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10α-*tert*-Butyl-3,3aα,4,5,6,6aα,7,8,9,10-decahydro-7α-methyl-1*H*-naphtho-[1,8a-*c*]furan-1,8-dione

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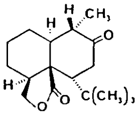
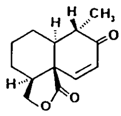
Abstract. $C_{17}H_{26}O_3$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}598\,(2)$, $b = 9{\cdot}382\,(3)$, $c = 13{\cdot}985\,(3)$ Å, $Z = 4$, $D_c = 1{\cdot}214$, $D_m = 1{\cdot}21\,(3)$ Mg m^{-3}, $\lambda = 1{\cdot}5418$ Å, $F(000) = 608$, $M_r = 278$. The structure, which was refined to $R = 0{\cdot}03$ for 882 observed reflections, reveals the conformation of a single enantiomer of the title compound in which the *tert*-butyl group assumes an axial orientation.

Introduction. The title compound (I) was synthesized by the addition of *tert*-butyllithium to a racemic mixture of compound (II)* under conditions which are described elsewhere (Goldsmith & Thottathil, 1981).

Because of steric hindrance to the equatorial approach of the *tert*-butyllithium by the lactone ring system, axial addition of the *tert*-butyl group was expected. The crystal structure was determined to establish the conformation of the product.



(I)



(II)

Crystals of (I) were grown from a mixture of ether and pentane as colorless needles. A crystal with approximate dimensions 0·4 × 0·2 × 0·2 mm was mounted on a glass fiber using epoxy cement so that the longest crystal dimension was approximately parallel to the fiber axis. Unit-cell parameters and the orientation matrix were determined on a Nicolet R3 four-circle diffractometer at room temperature using Ni-filtered Cu $K\alpha$ radiation. 15 reflections whose Bragg angles varied from $2\theta = 12{\cdot}11$ to 25·24° were centered by the machine and used in unconstrained least-squares refinement of the lattice parameters and orientation matrix. Values are given in the *Abstract*. ω scans of several low-2θ-angle reflections gave peak widths at half-height of less than 0·3°, indicating a satisfactory mosaic spread for the crystal. The density was determined by flotation in an aqueous solution of sodium chloride. Axial photographs indicated that the crystals were orthorhombic. The absence of $h00$ reflections with $h = 2n + 1$; $0k0$ with $k = 2n + 1$; and $00l$ with $l = 2n + 1$ is consistent only with the space group $P2_12_12_1$.

Intensity data were collected using the θ–2θ scan technique with a scan rate ranging from 4·88 to 29·3° min^{-1}. A scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning and at the end of each scan with a total background to scan time ratio of 1. No. significant fluctuations were observed in the intensities of three standard reflections monitored every 100 reflections. Data with $2\theta = 4$–100° (928 total) were corrected for Lorentz and polarization effects but not for absorption. The standard deviation for each reflection was calculated on the basis of counting statistics.

The structure was solved by direct methods and refined by full-matrix least squares with *SHELX* 76 (Sheldrick, 1976). After anisotropic refinement of the non-H atoms, a difference Fourier map revealed the positions of all the H atoms. Refinement cycles of all positional parameters with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms were continued using the 882 reflections with $F > 3\sigma$ until the shift/e.s.d. for each parameter was less than 1.

Final R and R_g $[=(\sum w\Delta^2/\sum wF_o^2)^{1/2}]$ are 0·030 and 0·027 respectively. The final electron-density difference map showed no peak exceeding 0·14 e Å^{-3} in height. Refinement of each of the two possible enantiomers showed no difference in R value and no assignment of absolute configuration could be made.*

Discussion. Coordinates of the atoms are given in Table 1; bond lengths and selected angles are shown in Fig. 1.

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* Molecular formula (II) represents only one enantiomer of the racemate used for the preparation of (I).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36487 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i U_{ii}.$$

	x	y	z	B_{eq} or B (Å^2)
C(1)	0·2124 (4)	0·7167 (4)	0·3441 (3)	3·35 (11)
C(2)	0·1268 (3)	0·5920 (4)	0·3596 (3)	3·12 (10)
C(3)	0·1745 (3)	0·4454 (4)	0·3196 (3)	3·35 (11)
C(4)	0·2091 (4)	0·4729 (5)	0·2141 (3)	4·16 (14)
C(5)	0·2968 (4)	0·5876 (4)	0·2057 (3)	4·18 (13)
C(6)	0·2557 (4)	0·7315 (4)	0·2394 (3)	3·86 (12)
C(7)	0·1652 (4)	0·8579 (4)	0·3839 (3)	4·62 (14)
C(8)	0·1416 (5)	0·8416 (6)	0·4909 (4)	4·80 (17)
C(9)	0·0478 (5)	0·7312 (5)	0·5057 (4)	5·92 (16)
C(10)	0·0804 (4)	0·5835 (4)	0·4638 (3)	4·22 (12)
C(11)	0·3488 (5)	0·8458 (6)	0·2281 (4)	5·91 (18)
C(12)	0·0114 (4)	0·6119 (4)	0·3067 (4)	5·02 (15)
C(13)	0·3597 (4)	0·4473 (6)	0·4274 (4)	4·93 (16)
C(14)	−0·0296 (5)	0·5002 (6)	0·4491 (5)	6·78 (20)
C(15)	0·2651 (3)	0·3577 (4)	0·3798 (3)	3·45 (10)
C(16)	0·2046 (5)	0·2682 (5)	0·4558 (4)	4·89 (15)
C(17)	0·3256 (5)	0·2503 (5)	0·3129 (4)	5·08 (15)
O(1)	−0·0074 (3)	0·6663 (3)	0·2307 (3)	6·75 (12)
O(2)	−0·0748 (2)	0·5511 (4)	0·3583 (3)	7·04 (12)
O(3)	0·3933 (3)	0·5674 (3)	0·1740 (2)	5·99 (10)
H(1)	0·2857 (29)	0·6866 (33)	0·3827 (24)	3·21 (78)
H(3)	0·1135 (25)	0·3894 (29)	0·3168 (19)	1·22 (68)
H(4)	0·1382 (31)	0·5061 (37)	0·1772 (25)	4·07 (91)
H(4′)	0·2386 (31)	0·3949 (43)	0·1859 (26)	4·03 (100)
H(6)	0·1879 (29)	0·7603 (36)	0·1940 (23)	3·58 (80)
H(7)	0·0828 (36)	0·8889 (44)	0·3479 (27)	6·21 (112)
H(7′)	0·2214 (30)	0·9338 (38)	0·3758 (24)	3·95 (85)
H(8)	0·1087 (34)	0·9304 (51)	0·5179 (28)	5·89 (114)
H(8′)	0·2219 (38)	0·8065 (46)	0·5326 (31)	7·45 (141)
H(9)	0·0336 (34)	0·7124 (42)	0·5839 (29)	6·41 (111)
H(9′)	−0·0336 (41)	0·7816 (52)	0·4724 (32)	8·91 (139)
H(10)	0·1382 (33)	0·5371 (41)	0·5087 (26)	4·37 (96)
H(11)	0·3204 (36)	0·9440 (48)	0·2371 (30)	6·55 (118)
H(11′)	0·3895 (33)	0·8454 (44)	0·1705 (27)	4·61 (102)
H(11″)	0·4225 (40)	0·8153 (46)	0·2800 (30)	7·76 (141)
H(13)	0·3293 (33)	0·5157 (42)	0·4842 (29)	5·75 (111)
H(13′)	0·4046 (33)	0·4969 (39)	0·3770 (27)	4·90 (111)
H(13″)	0·4103 (40)	0·3932 (52)	0·4576 (33)	8·01 (151)
H(14)	−0·0843 (43)	0·5253 (56)	0·5048 (35)	9·70 (159)
H(14′)	−0·0212 (36)	0·4003 (46)	0·4444 (30)	5·72 (118)
H(16)	0·1561 (40)	0·3328 (48)	0·5092 (33)	7·18 (123)
H(16′)	0·2615 (32)	0·2143 (44)	0·4941 (30)	5·36 (111)
H(16″)	0·1454 (37)	0·2066 (43)	0·4305 (28)	5·89 (129)
H(17)	0·3766 (46)	0·3159 (57)	0·2583 (37)	10·98 (179)
H(17′)	0·2715 (35)	0·1990 (46)	0·2844 (32)	5·84 (139)
H(17″)	0·3784 (34)	0·1865 (42)	0·3509 (27)	5·65 (115)

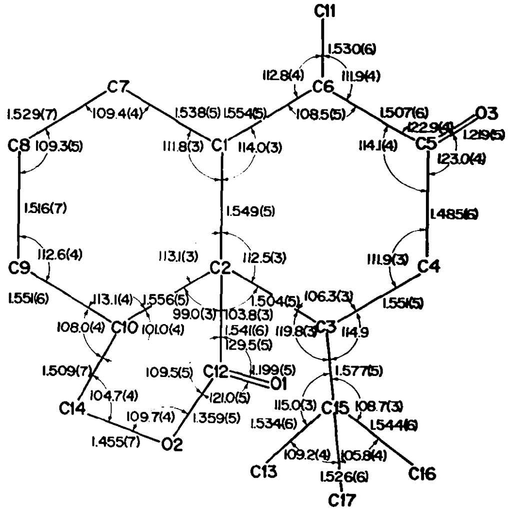

Fig. 1. Bond lengths (Å) and angles (°). The estimated errors in the least significant digit are shown parenthetically. The numbering system shown is that used in Table 1.

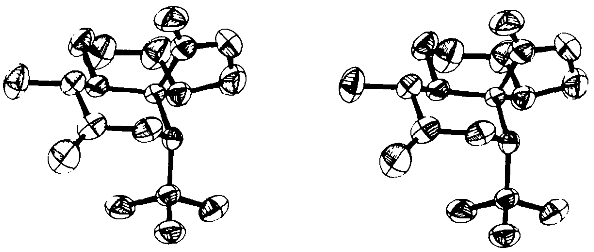

Fig. 2. A stereodrawing of the title compound. The thermal ellipsoids are drawn at the 50% probability level.

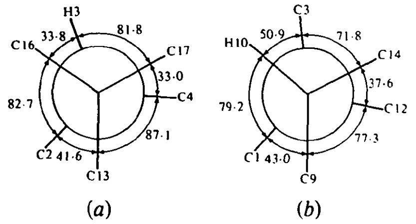

Fig. 3. Newman projection (*a*) along the C(15)—C(3) bond and (*b*) along the C(2)—C(10) bond showing torsion angles (°). E.s.d.'s are 0·4–0·5° for angles involving non-hydrogen atoms and 2–3° for angles involving H atoms.

The orientation of the *tert*-butyl group in this structure is of particular interest. The stereodrawing in Fig. 2 shows the *tert*-butyl group to be axial. The bond angles about C(15) vary from 106–109° and suggest no particular distortion, but the C(3)—C(15) bond is long [1·577 (5) Å]. The Newman projection along the C(3)—C(15) bond shown in Fig. 3(*a*) suggests a structure tending to an eclipsed conformation.

As is found in similar ring systems, the bond angles in the furanone ring suggest considerable strain. Comparisons of the bond angles at the carbonyl in similar fused-ring furanone systems (±)-decahydro-4,5-dihydroxy-4a,8-dimethylazuleno[6,5-*b*]furan-2(3*H*)-one (3a*α*,4*α*,4a*β*,5*α*,7a*α*,8*α*,9a*β*) (Declercq, Germain, Van Meerssche, Kok, De Clercq & Vandewalle, 1980) and (3a*SR*,4*RS*,5*SR*,7a*SR*)-4-(1-oxo-2-phenylethyl)-5,6-dimethyl-1,4,5,7a-tetrahydroisobenzofuran-3(3a*H*)-one (Jones & Kennard, 1978), 104·8 and 110·8° respectively, show similar distortions. The corresponding angle in the spiro compound 2′,2′,4,4,5′,5′,6,6-octamethyl-2′,4,5′,6-tetrahydrofuro[3,4-*d*]-1,3-oxathiole-2-spiro-3′-furan-4′(3′*H*)-one (Cheng, Wong-Ng & Nyburg, 1977), where there is no ring fusion, is 107·4°. A comparison of the torsion angles in the furanone ring with those of the two

Table 2. *Furanone torsion angles* (°)

	(*a*)	(*b*)	(*c*)
C(12)–C(2)–C(10)–C(14)	37·6	23·9	25·9
C(2)–C(12)–O(2)–C(14)	4·7	5·6	0
C(12)–O(2)–C(14)–C(10)	−20·9	−23·0	−25·8
O(2)–C(14)–C(10)–C(2)	36·9	30·0	16·5
C(10)–C(2)–C(12)–O(2)	−27·3	−13·9	−17·4

(*a*) Our determination, e.s.d.'s 0·4–0·5°. (*b*) Cheng *et al.* (1977). (*c*) Declercq *et al.* (1980).

similar fused-ring systems is given in Table 2. The furanone in the present structure appears more twisted than those above with the major difference being the torsion at the ring fusion, the C(2)—C(10) bond. The Newman projection along the C(2)—C(10) bond presented in Fig. 3(*b*) shows that the configuration at the ring junction tends toward eclipsed geometry [torsion angles C(14), C(10), C(2), C(12), and C(2), C(12), O(2), C(14) are 37·6 and 4·7° respectively].

We thank Drs Goldsmith and Thottathil for providing the crystals.

References

CHENG, P. T., WONG-NG, W. K. & NYBURG, S. C. (1977). *J. Cryst. Mol. Struct.* **7**, 115–121.

DECLERCQ, J. P., GERMAIN, G., VAN MEERSSCHE, M., KOK, P., DE CLERCQ, P. & VANDEWALLE, M. (1980). *Acta Cryst.* B**36**, 190–192.

GOLDSMITH, D. & THOTTATHIL, J. K. (1981). *J. Org. Chem.* Submitted for publication.

JONES, P. G. & KENNARD, O. (1978). *Acta Cryst.* B**34**, 2025–2027.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

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Iodure de Phénacyle

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Abstract. C_8H_7IO, monoclinic, $P2_1/c$, $a = 8{\cdot}560$ (6), $b = 10{\cdot}803$ (9), $c = 8{\cdot}889$ (6) Å, $\beta = 99{\cdot}84$ (6)°; $Z = 4$. The structure was solved by direct methods. Full-matrix least-squares refinement converged at $R = 0{\cdot}04$ for 1131 reflexions. The molecule exhibits a *gauche* conformation in which the dihedral angle between the C=O and C—I bonds is 93 (3)°. The shortest intermolecular I···I and I···O contacts are respectively 4·02 and 3·24 Å.

Introduction. Dans l'un de nos précédents mémoires (Bonniol, Galsomias & Petrissans, 1979), nous avons montré que la fréquence de la vibration de cisaillement $\delta(CH_2)$ d'un groupe méthylène placé en α d'un groupement carbonyle dépend de l'orientation spaciale de ce groupement. Cette propriété remarquable du vibrateur CH_2 a été mise en évidence dans le cadre d'une étude conformationnelle des halogénures de phénacyle C_6H_5—CO—CH_2X (X = Cl, Br, I), composés qui à l'état dissous se présentent sous des conformations *cis* et *gauche*.

En fait, si les structures de conformères *cis* sont connues (Barrans & Maisseu, 1966; Gupta & Prasad, 1971), il n'en est pas de même de celles des conformères *gauche* et lors de notre précédente étude (Bonniol, Galsomias & Petrissans, 1979) nous avons supposé pour ces dernières molécules que l'angle dièdre formé par les liaisons C=O et C—X est de 120°.

Des déterminations effectuées récemment au laboratoire (Ouamba, Bonniol & Petrissans, non publié) ayant montré que l'iodure de phénacyle se présente à l'état solide et dissous sous une forme *gauche* apparemment peu modifiée par le changement d'état physique, nous avons entrepris l'étude structurale de cette molécule (Fig. 1) par diffraction des rayons X.

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