

THE MOLECULAR AND CRYSTAL STRUCTURE OF 4,4-DIMETHYL-6,6-DIPHENYL-TETRAHYDRO-2H-PYRAN-2-ONEJiří NOVOTNÝ^a, Jan ONDRÁČEK^a, Marian SCHWARZ^b and Bohumil KRATOCHVÍL^{a*}^a Department of Mineralogy.

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The molecular and crystal structure of 4,4-dimethyl-6,6-diphenyl-tetrahydro-2H-pyran-2-one was solved by direct methods and anisotropically refined by the least squares method. The final *R*-factor value was 0.065 for 2181 observed reflections ($I > 1.96\sigma(I)$) and 272 refined parameters. The symmetry of the structure corresponds to the $P2_1/c$ space group with lattice parameters $a = 11.207(2)$, $b = 8.168(1)$, $c = 16.896(3)$ Å, $\beta = 90.05(1)^\circ$. The unit cell contains four formula units. A lactone structure was found for this geminally substituted heterocyclic compound and was also demonstrated by ¹H and ¹³C NMR spectroscopy. The lactone ring assumes the boat conformation.

It was found necessary in the study of the photochromic six-membered heterocyclic compounds¹ to determine the molecular and crystal structure of 4,4-dimethyl-6,6-diphenyl-tetrahydro-2H-pyran-2-one by X-ray diffraction methods. The lactone structure of this geminally substituted heterocycle was first demonstrated² by ¹H NMR spectroscopy; in contrast to the isomeric symmetrically substituted 3,3-dimethyl-1,5-diphenyl-1,5-pentadione (ref.³), the methyl groups in this compound are not equivalent.

EXPERIMENTAL

The studied compound was prepared² by Friedel-Crafts reaction of the dichloride of 3,3-dimethylglutaric acid with benzene with catalysis by aluminium chloride. The product was obtained in 65% yield and was recrystallized from methanol; the final m.p. was 90--91°C, which is in good agreement with the value of Brown and Greenberg² (92°C). For C₁₉H₂₀O₂ (280.4) calculated: 81.40% C, 7.19% H; found: 81.36% C, 7.17% H. The density of the substance was determined by the flotation method in a CCl₄-hexane mixture at 25°C. The NMR spectra were measured on a Bruker AM 400 instrument in CDCl₃ using tetramethylsilane ($\delta = 0$ ppm) as an internal standard. The experimental parameters were: for ¹H NMR (400.134 MHz), digital resolution 0.184 Hz/point, pulse width 5 μs, temperature 297 K; for ¹³C NMR (100.61 MHz), digital resolution 0.763 Hz/point, temperature 297 K, using the APT technique.

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^1H NMR spectrum (ppm): 1.04 s, 6 H (CH_3); 2.18 s, 2 H (at C19); 2.59 s, 2 H (at C15); 7.22 t, 2 H (at C4, C10, $^3J = 7.3$ Hz); 7.31 t, 4 H (at C3, C5, C9, C11, $^3J = 7.7$ Hz); 7.44 d, 4 H (at C2, C6, C8, C12, $^3J = 7.3$ Hz). ^{13}C NMR spectrum (ppm): 30.64 (C16); 31.54 (C17, C18);

TABLE I
Basic crystallographic data

$a = 11.207(2)$ Å	$\rho_o = 1.199$ kg m $^{-3}$
$b = 8.168(1)$ Å	$\rho_c = 1.204$ kg m $^{-3}$
$c = 16.896(3)$ Å	space group: $P2_1/c$
$\beta = 90.05(1)^\circ$	$\mu(\text{MoK}\alpha) = 0.07$ mm $^{-1}$
$V = 1546.7(3)$ Å 3	$F(000) = 600$
$Z = 4$	

TABLE II
Fractional coordinates ($\cdot 10^4$) of the nonhydrogen atoms and their equivalent temperature parameters ($\cdot 10^4$). $U_{\text{eq}} = (U_{11} + U_{22} + U_{33} + U_{13} \cos \beta)/3$

Atom	x	y	z	$U_{\text{eq}}, \text{Å}^2$
O1	2525(1)	2025(2)	4862(1)	361(5)
O2	2190(2)	2641(3)	6103(1)	634(7)
C1	3295(2)	1299(3)	3605(1)	351(7)
C2	3061(3)	744(4)	2849(2)	469(9)
C3	3850(3)	-316(4)	2477(2)	634(12)
C4	4856(3)	-864(4)	2860(2)	689(13)
C5	5103(3)	-301(4)	3603(2)	657(13)
C6	4335(3)	767(4)	3980(2)	490(9)
C7	1196(2)	2390(3)	3730(1)	316(7)
C8	425(2)	1262(3)	4068(2)	395(8)
C9	-740(2)	1087(4)	3787(2)	493(9)
C10	-1129(3)	2024(4)	3169(2)	526(10)
C11	-373(3)	3127(4)	2819(2)	558(9)
C12	787(3)	3307(4)	3099(2)	475(9)
C13	2482(2)	2535(3)	4026(1)	307(7)
C14	2130(2)	3087(3)	5424(1)	340(8)
C15	1659(2)	4679(3)	5139(2)	433(9)
C16	2499(2)	5539(3)	4549(1)	392(8)
C17	3523(3)	6330(5)	5018(2)	612(12)
C18	1800(4)	6868(5)	4114(2)	684(14)
C19	3025(2)	4253(3)	3970(2)	367(8)

44.02 (C19); 46.55 (C15); 86.79 (C13); 125.37 (C2, C6, C8, C12); 127.45 (C4, C10); 128.56 (C3, C5, C9, C11); 144.86 (C1, C7); 171.92 (C14).

Measurements on a CAD4 four-circle diffractometer from the Enraf-Nonius Co. were carried out using a single crystal with dimensions of $0.5 \times 0.35 \times 0.3$ mm. Measurements were carried out at 298 K using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The primary beam was passed through a graphite monochromator. The lattice parameter values were refined from a set of 25 centred reflections ($\Theta = 10\text{--}20^\circ$). The scanning speed was $3.5\text{--}16.5^\circ/\text{min}$ and a total of 10 198 reflections were measured in the reciprocal space region $-17 \leq h \leq 17$, $0 \leq k \leq 13$, $-25 \leq l \leq 25$, yielding 3 785 independent reflections after averaging. During the measurement, the intensities of three standard reflections exhibited a maximal fluctuation of only 0.2%. A total of 2 181 reflections were considered as independent on the basis of the condition $I > 1.96\sigma(I)$. Correction for absorption and extinction was neglected.

The phase problem was solved by direct methods and 272 parameters were refined by the full-matrix least squares method, in three blocks. The positions of the hydrogen atoms were first calculated theoretically and then refined. The following values were obtained in the final anisotropic cycle: $R = 0.065$, $wR = 0.062$, where $w = (\sigma^2(F_o) + 0.009F_o^2)^{-1}$ for 2 181 observed reflections, where the highest shift/error value was 0.037. The residual maximum on the final

TABLE III
Interatomic distances (in \AA) and angles (in $^\circ$)

C1—C2	1.381(4)	C2—C1—C6	118.5(2)
C1—C6	1.396(4)	C3—C2—C1	120.2(3)
C2—C3	1.389(5)	C4—C3—C2	120.8(3)
C3—C4	1.375(5)	C5—C4—C3	119.3(3)
C4—C5	1.366(5)	C4—C5—C6	120.7(3)
C5—C6	1.381(5)	C5—C6—C1	120.5(3)
C1—C13	1.535(3)	C1—C13—C7	110.9(2)
C7—C8	1.387(3)	C12—C7—C8	118.1(2)
C7—C12	1.382(4)	C7—C8—C9	120.7(2)
C8—C9	1.397(4)	C8—C9—C10	120.0(3)
C9—C10	1.367(4)	C9—C10—C11	120.0(3)
C10—C11	1.371(4)	C10—C11—C12	120.1(3)
C11—C12	1.390(4)	C11—C12—C7	121.0(3)
C7—C13	1.530(3)	C7—C13—O1	108.9(2)
C13—O1	1.473(3)	C1—C13—C19	110.9(2)
O1—C14	1.360(3)	O1—C14—O2	117.0(2)
C14—O2	1.205(3)	O1—C14—C15	116.6(2)
C14—C15	1.484(4)	O2—C14—C15	126.4(2)
C15—C16	1.541(4)	C14—C15—C16	113.1(2)
C16—C17	1.537(5)	C17—C16—C18	109.4(3)
C16—C18	1.527(5)	C15—C16—C17	108.3(2)
C16—C19	1.551(4)	C15—C16—C19	109.4(2)
C19—C13	1.532(3)	C18—C16—C19	111.9(2)
		C16—C19—C13	115.4(2)
		C19—C13—O1	107.8(2)

TABLE IV

The plane fitted through the atoms of the lactone ring and its torsion angles (in °)

Atom	Deviation from the plane ^a , Å	Atom	Deviation from the plane ^a , Å
lie in the plane		do not lie in the plane	
O1	0.011(1)	C13	0.588(2)
C19	-0.038(3)	C15	0.543(3)
C16	0.028(2)	O2	0.535(2)
C14	-0.032(2)	C18	0.954(4)
		C17	-1.387(3)

Torsion angle			
C13-O1-C14-C15	1.3(3)	C15-C16-C19-C13	8.4(3)
O1-C14-C15-C16	-49.4(3)	C16-C19-C13-O1	-51.8(3)
C14-C15-C16-C19	41.1(3)	C19-C13-O1-C14	48.2(2)

$$^a -0.9131(6) X - 0.0770(9) Y - 0.400(1) Z + 6.0110(4) = 0$$

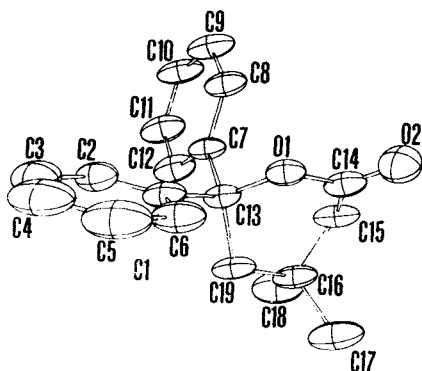


FIG. 1

The molecule of the studied compound (without hydrogen) with atom numbering

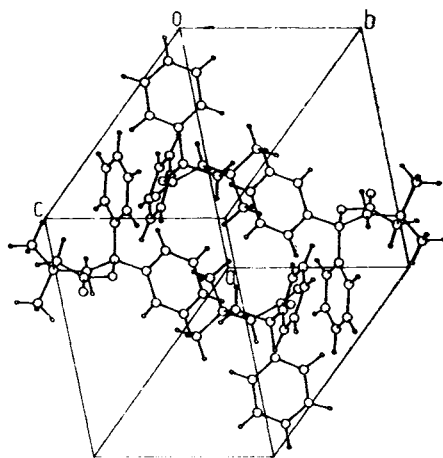


FIG. 2

Molecular packing

difference map had a value of $0.23 \text{ e} \text{ \AA}^{-3}$. Calculations were carried out on PDP 11/73 and EC 1 033 computers using the SDP (ref.⁴), SHELX 76 (ref.⁵), SHELXS 86 (ref.⁶) and PARST (ref.⁷) programs. The atomic scattering factors were those incorporated in the SHELX 76 program.

RESULTS AND DISCUSSION

High-resolution NMR spectroscopy was used to study the substance by assigning all the signals in the aromatic regions of the ^1H and ^{13}C NMR spectra. The basic crystallographic data for the studied compound are given in Table I. The final coordinates of the nonhydrogen atoms and their equivalent temperature factors are listed in Table II. Table III gives a survey of the important interatomic distances and angles.*

The 4,4-dimethyl-6,6-diphenyl-tetrahydro-2H-pyran-2-one molecule (Fig. 1) contains two phenyl rings, with planes mutually rotated by $98.27(9)^\circ$ and a lactone ring in the boat conformation. Table IV gives the deviations of the atoms from the plane fitted through the lactone ring and its endocyclic torsion angles, yielding the degree of deformation of the boat by the spirocarbon C13. This part of the lactone ring, which lies in the (O1, C14, C16, C19) plane, encloses an angle of $111.55(9)^\circ$ with the first phenyl ring (C1, C2, C3, C4, C5, C6) and an angle of $88.66(9)^\circ$ with the second phenyl ring (C7, C8, C9, C10, C11, C12).

No hydrogen bridges were found in the crystal structure of the studied compound (Fig. 2). The nearest distance between neighbouring molecules is $\text{O2} \dots \text{C2}^i$ ($i: x, 1/2 - y, 1/2 + z$) = $3.376(4) \text{ \AA}$.

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* Table II does not contain the hydrogen atom coordinates and Table III does not have the interatomic distances and angles that include hydrogen. This information is available from the authors.