

N1—C1	1.350 (7)	1.362 (7)	1.357 (4)
N1—C2	1.417 (7)	1.406 (7)	1.418 (4)
N2—C1	1.348 (7)	1.342 (7)	1.344 (4)
N2—C8	1.468 (7)	1.464 (7)	1.471 (4)
N2—C11	1.473 (7)	1.467 (7)	1.473 (4)
C8—C9	1.506 (10)	1.501 (10)	1.484 (6)
C10—C11	1.501 (10)	1.510 (10)	1.496 (5)
C7—C12			1.508 (6)
C10—O1—C9	109.8 (5)	110.6 (5)	109.1 (3)
C1—N1—C2	128.1 (5)	126.2 (5)	125.6 (3)
C1—N2—C8	122.1 (5)	123.6 (4)	122.8 (3)
C1—N2—C11	124.7 (4)	125.0 (5)	123.9 (3)
C11—N2—C8	111.2 (5)	111.2 (5)	111.2 (3)
N2—C1—N1	116.5 (4)	116.3 (5)	116.2 (3)
N2—C1—S1	121.6 (4)	122.4 (4)	122.9 (2)
N1—C1—S1	121.9 (4)	121.2 (4)	121.0 (3)
C3—C2—C7	119.6 (5)	118.6 (6)	120.2 (3)
C7—C2—N1	121.8 (5)	120.3 (5)	121.1 (3)
C3—C2—N1	118.4 (5)	121.0 (6)	118.5 (3)
C6—C7—C2	119.3 (6)	120.9 (7)	117.4 (4)
N2—C8—C9	108.8 (5)	110.2 (5)	110.1 (3)
O1—C9—C8	113.4 (6)	110.2 (6)	112.6 (3)
O1—C10—C11	111.7 (6)	112.2 (5)	111.8 (3)
N2—C11—C10	110.3 (5)	108.1 (6)	110.2 (3)
C2—C7—C12			121.4 (4)
C6—C7—C12			121.1 (4)
C2—N1—C1—N2	169.2 (5)	170.0 (5)	166.0 (3)
C2—N1—C1—S1	-12.7 (8)	-12.8 (8)	-15.8 (4)
C1—N1—C2—C3	137.3 (6)	-56.2 (8)	122.5 (4)
C1—N1—C2—C7	-46.5 (8)	125.8 (6)	-63.6 (4)
C8—N2—C1—N1	175.2 (6)	166.7 (5)	178.3 (3)
C8—N2—C1—S1	-2.9 (8)	-10.4 (8)	0.1 (4)
C11—N2—C1—N1	-22.0 (9)	-19.1 (9)	19.6 (6)
C11—N2—C1—S1	159.9 (5)	163.7 (5)	162.2 (3)
C1—N2—C8—C9	-141.0 (6)	117.6 (6)	-143.4 (3)
C1—N2—C11—C10	140.5 (6)	-118.7 (7)	143.4 (3)

Both of the structures were solved by direct methods and refined by the full-matrix least-squares technique. All H atoms in both structures were located from difference maps and refined isotropically. The *PARST* (Nardelli, 1983) program was used for geometric calculations.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993); geometric calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1225). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrogen Bonding versus van der Waals Repulsion in 1,3,5-Trideoxy-1,3,5-tris-(trimethylammonio)-*cis*-inositol Triiodide Sesquihydrate, C₁₅H₃₆N₃O₃³⁺·3I⁻·1.5H₂O

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Abstract

The crystal structure of the trimethylammonio-*cis*-inositol molecule displays one bifurcated intramolecular hydrogen bond of the form O—H···O, a strong intermolecular O—H···OW contact and possible intermolecular C—H···O and O—H···I interactions. C—H···I interactions may also be considered. As a result of the three bulky N(CH₃)₃ groups and the OH groups, increased puckering of the cyclohexane ring is observed compared with an undistorted ideal cyclohexane chair conformation.

Comment

This paper reports the structure of a cyclohexane chair substituted by bulky N(CH₃)₃ groups and OH groups. Intra- and intermolecular hydrogen bonds are competitors in this structure. Intramolecular three-center bonds, intermolecular OH···OW, CH···OW, OH···I and possible CH···I interactions are discussed. Fundamental work is summarized by Jeffrey & Saenger (1994). Additional information on OH···O and CH···O interactions is given by Steiner & Saenger (1993, 1994) and by

Steiner (1995). Crystallographic evidence for the existence of $\text{CH}\cdots\text{X}$ ($\text{X} = \text{O}, \text{N}, \text{Cl}$) hydrogen bonds has been described by Taylor & Kennard (1982).

Cyclohexane molecules having a *syn*-1,3,5-triaxial orientation of donor groups X ($\text{X} = \text{OH}$ or NH_2) are of interest because of their optimal steric arrangement for metal binding. Their high affinity for Fe^{III} and their different complexation properties for a variety of mono-, di-, tri- and tetravalent metal ions have been extensively studied by X-ray analysis, spectroscopic methods and molecular-mechanics calculations (Angyal, 1980; Hegetschweiler, Ghisletta, Fässler, Nesper, Schmalte & Rihs, 1993; Hegetschweiler, Hancock, Ghisletta, Kradolfer, Gramlich & Schmalte, 1993; Hausherr-Primo, Hegetschweiler, Rügger, Odier, Hancock, Schmalte & Gramlich, 1994; Hegetschweiler, Kradolfer, Gramlich & Hancock, 1995; Hancock & Hegetschweiler, 1993). On the one hand, the free ligands are destabilized by van der Waals repulsion of the electronegative OH or NH_2 groups, while on the other hand they are stabilized by attractive forces of intramolecular hydrogen bonds of the type $\text{X}-\text{H}\cdots\text{X}$. With respect to this interesting contradiction the question arises whether more than one intramolecular $\text{X}-\text{H}\cdots\text{X}$ hydrogen bond can be formed in the same molecule.

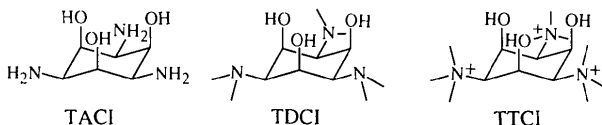


Fig. 1(a) shows some possible hydrogen-bonding schemes and Fig. 1(b) the observed intramolecular hydrogen bonds for the above-mentioned molecules. Up to now two examples are known in which equatorial N atoms can act as additional intramolecular acceptors: in $\text{TACI}\cdot 2\text{H}_2\text{O}$ (1,3,5-trideoxy-1,3,5-triamino-*cis*-inositol dihydrate) (Hegetschweiler, Hancock, Ghisletta, Kradolfer, Gramlich & Schmalte, 1993) and in TDCI [1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (Hegetschweiler, Erni, Schneider & Schmalte, 1990)]. Thus, the title compound, $\text{TTCI}\cdot 3\text{I}\cdot 1.5\text{H}_2\text{O}$, has been prepared in order to find out if additionally formed intra ($\text{X}-\text{H}\cdots\text{X}$) or intermolecular hydrogen bonds ($\text{X}-\text{H}\cdots\text{OH}_2$, $\text{X}-\text{H}\cdots\text{X}$) can occur when the N atoms are entirely blocked by space-filling CH_3 groups.

In molecules such as TACI, TDCI and TTCI, the axial hydroxy groups are well positioned to form intramolecular hydrogen bonds. Fig. 1 shows some possible $\text{O}-\text{H}\cdots\text{O}$ or $\text{O}-\text{H}\cdots\text{N}$ interactions. Both such types of intramolecular hydrogen bonds [(1) and (2)] may be realised in one molecule at the same time. The free donor, available for intermolecular hydrogen bonds, shown in (3) and (4), may also rotate towards the N-acceptor atom to form an additional $\text{O}-\text{H}\cdots\text{N}$ intramolecular hydrogen bond, whereas the conformation shown in (5) represents a bifurcated

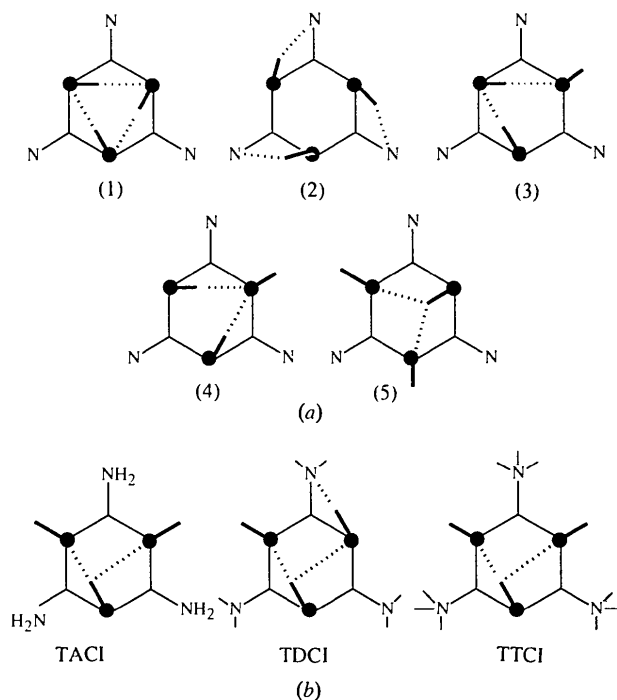


Fig. 1. (a) Possible hydrogen-bonding schemes and (b) observed intramolecular hydrogen bonds for cyclohexane molecules with a *syn*-1,3,5-triaxial orientation of donor groups X ($\text{X} = \text{OH}$ and NH_2).

hydrogen-bonding type that is extensively discussed, together with more complex hydrogen bonds found in biological systems, by Jeffrey & Saenger (1994). Additional water molecules and I^- ions, as well as participating in intermolecular bonding, will influence or even determine the number of possible intramolecular hydrogen bonds in the ring system. In $\text{TACI}\cdot 2\text{H}_2\text{O}$, the two water O atoms participate as donors and acceptors in intermolecular hydrogen bonds. The crystal packing also causes intermolecular hydrogen bonds between the axial OH and the NH_2 groups and between different TACI molecules. Thus, only one OH group can act as a donor for the bifurcated intramolecular hydrogen bond (Hegetschweiler, Hancock, Ghisletta, Kradolfer, Gramlich & Schmalte, 1993). TDCI crystallizes without solvent molecules, but in the structure intermolecular hydrogen bonds of the type $\text{O}-\text{H}\cdots\text{N}(\text{CH}_3)_2$ compete with intramolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ bonds. As in TACI, only one bifurcated intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond and one $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond are realised.

Conformational analyses of the eight isomers of inositol carried out by *ab initio* calculations showed an excellent agreement between the calculated model of epi-inositol and TDCI, and confirmed the geometry of the intramolecular hydrogen bond (Liang, Ewig, Stouch & Hagler, 1994). TTCI crystallizes with 1.5 water molecules that are distributed over two sites and with three I^- ions, of which two appear to

be disordered. Within this molecule again only one bifurcated intramolecular $O-H \cdots O$ hydrogen-bonding system is observed, with two hydroxy O atoms as acceptors (Fig. 2). These acceptor atoms also function as donors in intermolecular hydrogen-bonding interactions of the types $O-H \cdots OW$ and $O-H \cdots I$ (Fig. 3). The intermolecular $O4 \cdots O1W$ distance [2.628 (8) Å] is short and corresponds to a minimum value of $O \cdots O$ distances (2.55 Å) theoretically calculated by Ferraris & Ivaldi (1988), but it is far from the shortest experimentally observed $O \cdots O$ distances of about 2.40 Å (Joswig, Fues & Ferraris, 1982). $C-H \cdots O$ hydrogen bonds in

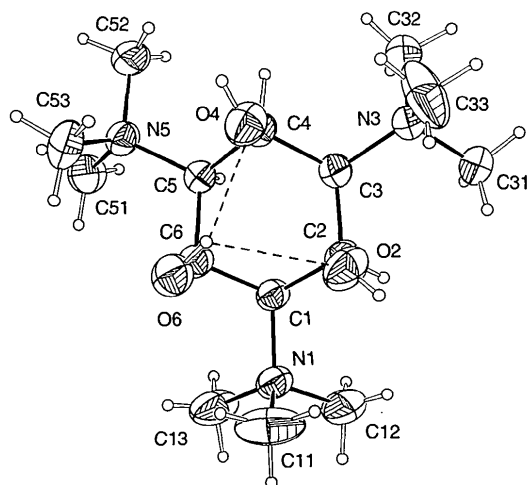


Fig. 2. ORTEP (Johnson, 1976) view of TtCI with atom-numbering scheme. The anisotropic displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The three-center hydrogen bond is indicated by broken lines.

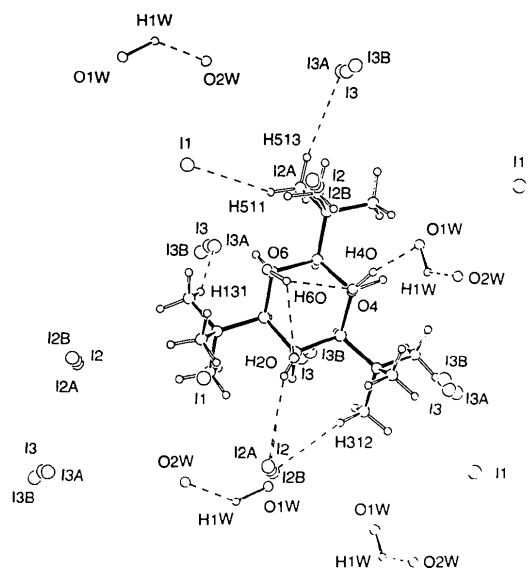


Fig. 3. A SCHAKAL (Keller, 1986) plot showing the hydrogen-bonding details in $TtCI \cdot 3I \cdot 1.5H_2O$.

crystal structures have been discussed extensively by Taylor & Kennard (1982) and reviewed by Desiraju (1991). The observed $C \cdots O$ distances and $C-H \cdots O$ angles in TtCI [ranging 2.96 (1) and 3.56 (1) Å and between 117 and 162°, respectively (see Table 3)] also indicate intermolecular hydrogen-bonding contacts.

Possible hydrogen bonds with $O \cdots I$ distances between 3.6 and 3.7 Å are discussed by Johansson, Molund & Oskarsson (1978). Some possible $CH \cdots I$ interactions are also listed in Table 3, but 23 further $CH \cdots I$ 'contacts' are not shown, as their $C \cdots I$ distances exceed 4.0 Å. However, all these corresponding $CH \cdots I$ angles range between 145 and 175°. Fig. 4 indicates the distribution of the water O atoms and the I^- ions in the structure. The hydrogen-bonding geometries of the title compound were calculated by using the program ORFFE (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971) and are listed in Table 3.

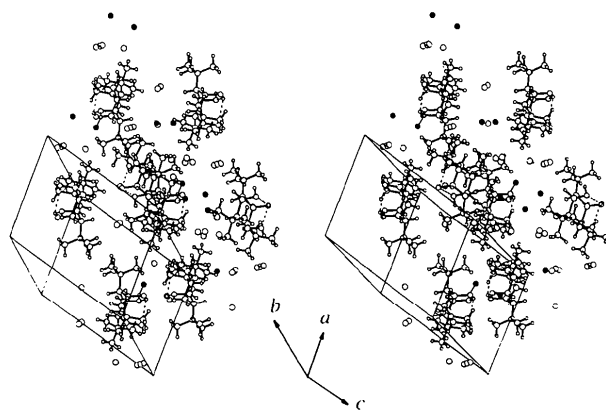


Fig. 4. A SCHAKAL (Keller, 1986) stereoview of a packing diagram of $TtCI \cdot 3I \cdot 1.5H_2O$.

Bulky substituents in a 1,3,5-*syn*-axial arrangement cause considerable van der Waals repulsion. This can be seen by viewing the molecules along the pseudo threefold axis (Fig. 1): the six axial substituents of a regular cyclohexane chair are located exactly above and below the corresponding C atoms. As shown in Fig. 2, the three O atoms of TtCI are significantly displaced from the ideal positions, therefore indicating a considerable amount of repulsion between the three axial hydroxy groups. Assuming C_{3v} symmetry, equal $O \cdots O$ distances should be found. The observed asymmetry is obviously a consequence of the presence of one bifurcated but asymmetric intramolecular hydrogen bond. Since the same hydrogen-bonding system occurs in TACI, TDCI and TtCI, it probably represents a low-energy conformation for such molecules. The $O \cdots O$ distances involved in the bifurcated intramolecular hydrogen bonds are 2.762 (2) and 2.827 (2) Å in TACI, 2.732 (2) and 2.862 (2) Å in TDCI, and 2.758 (5) and 2.883 (6) Å in TtCI. The repulsion between the

non-hydrogen-bonded O atoms results in significantly longer O···O distances of 2.935(3) Å for TACI and 3.006(2) Å for TDCI. This is not the case for the title compound, where the non-hydrogen-bonded O···O distance is shorter [O2···O4 2.824(6) Å] than one of the hydrogen-bonded O···O distances [O2···O6 2.883(6) Å]. If no water molecules were present in the crystal of TTCI, a second intramolecular hydrogen bond O4—H4O···O2 could possibly be formed, such as the one shown in (3). Furthermore, if it was possible to also remove the iodide I2 (I2A, I2B) from its (their) acceptor function(s) (see Fig. 3), the intramolecular hydrogen bonds may be completed as shown in (1).

Puckering parameters (Cremer & Pople, 1975) of the three ligands, calculated with *MOLEG* (Schweizer, 1985) are compared in Table 4. The undistorted cyclohexane chair has a Q_3 value of 0.630. The value of Q_3 for the unsubstituted TACI is significantly lower. This is consistent with a flattening of the ring due to the O···O repulsion. On the other hand, a significant increase for Q_3 is observed in the order TACI < TDCI < TTCI. This is obviously a consequence of the enlarged steric requirements of the three equatorial substituents. Thus, the axial–axial O···O and axial–equatorial O···N(CH₃)_n repulsions have opposite effects with respect to the ring puckering. This is also indicated by a comparison of the bond angles of the cyclohexane ring: the C—C ring angles around C1, C3 and C5 are larger (mean 113.1°) and those around C2, C4 and C6 are smaller (mean 104.7°) than the ideal tetrahedral angle of 109.5° (see Table 2). The mean C—C distances in the cyclohexane chairs of 1.533(3) Å for TACI and 1.535(2) Å for TDCI are in excellent agreement with the mean value of 1.535 Å for C_{sp³}—C_{sp³} distances listed in *International Tables for Crystallography* (1992, Vol. C), where 2814 distances are averaged (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1992). The mean C—C distance in the title compound is increased to 1.548(6) Å, probably due to the bulky substituents. The averaged values of the C_{ring}—NR and C_{ring}—OH distances are 1.468(3) and 1.427 Å, respectively, for TACI, 1.476(2) and 1.430(2) Å, respectively, for TDCI, but 1.547(5) and 1.412(5) Å, respectively, for TTCI, compared to values of 1.498 (for C_{sp³}—N⁺R) and 1.431 Å, respectively, given by Allen *et al.*, (1992).

Figs. 2 and 3 show considerable repulsion between the hydroxy O atoms and pairs of neighboring methyl groups which are parallel to the OH groups. The following values were calculated: O2···C11 3.004(8) and O2···C33 3.091(8) Å; O4···C33 2.957(8) and O4···C53 3.213(7) Å; O6···C11 3.010(9) and O6···C53 2.893(7) Å. This repulsion leads to increased C_{ring}—N—CH₃ angles of 114.7(3)–115.1(4)°, and to elongated C_{ring}—N bond lengths of 1.531(5)–1.556(5) Å. As a consequence, the axial hydroxy O atoms approach distances < 2.90 Å, and the C—C distances within the chair increase to the aforementioned

higher values. Both effects, the O···C repulsion and the O···O approach, are responsible not only for an increased puckering but also for the unusual C—C—C angles in the ring (Table 2). Methylation of the axial O atoms in TACI results in a loss of intramolecular hydrogen bonds. The O···O distances in this structure range between 2.95 and 3.11 Å (mean value 3.01 Å) (Hegetschweiler, Weber & Gramlich, 1995). These distances could be considered as a reference where no intramolecular hydrogen bonding is involved. This finding is also in agreement with the non-hydrogen-bonded O···O distances in TACI and TDCI. In the title compound, both the hydrogen-bonded and the non-bonded O···O distances are shorter than 2.90 Å, reflecting the unusual molecular geometry, mainly caused by the arrangement of the bulky methyl and hydroxy groups.

The mean value of the N—C trimethyl distances in TTCI is 1.502 Å. The C—C, C—N and C—O distances in TACI and TDCI agree well not only with the above-mentioned values but also with values found in crystal structures where N or O atoms are coordinated to metal ions (Schmalle, Hegetschweiler & Ghisletta, 1991; Hegetschweiler, Ghisletta, Fässler, Nesper, Schmalle & Rihs, 1993; Hegetschweiler, Hancock, Ghisletta, Kradolfer, Gramlich & Schmalle, 1993; Hegetschweiler, Weber & Gramlich, 1995).

Experimental

TACI and its *N*-methylated derivatives TDCI and the title compound have been prepared as described previously (Hegetschweiler, Erni, Schneider & Schmalle, 1990). It is interesting to note that all three ligands crystallize in the monoclinic space group $P2_1/n$. A safe and more efficient ligand preparation method and the structure of TACI were found later (Ghisletta, Jalett, Gerfin, Gramlich & Hegetschweiler, 1992; Hegetschweiler, Hancock, Ghisletta, Kradolfer, Gramlich & Schmalle, 1993). As TTCI is completely alkylated, the ligand bears three positive charges, thus, three counterions of iodide were necessary for crystallization. According to elemental analysis and the relatively large displacement parameters for the two water O atoms, it seems likely that the water positions are not fully occupied. Analysis for the air-dried product: calculated for C₁₅H₃₉N₃O_{4.5}I₃ C 25.23, H 5.50, N 5.88%; found C 25.26, H 5.56, N 5.73%.

Crystal data

C₁₅H₃₆N₃O₃³⁺·3I⁻·1.5H₂O

$M_r = 714.19$

Monoclinic

$P2_1/n$

$a = 9.690(3)$ Å

$b = 21.620(4)$ Å

$c = 12.835(3)$ Å

$\beta = 106.26(3)^\circ$

$V = 2581.4(11)$ Å³

$Z = 4$

$D_x = 1.838$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 8.3$ – 16.7°

$\mu = 3.656$ mm⁻¹

$T = 295(2)$ K

Plate

$0.70 \times 0.53 \times 0.18$ mm

Transparent, colorless

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.0398$
ω -2 θ scans	$\theta_{\text{max}} = 29.97^\circ$
Absorption correction: analytical	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.221$, $T_{\text{max}} = 0.723$	$k = 0 \rightarrow 30$
7808 measured reflections	$l = 0 \rightarrow 18$
7506 independent reflections	3 standard reflections
5250 observed reflections	monitored every 400 reflections
$[I > 2\sigma(I)]$	frequency: 180 min
	intensity decay: 2.1%

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 1.203 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.0472$	$\Delta\rho_{\text{min}} = -1.030 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1637$	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
$S = 1.285$	Extinction coefficient: 0.0031 (2)
7496 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
297 parameters	
Ring and OH H atoms refined freely	
$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 6.7866P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = -0.105$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
I1	0.13370 (4)	0.08326 (2)	0.26648 (3)	0.05453 (9)
I2	0.08036 (5)	0.34024 (2)	-0.00450 (4)	0.04415 (12)
I3	-0.12720 (6)	0.58628 (3)	0.51522 (5)	0.0580 (2)
I2A†	0.0521 (4)	0.3394 (2)	-0.0269 (3)	0.0409 (9)
I2B†	0.1015 (6)	0.3382 (3)	0.0121 (5)	0.0573 (14)
I3A†	0.1417 (7)	0.4233 (3)	0.4970 (5)	0.069 (2)
I3B†	0.1036 (6)	0.4034 (3)	0.4905 (5)	0.0587 (13)
C1	-0.2081 (4)	0.4298 (2)	0.2257 (3)	0.0333 (8)
C2	-0.1540 (4)	0.3668 (2)	0.1942 (3)	0.0364 (9)
C3	-0.1743 (5)	0.3209 (2)	0.2817 (4)	0.0378 (9)
C4	-0.3305 (4)	0.3146 (2)	0.2878 (3)	0.0344 (9)
C5	-0.3698 (4)	0.3807 (2)	0.3181 (3)	0.0327 (8)
C6	-0.3659 (4)	0.4280 (2)	0.2285 (3)	0.0333 (8)
O2	-0.2289 (4)	0.3469 (2)	0.0883 (3)	0.0499 (8)
O4	-0.4259 (4)	0.2949 (2)	0.1893 (3)	0.0462 (8)
O6	-0.4636 (4)	0.4170 (2)	0.1258 (3)	0.0456 (8)
N1	-0.1740 (4)	0.4855 (2)	0.1601 (3)	0.0354 (7)
C11	-0.2449 (8)	0.4830 (3)	0.0397 (4)	0.077 (2)
C12	-0.0154 (6)	0.4897 (3)	0.1760 (6)	0.068 (2)
C13	-0.2169 (7)	0.5432 (2)	0.2045 (5)	0.075 (2)
N3	-0.1016 (4)	0.2571 (2)	0.2783 (4)	0.0452 (9)
C31	0.0494 (5)	0.2655 (2)	0.2724 (5)	0.0535 (12)
C32	-0.0890 (7)	0.2243 (3)	0.3851 (6)	0.079 (2)
C33	-0.1785 (8)	0.2155 (3)	0.1865 (7)	0.085 (2)
N5	-0.5072 (4)	0.3848 (2)	0.3543 (3)	0.0369 (8)
C51	-0.5010 (6)	0.4434 (2)	0.4187 (4)	0.0480 (11)
C52	-0.5135 (6)	0.3324 (2)	0.4303 (5)	0.0556 (12)
C53	-0.6445 (5)	0.3853 (3)	0.2629 (5)	0.0553 (14)
O1W	0.3962 (8)	0.2132 (3)	0.2314 (5)	0.106 (2)
O2W	0.3243 (6)	0.1173 (4)	0.0778 (5)	0.076 (2)

† Disordered; U_{iso} (see text).Table 2. Selected geometric parameters (\AA , $^\circ$)

C1—C6	1.540 (6)	O2—H2O	0.66 (6)
C1—N1	1.556 (5)	O4—H4O	0.83 (8)
C1—C2	1.554 (6)	O6—H6O	0.79 (8)

C2—O2	1.417 (5)	N1—C13	1.479 (6)
C2—C3	1.551 (6)	N1—C12	1.495 (7)
C3—C4	1.543 (6)	N1—C11	1.506 (6)
C3—N3	1.556 (5)	N3—C31	1.497 (6)
C4—O4	1.407 (5)	N3—C33	1.504 (8)
C4—C5	1.555 (6)	N3—C32	1.518 (7)
C5—N5	1.531 (5)	N5—C51	1.504 (6)
C5—C6	1.547 (6)	N5—C53	1.507 (6)
C6—O6	1.412 (5)	N5—C52	1.509 (6)
C6—C1—N1	113.3 (3)	C13—N1—C12	106.5 (4)
C6—C1—C2	113.2 (3)	C13—N1—C11	109.2 (5)
N1—C1—C2	113.5 (3)	C12—N1—C11	107.4 (4)
O2—C2—C3	111.4 (3)	C13—N1—C1	108.6 (3)
O2—C2—C1	113.4 (3)	C12—N1—C1	109.8 (3)
C3—C2—C1	104.6 (3)	C11—N1—C1	115.1 (4)
C4—C3—C2	114.7 (3)	C31—N3—C33	108.1 (5)
C4—C3—N3	112.4 (3)	C31—N3—C32	105.7 (4)
C2—C3—N3	113.4 (4)	C33—N3—C32	109.0 (5)
O4—C4—C3	112.9 (4)	C31—N3—C3	110.4 (3)
O4—C4—C5	111.0 (3)	C33—N3—C3	115.1 (4)
C3—C4—C5	104.1 (3)	C32—N3—C3	108.2 (4)
N5—C5—C6	113.0 (3)	C51—N5—C53	108.2 (4)
N5—C5—C4	115.1 (3)	C51—N5—C52	106.3 (4)
C6—C5—C4	111.3 (3)	C53—N5—C52	108.8 (4)
O6—C6—C1	113.1 (3)	C51—N5—C5	108.2 (3)
O6—C6—C5	115.7 (3)	C53—N5—C5	114.7 (3)
C1—C6—C5	105.4 (3)	C52—N5—C5	110.4 (3)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4O \cdots O1W ⁿ	0.83 (8)	1.82 (8)	2.628 (8)	163 (8)
O6—H6O \cdots O4	0.79 (8)	2.10 (8)	2.758 (5)	141 (7)
O6—H6O \cdots O2	0.79 (8)	2.44 (8)	2.883 (6)	116 (6)
O2—H2O \cdots I2A	0.66 (6)	2.83 (6)	3.447 (6)	155 (5)
O2—H2O \cdots I2	0.66 (6)	2.93 (6)	3.524 (4)	150 (5)
O2—H2O \cdots I2B	0.66 (6)	3.04 (6)	3.604 (8)	146 (5)
C5—H5 \cdots O2W ⁿ	1.08 (4)	2.40 (4)	3.338 (7)	145 (3)
C33—H332 \cdots O2	0.96 (2)	2.47 (3)	3.091 (8)	123 (1)
C33—H333 \cdots O4	0.96 (3)	2.39 (4)	2.957 (8)	117 (2)
C51—H512 \cdots O2W ⁿ	0.96 (2)	2.66 (2)	3.497 (7)	146 (2)
C52—H521 \cdots O1W ⁿ	0.96 (1)	2.63 (1)	3.560 (8)	162 (1)
C52—H523 \cdots O2W ⁿ	0.96 (2)	2.62 (2)	3.466 (8)	147 (2)
C1—H1 \cdots I3B	0.96 (4)	3.03 (4)	3.905 (6)	152 (3)
C1—H1 \cdots I3 ⁱⁱⁱ	0.96 (4)	3.08 (4)	3.960 (4)	152 (3)
C3—H3 \cdots I3B	1.06 (6)	2.68 (6)	3.684 (7)	157 (6)
C3—H3 \cdots I3 ⁱⁱⁱ	1.06 (6)	2.91 (6)	3.884 (4)	153 (6)
C11—H111 \cdots I1 ⁱⁱ	0.96 (4)	3.14 (1)	3.664 (6)	116 (3)
C13—H131 \cdots I3A ⁱⁱⁱ	0.96 (1)	2.85 (1)	3.76 (1)	160 (3)
C13—H131 \cdots I3B ⁱⁱⁱ	0.96 (1)	3.03 (1)	3.931 (9)	157 (2)
C13—H131 \cdots I3	0.96 (1)	3.04 (2)	3.949 (7)	159 (3)
C31—H312 \cdots I2	0.96 (2)	3.04 (2)	3.991 (6)	173 (1)
C51—H511 \cdots I1 ⁱⁱ	0.96 (1)	2.95 (1)	3.838 (5)	154 (3)
C51—H513 \cdots I3A ⁱ	0.96 (3)	2.95 (3)	3.89 (1)	165 (2)
C51—H513 \cdots I3 ^v	0.96 (3)	3.06 (3)	3.978 (6)	161 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $-x, 1-y, 1-z$; (iv) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $-1-x, 1-y, 1-z$.Table 4. Puckering parameters Q (\AA), φ and θ ($^\circ$) for the ring atoms C1 to C6 in the TACI molecule and for its methylated derivatives TDCI and TTCI

	TACI	TDCI	TTCI
Q_2	0.039	0.072	0.037
Q_3	0.553	-0.582	-0.648
φ	0.554	-0.586	-0.649
Q	246.39	-45.23	247.15
θ	4.03	-7.05	-3.27

Data collection, unit-cell parameter refinement and crystal-face indexing were carried out with *Enraf-Nonius CAD-4 Software* (Enraf-Nonius, 1989). Data reduction and the numerical absorption correction, which was based on eight crystal faces, were performed using the *MolEN* program package (Fair, 1990). The crystal structure of TTCI was determined by using

the Patterson method and refined by full-matrix least-squares techniques. For all non-H atoms, anisotropic displacement parameters were refined, except the disordered parts of I2 and I3. Two pairs of peaks in the difference electron-density map relating to I2 and I3 were refined as disordered parts of these ions, with site occupations of 80% for both I2 and I3. For the isotropically refined split positions I2A, I2B, I3A and I3B, 10% site occupations were assumed according to their isotropic displacement parameter values from a previous refinement. Test refinements in which these peaks were treated as parts of water O atoms, assuming a statistical disorder between I⁻ ions and water, failed completely. The cyclohexane H atoms H1 to H6 and the hydroxy H atoms H2O, H4O and H6O were refined with individual isotropic displacement parameters. The H-atom positions of the methyl groups were geometrically idealized and their isotropic displacement parameters were assigned as 1.5U_{eq} of the preceding C atom. Only one water H atom could be located in the difference electron-density map, but it was not refined.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976); *SCHAKAL86* (Keller, 1986). Software used to prepare material for publication: CIF (Hall, Allen & Brown, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(4-Methoxyphenoxy)-1,2-benzisothiazole 1,1-Dioxide: its Relation to Mechanistic Behaviour in Catalytic Transfer Hydrogenolysis

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Abstract

Conjugation of oxygen with an aromatic ring, as in a phenol, gives a C—O bond length of about 1.35 Å, whereas the C—O bond length in an aliphatic alcohol is about 1.45 Å. A saccharyl ether derivative of a phenol changes the phenolic C—O bond length to 1.42 Å and makes the bond chemically more susceptible

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