The five-membered ring Cu, O, C, C, N has a skew-envelope form, where the atom out of the plane defined by the remaining four atoms differs in every compound. It is C(3) for (I) and N(4) for (II).

The Cu—O(*W*1)(aqua) apical bond length alters from 2.23 (4) Å in (I) to 2.308 (6) Å in (II). Values of 2.24 (1) and 2.368 (5) Å are reported for aqua(1,10-phenanthroline)(L-phenylalaninato)copper(II) nitrate monohydrate (Solans, Ruíz-Ramírez, Martínez, Gasque & Briansó, 1988) and aqua(aspartato)(2,2′-bipyridine)copper(II) trihydrate (Antolini, Marcotrigiano, Menabue & Pellacani, 1983), respectively.

The N(3)—Cu—O(1) bond angle is 84.5 (2)° for (I) and the N(4)—Cu—O(1) bond angle is 84.0 (2)° for (II); these angles correlate with the mean metal–ligand bond lengths (1.976 and 1.959 Å respectively). This correlation is based on the constancy of the O(1)···N(3) distances (average 2.66 Å). The mean donor–metal distance increases linearly from 2.0 to 2.5 Å as the interionic angle decreases from 84 to 64° (Freeman, 1967).

In (I) the water molecule coordinated to the Cu is hydrogen bonded to another water molecule and to atom O(2) of an alaninate ligand in a neighbouring complex. This second hydrogen bond is to a chloride ion in (II).

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4-Iodo-2,2,6,6-tetramethylheptane-3,5-dione

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Abstract. $C_{11}H_{19}IO_2$, $M_r = 310.18$, monoclinic, $P2_1/c$, $a = 9.188$ (3), $b = 14.229$ (2), $c = 10.628$ (12), $\beta = 104.74$ (6)°, $V = 1344$ (3) Å^3, $Z = 4$, $D_x = 1.53$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.34$ mm^{-1}, $F(000) = 616$, $T = 250$ K, $R = 0.039$ for 1562 unique reflexions [$I > 3\sigma(I)$]. The title compound was prepared as stable single crystals (m.p. 343 K) by the action of iodine on 2,2,6,6-tetramethylheptane-3,5-dione in ether. The molecule is highly dissymmetric with the carbonyl groups non-coplanar. Infrared (both for the solid state and CCl_4 solution) and nuclear magnetic resonance (for CCl_4 solution) spectra were also recorded.

Introduction. The preparation of 4-iodo-2,2,6,6-tetramethylheptane-3,5-dione (Ithd) was first reported by Schoppee & Stevenson (1972) with iodine chloride as an iodination agent. In the course of research on new ligands for volatile metal-organic componds, we incidentally obtained an iodinated compound by reacting iodine with 2,2,6,6-tetramethylheptane-3,5-dione (Hthd). It proved to be

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4-iodo-2,2,6,6-tetramethylheptane-3,5-dione but did not correspond to the compound described by Schoppee & Stevenson. For that reason we undertook a thorough structural study.

Experimental. *Synthesis.* A solution of iodine in ether (8×10^{-2} mol in 250 ml) was added dropwise to a solution of Hthd (Lancaster) in ether (8×10^{-2} mol in 150 ml). The mixture was refluxed for several hours. After addition of a few crystals of anhydrous copper chloride, the mixture was maintained overnight under stirring. It was washed successively with water, a solution of sodium hydrogenocarbonate, a solution of sodium thiosulfate and again with water. The ether phase was collected and dried over calcium sulfate. The evaporation of ether yielded a green-brown liquid containing small acicular transparent crystals of Ithd which were filtered off. After several days of evaporation, larger elongated single crystals had formed. They were filtered and rinsed with *n*-hexane. $T_f = 343$ K. Analysis: measured C 41.4, H 6.01%; calculated for $C_{11}H_{19}IO_2$, C 42.59, H 6.18%.

Crystal structure determination. A single crystal ($0.25 \times 0.30 \times 0.40$ mm) was mounted on an Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer equipped with a liquid nitrogen low-temperature device and a graphite-monochromated Mo $K\alpha$ radiation source. Accurate unit-cell constants were derived from the setting angles of 22 reflexions ($27.6 \leq 2\theta \leq 35.2°$). The intensity data were collected at 250 K up to a maximum Bragg angle $\theta = 25°$ covering the range $0 \leq h \leq 10$, $0 \leq k \leq 16$, $-12 \leq l \leq 12$ [θ–2θ-scan mode, ω-scan width $(0.90 + 0.35\tan\theta)°$, ω-scan speed 1.7–10° min^{-1} according to count rate]. Intensity standards (202, 012, 110) were measured every hour and showed no significant variation. Orientation controls (025, 504, 465) were monitored every 150 reflexions. 2625 reflexions were measured, 2432 were unique ($R_{\rm int} = 0.010$) of which 1562 had $I > 3\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by Patterson and Fourier and difference Fourier syntheses, and refined by full-matrix least-squares refinements using the *SHELX76* program (Sheldrick, 1976). Atomic scattering factors and anomalous terms were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). $\sum w(F_o - |F_c|)^2$ was minimized, $w = 0.973/[\sigma^2(F) + 0.0014F^2]$. Anisotropic thermal parameters were refined for all non-H atoms. All H atoms were located from difference Fourier maps. The positional and isotropic displacement parameters of the H atom of the CH group were refined. The methyl H atoms were constrained to ride over the corresponding C atoms [C—H distances set to 0.97 Å, H-atom angles idealized, $U_{\rm iso}$(H) set equal to $U_{\rm eq}$(C)]. Final maximum (variable shift)/e.s.d. = 0.11, $R = 0.039$, $wR = 0.050$, $S = 1.08$, for 132 variables and 1562 observations with $I > 3\sigma(I)$. Maximum fluctuation in the final ΔF map was in the range -0.95–0.58 e Å^{-3}. The refined positional and thermal parameters are reported in Table 1,* bond lengths and angles in Table 2, and Fig. 1 shows a thermal ellipsoid plot with the atom-numbering scheme.

Table 1. *Final least-squares atomic parameters with e.s.d.'s in parentheses for* $C_{11}H_{19}IO_2$

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (*U*1**U*1**U*2**U*2**U*3**U*3)**(1/3) where *U*1, *U*2 and *U*3 are root-mean-square amplitudes of the vibrational tensor. Atom H(3) was refined isotropically.

	x	y	z	$U_{\rm eq}/U_{\rm iso}$ (Å^2)
I	0.11107 (5)	0.11705 (3)	0.35386 (5)	0.0586 (6)
O(1)	0.4335 (6)	0.1039 (4)	0.5517 (5)	0.064 (6)
O(2)	0.3091 (5)	0.2984 (3)	0.5741 (4)	0.048 (4)
C(1)	0.5942 (6)	0.1885 (5)	0.4456 (6)	0.046 (6)
C(11)	0.6113 (8)	0.1293 (5)	0.3312 (7)	0.061 (8)
C(21)	0.5997 (7)	0.2929 (5)	0.4127 (9)	0.060 (8)
C(31)	0.7202 (8)	0.1656 (7)	0.5663 (7)	0.07 (1)
C(2)	0.4431 (6)	0.1604 (4)	0.4717 (6)	0.043 (5)
C(3)	0.3032 (6)	0.2088 (4)	0.3867 (6)	0.036 (5)
C(4)	0.2655 (5)	0.2948 (4)	0.4564 (5)	0.036 (5)
C(5)	0.1750 (7)	0.3770 (4)	0.3809 (6)	0.041 (5)
C(15)	0.1518 (8)	0.3711 (5)	0.2334 (6)	0.056 (7)
C(25)	0.0207 (7)	0.3770 (5)	0.4125 (7)	0.058 (7)
C(35)	0.2557 (8)	0.4671 (5)	0.4323 (8)	0.069 (9)
H(3)	0.312 (5)	0.219 (4)	0.299 (5)	0.07 (1)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and non-bonded intramolecular contacts* (Å) *with e.s.d.'s in parentheses for* $C_{11}H_{19}IO_2$

C(1)—C(11)	1.520 (10)	C(3)—H(3)	0.96 (6)
C(1)—C(21)	1.530 (10)	C(3)—C(4)	1.515 (8)
C(1)—C(31)	1.529 (9)	C(4)—O(2)	1.213 (7)
C(1)—C(2)	1.536 (9)	C(4)—C(5)	1.538 (7)
C(2)—O(1)	1.190 (8)	C(5)—C(15)	1.530 (9)
C(2)—C(3)	1.534 (7)	C(5)—C(25)	1.537 (10)
C(3)—I	2.151 (5)	C(5)—C(35)	1.512 (9)
C(11)—C(1)—C(21)	109.8 (6)	H(3)—C(3)—I	102 (3)
C(11)—C(1)—C(31)	110.1 (6)	C(4)—C(3)—I	106.8 (3)
C(21)—C(1)—C(31)	109.6 (6)	C(4)—C(3)—H(3)	115 (3)
C(2)—C(1)—C(11)	106.4 (5)	C(3)—C(4)—C(5)	121.3 (5)
C(2)—C(1)—C(21)	112.2 (5)	C(3)—C(4)—O(2)	118.8 (5)
C(2)—C(1)—C(31)	108.6 (5)	C(5)—C(4)—O(2)	119.9 (5)
C(1)—C(2)—C(3)	115.9 (5)	C(4)—C(5)—C(15)	114.1 (5)
C(1)—C(2)—O(1)	122.7 (5)	C(4)—C(5)—C(25)	107.0 (5)
C(3)—C(2)—O(1)	121.4 (6)	C(4)—C(5)—C(35)	107.8 (4)
C(2)—C(3)—I	110.6 (4)	C(15)—C(5)—C(25)	109.2 (5)
C(2)—C(3)—H(3)	112 (3)	C(15)—C(5)—C(35)	110.1 (6)
C(2)—C(3)—C(4)	109.6 (4)	C(25)—C(5)—C(35)	108.5 (6)
I···O(1)	3.172 (5)	I···O(2)	3.644 (4)

NMR and IR spectra. The NMR spectrum was recorded on a Hitachi–Perkin–Elmer R24A (60 MHz) instrument for a CCl_4 solution, using $(CH_3)_4Si$ as internal reference. IR absorption spectra

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55131 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0268]

were recorded with a Perkin–Elmer IR-FT 1710 spectrometer for a CCl_4 solution and the solid state.

Discussion. The compound prepared by Schoppee & Stevenson (1972) as 4-iodo-2,2,6,6-tetramethylheptane-3,5-dione by reacting iodine chloride with 2,2,6,6-tetramethylheptane-3,5-dione melted at 286–288 K and slowly decomposed even when stored at 243 K. The present compound melts at 343 K which is more consistent with the values reported for the chlorine (292–293 K) and bromine derivatives (317–318 K) (Schoppee & Stevenson, 1972). It can be kept at room temperature without decomposition but a faint colouration of the plastic container occurs owing to iodine liberation either from the crystals or more probably from tiny iodine inclusions, visible on microscope examination.

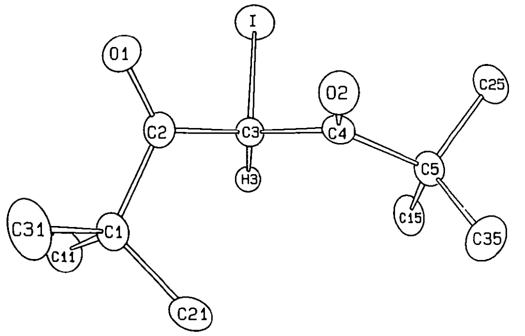

Fig. 1. The molecule of 4-iodo-2,2,6,6-tetramethylheptane-3,5-dione drawn using *ORTEP* (Johnson, 1965).

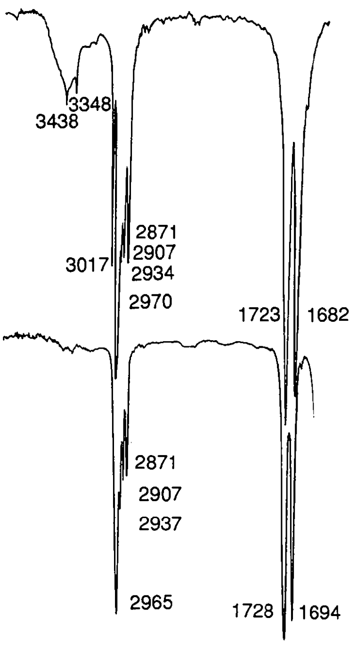

Fig. 2. Infrared absorption spectra of 4-iodo-2,2,6,6-tetramethylheptane-3,5-dione for the solid state (top) and CCl_4 solution (bottom).

A salient feature is the non-coplanarity of the carbonyl groups: the angle between the planes O(1)—C(1)—C(2)—C(3) and O(2)—C(3)—C(4)—C(5) is 101.2 (2)°. Consequently the I···O contacts are dissymmetrical: I···O(1) = 3.172 (5) Å is markedly shorter than the sum of van der Waals radii of the elements (1.40 + 2.20 = 3.60 Å) (Pauling, 1960), while I···O(2) = 3.644 (4) Å corresponds to a van der Waals contact. The C—O bonds are slightly, if not significantly, different from each other, C(2)—O(1) being shorter [1.190 (8) Å] than C(4)—O(2) [1.213 (7) Å], the shortest bond corresponding to the closest O atom to the I atom.

The IR absorption spectrum in the solid state (Fig. 2) shows two C═O stretching bands at 1682 and 1723 cm^{-1}. The angle between the directions of the C═O bonds is 50°. By introducing this value in the model proposed by Cotton & Lukehart (1971), it is inferred that the ratio of the intensities of the symmetric and antisymmetric bands generated by a strong coupling would be $I_{sym}/I_{asym} = 4.6$. Since the observed bands have nearly equal intensities, the C═O bonds are most likely to vibrate independently. The dissymmetry of the non-bonded intramolecular contacts between the O and I atoms might be responsible for the absence of coupling. Indeed, besides the differences in I···O separations mentioned above, the dissymmetry is marked by the O—C—C—I torsion angles, which show that the dipole C(3)—I is approximately parallel to the dipole C(2)—O(1) [O(1)—C(2)—C(3)—I = 31°] and approximately perpendicular to the dipole C(4)—O(2) [O(2)—C(4)—C(3)—I = 83°].

Another feature of the solid-state IR spectrum is the presence of a sharp medium band at 3017 cm^{-1} on the high-energy side of the ^{t}Bu C—H stretching massif. This band, attributable to the $\nu(C_\alpha—H)$ stretching, is not present in the IR spectrum for CCl_4 solution (Fig. 2). However, the energies of the C═O streching bands are slightly increased at 1694 and 1728 cm^{-1} and no O—H strectching band shows up, which precludes the formation of an enol. This was confirmed by proton NMR spectroscopy in CCl_4 solution which showed only two singlets at 1.24 and 5.76 p.p.m. with a ratio of relative intensities equal to 18:1, clearly indicating that no noticeable enolic form was present.

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Stereochemical Investigation of 2,3,4,6-Tetra-*O*-acetyl-1-*S*-benzhydroximoyl-*α*-D-glucopyranose

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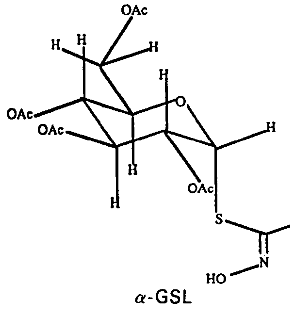
Abstract. 2,3,4,6-Tetra-*O*-acetyl-1-*S*-benzhydroximoyl-1-thio-*α*-D-glucopyranose (*α*-GSL) is the first synthetic *α*-glucosinolate. $C_{21}H_{25}NO_{10}S$, $M_r = 483.5$, monoclinic, $C2$, $a = 16.247$ (9), $b = 11.182$ (7), $c = 13.420$ (6) Å, $\beta = 91.62$ (4)°, $V = 2437.33$ Å^3, $Z = 4$, $D_m = 1.309$, $D_x = 1.317$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.711 Å, $F(000) = 1016$, room temperature, final $R = 0.052$ for 3712 unique reflections. The stereochemistry around the C=N bond was determined. The glucose residue has the expected $^4C_1$ conformation and the hydroxyl group on the N atom is found to be *syn* to the sugar ring. The crystal structure is stabilized by packing interactions. The structural features at the glucosidic position are: C(1)—S = 1.838 (3), C(7)=N = 1.273 (5) Å, φ [O(5)—C(1)—S—C(7)] = 54.9, ψ [C(1)—S—C(7)—C(8)] = 42, C(1)—S—C(7) = 98.5 (2)°. The observed conformational behaviour has been analyzed and compared with other known structures of thiosugars.

Introduction. Natural glucosinolates (GSL) occurring mainly in the family *Cruciferae* display exclusively a *β*-D-thioglucosyl configuration at the anomeric carbon and a *syn* relationship on the aglycon between the sulfur and oxygen atoms (Kjaer, 1978; Fenwick, 1983). In the course of our studies on the elaboration of potent artificial analogues of natural GSL with aim of understanding their biosynthesis and biodegradation, we have developed the synthesis of *α*-glucosinolates.

The investigation of the crystal structure of the first member (*α*-GSL) of this new family of compounds was undertaken in order to determine the geometry around the C=N bond. It was also of interest to provide more crystallographic information on thiosugars, because few X-ray structures of these compounds are available from the literature, for example: Takagi & Jeffrey (1978), Ducruix & Pascard (1977) and see Fig. 1.



α-GSL

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