

Structure of 5,5-Dimethyl-3-[β -(2'-hydroxystyryl)]-2-cyclohexenone: a Condensation Product of Isophorone Dienamine and Salicylaldehyde

BY V. M. LYNCH, S. N. THOMAS AND S. H. SIMONSEN

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, USA

T. VEDAGIRISHWARA RAO AND G. K. TRIVEDI

Indian Institute of Technology, Bombay, India 400076

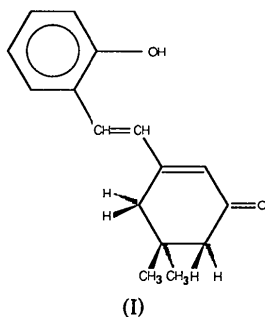
AND S. K. ARORA

College of Pharmacy, University of Texas at Austin, Austin, Texas 78712, USA

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Abstract. $C_{16}H_{18}O_2$, $M_r = 242.32$, monoclinic, $P2_1/n$, $a = 13.552(4)$, $b = 5.852(2)$, $c = 17.221(2)$ Å, $\beta = 104.55(1)^\circ$, $V = 1321.9(6)$ Å³, $Z = 4$, $D_m = 1.20$, $D_x = 1.22$ g cm⁻³ (163 K), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.735$ cm⁻¹, $F(000) = 520$, $T = 163$ K, $R = 0.0514$ for 1685 reflections. The molecules are observed as hydrogen-bonded dimers with O(5)···O(15) (related by $-x, 1-y, 1-z$) and H(5)···O(15) at distances of 2.686(2) and 1.72(4) Å, respectively, while the O(5)–H(5)···O(15) angle is 170(3)°. The phenyl and the cyclohexenone moieties are nearly coplanar which is indicative of a delocalized π -electron system. The near planarity of the molecule results in a close, intramolecular contact between O(5) and H(8) [2.18(2) Å] which is partially compensated for by a rather large angle at C(6) [C(5)–C(6)–C(7) 125.0(2)°].

Experimental. The title compound (I) was prepared by addition of salicylaldehyde (2.44 g, 0.02 mol) in 5 ml of hexane to freshly distilled isophorone dienamine (4.14 g, 0.02 mol) in 5 ml of anhydrous hexane. Mildly exothermic reaction resulted in a dark-green solution, which formed a sticky solid after one week in deep freeze. Separation over silica gel (150 g), eluting with a 3 : 17 ethyl acetate : hexane solution afforded the title



compound (m.p. 437–438 K) in 37% yield (1.8 g, 0.0074 mol). Yellow plate, 0.07 × 0.26 × 0.60 mm from CHCl_3 . Crystal density by flotation in ZnCl_2 solution. Syntex $P2_1$ diffractometer, graphite monochromator, Syntex LT-1 low-temperature delivery system (163 K). Lattice parameters from least-squares refinement of 45 reflections with $18.8 < 2\theta < 28.4^\circ$. ω -scan technique (2676 reflections, no redundant data), 2θ range 4.0–52.5°, 1° ω scan at 2–5° min⁻¹ ($h = 0 \rightarrow 16$, $k = 0 \rightarrow 7$, $l = -21 \rightarrow 20$). Space group determined from systematic absences. Four reflections (400, 301, 002, 211) were remeasured every 96 reflections to monitor instrument and crystal stability. Maximum decay correction < 1% (Henslee & Davis, 1975). Data corrected for Lp effects but not for absorption. Data reduction described in Riley & Davis (1976). Sixteen reflections (258, 336, 351, 541, 617, 6,2,18, 7,3,16, 7,5,10, 8,13, 8,4,16, 9,2,12, 939, 951, 10,5,4, 11,5,2, 14,3,2) were deleted because of a counter malfunction that went undetected during data collection. Reflections having $F_o < 4\sigma(F_o)$ considered unobserved (975 reflections omitted). Structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least-squares procedures (Sheldrick, 1976) with anisotropic thermal parameters for the non-H atoms. H atoms from a ΔF map and refined with isotropic thermal parameters. 235 parameters refined. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = (0.5kI^{-1/2})\{[\sigma(I)]^2 + (0.04I)^2\}^{1/2}$. Intensity (I) given by $(I_{\text{peak}} - I_{\text{background}}) \times (\text{scan rate})$, 0.04 is a factor to downweight intense reflections and to account for instrument instability, and k is the correction due to Lp effects and decay. $\sigma(I)$ estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$. Final $R = 0.0514$ for 1685 reflections, $wR = 0.0518$ ($R_{\text{all}} = 0.0920$, $wR_{\text{all}} = 0.0578$) and goodness of fit = 1.341. Maximum $|\Delta/\sigma| < 0.1$ in the final refine-

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for non-H atoms of 5,5-dimethyl-3-[β -(2'-hydroxystyryl)]-2-cyclohexenone

For anisotropic atoms, the U value is U_{eq} , calculated as $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i th and j th direct-space unit-cell vectors.

	x	y	z	U
O5	0.01621 (15)	0.3244 (3)	0.66266 (11)	0.0384 (7)
O15	0.11455 (13)	0.3801 (3)	0.29748 (10)	0.0354 (7)
C1	0.1505 (2)	-0.1838 (5)	0.7559 (2)	0.0351 (10)
C2	0.1329 (2)	-0.1727 (6)	0.8316 (2)	0.0402 (11)
C3	0.0773 (2)	0.0068 (6)	0.8505 (2)	0.0394 (10)
C4	0.0397 (2)	0.1730 (5)	0.7947 (2)	0.0329 (10)
C5	0.0558 (2)	0.1617 (5)	0.71796 (14)	0.0276 (9)
C6	0.1130 (2)	-0.0183 (4)	0.69736 (14)	0.0262 (8)
C7	0.1403 (2)	-0.0405 (5)	0.62005 (14)	0.0273 (8)
C8	0.1140 (2)	0.0971 (5)	0.55606 (14)	0.0283 (9)
C9	0.1489 (2)	0.0763 (4)	0.48296 (14)	0.0269 (8)
C10	0.2212 (2)	-0.1101 (5)	0.4721 (2)	0.0281 (9)
C11	0.2871 (2)	-0.0431 (4)	0.41511 (14)	0.0262 (8)
C12	0.3446 (2)	-0.2511 (5)	0.3959 (2)	0.0356 (10)
C13	0.3637 (2)	0.1401 (5)	0.4541 (2)	0.0325 (10)
C14	0.2165 (2)	0.0460 (5)	0.33654 (15)	0.0299 (9)
C15	0.1452 (2)	0.2321 (5)	0.34923 (14)	0.0275 (9)
C16	0.1144 (2)	0.2299 (5)	0.42375 (14)	0.0279 (9)

Mann (1968), with anomalous-dispersion corrections from Cromer & Liberman (1970), while scattering factors for the H atoms were from Stewart, Davidson & Simpson (1965); linear absorption coefficient from *International Tables for X-ray Crystallography* (1974). The least-squares-planes program was supplied by Cordes (1983); other computer programs from reference 11 of Gadol & Davis (1982).*

Related literature. The synthesis of the title compound is an extension to dienamines of a method (Paquette, 1965) for the synthesis of xanthenes by the self-trapping of an enamine-*O*-hydroxyaldehyde condensation product.

* Lists of anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles, least-squares planes, H-atom parameters, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51339 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$) for the non-H atoms of 5,5-dimethyl-3-[β -(2'-hydroxystyryl)]-2-cyclohexenone

1	2	3	1-2	1-2-3
C5	O5		1.358 (3)	
C15	O15		1.237 (3)	
C2	C1	C6	1.384 (4)	121.9 (3)
C6	C1		1.398 (4)	
C3	C2	C1	1.378 (5)	119.5 (3)
C4	C3	C2	1.372 (4)	120.3 (3)
C5	C4	C3	1.394 (4)	120.7 (3)
C6	C5	O5	1.405 (4)	119.6 (2)
C6	C5	C4		120.2 (2)
O5	C5	C4		120.2 (2)
C7	C6	C1	1.474 (4)	117.5 (2)
C7	C6	C5		125.0 (2)
C1	C6	C5		117.4 (2)
C8	C7	C6	1.339 (4)	127.9 (3)
C9	C8	C7	1.457 (4)	125.7 (3)
C10	C9	C16	1.509 (4)	120.0 (2)
C10	C9	C8		121.9 (2)
C16	C9	C8	1.352 (3)	118.1 (2)
C11	C10	C9	1.535 (4)	113.2 (2)
C12	C11	C13	1.526 (4)	109.1 (2)
C12	C11	C14		108.6 (2)
C12	C11	C10		110.2 (2)
C13	C11	C14	1.526 (4)	110.7 (2)
C13	C11	C10		109.8 (2)
C14	C11	C10	1.539 (3)	108.5 (2)
C15	C14	C11	1.508 (4)	113.4 (2)
C16	C15	O15	1.445 (4)	121.8 (2)
C16	C15	C14		117.4 (2)
O15	C15	C14		120.8 (2)
C9	C16	C15		123.6 (2)

ment cycle; the minimum and maximum peaks in the final $\Delta\rho$ map were -0.24 and 0.25 e \AA^{-3} , respectively. Atomic parameters are listed in Table 1, bond lengths and angles for the non-H atoms are listed in Table 2, while the atom-labelling scheme is shown in Fig. 1 and a view of the molecular packing is shown in Fig. 2. Scattering factors for the non-H atoms from Cromer &

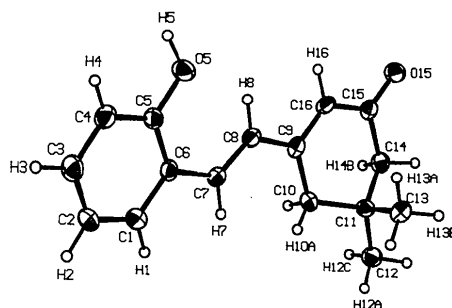


Fig. 1. View of molecule showing the atom-labelling scheme. Thermal ellipsoids are scaled to the 50% probability level.

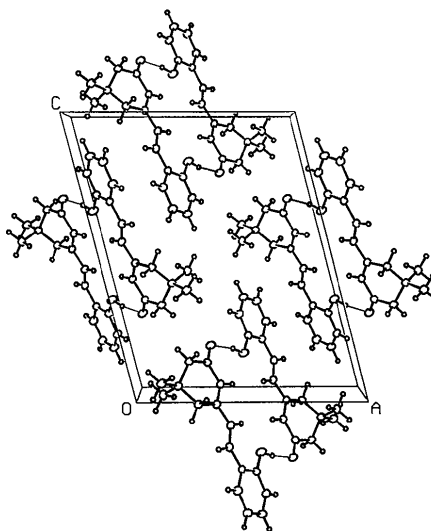


Fig. 2. View of the molecular packing down the b axis illustrating the hydrogen bonding between molecules.

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Structure of (4' *R*)-4'-Methoxycarbonyl-17 β -methoxymethyl-2,5 β -ethanoestr-3-one, a Bridged Steroid Derivative

BY HANS PREUT, SIMONE BATHE-BURMEISTER AND WOLFGANG KREISER

Fachbereich Chemie, Universität Dortmund, Postfach 500500, D-4600 Dortmund 50, Federal Republic of Germany

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Abstract. $C_{24}H_{36}O_5$, $M_r = 404.55$, monoclinic, $C2$, $a = 12.978$ (7), $b = 7.076$ (5), $c = 24.598$ (9) Å, $\beta = 97.20$ (5)°, $V = 2241$ (2) Å³, $Z = 4$, $D_x = 1.199$ Mg m⁻³, $F(000) = 880$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.08$ mm⁻¹, $T = 291$ (1) K, final $R = 0.048$ for 2915 unique observed [$F \geq 3.0\sigma(F)$] diffractometer data. The reaction product of 17 β -methoxymethyl-estr-4-en-3-one with methyl acrylate leads to a novel [2.2.2]bicyclooctane framework. The constitution and configuration of this product has been clarified by X-ray analysis. Surprisingly, the newly introduced methoxycarbonyl-ethano bridge was located on the β -face [*syn* to the angular methyl C(18)]. The chiral center at C(4') displays *R* configuration.

Experimental. Following the conditions of Weber, Spitzner & Kraus (1981) an excess of methyl acrylate at 205 K was added to a THF solution of 17 β -

methoxymethylestra-4-en-3-one in the presence of LDA. The product can either be interpreted as the result of a tandem Michael addition or a Diels–Alder reaction. The oily product was purified by using preparative TLC and then crystallized from methanol at 273 K, m.p. 357–358 K. Crystal size $\sim 0.45 \times 0.13 \times 0.22$ mm, $\omega/2\theta$ scan, scan speed 1.7–5.0° min⁻¹ in θ , Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25 reflections up to $2\theta = 24.4^\circ$; six standard reflections recorded every 2.5 h, only random deviations; 8124 reflections measured, $1.5^\circ \leq \theta \leq 25.0^\circ$, $-15 \leq h \leq 15$, $-8 \leq k \leq 8$, $-29 \leq l \leq 29$; after averaging ($R_{\text{int}} = 0.026$): 3950 unique reflections, 2915 with $F \geq$

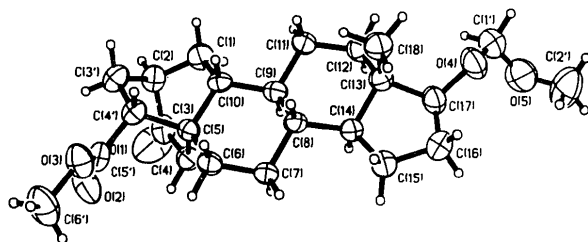


Fig. 1. General view (*SHELXTL PLUS* graphic) of the molecule, showing the atom-numbering scheme.

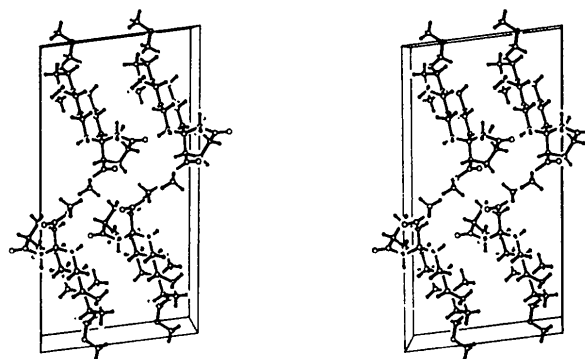


Fig. 2. Stereoscopic view (*SHELXTL PLUS* graphic) of the unit cell (a horizontal, c vertical).