A Neutron Diffraction Study of Pyridinium-1-dicyanomethylide, C8D5N3, at 294 K and 118 K

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Abstract

A neutron diffraction study of perdeuterated pyridinium-1-dicyanomethylide has been carried out at room temperature and at 118 K at the high-flux beam reactor of the Institut Laue–Langevin. Low temperature was obtained with a cryostat based on the Joule–Thomson expansion of gaseous helium, with a maximum long-term variation of ± 1 K. The crystals are monoclinic, space group $P2_1/m$. The data refinements, including extinction parameters, gave final $R_w(F^2)$ values of 0·038 (RT, 552 independent reflections) and 0·028 (118 K, 1869 independent reflections). A TLS thermal analysis indicated rigid-body behaviour of the non-deuterium atoms. The non-planarity of the molecule was confirmed. The bond distances were corrected for thermal motion and their e.s.d.'s ranged from 0·0012 to 0·0030 Å (RT) and from 0·0003 to 0·0008 Å (118 K). [Crystal data: at 294 K, $a = 7\cdot170$ (3), $b = 12\cdot523$ (5), $c = 3\cdot878$ (1) Å, $\beta = 94\cdot88$ (1)°, $D_x = 1\cdot418$ Mg m^{-3}; at 118 K, $a = 7\cdot106$ (3), $b = 12\cdot461$ (5), $c = 3\cdot802$ (1) Å, $\beta = 95\cdot47$ (1)°, $D_x = 1\cdot468$ Mg m^{-3}.]

Introduction

The structure of pyridinium-1-dicyanomethylide (hereafter PDM) was first solved by Bugg & Sass (1965) from Weissenberg photographs. PDM belongs to the ylide family and its study is interesting from the electron-distribution point of view. This work is the neutron diffraction part of an electron density determination of PDM by the X–N method. Two series of data collections have been performed at the high-flux reactor of the Institut Laue–Langevin at Grenoble. The first, at room temperature, was for a six-day allocated time and an ω step-scan technique was chosen to save time (detector displacement would have been slower).

For the second, at 118 K, the $\omega/2\theta$ step-scan technique could be used since we had 21 days for measurements.

Experimental

Deuterated crystals were grown by slow evaporation of a solution of PDM (deuterated) in N,N-dimethylformamide at room temperature. The same sample was used in the two series of measurements. It came from an as-grown small stick about 12 mm long which was cut by a dissolving saw into two halves to obtain a more suitable length of about 6 mm (beam homogeneity) and a volume of 8·2 mm^3. Its colour was light yellow and it was not optically transparent, though monocrystalline. It had nine boundary planes (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (01$\bar{1}$), (0$\bar{1}$1), (1$\bar{1}$1), ($\bar{1}$1$\bar{1}$) and (305) (the last being an approximation of the sawed face) at 0·012, 2·179, 0·24, 0·54, 0·0, 0·0, 0·0, 0·0 and 5·98 mm, respectively, from the origin located at the intersection of (01$\bar{1}$), (0$\bar{1}$1), (1$\bar{1}$1) and ($\bar{1}$1$\bar{1}$). The two {010} faces were irregularly shaped due to the growth and had to be approximated by mean planes (distances indicated above) for absorption and extinction corrections.

Cell parameters were determined (X-ray diffraction, four-circle Philips PW 1100 diffractometer) by least squares from the setting angles of 25 reflections (38·0 < θ < 47·6°, Cu $K\alpha$ radiation, at 294 K and 16·5 < θ < 21·2°, Mo $K\alpha$ radiation, at 118 K). Results are listed in Table 1.* The choice of unit cell differs from that of Bugg & Sass (1965). The absorption coefficient was measured by the attenuation of a narrow beam of neutrons ($\lambda = 0\cdot8317$ Å) passing through a deuterated

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34932 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Crystal data

Pyridinium-1-dicyanomethylide, $C_8D_5N_3$
$M_r = 148.18$
Space group $P2_1/m$
$Z = 2$

294 K	118 K
$a = 7.170(3)$ Å	$a = 7.106(3)$ Å
$b = 12.523(5)$	$b = 12.461(5)$
$c = 3.878(1)$	$c = 3.802(1)$
$\beta = 94.88(1)°$	$\beta = 95.47(1)°$
$U = 346.942$ Å^3	$U = 335.126$ Å^3
$D_x = 1.418$ Mg m^{-3}	$D_x = 1.468$ Mg m^{-3}

PDM crystal of known thickness and resulted in a value of 0.031 mm^{-1}.

Data were collected on the D9 four-circle diffractometer of the Institut Laue–Langevin. In the two series of measurements the crystal was mounted with c close to, but not along, the φ axis of the diffractometer. The low temperature was obtained using a Displex cooler, from Air Products and Chemical Inc., with an observed stability of ± 1 K (long-term variations) for the 21 d of measurements. In the room-temperature measurements the intensity I of the unique standard reflection showed a slow and continuous decrease of about $0.04I$, due to a small variation in the alignment of the crystal. A fraction of the collected data were then remeasured with an updated orientation matrix. No such behaviour was observed for the two standards at 118 K. The F_o^2 values were obtained with the minimal $\sigma(I)/I$ criterion (Lehmann & Larsen, 1974).

Room-temperature data collection

Two octants of the Ewald sphere were measured (h both positive and negative) as well as a small part (132 reflections) with k negative ($k = -1$ and -2) giving 800 reflections (sin $\theta/\lambda \leq 0.65$ Å^{-1}) comprising Friedel pairs (in the zero layer) and doubly measured ones. After averaging, and discarding four data, 552 unique reflections were left for the refinement.

118 K data collection

Measurements also covered two octants but with $-21 < k < 4$ and sin $\theta/\lambda \leq 0.877$ Å^{-1}. 2231 reflections were measured giving 1885 data after averaging (338 equivalent reflections). 16 data were discarded leaving 1869 reflections for the refinement.

Refinement of the structure

Data were corrected for absorption by the Gaussian-grid integration method (Coppens, Leiserowitz & Rabinovich, 1965). The 26 coordinates and 52 aniso-

Table 2. Final fractional coordinates ($\times 10^5$)

294 K

	x	y	z
C(1)	95418 (25)	−25000	−13950 (56)
C(2)	86717 (16)	−34500 (10)	−6740 (40)
C(3)	69975 (15)	−34344 (8)	7747 (36)
C(4)	44361 (21)	−25000	30469 (51)
C(5)	36158 (16)	−34596 (9)	38879 (39)
N(1)	61605 (16)	−25000	15166 (36)
N(2)	28971 (14)	−42429 (7)	46504 (35)
D(1)	108819 (32)	−25000	−25149 (72)
D(2)	92760 (23)	−42090 (12)	−12469 (54)
D(3)	62822 (21)	−41553 (9)	14372 (49)

118 K

	x	y	z
C(1)	96617 (6)	−25000	−16018 (14)
C(2)	87753 (5)	−34601 (3)	−8690 (11)
C(3)	70697 (5)	−34473 (2)	5985 (10)
C(4)	44856 (6)	−25000	28745 (14)
C(5)	36626 (5)	−34694 (3)	37661 (10)
N(1)	62312 (4)	−25000	13448 (9)
N(2)	29362 (4)	−42590 (2)	45787 (9)
D(1)	110003 (8)	−25000	−27386 (21)
D(2)	93799 (7)	−42301 (4)	−14607 (15)
D(3)	63511 (6)	−41761 (3)	12655 (14)

Table 3. Mosaic-spread distribution

Mosaic tensor $\times 10^8$ (Thornley & Nelmes, 1974)

	R_{11}	R_{22}	R_{33}	R_{12}	R_{13}	R_{23}
294 K	4.4 (2)	7.5 (6)	9.1 (3)	1.5 (2)	−1.2 (4)	−2.3 (8)
118 K	67 (3)	219 (10)	144 (4)	−18 (4)	−1 (2)	−26 (5)

Principal axes and directions

	294 K				118 K		
η_i	Direction cosines*			η_i	Direction cosines*		
6.4″	0.92	−0.38	−0.01	26.4″	0.99	0.11	−0.03
8.2	0.30	0.71	0.64	49.8	−0.11	0.94	−0.31
10.8	−0.23	−0.59	0.77	38.1	−0.01	0.31	0.95

* Direction cosines are given relative to orthogonal ångström space along a, b and c.

tropic temperature factors of the atoms, the scale factor and the 6 anisotropic type 1 extinction parameters [Lorentzian distribution; Thornley & Nelmes (1974) model for the mosaic distribution] were refined by least squares, including all the data (even those with $F_o^2 \leq 0$), with LINEX (Becker & Coppens, 1975). The minimized quantity was $\sum w|F_o^2 - k^2 F_c^2|^2$ with $w^{-1} = \sigma^2_{counting}(F_o^2)$.

The resulting atomic parameters are reported in Table 2, the extinction parameters in Table 3 and the final agreement factors in Table 4. The neutron scattering lengths were (in fm) $b_C = 6.648$, $b_N = 9.40$ and $b_D = 6.672$ (Shull, 1972). An additional refinement of these quantities yielded on average $b_C = 6.670$ (20), $b_N = 9.384$ (20), $b_D = 6.639$ (23) and $b_C = 6.669$ (8), $b_N = 9.381$ (8), $b_D = 6.636$ (9) fm for the 294 and 118 K data sets respectively. Difference syntheses showed residual peaks of 0.4 (294 K) and

Table 4. *Additional experimental information and refinement results*

	294 K	118 K
Wavelength [Cu (200) monochromator Laue case]	0·7414 (20) Å	0·8317 (20) Å
Scan width $\Delta\theta$ variable with θ		
Range of variation of $\Delta\theta$	1·7, 2·04°	2·24, 3·24°
$R_1 = \sum_{\text{all}}|F_o - k|F_c||/\sum_{\text{all}} F_o$	0·044	0·030
$R_2 = \left[\sum_{\text{all}} w'|F_o - k|F_c||^2/\sum_{\text{all}} w' F_o^2\right]^{1/2}$	0·019	0·015
$R_3 = \sum_{\text{all}} |F_o^2 - (kF_c)^2|/\sum_{\text{all}} F_o^2$	0·033	0·023
$R_4 = \left[\sum_{\text{all}} w|F_o^2 - (kF_c)^2|^2/\sum_{\text{all}} wF_o^4\right]^{1/2}$	0·038	0·028
$\left(\sum_{\text{all}} w|F_o - kF_c|^2/(N_o - N_v)\right)^{1/2}$	1·96	1·81
Transmission-factor range	0·969–0·988	0·965–0·988

Extinction factors y less than 0·9 ($F_{corr}^2 = F_o^2/y$)

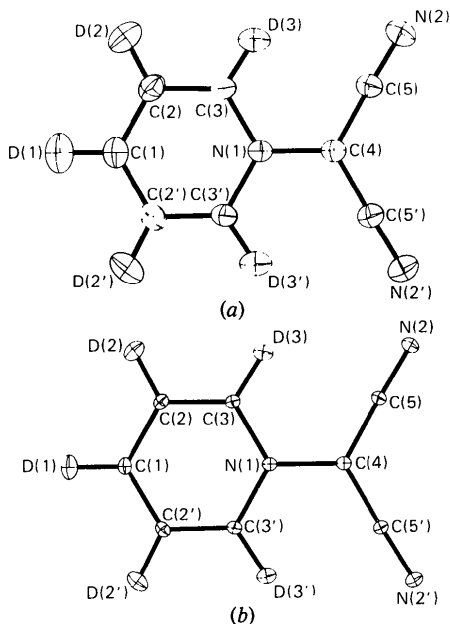| 294 K		118 K	
y_{300}	= 0·88	$y_{1\bar{1}\bar{1}}$	= 0·75
y_{020}	= 0·79		
y_{060}	= 0·85	$y_{1,\bar{1}\bar{1},1}$	= 0·84
$y_{0,10,0}$	= 0·88		
y_{111}	= 0·53	y_{202}	= 0·80
$y_{1,11,1}$	= 0·84		
y_{131}	= 0·87	$y_{0,\bar{1}\bar{2},0}$	= 0·88
y_{261}	= 0·88		
y_{202}	= 0·75		

Fig. 1. PDM 30% probability thermal ellipsoids at (a) 294 K and (b) 118 K (*ORTEP*, Johnson, 1965).

1·1 fm Å^{-3} (118 K) to be compared to Fourier synthesis peaks of 82·4 (3010 independent F_c) and 140·2 fm Å^{-3} (1869 independent F_c) respectively, corresponding to N(1) (see Fig. 1 for numbering).

Comparison of the values of the mosaic-spread tensors **Z** (Table 3) for the two temperatures, as well as those of the y extinction factors (Table 4), shows an important modification of the mosaic distribution upon cooling of the crystal, making it less sensitive to extinction. At the same time, the widths of the rocking curves of the reflections were larger in the low-temperature measurements [e.g. 0·25° full-width for the 202 reflection at 294 K and 0·4° at 118 K].

Thermal motion

The **T**, **L** and **S** tensors of the rigid-body model of Schomaker & Trueblood (1968) were fitted to the U_{ij} values of the C and N atoms, Table 5. The small r.m.s. ΔU_{ij} values (0·0015 Å^2 at 294 K and 0·0006 Å^2 at 118 K) indicate that these atoms form a reasonable rigid body. However, the deuterium ΔU_{ij} values calculated from these **T**, **L** and **S** tensors are one order of magnitude greater than those of the heavier atoms, proving that these atoms are not rigidly linked to the C and N atom skeleton. In Table 5, eigenvalues and eigenvectors of the inertia tensor **I** and of the **L** and **T** tensors are also reported. They show that the eigenvectors of **L** and **T** are close to those of **I** (especially for **L**) and that the largest libration is about the axis of smallest inertia. Corrections to bond lengths were obtained from the rigid-body librations. For the D atoms, an additional Δd_{riding} correction based on the riding model (Busing & Levy, 1964) was added to $\Delta d_{\text{rigid-body}}$ so that the total correction was $\Delta d = \Delta d_{\text{rigid-body}} + \Delta d_{\text{riding}}$. Δd_{riding} was obtained from the residual tensor $\Delta U_{ij} = (U_{ij})_o - (U_{ij})_{\text{rigid-body}}$ for the D atoms and $\Delta U_{ij} = 0$ for other atoms (Johnson, 1970). The corrected distances are reported in Fig. 2. Δd_{riding} values were found to be 0·0244, 0·0193 and 0·0202 Å at 294 K and 0·0159, 0·0120 and 0·0133 Å at 118 K for D(1), D(2) and D(3) respectively.

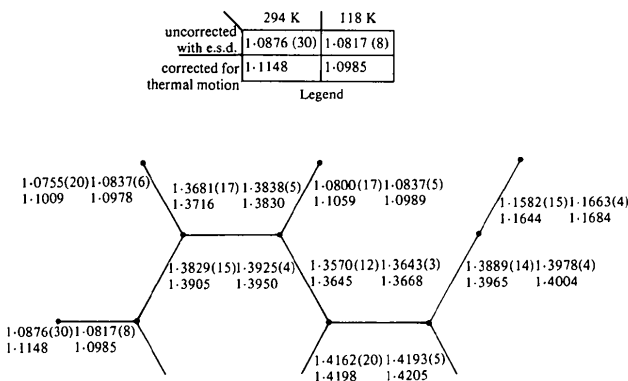|	294 K	118 K
uncorrected with e.s.d.	1·0876 (30)	1·0817 (8)
corrected for thermal motion	1·1148	1·0985

Legend

Fig. 2. Bond distances (Å).

Table 5. *Rigid-body analysis*

Calculations were based on non-deuterium atom U_{ij} orthogonal ångström space along a, b and c*.

294 K

Translation tensor **T** ($Å^2 \times 10^4$)			Librational tensor **L** ($rad^2 \times 10^4$)		
380 (6)	0	−41 (7)	89 (5)	0	−26 (3)
	261 (7)	0		21 (3)	0
		364 (9)			41 (2)

Cross tensor **S**
(Å rad × 10^5)

0	−75 (44)	0
28 (25)	0	31 (20)
0	133 (24)	0

The origin is at $(x,y,z)\ddagger = (0.5959, -0.25, 0.1775)$. The r.m.s. difference between observed and calculated U_{ij} values is 0.0015 $Å^2$. The e.s.d. of U_{ij} values is 0.0018 $Å^2$.

		Eigenvalues	Eigenvectors†		
I		135 (at. wt $Å^2$)	0.9049	0.0	−0.4256
(tensor of inertia)		297	0.0	1.0	0.0
		432	0.4256	0.0	0.9049
L		100 ($rad^2 \times 10^{-4}$)	0.9192	0.0	−0.3937
		21	0.0	1.0	0.0
		30	0.3937	0.0	0.9192
T		413 ($Å^2 \times 10^{-4}$)	0.7722	0.0	−0.6354
		261	0.0	1.0	0.0
		330	0.6354	0.0	0.7722

118 K

Translational tensor **T** ($Å^2 \times 10^4$)			Librational tensor **L** ($rad^2 \times 10^4$)		
127 (3)	0	−9 (3)	30 (2)	0	−9 (1)
	88 (3)	0		7 (1)	0
		120 (4)			14 (1)

Cross tensor **S**
(Å rad × 10^5)

0	−19 (18)	0
14 (10)	0	19 (8)
0	32 (10)	0

The origin is at $(x,y,z)\ddagger = (0.6029, -0.25, 0.1621)$. The r.m.s. difference between observed and calculated U_{ij} values is 0.0006 $Å^2$. The e.s.d. of U_{ij} values is 0.0007 $Å^2$.

		Eigenvalues	Eigenvectors†		
I		137 (at. wt $Å^2$)	0.9062	0.0	−0.4228
		300	0.0	1.0	0.0
		437	0.4228	0.0	0.9062
L		34 ($rad^2 \times 10^{-4}$)	0.9142	0.0	−0.4053
		7	0.0	1.0	0.0
		10	0.4053	0.0	0.9142
T		133 ($Å^2 \times 10^{-4}$)	0.8131	0.0	−0.5822
		88	0.0	1.0	0.0
		113	0.5822	0.0	0.8131

† Orthogonal ångström space along a, b and c*.
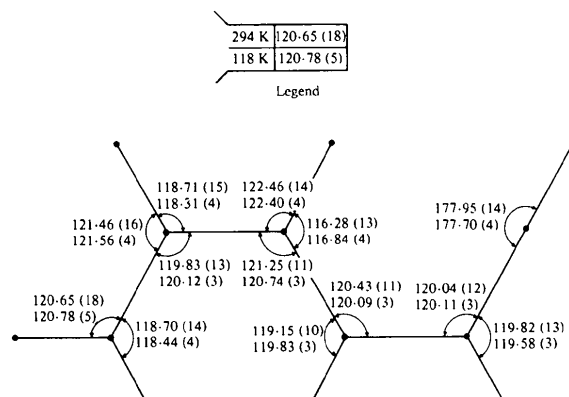‡ Crystallographic fractional coordinates.

Fig. 3. Bond angles (°).

Description and discussion of the structure

The atomic notation and thermal ellipsoids are shown in Fig. 1. The dimensions of the molecule are shown in Figs. 2 and 3. Bond lengths and angles compare well with those obtained by Bugg & Sass (1965) except for the C(5)—N(2) length [1.1582 Å (uncorrected) instead of 1.13 Å in their results]. The 1.40 Å found for the C(4)—C(5) distance, intermediate between a $C(sp^3)$—$C(sp^3)$ and a $C(sp^2)$—$C(sp^2)$ bond length, is confirmed. Another small difference is in the angle C(4)—C(5)—N(2) (177.95 instead of 180°). Noticeable also is the dissymmetry between the angles C(2)—C(3)—D(3) (122.40°) and D(3)—C(3)—N(1) (116.84°) as well as C(1)—C(2)—D(2) (121.56°) and C(3)—C(2)—D(2) (118.31°).

Table 6. *Least-squares planes and deviations* (Å) *of the atoms from the planes*

Atoms used in fitting the least-squares planes are denoted by asterisks.

Plane (I) : $0.4874 (3)X + 0.0Y + 0.8732 (2)Z = 2.3325 (21)$ (294 K)
$\qquad\quad 0.4910 (1)X + 0.0Y + 0.8712 (1)Z = 2.2421 (5)$ (118 K)

Plane (II): $0.5462 (12)X + 0.0Y + 0.8736 (8)Z = 2.4918 (21)$ (294 K)
$\qquad\quad 0.5668 (3)X + 0.0Y + 0.8238 (2)Z = 2.4462 (6)$ (118 K)

X, Y, Z are atomic coordinates in Å referred to the axes a*, b and c.

	Plane (I)			Plane (II)	
	294 K	118 K		294 K	118 K
C(1)*	0.0096 (20)	0.0129 (5)	C(1)	−0.2911 (20)	−0.3868 (5)
C(2)*	−0.0029 (15)	0.0000 (4)	C(2)	−0.2302 (15)	−0.3103 (4)
C(3)*	−0.0062 (13)	−0.0056 (4)	C(3)	−0.1330 (13)	−0.1813 (4)
C(4)*	0.0077 (19)	0.0032 (5)	C(4)*	−0.0024 (19)	−0.0023 (5)
C(5)	0.0505 (14)	0.0613 (4)	C(5)*	0.0026 (14)	0.0025 (4)
C(2')*	−0.0029 (15)	0.0000 (4)	C(5')*	0.0026 (14)	0.0025 (4)
C(3')*	−0.0062 (13)	−0.0056 (4)	N(1)	−0.0901 (13)	−0.1257 (4)
N(1)*	−0.0018 (13)	−0.0002 (4)	N(2)*	−0.0014 (13)	−0.0013 (3)
N(2)	0.0967 (13)	0.1210 (3)	N(2')*	−0.0014 (13)	−0.0013 (3)
D(1)*	0.0257 (27)	0.0223 (8)	D(1)	−0.3818 (27)	−0.4927 (8)
D(2)*	−0.0186 (20)	−0.0216 (6)	D(2)	−0.2490 (20)	−0.3337 (6)
D(3)*	0.0072 (18)	0.0081 (5)	D(3)	−0.1056 (18)	−0.1422 (5)
D(2')*	−0.0186 (20)	−0.0216 (6)	R.m.s.	0.0021	0.0021
D(3')*	0.0072 (18)	0.0081 (5)	deviation		
R.m.s.	0.0119	0.0122	of fitted atoms		
deviation					
of fitted atoms					

Table 7. *The shortest intermolecular distances* (Å)

Some distances, equivalent by lattice translations, are not reported [*e.g.* $C(3)_{x,y,z} \cdots C(2)_{x,y,z+1}$ is equivalent to $C(2)_{x,y,z} \cdots C(3)_{x,y,z-1}$].

	294 K	118 K
$C(2)\cdots C^i(3)$	3·429 (2)	3·3531 (5)
$C(3)\cdots C^i(5)$	3·451 (2)	3·3781 (5)
$C(2')\cdots C^i(3')$	3·429 (2)	3·3531 (5)
$C(3')\cdots C^i(5')$	3·451 (2)	3·3781 (5)
$C(5)\cdots D^{ii}(1)$	2·774 (3)	2·6988 (7)
$C(5')\cdots D^{ii}(1)$	2·774 (3)	2·6988 (7)
$N(2')\cdots D^{iii}(3')$	2·553 (2)	2·5304 (5)
$N(2')\cdots D^{iv}(2')$	2·553 (2)	2·5304 (5)
$N(2)\cdots D^{v}(2')$	2·753 (2)	2·6994 (6)

Symmetry code

(i)	$x, y, z - 1$	(iv)	$1 - x, y + \tfrac{1}{2}, 1 - z$
(ii)	$x - 1, y, z + 1$	(v)	$1 - x, y - \tfrac{1}{2}, -z$
(iii)	$1 - x, y - \tfrac{1}{2}, 1 - z$		

The non-planarity of the molecule, presumably related to a residual electronic charge on C(4), is confirmed by an angle of 2·38° between C(4)–C(5) and the best least-squares plane through C(4) and the pyridinium ring (294 K). Table 6 gives the least-squares analysis of the planarity of these last atoms as well as the best plane through C(4), C(5), N(2), C(5') and N(2'). The two planes make an angle of 5·12° (118 K) whereas a value of 3·94° is found for the room-temperature data.

Short intermolecular atomic distances are reported in Table 7.

X-ray data at the same temperatures have already been collected and their study is at present in progress.

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Structure of Digoxin

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Abstract

The three-dimensional structure of digoxin, a cardiac glycoside, was determined by X-ray diffraction analysis. Digoxin ($C_{41}H_{64}O_{14}$) crystallizes in the triclinic system, space group $P1$, with cell parameters $a = 7.404$ (2), $b = 12.781$ (2), $c = 12.677$ (2) Å, $\alpha = 91.15$ (1), $\beta = 119.89$ (2) and $\gamma = 104.78$ (2)° ($\lambda = 1.5418$ Å), $V = 990$ Å³, $Z = 1$. The structure was solved by vector-search methods using digoxigenin as known fragment followed by tangent-refinement recycling procedures. Refinement was carried out by block-diagonal least-squares calculations to an R factor of 4·2%. The molecule has an extended structure with its aglycone moiety in the $3\beta,12\beta,14\beta$-trihydroxy-5β-card-20(22)-enolide conformation and the three digitoxoses joined to the aglycone in a series of $\beta(1 \rightarrow 4)$-D-glycosidic linkages. The first and second digitoxoses