9. Preparation, Characterisation, and Structure of *N*-Methylated Derivatives of 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol: Polyalcohols with Unusual Acidity

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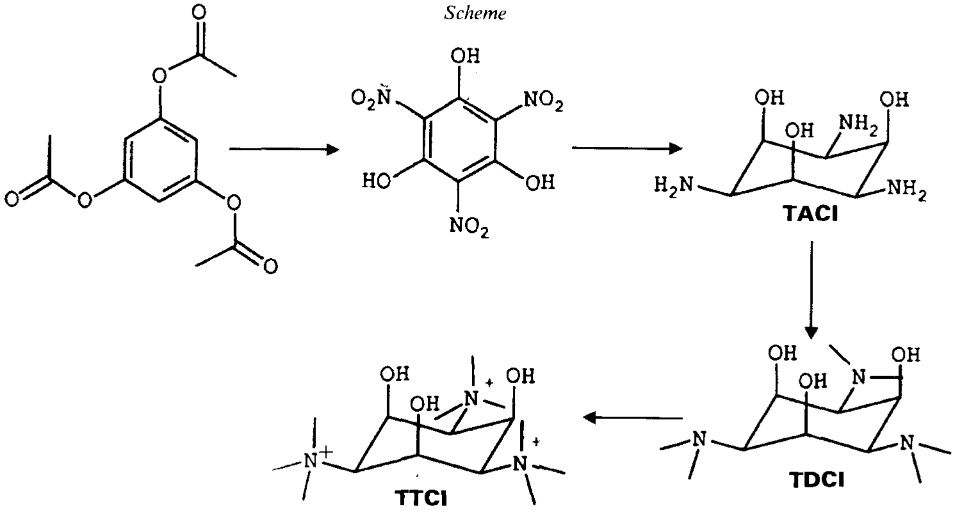
1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (TDCI) and 1,3,5-trideoxy-1,3,5-tris(trimethylammonio)-*cis*-inositol (TTCI) were prepared by methylation of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (TACI). The ability of TDCI to form both intermolecular and intramolecular H-bonds, as demonstrated by X-ray diffraction, is probably responsible for the good solubility of TDCI in almost every common solvent. TTCI was found to be a polyol of unusual high acidity ($pK_1 = 8.14 \pm 0.02$, $pK_2 = 13.0 \pm 0.2$). This phenomenon could be explained by electrostatic interactions between the charged substituents of the cyclohexane residue.

Introduction. – Aliphatic and alicyclic polyhydroxy compounds are wide spread in nature and have, therefore, been extensively investigated. They are generally considered to be highly hydrophilic and insoluble in non-polar solvents. The acidity of the OH groups is usally only slightly enhanced, compared to aliphatic monohydroxy compounds or H_2O, and interactions with metal ions are known to be weak or even negligible. Metal-complex formation of sugars and cyclitols was investigated by *Angyal* [1]. He found that *cis*-inositol has some enhanced affinity to metal ions due to the unique configuration with three axial OH groups on the same side of the molecule in either of its two chair conformations. A similar conformation of either three OH or three NH_2 groups is found in 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (TACI), and metal binding is possible by the OH or the NH_2 groups, depending on the nature of the metal. Developing new chelating agents for Fe(III), we found that TACI has a very high affinity for this cation. The complexes decay, however, probably due to the oxidation of the NH_2 groups catalyzed by Fe(III). Using the two methylated derivatives, 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (TDCI) and 1,3,5-trideoxy-1,3,5-tris(trimethylammonio)-*cis*-inositol (TTCI), this oxidation could be prevented, and very stable complexes of Fe(III) could be observed. The more bulky dimethylamino and trimethylammonio groups also stabilize the conformation of three axial OH groups, as required for the coordination with Fe(III). Both, TDCI and TTCI are unusual polyalcohols with regard to the qualities mentioned above. We report here the syntheses, structure, and some remarkable properties of these two new ligands. The equilibrium data of the metal complexes will be published separately.

Results and Discussion. – *Preparation of TDCI and TTCI.* The synthesis of TACI is reported by *Quadbeck* and *Röhm* [2] and *Lichtenthaler* and *Leinert* [3]. We slightly

Scheme



modified their method to avoid some experimental difficulties *(Scheme)*. Trinitrophloroglucinol could be easily prepared by nitration of phloroglucinol-triacetate in HNO_3 as described in [4], and it was not necessary to use the highly explosive trinitrosophloroglucinol [5]. The HNO_3 was neutralized with KOH. To get rid of the large excess of KNO_3, the product was precipitated as an almost insoluble Ba salt from aqueous solution. Trinitrophloroglucinol was liberated by the addition of H_2SO_4 and obtained in good quality and yield. In the subsequent step, the desired TACI · 1.5 H_2SO_4 could be produced by direct hydrogenation of trinitrophloroglucinol. The isolation of the highly air-sensitive intermediate triaminophloroglucinol was not necessary. The methylation of TACI with HCHO and HCOOH *(Leuckart-Wallach)* failed (formation of stereoisomers), and the reaction with MeI was not successful either. However, we could obtain the dimethylamino derivative TDCI by catalytic hydrogenation of TACI in the presence of HCHO with Pt as catalyst. The final methylation to TTCI is difficult, because the already charged intermediate mono- and diquaternary ammonium cations form insoluble salts and precipitate easily. TTCI can be produced though, using an excess of MeI in MeOH/H_2O.

Characterisation and Molecular Structure. TDCI crystallizes (from boiling hexane) in large monoclinic platelets (up to several mm). It is surprisingly well soluble in almost every solvent like H_2O, acetone, CH_2Cl_2, and even warm hexane. The rather unusual high solubility in non-polar solvents most likely originates from intramolecular H-bonding. Two intramolecular H-bonds can be observed in the solid state according to the X-ray structure analysis *(Fig. 1)*: O(4)–H···O(2) and O(6)–H···N(1). The molecular packing given in the *ORTEP* stereo plot of *Fig. 2* shows that there is only one intermolecular H-bond of the type O(2)–H···N(5) in the structure, forming endless chains of alternate molecules along axis *b*. (For the interatomic distances and angles of all three H-bonds, *cf. Table 5*.) In the solid state, the molecular symmetry is low. In solution, however, ^1H- and ^{13}C-NMR spectra of all the three derivatives TACI, TDCI, and TTCI demonstrate clearly that the highest possible symmetry C_{3v} must be taken into account. As expected, two signals for TACI and each three signals for TDCI and TTCI, respectively, could be

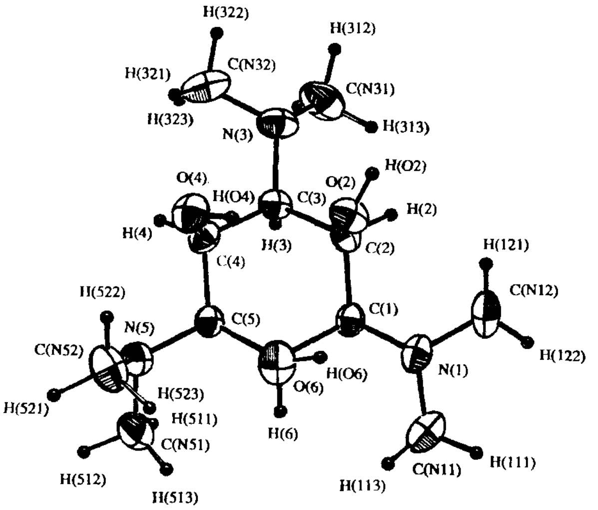


Fig. 1. *Crystal structure of TDCI: ORTEP plot* [6] *with numbering scheme and vibrational ellipsoides at the 50% probability level.* H-Atoms are shown as spheres of arbitrary size.

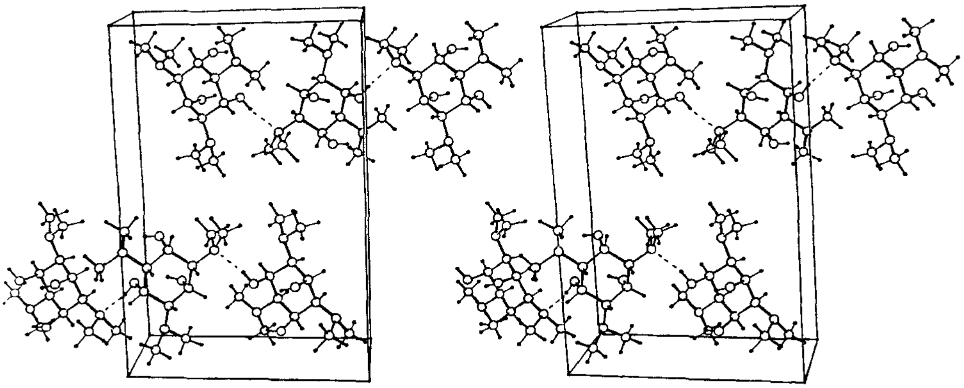


Fig. 2. *Stereoview of the monoclinic crystal structure of TDCI.* Intermolecular H-bonds are indicated by broken lines.

observed in the ^{13}C-NMR spectrum. For all three compounds, the six ring protons give two *multiplets* in the ^{1}H-NMR spectrum with significant long-range coupling between equatorial protons. For instance, the spectrum of TACI could be rationalized as $AA'A''XX'X''$ system with J_{XA} of 3.6, J_{XX} of 1.2, and J_{AA} of 0 Hz. The interpretation as first-order spectrum as given in [3], therefore, seems to be inaccurate.

*p*K *Values.* TACI and TDCI are weak bases as expected for alicyclic amines. The neutralisation curve of the corresponding ammonium compounds together with the neutralisation curve of TTCI is shown in *Fig. 3*, the p*K* values are presented in *Table 1*. TTCI can be doubly deprotonated in aqueous solution. The high acidity is unusual for a saturated polyol. The p*K* values of aliphatic polyols like sorbitol [7], glycerol, or ethane-

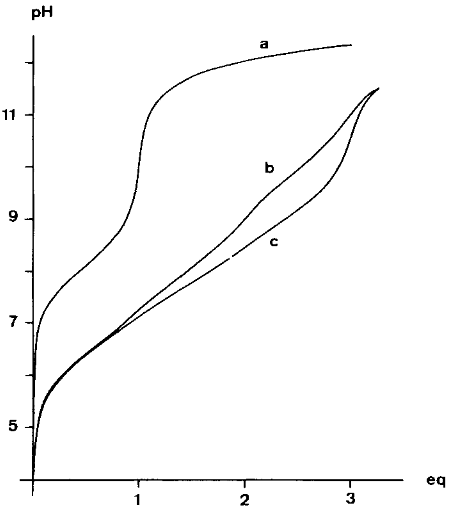
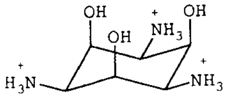
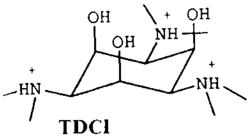
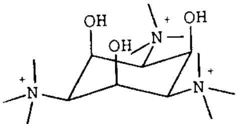


Fig. 3. *Neutralization of the ligands TTCI (*a*), TDCI · 3 HCl (*b*), TACI · 3 HCl (*c*) in 1* M *KCl with 1* M *KOH* (25°). eq. = mol KOH/mol ligand.

Table 1. *pK Values of 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol and Its* N*-Methylated Derivatives*

Compound	pK_1	pK_2	pK_3
 **TACI**	6.43 ± 0.02	7.78 ± 0.02	9.13 ± 0.02
 **TDCI**	6.45 ± 0.02	8.07 ± 0.02	9.95 ± 0.02
 **TTCI**	8.14 ± 0.02	13.0 ± 0.2	–

diol [8] are in the range of 13.5 to 15. Only for fluorinated alcohols, comparable acidities can be observed (hexafluoroisopropanol: 9.42 [9], perfluoropinacol: 5.95 [10]). Moreover, the difference of acidity between the three OH groups is surprisingly high compared to the values observed for the ammonium groups in TACI and TDCI. For a large variety of aliphatic polyamines, *Miescher* and coworkers [11] pointed out, that ΔpK is basically a function of chain length between the two examined ammonium groups. For all, TACI, TDCI, and TTCI, the considered functional groups are separated by three C-atoms.

Comparing these three compounds with the aliphatic reference propane-1,3-diamine ($\Delta pK_{1,2} = 2$), it is noteworthy that the values for TACI ($\Delta pK_{1,2} = 1.35$, $\Delta pK_{2,3} = 1.35$) and TDCI ($\Delta pK_{1,2} = 1.62$, $\Delta pK_{2,3} = 1.88$) are slightly diminished, whereas the value for TTCI ($\Delta pK_{1,2} = 4.9$) fits rather in the range expected for a chain length of one atom only. This result is obviously a consequence of the particular structure of TACI and its derivatives. The bulky substituents in equatorial position prevent chair conversion and enforce a short distance between the axial OH groups (average O···O distance in TDCI: 2.87 Å), whereas the distance between the equatorial amino groups is large (average N···N distance in TDCI: 4.98 Å). Thus, TDCI and TTCI are instructive models to elucidate the influence of conformation on ΔpK.

It should be noted that the measured pK values are macroscopic equilibrium constants ($pK_i = -\log[H_{-i}A][H^+]/[H_{1-i}A]$). In the case of $A = H_3TACI$ or H_3TDCI, different tautomers must be considered for the deprotonated forms $H_{-1}A$ and $H_{-2}A$ due to the possible deprotonation on the OH or the ammonium groups. If it is assumed, however, that the acidity of the OH groups in H_3TACI and H_3TDCI is comparable to that of TTCI, deprotonation will mainly occur on the ammonium groups, and the measured values represent closely their intrinsic acidity.

Both phenomena, the high acidity and the unusual $\Delta pK_{1,2}$ of TTCI can be explained in terms of long-range coulombic interactions using a point charge model as described in [12]. The charged substituents of the cyclohexane residue yield an additional electrostatic energy φ for deprotonation compared to the isosteric but uncharged 1,3,5-tri(*tert*-butyl)-1,3,5-trideoxy-*cis*-inositol (TBCI). Considering the interactions shown in *Fig. 4*, φ was calculated to be $(1/b + 2/c)e^2/4\pi\varepsilon_0\varepsilon_{\text{eff}}$ for TTCI, $(1/b + 2/c - 1/a)e^2/4\pi\varepsilon_0\varepsilon_{\text{eff}}$ for H_{-1}TTCI and $(1/b + 2/c - 2/a)e^2/4\pi\varepsilon_0\varepsilon_{\text{eff}}$ for H_{-2}TTCI. The effective dielectric constant $\varepsilon_{\text{eff}} = 20$ was derived from $\Delta pK_{1,2}$ diminished by the statistical factor 0.47. The value $pK = 19$ was then evaluated for TBCI accounting for loss of interionic repulsion and the pK_3 of TTCI was estimated to be 18.

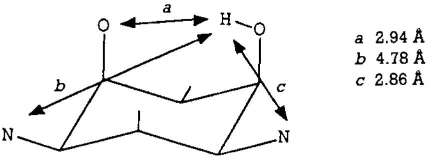


Fig. 4. *Electrostatic interactions used for the calculation of pK values of TTCI.* The distances are average values from the X-ray structure of TDCI.

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Experimental. – *General.* M.p.: *Büchi SMP-20*; not corrected. UV/VIS Spectra: *Uvikon 810*, $\lambda_{\max}(\log \varepsilon)$ in nm. IR spectra: *Beckman IR-4250*, in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker HX-90E* and *Bruker WM-250*, δ[ppm] scale, TSP (= 0 ppm) as internal standard. MS: Prof. *J. Seibl*, Laboratorium für org. Chemie, ETH Zürich, *Hitachi Perkin-Elmer RMU 6M*, data given as *m/z*(%). C,H,N Analyses: *D. Manser*, Laboratorium für org. Chemie, ETH Zürich.

pK Determination. A soln. (100 ml) containing $2 \cdot 10^{-2}$ M TACI · 3 HCl or $2 \cdot 10^{-2}$ M TDCI 3 · HCl, or 10^{-2} M TTCI in 1M KCl was adjusted to 25° and kept under N_2. Base (1M KOH) was added in increments of 0.1 ml or less with a *Mettler DV 11* burette. Points with [OH]/[A] between 0 and 3 (A = TACI and TDCI) or between 0 and 2

(A = TTCI) were used to calculate 3 or 2 p*K* values according to the method of minimization of the weighted residuals of the mass-balance equations [13]. A pH electrode (*Möller*) with a built-in reference was used, which was calibrated before and after each determination of the p*K*'s by titration of 100 ml $2 \cdot 10^{-2}$ M HCl in 1M KCl with 1M KOH.

Phloroglucinoltriacetate was prepared according to the method of *Heller* [14]. Colorless crystals (95%). M.p. 106°. IR (KBr): 3100*m*, 1770*s*, 1605*m*, 1460*m*. ^{1}H-NMR (90 MHz, $CDCl_3$): 6.84 (*s*, 3 H); 2.23 (*s*, 9 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 168.4; 151.1; 112.7; 20.8. MS: 126 (100), 252 (5, M^+). Anal. calc. for $C_{12}H_{12}O_6$ (252.2): C 57.14, H 4.80; found: C 57.07, H 4.79.

Trinitrophloroglucinol was prepared following a modified procedure given in [4]: 600 g (9.5 mol) of HNO_3 (fuming, 100%) was cooled to 0°, and 100 g (0.4 mol) of phloroglucinoltriacetate were added in small portions. The resultant mixture was poured onto 1 kg of ice and slowly neutralized with 50% KOH, until the pH of the mixture was strongly alkaline (pH > 10). The cold mixture was filtered and the remaining solid dissolved in 3 l of hot H_2O. A soln. of 250 g (1.2 mol) of $BaCl_2$ was added, and a yellow solid precipitated, which was filtered and washed with H_2O. 100 g of this tribarium bis(trinitrophloroglucinolat) was suspended in 2.5 l of H_2O, and 340 ml (0.34 mol) of 1M aq. H_2SO_4 was added. The precipitated $BaSO_4$ was removed by filtration, and the soln. was concentrated *in vacuo* to a volume of 100 ml. The remaining suspension was heated to 95°, and small amounts of additional H_2O were added, until a clear soln. was obtained. On cooling to 4°, a yellow solid crystallized. Yield: 60 g (0.21 mol, 53%) of trinitrophloroglucinol monohydrat. M.p. 167°. UV (H_2O): 5M HCl: 316 ($1.1 \cdot 10^4$), pH 2.5: 378 ($1.9 \cdot 10^4$), pH 4.7: 368 ($2 \cdot 10^4$), pH 12: 398 ($1.7 \cdot 10^4$). IR (KBr): identical with the spectrum reported in [15]. ^{13}C-NMR (62.9 MHz, (D_6)acetone): 151.9; 121.6.

*1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol sulfate* was prepared following a modified procedure given in [3]: 4.4 g PtO_2 was suspended in 255 ml of 1M aq. H_2SO_4. The mixture was placed in a glass autoclave fitted with a *Teflon* stirrer and hydrogenated (9 bar). After 10 min, the hydrogenation was interrupted, and 47 g (168 mmol) of trinitrophloroglucinol were added. The hydrogenation (9 bar) was continued for 10 d, and the suspension obtained was diluted with H_2O, until the white solid was completely dissolved. The Pt was removed by filtration, and the product was precipitated by slow addition of 1.2 l of MeOH. The product was finally recrystallized 6 times from H_2O/MeOH as described in [3]. Yield: 27 g (50%). IR (KBr): 3700–2200, 1590*m*, 1510*s*, 1430*w*, 1405*w*, 1390*w*, 1380*w*, 1360*w*, 1345*w*, 1315*w*, 1290*w*, 1235*w*, 1190*m*, 1120*s*, 1050*s*, 1035*s*, 910*m*, 905*m*, 810*w*, 725*m*, 620*m*, 590*m*. ^{1}H-NMR (90 MHz, D_2O): 4.8 (*s*, HDO); 4.5 (*m*, 3 H); 3.8 (*m*, 3 H). ^{13}C-NMR (62.9 MHz, D_2O): 65.6, 50.5. Anal. calc. for $C_6H_{15}N_3O_3 \cdot 1.5\ H_2SO_4$ (324.32): C 22.22, H 5.59, N 12.96, S 14.83; found: C 22.22, H 5.69, N 12.80, S 14.91.

*1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol trihydrochloride* could be obtained by ion-exchange chromatography (*Dowex 1*, Cl^- form). Recrystallization from aq. HCl (38%). ^{1}H-NMR (90 MHz, D_2O): identical with TACI · 1.5 H_2SO_4.

*1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol* was obtained by ion exchange (*Dowex 1*, OH^- form) as described in [3]. ^{1}H-NMR (90 MHz, D_2O): 4.8 (*s*, HDO); 3.83 (*m*, 3 H); 2.8 (*m*, 3 H). ^{13}C-NMR (62.9 MHz, D_2O): 73.7; 51.7. MS: 71 (100), 178 (4, $[M + 1]^+$).

*1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol Trihydrochloride Dihydrate.* PtO_2 (2.2 g) suspended in 200 ml of H_2O, was reduced by hydrogenation in a glass autoclave as mentioned above. TACI · 1.5 H_2SO_4 (15 g) and a 40% aq. soln. of HCHO (40 g) was added, and the hydrogenation was continued for 2 d. The catalyst was then separated from the soln., and the solvent removed under reduced pressure. The white solid was redissolved in 100 ml of H_2O, and SO_4^{2-} was exchanged against Cl^- by chromatography on *Dowex 1*. The solvent was removed again *in vacuo*, and the white solid was recrystallized from 300 ml of boiling MeOH. Yield 12 g (64%). ^{1}H-NMR (90 MHz, D_2O): 5.0 (*m*, 3 H); 4.8 (*s*, HDO); 3.6 (*m*, 3 H); 3.2 (*s*, 18 H). ^{13}C-NMR (62.9 MHz, D_2O): 64.6; 61.8; 42.4. MS: 127 (100), 261 (2, M^+), 262 (2, $[M + 1]^+$). Anal. calc. for $C_{12}H_{27}N_3O_3 \cdot 3\ HCl \cdot 2\ H_2O$ (406.78): C 35.43, H 8.42, N 10.33, Cl 26.15; found: C 35.28, H 8.04, N 10.23, Cl 26.40.

*1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol.* TDCI · 3 HCl · 2 H_2O (12 g, 29.5 mmol) was dissolved in 100 ml of H_2O and subjected to ion-exchange chromatography (*Dowex 1*, OH^- form). H_2O was removed under reduced pressure, and the white solid (TDCI · H_2O) was suspended in 500 ml of boiling hexane. The remaining H_2O was removed by azeotrope distillation, and the clear soln. was concentrated to a final volume of 300 ml. After filtration, a white solid crystallized at 4°. Recrystallization from hexane gave 7 g (91%) of TDCI. M.p. 118–119°. IR (KBr): 3450*s*, 2965*m*, 2877*m*, 2834*m*, 2782*m*, 1637*m*, 1476*m*, 1102*m*, 1039*m*, 905*m*, 882*m*. ^{1}H-NMR (90 MHz, $CDCl_3$): 4.35 (*m*, 3 H); 3.8 (*m*, 3 H); 2.47 (*s*, 18 H); 1.73 (*m*, 3 H). ^{13}C-NMR (62.9 MHz, D_2O): 66.6; 66.3; 42.3. Anal. calc. for $C_{12}H_{27}N_3O_3$ (261.37): C 55.15, H 10.41, N 16.08; found: C 55.08, H 10.34, N 15.96.

X-Ray Diffraction. Data collection was performed on a colorless crystal (0.34 × 0.53 × 0.58 mm) using an *Enraf-Nonius CAD-4* diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The ex-

Table 2. *X-Ray Crystal-Structure Results for 1,3,5-Trideoxy-1,3,5-tris(dimethylamino)*-cis-*Inositol* ($C_{12}H_{27}N_3O_3$)

Temperature of data collection		295 K
Unit cell dimensions	a [Å]	6.052(2)
	b [Å]	12.856(2)
	c [Å]	18.398(3)
	β [°]	94.44(2)
	V [Å^3]	1427.2(10)
Space group		$P2_1/n$
Molecules per unit cell		4
Maximum value of $(\sin\Theta)/\lambda$		0.7035
Method of measuring intensities		$\omega/2\Theta$ scan mode
Variable scan speeds		1.65 to 8.24°/min
No. of measured reflections		4432
value of R_{int} $\Sigma\|F - \langle F\rangle\|/\Sigma F$		0.044
No. of unique reflections		4287
No. of observed reflections ($I \geq 3\sigma(I)$)		2587
Numerical absorption correction (8 crystal faces) max/min transmission coefficients		0.9833/0.9724
Final value of	R (F)	0.045
	$R_w(F)$	0.041

Table 3. *Atomic Coordinates and Equivalent Isotropic Displacement Parameters of TDCI with e.s.d.'s in Parentheses.* The U_{eq} are defined by $1/3\,\Sigma_i \Sigma_j u_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Atom	x	y	z	U_{eq} [Å^2]	Atom	x	y	z	U_{iso} [Å^2]
N(1)	0.3858 (3)	0.4815 (1)	0.12385 (9)	0.0386 (4)	H(1)	0.270 (3)	0.354 (1)	0.175 (1)	0.035 (5)
N(3)	0.6061 (3)	0.3456 (1)	0.36983 (9)	0.0422 (4)	H(2)	0.389 (3)	0.460 (1)	0.270 (1)	0.023 (4)
N(5)	0.7395 (2)	0.1309 (1)	0.14981 (8)	0.0340 (3)	H(3)	0.409 (3)	0.277 (1)	0.289 (1)	0.029 (5)
O(2)	0.7055 (2)	0.4742 (1)	0.24486 (8)	0.0386 (3)	H(4)	0.733 (3)	0.178 (1)	0.287 (1)	0.026 (5)
O(4)	0.9323 (2)	0.2910 (1)	0.26198 (8)	0.0415 (4)	H(5)	0.475 (3)	0.186 (1)	0.192 (1)	0.026 (5)
O(6)	0.7581 (2)	0.3623 (1)	0.11283 (9)	0.0454 (4)	H(6)	0.482 (3)	0.285 (1)	0.088 (1)	0.028 (5)
C(1)	0.4129 (3)	0.3883 (1)	0.1703 (1)	0.0306 (4)	H(O2)	0.710 (4)	0.516 (2)	0.280 (1)	0.054 (7)
C(2)	0.5061 (3)	0.4151 (1)	0.2479 (1)	0.0317 (4)	H(O4)	0.914 (3)	0.350 (2)	0.249 (1)	0.041 (7)
C(3)	0.5459 (3)	0.3161 (1)	0.2936 (1)	0.0307 (4)	H(O6)	0.733 (5)	0.422 (2)	0.111 (2)	0.10 (1)
C(4)	0.7155 (3)	0.2458 (1)	0.2594 (1)	0.0312 (4)	H(111)	0.242 (4)	0.525 (2)	0.025 (1)	0.073 (8)
C(5)	0.6180 (3)	0.2171 (1)	0.1826 (1)	0.0285 (4)	H(112)	0.126 (4)	0.420 (2)	0.058 (1)	0.068 (8)
C(6)	0.5631 (3)	0.3111 (1)	0.1335 (1)	0.0314 (4)	H(113)	0.357 (4)	0.416 (2)	0.024 (1)	0.059 (8)
C(N11)	0.2684 (5)	0.4573 (2)	0.0535 (1)	0.0518 (6)	H(121)	0.356 (4)	0.593 (2)	0.200 (1)	0.070 (8)
C(N12)	0.2696 (5)	0.5658 (2)	0.1582 (2)	0.0608 (8)	H(122)	0.249 (4)	0.619 (2)	0.122 (1)	0.073 (8)
C(N31)	0.4061 (5)	0.3685 (2)	0.4069 (1)	0.0599 (7)	H(123)	0.114 (5)	0.541 (2)	0.176 (2)	0.10 (1)
C(N32)	0.7363 (5)	0.2684 (2)	0.4126 (1)	0.0607 (8)	H(311)	0.324 (4)	0.305 (2)	0.419 (1)	0.078 (8)
C(N51)	0.6072 (4)	0.0822 (1)	0.0893 (2)	0.0518 (6)	H(312)	0.446 (3)	0.405 (2)	0.454 (1)	0.057 (7)
C(N52)	0.9602 (4)	0.1566 (2)	0.1263 (2)	0.0537 (6)	H(313)	0.296 (5)	0.417 (2)	0.378 (2)	0.10 (1)
					H(321)	0.651 (4)	0.197 (2)	0.419 (1)	0.091 (9)
					H(322)	0.765 (4)	0.299 (2)	0.462 (1)	0.074 (8)
					H(323)	0.875 (4)	0.257 (2)	0.395 (1)	0.078 (9)
					H(511)	0.458 (4)	0.064 (2)	0.105 (1)	0.071 (8)
					H(512)	0.678 (4)	0.015 (2)	0.075 (1)	0.064 (7)
					H(513)	0.598 (4)	0.128 (2)	0.046 (1)	0.070 (8)
					H(521)	1.029 (4)	0.088 (2)	0.107 (1)	0.079 (8)
					H(522)	1.054 (4)	0.187 (2)	0.168 (1)	0.079 (9)
					H(523)	0.952 (4)	0.216 (2)	0.080 (1)	0.090 (9)

perimental details are shown in *Table 2*. Unit cell parameters were obtained by least-squares refinement of the setting angles of 24 automatically centered reflections in the range 11.8° $< \Theta <$ 16.3°. The structure could be solved in the space group $P2_1$ with the *Patterson* interpretation routine of *SHELXS86* [16]. Two fragments were reduced and the coordinates shifted approximately about $x - 0.25$, $y + 0.14$, $z - 0.25$ to fit in the space group $P2_1/n$. The refinement on F_{obs} was carried out with *SHELX76* [17]. All C-, N-, and O-atoms were refined with anisotropic displacement parameters. The 27 H-atoms were located from difference *Fourier* maps. 271 parameters (including positional and isotropic displacement parameters for the H-atoms) and 2587 observed reflections were used in the final full-matrix least-squares refinement. The ratio of maximum shift to error in the final refinement cycle was 0.024 (H-atom parameter), max/min, electron densities in the final difference *Fourier* synthesis were 0.25 and −0.26 e/Å^3, respectively. The atomic coordinates are shown in *Table 3*, bond distances and angles are listed in *Table 4*. The interatomic distances and angles of the H-bonds in TDCI are listed in *Table 5*.

Table 4. *Bond Lengths* [Å] *and Angles* [°] *of TDCI with e.s.d.'s in Parentheses*

Bond Lengths					
C(1)–C(2)	1.534 (3)	N(3)–C(N31)	1.464 (3)	C(4)–C(5)	1.533 (2)
C(1)–N(1)	1.473 (2)	N(5)–C(N51)	1.462 (3)	C(5)–C(6)	1.531 (2)
C(2)–O(2)	1.431 (2)	H(O2)–O(2)	0.83 (2)	C(6)–O(6)	1.428 (2)
C(3)–N(3)	1.472 (2)	H(O6)–O(6)	0.78 (3)	N(1)–C(N12)	1.462 (3)
C(4)–O(4)	1.432 (2)	C(1)–C(6)	1.538 (3)	N(3)–C(N32)	1.459 (3)
C(5)–N(5)	1.484 (2)	C(2)–C(3)	1.534 (2)	N(5)–C(N52)	1.473 (3)
N(1)–C(N11)	1.460 (3)	C(3)–C(4)	1.538 (3)	H(O4)–O(4)	0.80 (2)
Bond Angles					
H(O2)–O(2)–C(2)	107 (2)	C(5)–C(6)–C(1)	111.0 (2)	N(3)–C(3)–C(4)	114.7 (2)
H(O6)–O(6)–C(6)	107 (2)	C(N12)–N(1)–C(1)	112.8 (2)	C(5)–C(4)–O(4)	114.5 (2)
N(1)–C(1)–C(2)	111.9 (1)	C(N31)–N(3)–C(3)	110.1 (2)	C(6)–C(5)–C(4)	113.9 (1)
C(1)–C(2)–O(2)	109.4 (1)	C(N32)–N(3)–C(N31)	108.5 (2)	N(5)–C(5)–C(6)	116.2 (2)
C(3)–C(2)–C(1)	110.7 (1)	C(N52)–N(5)–C(5)	116.2 (2)	C(5)–C(6)–O(6)	112.0 (2)
N(3)–C(3)–C(2)	108.9 (1)	H(O4)–O(4)–C(4)	106 (2)	C(N11)–N(1)–C(1)	111.4 (2)
C(3)–C(4)–O(4)	112.7 (1)	C(6)–C(1)–C(2)	111.6 (1)	C(N12)–N(1)–C(N11)	108.9 (2)
C(5)–C(4)–C(3)	107.3 (1)	N(1)–C(1)–C(6)	108.2 (1)	C(N32)–N(3)–C(3)	114.9 (2)
N(5)–C(5)–C(4)	112.8 (1)	C(3)–C(2)–O(2)	111.4 (2)	C(N51)–N(5)–C(5)	111.8 (2)
C(1)–C(6)–O(6)	110.4 (2)	C(4)–C(3)–C(2)	110.2 (2)	C(N52)–N(5)–C(N51)	109.2 (2)

Table 5. *Interatomic Distances* (*d* [Å] *and Angles*(α [°]) of the *H-Bonds in the Crystal Structure of TDCI with e.s.d.'s in Parentheses*

X–H···Y	*d*(XH)	*d*(HY)	*d*(XY)	α(XHY)
Intramolecular				
O(4)–H···O(2)	0.80 (2)	2.03 (2)	2.732 (2)	146 (2)
O(6)–H···N(1)	0.78 (3)	2.26 (3)	2.745 (2)	121 (3)
Intermolecular				
O(2)–H···N(5)	0.83 (2)	1.98 (2)	2.797 (2)	168 (2)

*1,3,5-Trideoxy-1,3,5-tris(trimethylammonio)-*cis*-inositol Triiodide.* TDCI (7 g, 26.78 mmol) was dissolved in a mixture of 80 ml of MeOH and 20 ml of H_2O. MeI (15 g, 0.106 mol) was added, and the soln. was refluxed for 36 h. NaOH was then added, until the suspension reacted slightly alkaline. An additional portion of MeI (10 g 70.5 mmol) was added, and the mixture was kept under reflux for another 24 h. The suspension was filtered, and the remaining white solid was recrystallized from MeOH/H_2O. Yield: 12 g (64%). ^{1}H-NMR: 5.6 (*m*, 3 H); 4.8 (*s*, HDO); 3.7 (*m*, 3 H); 3.65 (*s*, 27 H). ^{13}C-NMR: 69.9; 65.3; 55.2. Anal. calc. for $C_{15}H_{36}I_3N_3O_3 \cdot 0.5\,H_2O$ (696.19): C 25.88, H 5.36, I 54.68, N 6.04; found: C 25.63, H 5.10, I 54,39, N 6.03.

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