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Crystal structure analysis of *trans*-1,3,5,7-tetraazadecalin (4)

The X-ray diffraction measurements were carried out at 100 K on an automated CAD4 diffractometer equipped with a graphite monochromator, using MoK α ($\lambda = 0.7107 \text{ \AA}$) radiation. Intensity data were collected by the ω -2 θ scan mode. Possible deterioration of the analyzed crystal was tested by detecting periodically the intensities of three reference reflections from different zones of the reciprocal space, and was found negligible during the experiment. No corrections for absorption or secondary extinction effects were applied. The structure were solved by direct methods (SHELXS-86)¹, and refined by full-matrix least-squares (SHELXL-93)². Non-hydrogen atoms were treated anisotropically. All the hydrogen atoms were located on difference-Fourier maps; their final positions were slightly adjusted to correspond to standard C-H bond lengths.

Crystal data (at 100K):

C₆H₁₄N₄ · 4H₂O, formula weight 214.26, monoclinic, space group *P2₁/c*,
 $a = 6.020(3)$, $b = 8.730(1)$, $c = 11.667(2) \text{ \AA}$, $\beta = 102.58(2)^\circ$, $V = 598.4(3) \text{ \AA}^3$,
 $Z = 2$, $D_{\text{calc}} = 1.189 \text{ g.cm}^{-3}$, $F(000) = 236$, $\mu(\text{MoK}\alpha) = 0.97 \text{ cm}^{-1}$.

Data Collection and Refinement: Diffraction data measured out to $2\theta_{\text{max}} = 56^\circ$ with a constant scan rate of 4 deg/min. A total of 1363 unique reflections with positive intensities were recorded. The final refinement, based on F^2 , converged at $R=0.047$ for 1230 observations having $F_o > 4\sigma(F_o)$ and $R=0.051$ for 1363 unique data. At convergence, $S = 1.12$ and $|\Delta\rho| \leq 0.37 \text{ e.\AA}^{-3}$. In the crystal, the molecular units are located on crystallographic inversion centers at $\frac{1}{2}, 0, \frac{1}{2}$.

The tetraazadecaline compound crystallized as tetrahydrate. The crystal structure is characterized by a three-dimensional network of nearly linear hydrogen bonds between the tetraazadecaline and water species. All hydrogen bonding sites are utilized to full capacity providing a tetrahedral environment around the O and N sites.

1. G. M. Sheldrick. SHELXS-86. In "Crystallographic Computing 3"; G.M. Sheldrick, C. Kruger and R. Goddard, Eds.; Oxford University Press 1985; pp 175-189; *Acta Cryst.* **A46**, 467-473 (1990).

2. G. M. Sheldrick. SHELXL-93. Program for the Refinement of Crystal Structures from Diffraction Data, University of Goettingen, Germany, 1993.

Anisotropic thermal parameters ($\text{\AA}^2$) of the nonhydrogen atoms of 4

<i>atom</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0239(5)	0.0214(6)	0.0255(5)	0.0007(4)	0.0104(4)	-0.0014(4)
C2	0.0283(7)	0.0207(6)	0.0312(7)	0.0026(5)	0.0118(5)	-0.0010(5)
N3	0.0236(6)	0.0245(6)	0.0269(6)	0.0018(4)	0.0093(4)	-0.0049(4)
C4	0.0232(6)	0.0249(6)	0.0248(6)	0.0018(5)	0.0101(5)	-0.0043(5)
C10	0.0177(6)	0.0212(6)	0.0231(6)	0.0022(4)	0.0072(4)	-0.0010(4)
O1	0.0414(6)	0.0211(5)	0.0318(5)	0.0008(4)	0.0208(4)	0.0015(4)
O2	0.0246(5)	0.0220(5)	0.0383(6)	-0.0018(4)	0.0142(4)	0.0009(3)

The anisotropic temperature factor is in the form -

$$\exp [-2\pi^2 (U_{11} h^2 (a^*)^2 + \dots + 2U_{12} hk (a^*) (b^*) + \dots)]$$

Atomic coordinates and equivalent isotropic thermal parameters of 4

<i>atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}(\text{\AA}^2)$
N1	0.4669(1)	0.1615(1)	0.6030(1)	0.0228(3)
C2	0.5291(2)	0.2867(1)	0.5311(1)	0.0259(4)
N3	0.7085(1)	0.2498(1)	0.4686(1)	0.0244(3)
C4	0.6550(2)	0.1099(1)	0.3979(1)	0.0235(4)
C10	0.5952(1)	-0.0236(1)	0.4694(1)	0.0202(4)
O1	0.8724(1)	0.0766(1)	0.8040(1)	0.0295(3)
O2	0.9067(1)	-0.2341(1)	0.8191(1)	0.0272(3)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor

Atomic coordinates of the hydrogen atoms of Fu15

<i>atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H1	0.5878	0.1415	0.6655
H2a	0.3940	0.3173	0.4740
H2b	0.5781	0.3739	0.5818
H3	0.8400	0.2396	0.5274
H4a	0.5280	0.1300	0.3327
H4b	0.7851	0.0821	0.3657
H10	0.7302	-0.0480	0.5304
H(O1)a	0.8805	-0.0310	0.8123
H(O1)b	0.8144	0.1104	0.8679
H(O2)a	0.7786	-0.2644	0.8460
H(O2)b	0.9448	-0.3068	0.7670

Bond distances (Å) , bond and torsion angles (°) of 4

(a) Bond distances .

N1 - C2	1.474(2)	C4 - C10	1.522(2)
N1 - C9	1.471(2)	C10 - N5	1.471(2)
C2 - N3	1.465(2)	C10 - C9	1.533(2)
N3 - C4	1.469(2)		

(b) Bond angles .

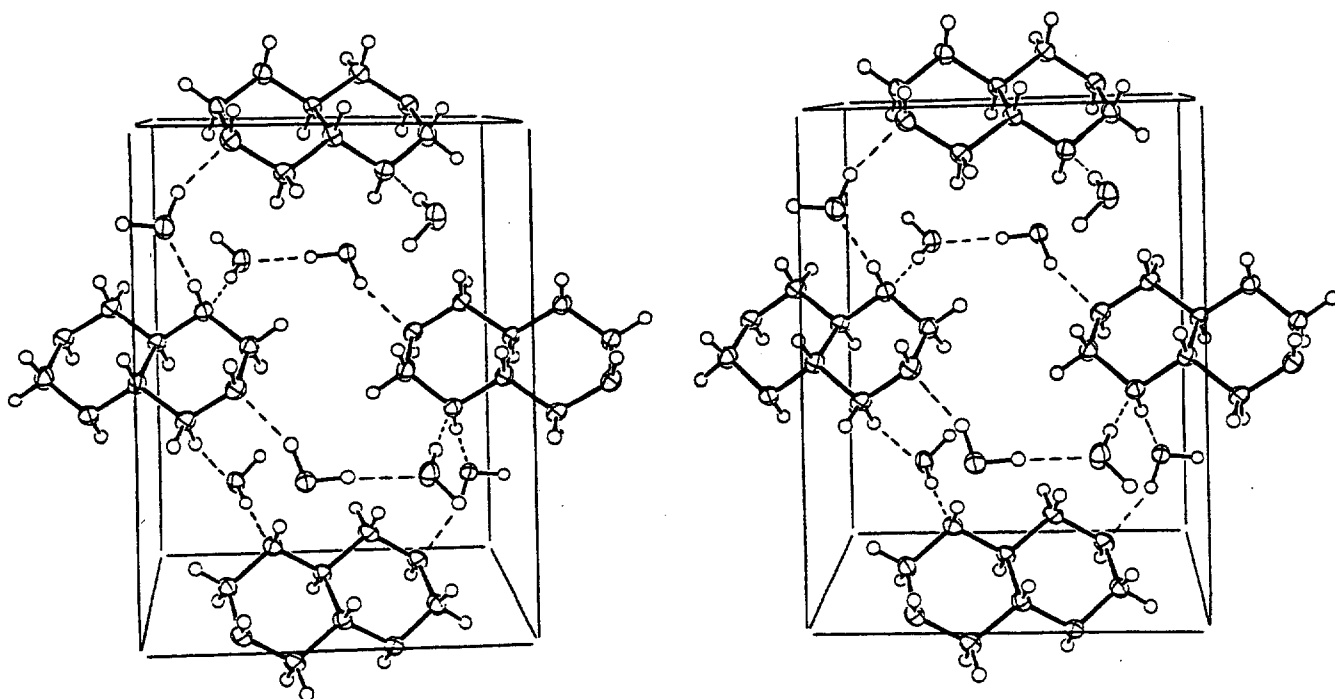
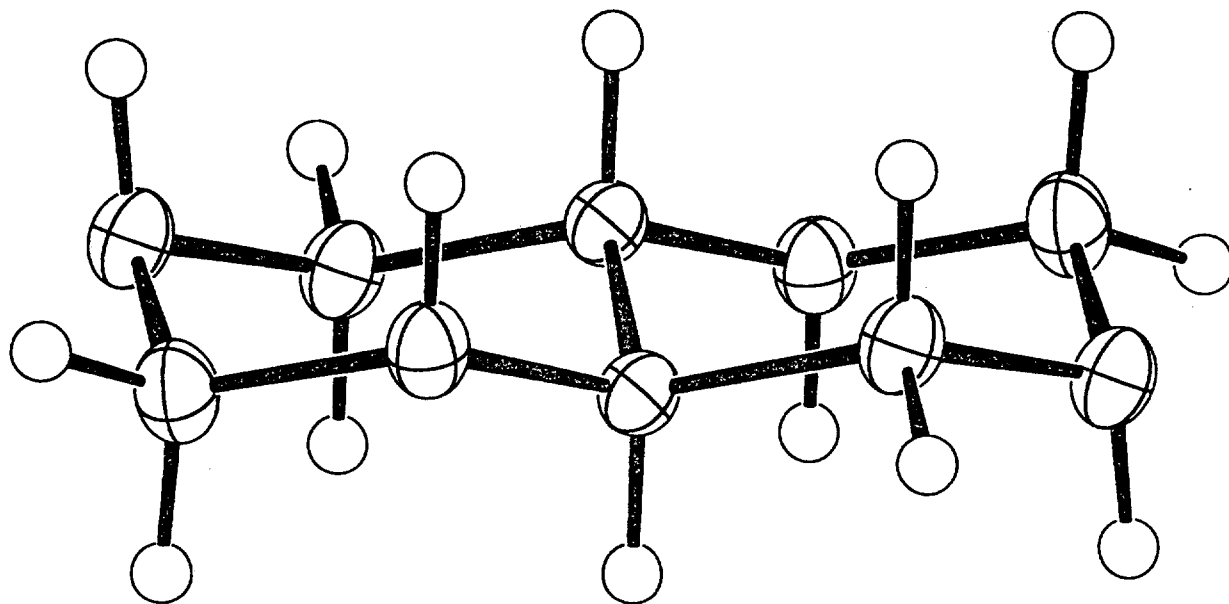
C2 - N1 - C9	110.1(1)	C4 - C10 - C9	109.8(1)
N1 - C2 - N3	115.2(1)	C4 - C10 - N5	111.9(1)
C2 - N3 - C4	111.6(1)	N5 - C10 - C9	111.4(1)
N3 - C4 - C10	112.2(1)		

(c) Torsion angles .

C2 -N1 -C9 -C10	55.2(1)	N3 -C4 -C10 -N5	177.7(1)
C2 -N1 -C9 -C8	178.6(1)	N3 -C4 -C10 -C9	53.5(1)
C9 -N1 -C2 -N3	-54.8(1)	C4 -C10 -C9 -N1	-55.5(1)
N1 -C2 -N3 -C4	53.1(1)	N5 -C10 -C9 -N1	180.0(1)
C2 -N3 -C4 -C10	-51.9(1)	C4 -C10 -C9 -C8	180.0(1)

Intermolecular hydrogen bonding in the crystal structure of 4

NH(1)··· O(1) (at x, y, z)	3.085(2) Å
NH(3)··· O(2) (at 2-x, y+½, 1½-z)	3.004(2) Å
OH(1)··· O(2) (at x, y, z)	2.723(1) Å
OH(1)··· N(3) (at x, ½-y, z+½)	2.790(2) Å
OH(2)··· O(1) (at 2-x, y-½, 1½-z)	2.719(1) Å
OH(2)··· N(1) (at 1-x, y-½, 1½-z)	2.758(2) Å



ORTEP drawing from the X-ray analysis of *trans*-1,3,5,7-TAD (4) with 50% probability ellipsoids of the non-hydrogen atoms and stereoview of the unit cell down the *a* axis (indicating intermolecular hydrogen bonding scheme with water in the crystal).

Crystal structure analysis of 1,3,5,7-tetraacetyl-*trans*-1,3,5,7-tetraazadecalin (12).

The X-ray diffraction measurements were carried out at room temperature (ca. 298 K) on an automated CAD4 diffractometer equipped with a graphite monochromator, using MoK α (λ = 0.7107 Å) radiation. Intensity data were collected by the ω -2 θ scan mode. Possible deterioration of the analyzed crystal was tested by detecting periodically the intensities of three reference reflections from different zones of the reciprocal space, and was found negligible during the experiment. No corrections for absorption or secondary extinction effects were applied. The structure were solved by direct methods (SHELXS-86)¹, and refined by full-matrix least-squares (SHELXL-93)². Non-hydrogen atoms were treated anisotropically. All the hydrogen atoms were located on difference-Fourier maps; their final positions were slightly adjusted to correspond to standard C-H bond lengths.

Crystal data: C₁₄H₂₂O₄N₄, formula weight 310.35, monoclinic, space group *C2/c*, a = 15.595(2), b = 5.489(1), c = 17.876(2) Å, β = 92.49(1)°, V = 1528.8(4) Å³, Z = 4, D_{calc} = 1.348 g.cm⁻³, $F(000)$ = 664, $\mu(\text{MoK}\alpha)$ = 1.00 cm⁻¹.

Data Collection and Refinement: Diffraction data measured out to $2\theta_{\text{max}}$ = 54° with a constant scan rate of 4 deg/min. A total of 1560 unique reflections with positive intensities were recorded. The final refinement, based on F^2 , converged at $R=0.042$ for 1350 observations having $F_o > 4\sigma(F_o)$ and $R=0.049$ for 1560 unique data. At convergence, S = 1.09 and $|\Delta\rho| \leq 0.21$ e.Å⁻³. In the crystal, the molecular units are located on crystallographic inversion centers at $\frac{1}{4}, \frac{1}{4}, 0$.

1. G. M. Sheldrick. SHELXS-86. In "Crystallographic Computing 3"; G.M. Sheldrick, C. Kruger and R. Goddard, Eds.; Oxford University Press 1985; pp 175-189; *Acta Cryst.* A46, 467-473 (1990).

2. G. M. Sheldrick. SHELXL-93. Program for the Refinement of Crystal Structures from Diffraction Data, University of Goettingen, Germany, 1993.

Atomic coordinates and equivalent isotropic thermal parameters of 12

<i>atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}(\text{\AA}^2)$
N1	0.6880(1)	0.3653(2)	0.4152(1)	0.0340(4)
C2	0.7091(1)	0.3279(2)	0.4956(1)	0.0337(4)
C3	0.6347(1)	0.2070(3)	0.5341(1)	0.0402(5)
N4	0.6636(1)	0.1378(2)	0.6107(1)	0.0377(4)
C5	0.7481(1)	0.2254(2)	0.6356(1)	0.0367(4)
C6	0.6331(1)	0.5522(2)	0.3966(1)	0.0388(4)
C7	0.6165(1)	0.6122(3)	0.3151(1)	0.0527(6)
O8	0.5973(1)	0.6634(2)	0.4453(1)	0.0568(5)
C9	0.6263(1)	-0.0433(3)	0.6493(1)	0.0433(6)
C10	0.5416(1)	-0.1381(3)	0.6187(1)	0.0530(6)
O11	0.6596(1)	-0.1226(3)	0.7075(1)	0.0712(6)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor

Atomic coordinates of the hydrogen atoms of 12

<i>atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H2	0.7203	0.4868	0.5190
H3a	0.5867	0.3191	0.5357
H3b	0.6159	0.0635	0.5062
H5a	0.7618	0.1689	0.6861
H5b	0.7485	0.4021	0.6359
H7a	0.6130	0.4642	0.2866
H7b	0.6626	0.7108	0.2980
H7c	0.5634	0.6998	0.3089
H10a	0.5507	-0.2419	0.5766
H10b	0.5056	-0.0038	0.6032
H10c	0.5143	-0.2291	0.6569

Anisotropic thermal parameters ($\text{\AA}^2$) of the nonhydrogen atoms of 12

<i>atom</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0375(6)	0.0347(7)	0.0294(6)	0.0019(5)	-0.0041(5)	0.0013(5)
C2	0.0379(8)	0.0339(8)	0.0287(7)	0.0001(5)	-0.0040(5)	0.0017(6)
C3	0.0378(8)	0.0487(9)	0.0338(8)	0.0051(6)	-0.0039(6)	0.0012(6)
N4	0.0368(7)	0.0459(8)	0.0299(6)	0.0027(5)	-0.0029(5)	-0.0023(5)
C5	0.0420(8)	0.0391(8)	0.0286(6)	-0.0041(6)	-0.0042(6)	-0.0005(6)
C6	0.0439(8)	0.0343(8)	0.0378(8)	0.0024(6)	-0.0029(6)	0.0015(6)
C7	0.0629(11)	0.0527(10)	0.0416(9)	0.0091(8)	-0.0084(8)	0.0113(8)
O8	0.0731(9)	0.0511(8)	0.0460(7)	0.0023(5)	0.0011(6)	0.0241(6)
C9	0.0469(9)	0.0455(9)	0.0374(8)	0.0048(7)	0.0000(6)	-0.0015(7)
C10	0.0485(9)	0.0588(11)	0.0515(10)	0.0069(8)	-0.0003(8)	-0.0120(8)
O11	0.0751(10)	0.0818(11)	0.0546(8)	0.0324(7)	-0.0203(7)	-0.0213(8)

The anisotropic temperature factor is in the form -

$$\exp [-2\pi^2 (U_{11} h^2 (a^*)^2 + \dots + 2U_{12} hk (a^*) (b^*) + \dots)]$$

Bond distances (Å) and bond angles (°) of 12**(a) Bond distances .**

N1 - C2	1.475(2)	N4 - C5	1.453(2)
N1 - C5'	1.463(2)	N4 - C9	1.355(2)
N1 - C6	1.368(2)	C6 - C7	1.505(2)
C2 - C3	1.526(2)	C6 - O8	1.219(2)
C2 - C2'	1.538(2)	C9 - C10	1.500(2)
C3 - N4	1.474(2)	C9 - O11	1.224(2)

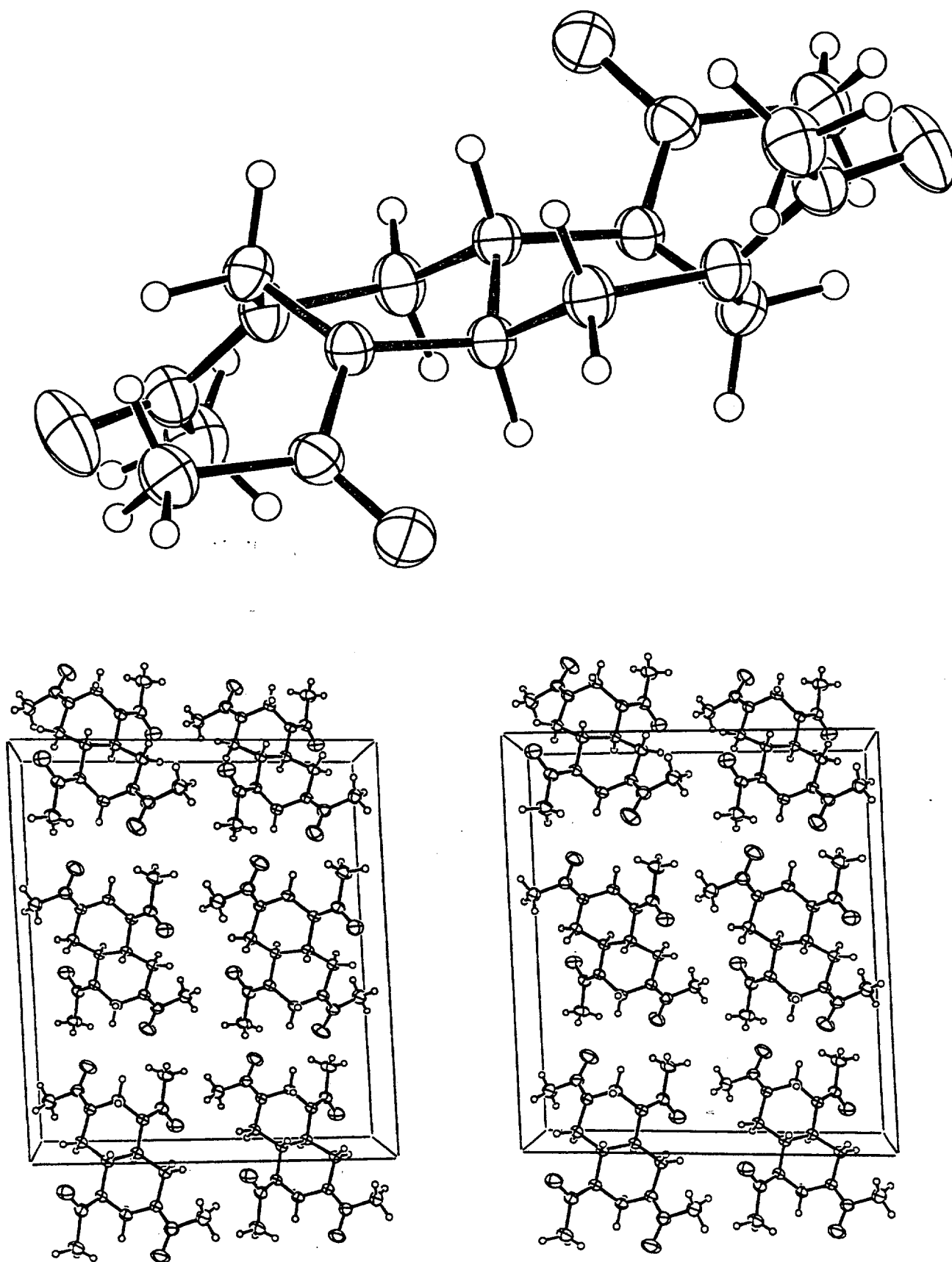
(b) Bond angles .

C5' - N1 - C6	122.7(1)	C5 - N4 - C9	119.4(1)
C2 - N1 - C6	116.9(1)	N4 - C5 - N1'	109.3(1)
C2 - N1 - C5'	115.3(1)	N1 - C6 - O8	120.3(1)
N1 - C2 - C2'	109.0(1)	N1 - C6 - C7	118.6(1)
N1 - C2 - C3	110.9(1)	C7 - C6 - O8	121.1(1)
C3 - C2 - C2'	110.9(1)	N4 - C9 - O11	121.1(1)
C2 - C3 - N4	108.8(1)	N4 - C9 - C10	117.4(1)
C3 - N4 - C9	122.7(1)	C10 - C9 - O11	121.4(1)
C3 - N4 - C5	115.8(1)		

(c) Torsion angles .

C5' - N1 - C6 - C7	20.7(2)	N1 - C2 - C3 - N4	171.0(1)
C2 - N1 - C6 - C7	174.2(1)	C3 - C2 - C2' - C3'	180.0(1)
C5' - N1 - C6 - O8	-160.9(1)	C2' - C2 - C3 - N4	49.7(2)
C2 - N1 - C6 - O8	-7.3(2)	C2 - C3 - N4 - C5	8.0(2)
C6 - N1 - C5' - N4'	104.3(1)	C2 - C3 - N4 - C9	-155.6(1)
C2 - N1 - C5' - N4'	-49.6(2)	C3 - N4 - C9 - C10	-13.2(2)
C5' - N1 - C2 - C2'	-6.5(2)	C3 - N4 - C9 - O11	168.3(1)
C5' - N1 - C2 - C3	-128.9(1)	C3 - N4 - C5 - N1'	-58.6(2)
C6 - N1 - C2 - C2'	-162.0(1)	C5 - N4 - C9 - C10	-176.3(1)
C6 - N1 - C2 - C3	75.6(2)	C5 - N4 - C9 - O11	5.2(2)
N1 - C2 - C2' - C3'	57.6(1)	C9 - N4 - C5 - N1'	105.7(1)
N1 - C2 - C2' - N1'	180.0(1)		

Primed atoms are related to the corresponding non-primed atoms by inversion at 0.75,0.25,0.50 .



ORTEP drawing from the X-ray analysis of 1,3,5,7-tetraacetyl-*trans*-1,3,5,7-tetraazadecalin (**12**) with 50% probability ellipsoids of the non-hydrogen atoms and packing diagram stereoviewed down the short *b* axis of the unit cell.

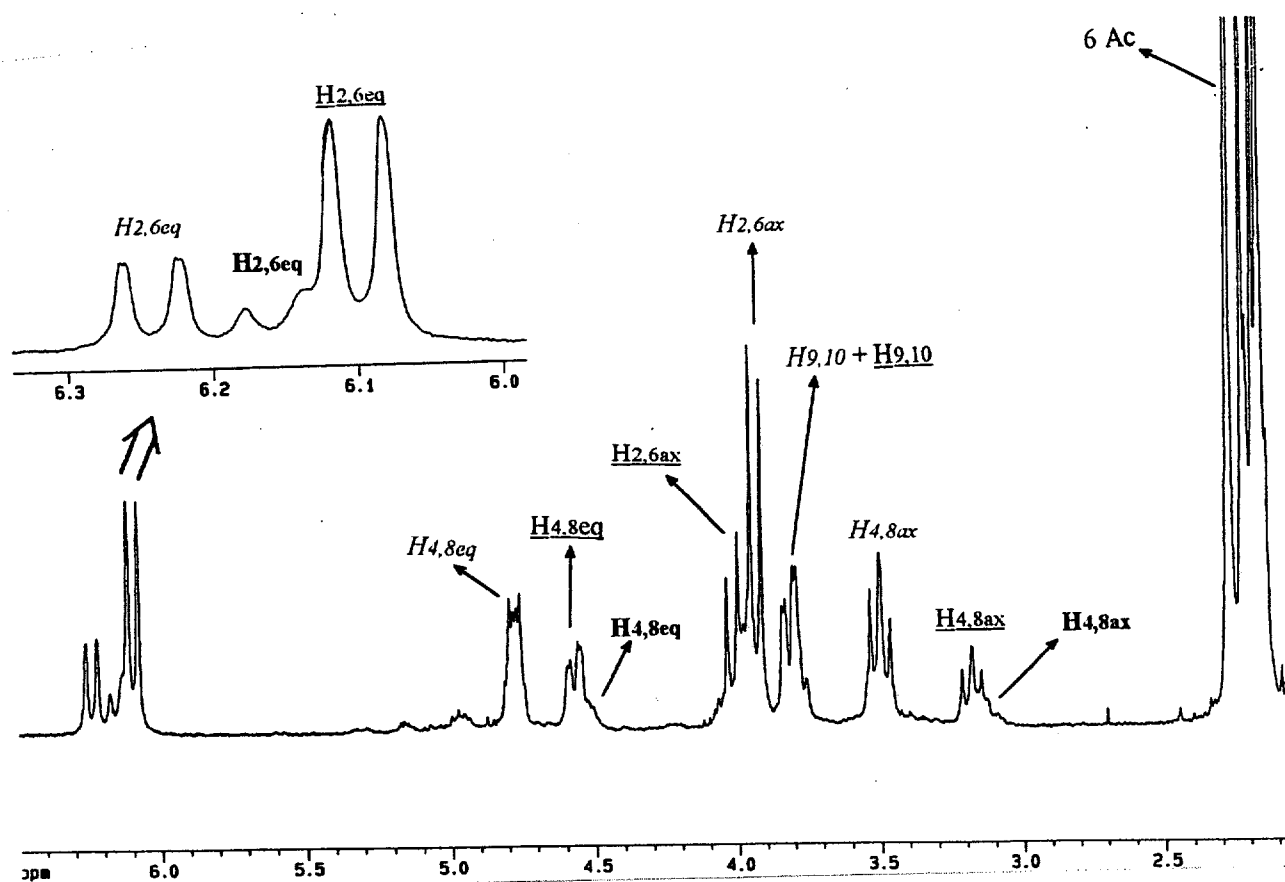


Figure 3. ¹H NMR (360 MHz) of *cis*-TATAD (10) showing at least three tetraacetyl species at 296 K: isomer **A** (underlined), isomer **D** (*italic*) and a third isomer (**bold**) (see text).

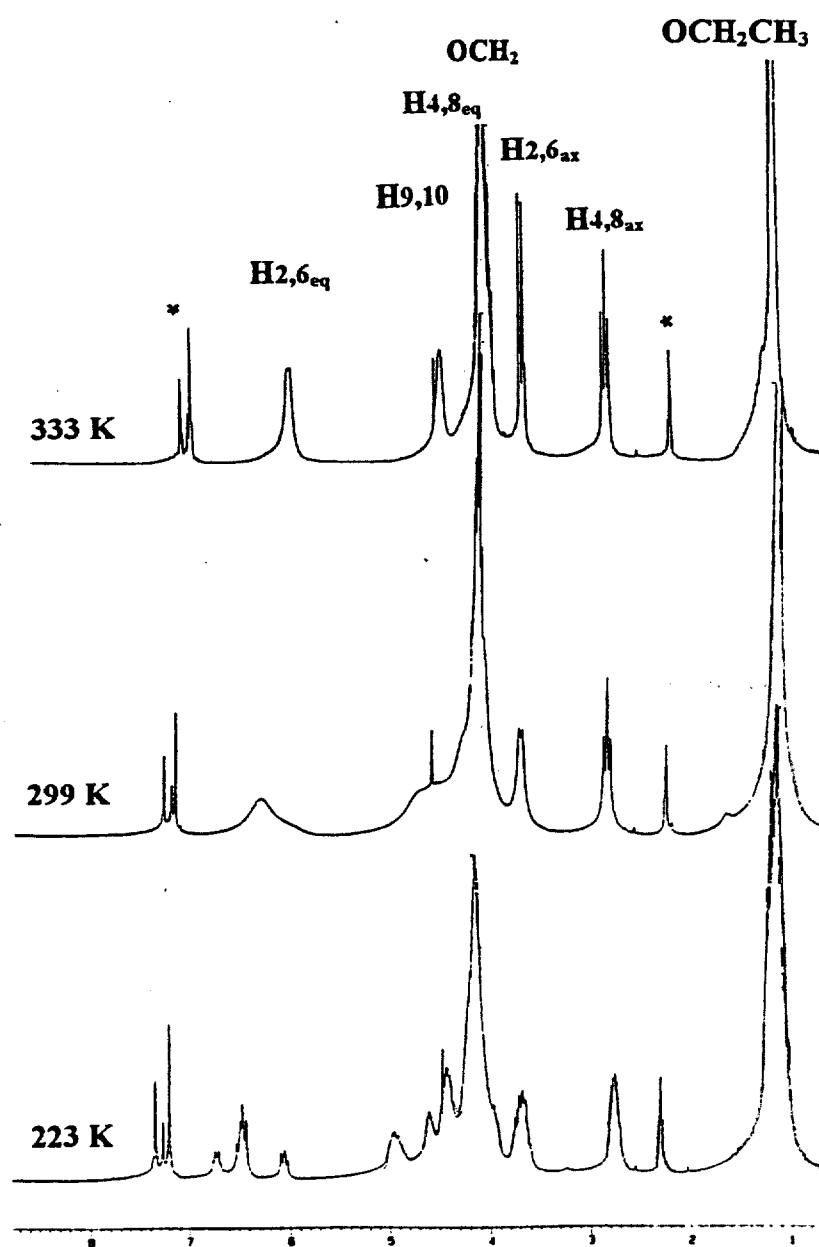


Figure 4. VT-¹H NMR spectra of *cis*-TECTAD (11), showing all resonances of the H_{2,6}; H_{4,6}; H_{9,10}; and OEt. (asteriks refer to signals of residual ¹H in toluene-*d*₈).

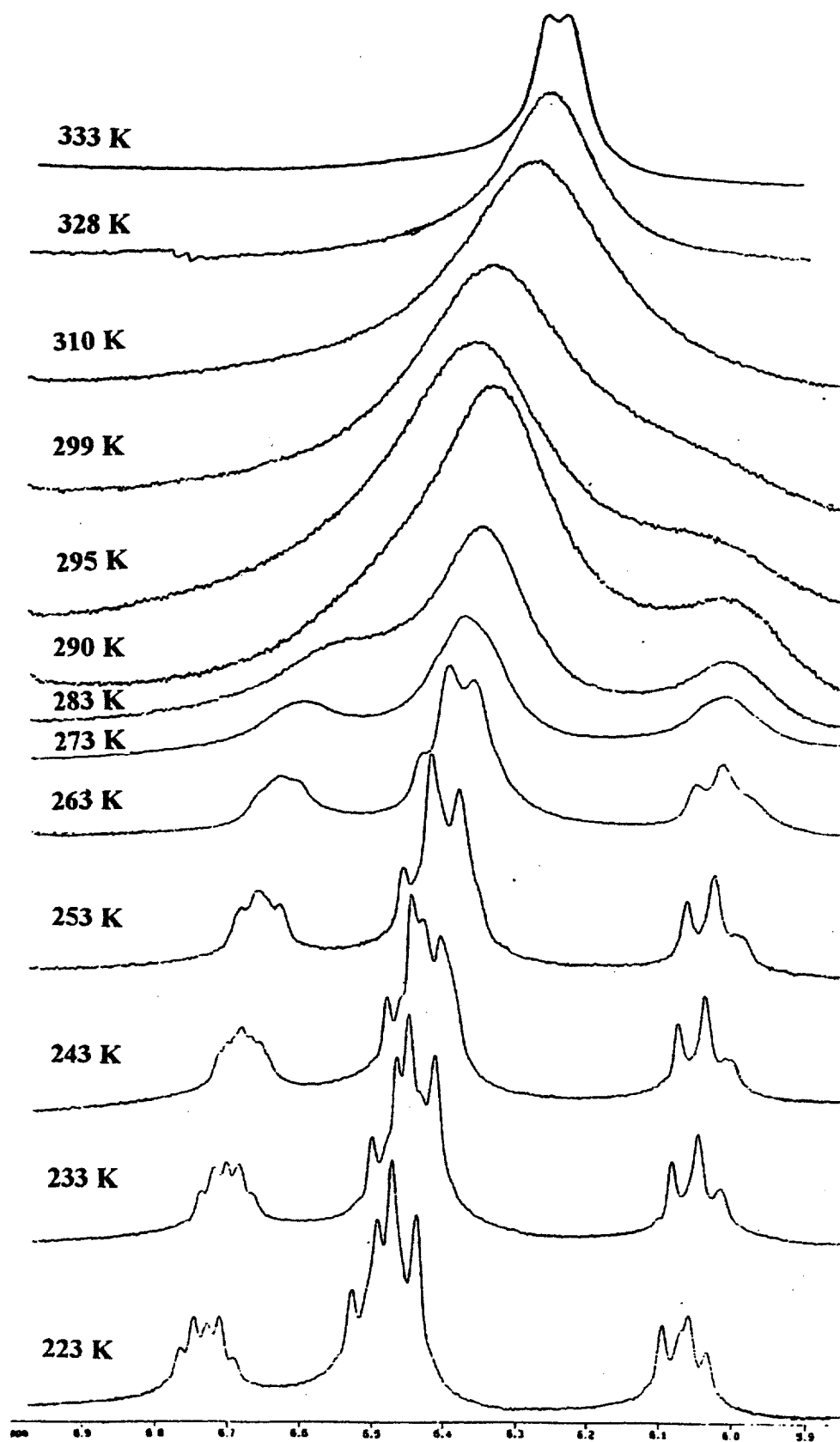


Figure 5. VT-¹H NMR measurements of the H2(6)eq proton of *cis*-TECTAD (11) in toluene-d₈.