C1—C11	123·3 (2)	C12—C11—C1	125·1 (2)
C6—C1—C11	123·5 (2)	C16—C11—C1	124·9 (2)

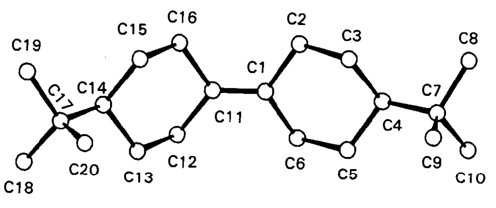

Fig. 1. Atomic numbering and molecular structure of the title compound.

Unexpectedly, it was found that the present compound exhibits a positioning of the two rings that differs from that of the bicyclohexylidene (Sasvári & Löw, 1965), and confirms one of the conformations suggested by Asveld & Kellogg.

The center of symmetry of the molecule of bicyclohexylidene is absent in the present compound and the two rings are distorted differently. From crystallographic data reported by Sasvári & Löw, asymmetry parameters (Duax & Norton, 1975) were calculated. The same was done for the two rings of the present compound.

The Duax & Norton mirror-plane asymmetry parameters $\Delta C_s(2)$, $\Delta C_s(3)$, $\Delta C_s(12)$ and $\Delta C_s(13)$ have values of 11·7 (6), 10·6 (6), 1·8 (5) and 1·8 (5), respectively. These are greater than those for bicyclohexylidene: 1·0 (5) and 1·3 (5) and show the influence of the *tert*-butyl group on the conformation of the cyclohexane. Apart from this influence, the packing of the molecules affects the two rings differently. The C1–C6 ring is the more distorted, as is shown by the previously given parameters and by the twofold asymmetry parameters $\Delta C_2(2–3)$ and $\Delta C_2(3–4)$ that have values of 15·6 (6) and 6·9 (6) greater than the pair 1·9 (6) and 1·6 (5) for the C11–C16 ring, and 1·5 (6) and 1·4 (5) for the bicyclohexylidene ring.

To confirm the deviation from the predicted C_{2v} symmetry (Kellogg & Kaiser, 1975), two different molecules were generated through a mirror plane perpendicular to the double bond with C1–C6 and C11–C16 ring conformations, respectively. Both models yielded, as expected, R factors as high as 0·50 and distances from atoms of different molecules shorter than van der Waals values. The most remarkable short distances are between H atoms of C9—C19 and C18—C19 in the first case and H atoms of C8—C13 and C9—C18 in the second. The C atoms mentioned are shown in Fig. 2, in their actual positions. The packing effect results in a displacement of the C7 *tert*-butyl group towards the mirror plane perpendicular to the double bond and a displacement of the C17 *tert*-butyl group away from it. Both displacements distort the chair conformation and twist mainly the

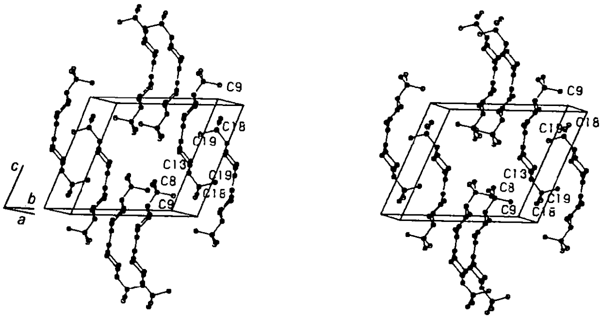

Fig. 2. Stereoscopic diagram of the packing of the molecules in the crystal structure.

chair C1—C6. As a result the *tert*-butyl groups occupy positions intermediate between equatorial and axial.

The shortest intermolecular H—H distance is 2·36 Å, in agreement with the hydrogen van del Waals diameter of 2·34 Å. The double-bond length of 1·339 (3) Å is equal to that reported by Sasvári & Löw.

The molecules are held together by van der Waals interactions.

The authors thank Professor Svend Rasmussen, Department of Inorganic Chemistry, University of Aarhus, for the use of the diffractometer, Professor Rita Hazell for helpful discussions and I.Q. Rodolfo Valentin for writing the program for molecular-geometry calculation and plotting.

References

Asveld, W. H. & Kellogg, R. M. (1982). *J. Org. Chem.* **47**, 1250–1257.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure.* New York: IFI/Plenum Data Company.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Kellogg, R. M. & Kaiser, J. K. (1975). *J. Org. Chem.* **40**, No. 17, 2575.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sasvári, K. & Löw, M. (1965). *Acta Cryst.* **19**, 840.

Sheldrick, J. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1988). C**44**, 2191–2193

Structure of Hexacyclo[7.4.2.$0^{1,9}$.$0^{3,7}$.$0^{4,14}$.$0^{6,15}$]pentadeca-10,12-diene-2,8-dione*

By N. N. Dhaneshwar, S. S. Tavale and T. N. Guru Row†

Physical and Structural Chemistry Unit, National Chemical Laboratory, Pune 411 008, *India*

and U. R. Zope, B. Pandey and N. R. Ayyangar

Organic Chemistry Division, National Chemical Laboratory, Pune 411 008, *India*

(*Received* 23 *May* 1988; *accepted* 25 *July* 1988)

Abstract. $C_{15}H_{12}O_2$, $M_r = 224·25$, monoclinic, $P2_1/n$, $a = 7·192$ (1), $b = 10·821$ (1), $c = 14·093$ (2) Å, $\beta = 97·48$ (1)°, $V = 1087·5$ (2) Å^3, $Z = 4$, $D_m = 1·34$ (1), $D_x = 1·36$ (1) Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu = 0·729$ mm^{-1}, $F(000) = 472$, $T = 293$ K, $R = 0·055$ ($wR = 0·056$) for 1323 observed reflections. The carbon skeleton consists of four 'envelope' five-membered rings, one planar four-membered ring and two six-membered rings. The diene ring is planar while the dione-bearing ring has a boat conformation.

Introduction. The transformation of aromatics to cycloalkanes *via* strained polycyclic systems is increasingly becoming a standard synthetic protocol towards complex organic natural products (Wender, 1983; Solott & Gilbert, 1980; Eaton, Ravi Shanker, Price, Pluth, Gilbert, Alster & Sandus, 1984). The nature of bonding in the cyclobutane-ring framework of polycyclic systems of cubane and homocubane is also of interest. With a view to examine whether [2 + 2]-*ortho* addition or [3 + 2]-*meta* addition (Mehta, Murthy, Reddy & Reddy, 1986; Bryce-Smith & Gilbert, 1976) is operative in an intramolecular benzene olefin photoaddition, the major Diels–Alder isomer of cyclopentadiene and 1,4-naphthoquinone was irradiated at 254 nm and crystals were obtained by repeated slow crystallization from a 3:1 mixture of petroleum ether and benzene. The X-ray structure was essential for stereoselective synthetic manipulations of the diene functionality.

Experimental. Crystal ~0·1 × 0·25 × 0·8 mm, D_m by flotation in aqueous KI, Nonius CAD-4F-11M diffractometer, Cu $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1}, $\theta \leq 60°$, $0 \leq h \leq 8$, $0 \leq k \leq 12$, $-15 \leq l \leq 15$, 1708 reflections collected, 1323 judged significant [$|F_o| > 3\sigma(|F_o|)$], lattice parameters from 25 reflections ($16·5 \leq 2\theta \leq 51·8°$), three standard reflections (501, $22\bar{8}$ and 244) every 2000 s, 4% variation in intensity. No correction for absorption. Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement (on F) of scale factor, positional and anisotropic thermal parameters for H atoms, initial H positions

---

* NCL Communication No. 4427.

† To whom all correspondence is to be addressed.

0108-2701/88/122191-03$03.00