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(+)-3,5-*O*-(*R*)-Benzylidene-6-deoxy-6-iodo-1,2-*O*-isopropylidene-α-D-glucofuranose

By Peter P. Giannousis, Gretchen E. Hofmeister, Kevin L. McLaren and Michael C. Nolan

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, *USA*

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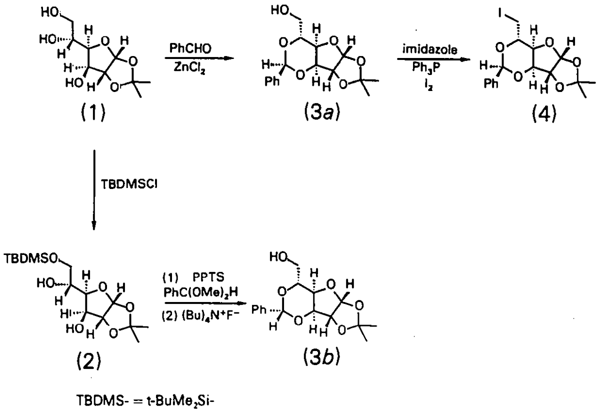
Abstract. 2,2-Dimethyl-5-iodomethyl-7-phenyl-[1′,3′]-dioxolo[4′,5′:4,5]furo[3,2-*d*][1,3]dioxane, $C_{16}H_{19}IO_5$, $M_r = 418{\cdot}23$, monoclinic, $P2_1$, $a = 6{\cdot}0913$ (6), $b = 9{\cdot}1636$ (7), $c = 14{\cdot}7957$ (9) Å, $\beta = 94{\cdot}172$ (6)°, $V = 823{\cdot}7$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}686$ g cm^{-3}, $\lambda = 0{\cdot}71073$ Å, Mo $K\alpha$, $\mu = 19{\cdot}398$ cm^{-1}, $F(000) = 416$, $T = 298$ K, $R = 0{\cdot}016$ for 1890 independent reflections with $F^2 > 3\sigma(F^2)$. The dioxane ring is in the chair conformation, where the iodomethyl is axial and *trans* to the phenyl group.

Introduction. In connection with a program directed towards the synthesis of a series of 6-substituted glucose analogs, a reliable source of the protected glucose derivatives 3,5-*O*-benzylidene-1,2-*O*-isopropylidene-α-D-glucofuranose was required.



The traditional zinc-halide-catalyzed acetalization of the D-glucose acetonide (1) has been presumed to give thermodynamically the more stable product (3*a*) [Brigl & Grüner (1932) and references cited therein]. However, pyridinium-tosylate-catalyzed acetal exchange between benzaldehyde dimethyl acetal and 6-*O*-(*tert*-butyldiphenylsilyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (2) gave an isomeric compound (3*b*) (Åkerfeldt & Bartlett, 1986). The hydroxy compound (3*a*) was converted to the corresponding iodide (4). It was of interest to determine the configuration of the phenyl group of the benzylidene acetal relative to that of the iodomethyl side chain in compound (3*a*) as compared to isomer (3*b*).

The configuration of the benzylic carbon was assigned unambiguously by two-dimensional NOESY ^{1}H NMR spectroscopy. For iodide (4), nuclear Overhauser interaction is seen between the benzylic methine H(C7) and the methylene hydrogens H′(C6) and H″(C6) (Åkerfeldt & Bartlett, 1986). Thus in compound (4), and hence in (3*a*), the phenyl group and C(6) are *trans* with respect to the 1,3-dioxane ring, *S*-benzal configuration (Åkerfeldt & Bartlett, 1986).

Experimental. Clear colorless crystals obtained from ethanol/hexane were kindly provided by Karin S. Åkerfeldt and Professor Paul A. Bartlett. Density was not measured. Crystal 0·36 × 0·38 × 0·12 mm. Precession photographs, monoclinic space group $P2_1$, $0k0$, $k = 2n$. Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 24 reflections, $26 < 2\theta < 31°$, graphite-monochromatized Mo $K\alpha$, θ–2θ scans. 2361 intensities collected during 30 h in hemisphere h, $\pm k$, $\pm l$ ($h = 0$ to 5, $k = -9$ to 9, $l = -15$ to 15), $3 < 2\theta < 45°$, scan speed 0·91 to 6·67° min^{-1}. Average of 3·4% decrease in intensity in three intensity standards equally distributed over reciprocal space during 24 h of X-ray exposure time; linear correction applied. No crystal reorientation required in data collection. Data correction for background, scan speed,

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Lorentz and polarization factors (*SDP*; Frenz, 1982); empirical absorption correction (minimum transmission 73%) based on ψ scans over four reflections. 1890 independent reflections with $F^2 > 3\sigma(F^2)$. Position (x,z) for iodine (I) determined from Patterson map. Subsequent full-matrix least-squares refinements and Fourier synthesis gave positions of the remaining non-hydrogen atoms. All hydrogen atoms were assigned idealized coordinates with C—H = 0·95 Å and isotropic thermal parameters (B = 3·6–6·8 Å^2) based on the magnitudes of the thermal parameters of their parent C atoms. Secondary-extinction coefficient refined to 1·45 × 10^{-6} (Zachariasen, 1968). Final least-squares cycle R = 1·6%, wR = 2·5%, $\sum w(\Delta F)^2$ minimized where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]$, p = 0·03, GOF = 1·47, $(\Delta/\sigma)_{\max}$ = 0·05. Highest peak in final difference Fourier map = 0·435 e Å^{-3}, most peaks associated with iodine. Least-squares refinement using enantiomeric structure generated from final coordinates of (4) gave final R = 2·8%, with $(\Delta/\sigma)_{\max}$ = 0·00, supporting the absolute configuration assigned to the molecule. Atomic scattering factors of I, C, O and H atoms and f' and f'' values taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are listed in Table 1. Representative bond distances, angles and torsional angles are listed in Table 2.* The molecular structure of the title compound is shown in Fig. 1 along with the crystallographic numbering scheme.

Table 1. *Positional parameters and equivalent isotropic thermal parameters with estimated standard deviations in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
I	0·15345 (3)	0·000	0·13798 (1)	4·941 (5)
O(1)	−0·2278 (4)	0·3183 (2)	0·5800 (1)	4·22 (4)
O(2)	−0·4419 (3)	0·1331 (2)	0·5213 (1)	3·42 (4)
O(3)	−0·4323 (3)	0·2962 (2)	0·3017 (1)	3·02 (4)
O(4)	−0·0708 (3)	0·2805 (2)	0·4415 (1)	3·47 (4)
O(5)	−0·0914 (3)	0·2760 (2)	0·2404 (1)	2·98 (3)
C(1)	−0·2509 (5)	0·3384 (3)	0·4858 (2)	3·15 (5)
C(2)	−0·4489 (5)	0·2444 (2)	0·4551 (2)	2·84 (5)
C(3)	−0·3860 (4)	0·1826 (2)	0·3664 (2)	2·84 (5)
C(4)	−0·1394 (4)	0·1606 (3)	0·3855 (2)	2·98 (5)
C(5)	−0·0153 (4)	0·1603 (3)	0·2994 (2)	3·09 (5)
C(6)	−0·0325 (4)	0·0120 (3)	0·2560 (2)	3·73 (5)
C(7)	−0·3213 (4)	0·2787 (3)	0·2212 (2)	2·87 (5)
C(8)	−0·3826 (4)	0·4067 (3)	0·1614 (2)	2·78 (5)
C(9)	−0·2297 (5)	0·5119 (3)	0·1427 (2)	4·10 (6)
C(10)	−0·2956 (6)	0·6312 (3)	0·0889 (2)	5·22 (7)
C(11)	−0·5067 (6)	0·6444 (3)	0·0536 (2)	4·88 (7)
C(12)	−0·6585 (6)	0·5398 (3)	0·0722 (2)	5·12 (7)
C(13)	−0·5956 (5)	0·4198 (3)	0·1259 (2)	4·06 (6)
C(14)	−0·3529 (5)	0·1922 (3)	0·6048 (2)	3·27 (5)
C(15)	−0·5353 (7)	0·2412 (4)	0·6606 (2)	5·22 (8)
C(16)	−0·1976 (6)	0·0828 (4)	0·6518 (2)	4·87 (7)

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

C(6)—I	2·153 (2)	O(1)—C(1)	1·402 (3)
O(1)—C(14)	1·446 (3)	O(2)—C(2)	1·412 (3)
O(2)—C(14)	1·420 (3)	O(3)—C(3)	1·429 (3)
O(3)—C(7)	1·420 (3)	O(4)—C(1)	1·422 (3)
O(4)—C(4)	1·420 (3)	O(5)—C(5)	1·429 (3)
O(5)—C(7)	1·409 (3)	C(1)—C(2)	1·525 (3)
C(2)—C(3)	1·504 (3)	C(3)—C(4)	1·522 (4)
C(4)—C(5)	1·527 (4)	C(5)—C(6)	1·503 (4)
C(7)—C(8)	1·500 (3)	C(8)—C(9)	1·382 (4)
C(8)—C(13)	1·369 (4)	C(9)—C(10)	1·394 (5)
C(10)—C(11)	1·358 (5)	C(11)—C(12)	1·373 (5)
C(12)—C(13)	1·395 (4)	C(14)—C(15)	1·501 (5)
C(14)—C(16)	1·512 (4)		

I—C(6)—C(5)	111·6 (2)	C(6)—C(5)—O(5)	113·6 (2)
C(5)—O(5)—C(7)	114·2 (2)	O(5)—C(7)—O(3)	111·1 (2)
C(7)—O(3)—C(3)	113·4 (2)	O(3)—C(3)—C(4)	111·4 (2)
C(3)—C(4)—C(5)	112·8 (2)	C(4)—C(5)—C(6)	109·5 (2)
C(4)—C(5)—O(5)	110·5 (2)	O(5)—C(7)—C(8)	109·5 (2)
O(3)—C(7)—C(8)	107·0 (2)	C(5)—C(4)—O(4)	110·2 (2)
C(4)—O(4)—C(1)	110·7 (2)	O(4)- C(1) C(2)	105·8 (2)
C(1)—C(2)—C(3)	103·1 (2)	C(2)—C(3)—O(3)	105·1 (2)
C(2)—C(3)—C(4)	101·5 (2)	C(3)—C(4)—O(4)	104·5 (2)
C(3)—C(2)—O(2)	109·6 (2)	C(2)—O(2)—C(14)	108·5 (2)
O(2)—C(14)—O(1)	105·0 (2)	C(14)—O(1)—C(1)	109·9 (2)
O(1)—C(1)—O(4)	112·6 (2)	O(1)—C(1)—C(2)	104·0 (2)
C(1)—C(2)—O(2)	102·6 (2)	O(2)—C(14)—C(15)	110·0 (2)
O(2)—C(14)—C(16)	109·5 (2)	O(1)—C(14)—C(15)	109·0 (2)
O(1)—C(14)—C(16)	108·8 (2)	C(15)—C(14)—C(16)	114·1 (3)

H(1)—C(1)—C(2)—H(2)	−26·5	H(2)—C(2)—C(3)—H(3)	−76·1
H(3)—C(3)—C(4)—H(4)	−39·9	H(4)—C(4)—C(5)—H(5)	−78·4
O(5)—C(5)—C(6)—I	59·0 (2)	O(5)—C(7)—C(8)—C(9)	−8·6 (3)
O(1)—C(1)—C(2)—O(2)	−28·5 (2)	C(3)—O(3)—C(7)—O(5)	−59·4 (2)
C(7)—O(5)—C(5)—C(4)	−52·5 (3)	O(4)—C(1)—C(2)—C(3)	−142·4 (2)

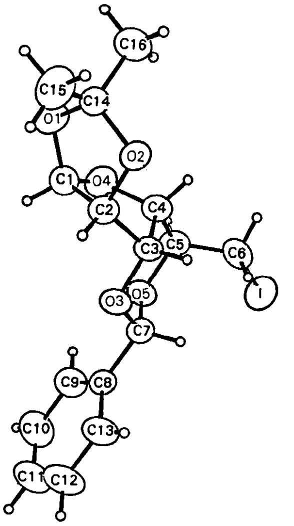

Fig. 1. Molecular structure of (4) with crystallographic numbering scheme.

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* Lists of structure factors, positional and anisotropic thermal parameters for all atoms, selected least-squares planes, and intramolecular bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44092 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Thus the structure of the compound is unambiguously shown to be (4), which arises from isomer (3*a*). All bond lengths and bond angles are fully consistent with literature values. The shortest non-hydrogen-atom intermolecular contact was 3·283 (3) Å between O(2) and C(1). There are no others shorter than 3·6 Å.

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Structure of Thiazolo[5,4-*d*]thiazole

By A. Bolognesi, M. Catellani, S. Destri and W. Porzio*

Istituto di Chimica delle Macromolecole del CNR, Via Bassini 15, 20133 *Milano, Italy*

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Abstract. $C_4H_2N_2S_2$, $M_r = 142{\cdot}20$, monoclinic, $P2_1/n$, $a = 7{\cdot}847$ (9), $b = 6{\cdot}606$ (9), $c = 5{\cdot}517$ (7) Å, $\beta = 107{\cdot}0$ (1)°, $V = 273{\cdot}5$ (9) Å^3, $Z = 2$, $D_x = 1{\cdot}73$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 8{\cdot}09$ cm^{-1}, $F(000) = 144$, $T = 293$ K, $R = 4{\cdot}9\%$ based on 780 independent reflections. The structure consists of the packing of planar molecules placed on inversion centers. The geometric features are compared with thiazole and thiophene analogues to provide evidence for variations in 'aromaticity'. Three short contacts [S···N 3·201 (4), N···N 3·24 (1), N···H—C 2·56 (3) Å] determine the intermolecular packing.

Introduction. For a number of years polymers exhibiting electroconducting properties have been extensively studied at our institute. Recently, polyheterocyclic systems have attracted our attention with the aim of overcoming the drawbacks of polyacetylene, namely air stability and processability. Moreover, our interest has also been devoted to the elucidation of conduction models for these materials and to the prediction of potential applicative developments. In particular, we have focused our attention on the different contributions which play a decisive role in understanding the complex phenomena occurring in the conduction process. As part of our research concerning polymeric systems having an N atom in the conjugation pathway we studied polythiazole and its oligomers, *i.e.*, 4,4′-dimethyl-2,2′-bithiazole as a model compound, in order to obtain precise inter- and intraring geometric parameters for *ab initio* calculations on these polymeric systems (Bolognesi, Catellani, Destri & Porzio, 1987). Here we present the crystal and molecular structure of thiazolo[5,4-*d*]thiazole with particular reference to known thiazole and thiophene analogues.

Experimental. The synthesis of thiazolo[5,4-*d*]thiazole was carried out by cyclization of dithiooxamide (Johnson, Rotenberg & Ketcham, 1970) and the product was crystallized from a solution of 50% aqueous ethanol. The experimental details and the crystal data are summarized in Table 1. Intensity data were collected on a Nonius CAD-4 computer-controlled diffractometer with a non-aligned crystal; subsequently the data were corrected for Lorentz and polarization effects, and an experimental absorption correction was applied (North, Phillips & Mathews, 1968). The absorption correction values range from 0·89 to 1·00. Unit-cell parameters and their e.s.d.'s were determined by an accurate centering of 25 strong reflections (θ range 8–15°) and then refined by least squares. The structure was solved by the Patterson method, by which the position of the S atom was determined. The positional and thermal parameters were refined using full-matrix least squares and minimizing $\sum w(F_o - KF_c)^2$, where $w = 1/\sigma^2$. After a difference Fourier map, which allowed the localization of all H atoms ($\Delta\rho$ max. and min. $\pm 0{\cdot}3$ e Å^{-3}), six

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* To whom correspondence should be addressed.

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