

SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1973). B29, 154.

Acta Cryst. (1976). B32, 2871

***trans*-1 β ,6 α -Dimethyl-8(*E*)-[1-ethoxyethylidene]-2 α -methoxybicyclo[4.3.0]nonan-7-one**

BY DONALD L. WARD AND JERROLD L. MARTIN

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, U.S.A.

(Received 24 November 1975; accepted 17 February 1976)

Abstract. C₁₆H₂₆O₃, orthorhombic, *P*2₁2₁2₁; *a* = 10.831 (3), *b* = 18.889 (8), *c* = 7.538 (6) Å, 23°C; *M* = 266.38, *Z* = 4, *D_x* = 1.147 g cm⁻³; the material was synthesized [Martin, J. L. (1976), Thesis, Michigan State Univ.] and recrystallized from methyl alcohol. The structure is interesting as it is *not* the one expected from the synthesis.

Introduction. The synthesis shown in Fig. 1 yielded a material which was not the one expected and attempts to elucidate its structure using IR, UV, and NMR spectra were not successful. The crystal and molecular structure determination of the title compound was undertaken to identify this material. The synthesis will be reported in detail in due course (Martin, 1976).

A single crystal of approximate dimensions 0.16 × 0.26 × 0.31 mm [*μ* for Mo *Kα* = 0.43 cm⁻¹] was mounted on a glass fiber with epoxy glue. The diffraction conditions *h*00: *h* = 2*n*; 0*k*0: *k* = 2*n*; 00*l*: *l* = 2*n*, the absence of other conditions, and the orthorhombic symmetry establish the space group *P*2₁2₁2₁. Diffraction data were measured at 23°C with a Picker FACS-I automatic diffractometer using zirconium-filtered Mo *Kα*

radiation. The cell parameters were determined by a least-squares fit to the angular settings (*2θ*, *ω*, *χ*, *φ*) of 12 reflections in the range 34 ≤ *2θ* ≤ 38° for which the *α*₁, *α*₂ doublet was clearly resolved [*λ* for Mo *Kα*₁ = 0.70926 Å]. The 1612 unique reflections (including 455 'unobserved') in the +*h*+*k*+*l* octant were collected for *2θ* ≤ 50° with the *θ*-2*θ* scan method: a scan speed of 1° (*2θ*) min⁻¹, 10 s backgrounds, scan ranges of 1° (*2θ*) plus the *α*₁-*α*₂ divergence; and three standard reflections measured after every 100 data were used to scale the data. The data were reduced and standard deviations calculated as a function of counting statistics as reported previously (Wei & Ward, 1976); the least-squares refinement weights were calculated from the standard deviations of the structure factors by

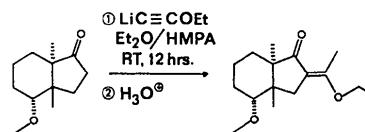


Fig. 1. Chemical synthesis of the title compound.

Table 1. Fractional coordinates ($\times 10^4$, except for H which are $\times 10^3$) and thermal parameters (\AA^2)

The anisotropic temperature factor has the form $\exp[-\frac{1}{2}\sum_i \sum_j (a_i^* a_j^* h_i h_j B_{ij})]$, where a_i^* is a reciprocal cell edge and h_i is one of the Miller indices.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
O(1)	1110 (3)	5725 (1)	7218 (4)	5.7 (2)	3.0 (1)	3.7 (1)	0.2 (1)	0.5 (1)	-0.0 (1)
O(2)	-42 (3)	2969 (1)	6611 (5)	5.1 (2)	4.5 (1)	8.0 (2)	-1.9 (1)	-1.2 (2)	-0.8 (2)
O(3)	3890 (3)	3262 (1)	7754 (4)	3.8 (2)	3.6 (1)	6.9 (2)	0.6 (1)	0.2 (2)	-0.6 (1)
C(1)	803 (4)	4577 (2)	8548 (5)	3.0 (2)	3.3 (2)	2.7 (2)	-0.1 (2)	0.1 (2)	0.0 (2)
C(2)	576 (4)	5371 (2)	8706 (6)	4.7 (2)	4.0 (2)	2.7 (2)	0.4 (2)	0.1 (2)	-0.7 (2)
C(3)	-799 (5)	5532 (3)	8913 (7)	4.6 (3)	6.0 (2)	5.0 (3)	1.9 (2)	0.3 (2)	-0.2 (2)
C(4)	-1635 (4)	5145 (3)	7599 (8)	3.8 (2)	8.5 (3)	5.8 (3)	1.5 (2)	0.2 (3)	-0.5 (3)
C(5)	-1367 (4)	4349 (3)	7423 (6)	2.7 (2)	7.0 (3)	5.2 (2)	-0.4 (2)	-0.4 (2)	-0.3 (2)
C(6)	7 (4)	4248 (3)	7046 (5)	3.3 (2)	4.0 (2)	3.1 (2)	-0.8 (2)	-0.2 (2)	-0.2 (2)
C(7)	542 (4)	3498 (2)	7009 (6)	4.3 (2)	3.8 (2)	3.7 (2)	-1.5 (2)	-0.2 (2)	-0.1 (2)
C(8)	1854 (4)	3571 (2)	7442 (5)	3.3 (2)	2.8 (2)	3.7 (2)	-0.3 (2)	0.3 (2)	-0.5 (2)
C(9)	2089 (3)	4310 (2)	8092 (5)	2.8 (2)	3.2 (2)	3.6 (2)	-0.6 (1)	0.1 (2)	0.2 (2)
C(10)	1453 (5)	6430 (2)	7547 (7)	8.1 (3)	3.0 (2)	5.9 (3)	0.4 (2)	-0.1 (3)	0.2 (2)
C(11)	480 (6)	4240 (3)	10357 (6)	4.8 (3)	4.4 (3)	3.2 (2)	-0.0 (2)	0.2 (2)	0.2 (2)
C(12)	292 (6)	4517 (3)	5151 (6)	4.6 (3)	4.5 (3)	2.9 (2)	-0.4 (2)	-0.2 (2)	-0.0 (2)
C(13)	2716 (4)	3062 (2)	7306 (6)	4.7 (2)	3.3 (2)	4.0 (2)	-0.6 (2)	0.6 (2)	-0.1 (2)
C(14)	2506 (7)	2326 (3)	6654 (12)	5.6 (3)	3.2 (2)	8.6 (4)	-0.2 (2)	0.2 (3)	-1.2 (3)
C(15)	4858 (6)	2762 (4)	7911 (14)	5.9 (4)	5.6 (3)	9.8 (5)	2.2 (3)	-0.3 (4)	-0.7 (4)
C(16)	5974 (6)	3117 (5)	8498 (19)	4.5 (3)	8.4 (4)	11.9 (6)	1.8 (3)	-2.4 (4)	-0.5 (5)

Table 1 (cont.)

	x	y	z	B _{iso}
H(1)	99 (3)	553 (2)	973 (5)	1.7 (7)
H(2)	-91 (4)	608 (2)	874 (6)	5.8 (11)
H(3)	-108 (5)	535 (3)	1010 (7)	7.3 (14)
H(4)	-158 (5)	533 (2)	639 (7)	5.1 (11)
H(5)	-253 (5)	519 (2)	789 (7)	6.4 (12)
H(6)	-182 (4)	413 (2)	654 (6)	2.7 (9)
H(7)	-156 (5)	402 (2)	877 (9)	8.1 (14)
H(8)	264 (4)	438 (2)	896 (6)	3.8 (10)
H(9)	247 (3)	458 (2)	727 (5)	1.6 (7)
H(10)	208 (5)	646 (2)	862 (8)	6.2 (13)
H(11)	74 (4)	670 (2)	784 (6)	5.5 (12)
H(12)	180 (3)	668 (2)	655 (5)	2.6 (9)
H(13)	-34 (4)	439 (2)	1065 (5)	3.5 (10)
H(14)	94 (5)	442 (2)	1134 (7)	5.7 (12)
H(15)	59 (3)	372 (2)	1046 (5)	3.3 (9)
H(16)	109 (5)	449 (2)	473 (6)	5.0 (12)
H(17)	8 (5)	500 (2)	495 (6)	4.3 (10)
H(18)	-26 (4)	419 (2)	436 (5)	3.1 (9)
H(19)	271 (4)	201 (2)	748 (6)	4.3 (12)
H(20)	317 (7)	219 (3)	570 (9)	9.1 (17)
H(21)	164 (5)	226 (2)	630 (6)	5.1 (12)
H(22)	498 (5)	250 (3)	701 (8)	7.2 (18)
H(23)	456 (6)	240 (4)	887 (9)	9.5 (21)
H(24)	594 (9)	334 (5)	949 (13)	12.1 (35)
H(25)	595 (10)	347 (5)	749 (15)	17.0 (38)
H(26)	674 (7)	275 (2)	876 (9)	10.7 (17)

$w = 1/[\sigma^2 + (0.02F)^2]^{1/2}$; absorption and extinction corrections were not applied to the data.

The crystal structure was solved with the program *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used in this study include the entire system of Zalkin's (1974) programs and programs written and/or modified locally. A CDC 6500 computer was used.

The structure was refined by full-matrix least squares to $R_1 = (\sum |F_o - F_c|) / \sum F_o = 0.060$, $R_2 = \{[\sum w(F_o - F_c)^2] / \sum w(F_o)^2\}^{1/2} = 0.041$, $R_3 = 0.101$ including the 455 zero-weighted data for which $I \leq \sigma(I)$, the standard deviation of an observation of unit weight = 1.050, and the atomic parameters listed in Table 1. The average and maximum shift-to-error ratios for the last cycle of least-squares refinement were 0.022 and 0.133 for non-hydrogen atoms and 0.072 and 0.441 for hydrogen atoms. The final difference map showed densities ranging from +0.29 to -0.28 e Å⁻³ with no indication of incorrectly placed or missing atoms. The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for hydrogen, the anomalous scattering

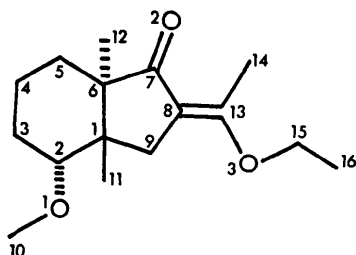


Fig. 2. Molecular structure and configuration.

Table 2. Interatomic distances (Å) and angles (°)

C(1)—C(2)	1.526 (5)	C(2)—C(1)—C(6)	111.2 (3)
C(1)—C(6)	1.553 (5)	C(2)—C(1)—C(9)	119.4 (3)
C(1)—C(9)	1.521 (6)	C(2)—C(1)—C(11)	107.5 (4)
C(1)—C(11)	1.544 (6)	C(6)—C(1)—C(9)	102.2 (3)
C(2)—C(3)	1.528 (7)	C(6)—C(1)—C(11)	110.7 (4)
C(2)—O(1)	1.427 (5)	C(9)—C(1)—C(11)	105.7 (4)
C(3)—C(4)	1.528 (7)	C(1)—C(2)—C(3)	111.1 (3)
C(4)—C(5)	1.537 (6)	C(1)—C(2)—O(1)	109.5 (3)
C(5)—C(6)	1.527 (6)	C(3)—C(2)—O(1)	112.5 (3)
C(6)—C(7)	1.531 (6)	C(2)—C(3)—C(4)	114.6 (4)
C(6)—C(12)	1.548 (6)	C(3)—C(4)—C(5)	114.4 (4)
C(7)—C(8)	1.464 (6)	C(4)—C(5)—C(6)	108.9 (4)
C(7)—O(2)	1.219 (4)	C(1)—C(6)—C(5)	110.8 (3)
C(8)—C(9)	1.502 (5)	C(1)—C(6)—C(7)	100.0 (3)
C(8)—C(13)	1.344 (5)	C(1)—C(6)—C(12)	115.5 (3)
C(10)—O(1)	1.405 (5)	C(5)—C(6)—C(7)	119.2 (4)
C(13)—C(14)	1.493 (6)	C(5)—C(6)—C(12)	109.0 (4)
C(13)—O(3)	1.368 (5)	C(7)—C(6)—C(12)	102.3 (4)
C(15)—C(16)	1.451 (9)	C(6)—C(7)—C(8)	106.0 (3)
C(15)—O(3)	1.416 (6)	C(6)—C(7)—O(2)	124.5 (4)
		C(8)—C(7)—O(2)	129.5 (3)
		C(7)—C(8)—C(9)	109.0 (4)
		C(7)—C(8)—C(13)	126.2 (4)
		C(9)—C(8)—C(13)	124.9 (4)
		C(1)—C(9)—C(8)	103.1 (3)
		C(8)—C(13)—C(14)	125.8 (5)
		C(8)—C(13)—O(3)	115.5 (3)
		C(14)—C(13)—O(3)	118.7 (4)
		C(16)—C(15)—O(3)	109.6 (5)
		C(2)—O(1)—C(10)	114.3 (4)
		C(13)—O(3)—C(15)	121.7 (4)

factors of Cromer & Liberman (1970) for the non-hydrogen atoms, and anomalous scattering factors of zero were assumed for hydrogen.* Interatomic distances and angles are listed in Table 2.

Discussion. The determination of the crystal and molecular structure of the title compound revealed that the addition of ethoxyacetylene occurs at the carbon C(8) α to the carbonyl carbon rather than, as was expected, at the carbonyl carbon C(7). The molecular structure and configuration are shown in Fig. 2.

Owing to the *trans* ring junction and the double bonds to adjacent carbon atoms in the five-membered ring, a major portion of the molecule is relatively planar. Eight atoms in particular are relatively coplanar, and the deviations of these atoms from the least-squares plane [$-2.089x - 4.692y + 7.156z - 3.228 = 0$ (x, y, z are fractional coordinates)] are: C(6) -0.181 ; C(7) 0.033 ; C(8) 0.034 ; C(9) 0.104 ; C(13) -0.004 ; C(14) -0.082 ; O(2) 0.118 ; and O(3) -0.023 Å. The small angles in the five-membered ring (averaging 101.8° at tetrahedral and 107.5° at trigonal carbon atoms) indicate considerable strain in this ring. Distances between carbon atoms in the six-membered ring averaging 1.533 Å and the bond angles averaging 111.8° do not indicate any appreciable strain in this ring. The carbon-hydrogen

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31800 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

interatomic distances range from 0.85 to 1.21 Å with an average of 0.98 Å and an average standard deviation of about 0.06 Å. Intermolecular contacts are reasonable and give no indication of hydrogen bonding.

The bond angles and distances are similar in several respects to those in 5 α -bromo-8 β ,9 α -dimethylhydri-dane-1,4-dione (Yordy & Neuman, 1974). The major structural differences between this molecule and the title compound are [all atom numbers are those of the present study]: the bromine replacing H(3); the carbonyl oxygen replacing both H(1) and the methoxy group at C(2); and two hydrogens replacing the group at C(8).

Of particular interest is the bond C(1)–C(6), which is shared by the two rings, and the geometries around C(1) and C(6). This bond length is 1.553 (5) Å in the present study, compared with 1.61 (2) Å in the compound reported by Yordy & Neuman (1974). The average difference between the two molecules in the angles around C(1) is 3.5 and around C(6) is 3.3°. The angle C(1)–C(6)–C(12) is 8.3° larger in the present study; this difference is probably due to the steric interaction between the methyl C(12) and the methoxy group. The angle C(6)–C(1)–C(9) is 8.2° smaller in the present study; this difference is probably due to the

extra strain in the five-membered ring when it has two adjacent double bonds to it. The significant differences between the bond angles and distances in the two compounds appear to be due to the steric and bond-strain effects of the differences in the chemical structures.

We thank the National Institutes of Health for support of the synthesis of the title compound (Grant 2 RO1 AM 10849-08) and Dr William H. Reusch for his helpful discussions.

References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 MARTIN, J. L. (1976). *Studies Toward the Total Synthesis of Tetracyclic Triterpenes*. Thesis, Michigan State Univ.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WEI, K.-T. & WARD, D. L. (1976). **B32**, 2768–2773.
 YORDY, J. D. & NEUMAN, M. A. (1974). *J. Cryst. Mol. Struct.* **4**, 121–127.
 ZALKIN, A. (1974). Private communication.

Acta Cryst. (1976). **B32**, 2873

Di- μ -iodo-bis[diiodobis(triphenylphosphine oxide)bismuth(III)]

BY F. LAZARINI AND S. MILIČEV

Department of Chemistry, Faculty of Natural Sciences and Technology, University of Ljubljana, Murnikova 6, 61000 Ljubljana, Yugoslavia

(Received 5 April 1976; accepted 27 April 1976)

Abstract. {BiI₃[(C₆H₅)₃PO]₂}₂, monoclinic, *P*2₁/*n* (alternative setting for *P*2₁/*c*, No. 14); *a* = 12.899 (5), *b* = 11.778 (1), *c* = 25.212 (3) Å, β = 102.95 (9)°; *D*_o = 2.01 (1) g cm⁻³, *Z* = 2, *D*_c = 2.039 g cm⁻³; *R* = 0.033 for 4331 reflexions [*I* > 1.5 σ (*I*)]. The structure consists of binuclear complex molecules with two distorted octahedra sharing an edge. Each of the Bi atoms is coordinated with two organic ligands, and two terminal and two bridging iodine atoms, arranged in *cis* positions.

Introduction. A series of coordination compounds was prepared in the systems Sb or Bi trihalide–triphenylphosphine oxide and triphenylarsine oxide and characterized using vibrational spectra (Miličev & Hadži, 1971, 1976). In order to establish the complete structures of these compounds crystal structure analysis was undertaken. As the first example the crystal structure of triiodobismuth(III)-tri- μ -iodotris(triphenylarsine

oxide)bismuth(III), I₃BiI₃Bi[(C₆H₅)₃AsO]₃, was reported (Lazarini, Golič & Pelizzi, 1975, 1976). The structure of the title compound, obtained under similar conditions, is different.

The unit-cell parameters were calculated by a least-squares method from Al-calibrated Weissenberg photographs (Cu *K* α ₁, λ = 1.54051 Å, *T* = 20°C). The intensity data were collected using an Enraf–Nonius CAD-4 diffractometer with the ω –2 θ scan and Mo *K* α radiation (graphite monochromator, λ = 0.7107 Å). A set of 6566 independent reflexions within the θ range 1.5–25° was recorded, and of these 4331 reflexions, having *I* > 1.5 σ (*I*) (calculations based on counting statistics), were used in the structure analysis. The intensities were corrected for Lorentz and polarization effects. Absorption correction was not applied (μ Mo *K* α = 71.2 cm⁻¹, approximate dimensions of the crystal 0.20 × 0.20 × 0.15 mm; μ r \approx 0.7).

The positions of one Bi and three I atoms were deter-