The Crystal Structure of 5α-Ergosta-7,22-dien-3-one 2,4-Dinitrophenylhydrazone at 243 K

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Abstract

$C_{34}H_{48}N_4O_4$ is monoclinic, $P2_1$. Experimental measurements were made at 243 ± 1 K: $a = 15.359$ (4), $b = 7.667$ (8), $c = 14.667$ (4) Å, $\beta = 114.44$ (3)°, $U = 1572.4$ Å³, $D_x = 1.218$ Mg m⁻³, $Z = 2$; 3459 unique reflexion intensities with $F > 4\sigma(F)$. The structure was refined to $R = 0.049$. The unsaturated B ring is an almost perfect half-chair, while the A and C rings adopt flattened chair conformations [$\omega = 46.3$ (4) and 51.4 (4)° respectively]. The D ring approximates a 13β-envelope.

Introduction

In a previous paper (Guy, Allen, Kennard & Sheldrick, 1977), we attempted to correlate the A-ring conformations of a number of 3-keto-5α-steroids with their relative rates of 2-condensation with benzaldehyde (Barton, McCapra, May & Thudium, 1960). Differences in condensation rate depend on small conformational changes in the A ring induced by the presence of remote substituents and/or points of unsaturation in the steroid skeleton (conformational transmission, Barton, McCapra, May & Thudium, 1960). During a search for steroids which might enable us to extend the above correlation we were provided with crystals of the

2,4-dinitrophenylhydrazone derivative of 5α-ergosta-7,22-dien-3-one (I). Although we anticipated that the introduction of such a bulky substituent at C(3) would have its own additional effect on the A ring (preventing an accurate correlation), we decided to proceed with X-ray analysis.

Experimental

Crystal data

$C_{34}H_{48}N_4O_4$, $M_r = 576.8$, monoclinic, $P2_1$, $a = 15.359$ (4), $b = 7.667$ (8), $c = 14.667$ (4) Å, $\beta = 114.44$ (3)°, $U = 1572.4$ Å³, $Z = 2$, $D_x = 1.218$ Mg m⁻³, Mo $K\alpha$ ($\lambda = 0.71069$ Å), μ(Mo $K\alpha$) = 0.05 mm⁻¹. Large orange prisms were obtained from toluene/methanol. Cell dimensions were obtained at 243 ± 1 K by least-squares analysis of zero-layer ω-angle measurements on a two-circle diffractometer.

Intensity data

Intensities were measured on an automated Stoe STADI-2 two-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a crystal 1.0 × 0.5 × 0.2 mm mounted about *b*. In an attempt to minimize any problems due to high thermal motion of the side chain, the experiment was carried out at 243 ± 1 K with the cooling apparatus of Bellard & Sheldrick (1978). The net intensities were corrected for Lorentz and polarization effects, but not for absorption. Of the 4626 reflexions measured (*h0l–h9l*) 3567 were unique; the 3459 unique data with $F > 4\sigma(F)$ were considered observed.

Structure analysis

Initial attempts to solve the structure made use of *SHELX* and the automated form of *XCSD* (programs written by Sheldrick, 1977). *XCSD* incorporates a pseudotangent expansion to select all or part of a starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973), the principle of magic integers (White & Woolfson, 1975), and the negative quartet test
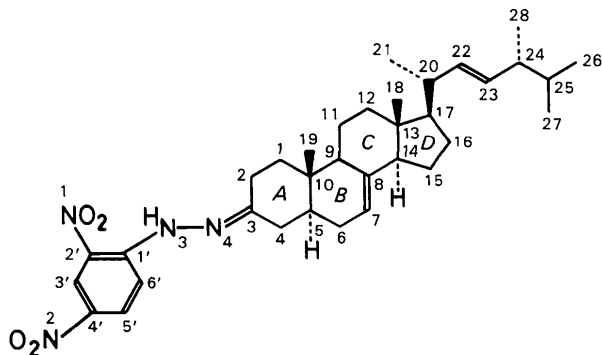
NQEST (De Titta, Edmonds, Langs & Hauptman, 1975). Both automated approaches were unsuccessful. Fixed phases were then assigned to six reflexions (Table 1); the program *XCSD* chose two further origin-defining reflexions and eight magic-integer reflexions to give a 16-reflexion starting set. One of the resultant E maps showed all non-H atoms except for six terminal C atoms of the side chain. Merit figures for this solution were NQEST $= -0.398$, Ra (a point-atom R factor based on observed peaks) $= 0.084$, and R_A (Roberts *et al.*, 1973) $= 0.299$. Two other incorrect solutions had marginally better NQEST, but higher Ra and R_A. It has been previously noted (Jones, Falvello & Kennard, 1978) that NQEST is not a reliable discriminator when weak reflexions are omitted from the data collection.

The remaining C atoms were located from a difference synthesis and isotropic full-matrix refinement, with interlayer scale factors included as parameters, gave $R = 0.15$. Anisotropic refinement proceeded to $R = 0.10$ and a difference map revealed all but five H atoms. Further refinement, in the course of which the missing H atoms were located, continued to a final $R = 0.049$ and $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0.057$. Five reflexions clearly in error were omitted. In the final cycles, C—H distances and H—C—H angles were constrained to 1.08 Å and 109.5° respectively; H atoms were given a common isotropic temperature factor. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.001F_o^2]$ gave mean $w\Delta^2$ values varying only slightly with sin θ or $|F_o|$. A final difference map had no peaks >0.22 e Å^{-3}.

Final parameters for the non-H atoms are in Table 2;* derived bond lengths, valence angles and intra-annular torsion angles* are in Tables 3, 4 and 5.

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* Lists of structure factors, anisotropic thermal parameters, H atom positions and a full table of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34477 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fixed-phase reflexions in starting set*

h	k	l	|E|	φ (°)
$\bar{9}$	0	5	4.63	0^a
$\bar{8}$	0	10	2.44	0^{b,c}
$\overline{14}$	0	8	1.91	180^{b,c}
$\bar{4}$	0	2	4.26	180^{b,c,d}
$\bar{5}$	0	3	3.71	180^e
$\overline{13}$	0	7	2.66	180^d

^{a} Origin definition (partial, see text).
^{b} $\sum_1$ relationship.
^{c} Seminvariant phase indications, obtained by combining quartets and triplets (Sheldrick, 1978).
^{d} Solution in *h0l* projection using *EEES* (Boeyens, 1977). All 20 best projection solutions had the same phases for these reflexions.
^{e} From $\bar{9}05$ and $\bar{4}02$.

Table 2. *Atom coordinates* ($\times 10^4$)

	x	y	z
C(1)	8469 (2)	9141 (3)	−926 (2)
C(2)	7601 (2)	9113 (4)	−1942 (2)
C(3)	7376 (2)	7323 (3)	−2396 (2)
C(4)	7542 (2)	5801 (3)	−1698 (2)
C(5)	8368 (2)	5979 (3)	−664 (1)
C(6)	8311 (2)	4533 (3)	24 (2)
C(7)	9040 (2)	4772 (4)	1083 (2)
C(8)	9512 (1)	6245 (3)	1427 (2)
C(9)	9346 (1)	7873 (3)	790 (1)
C(10)	8412 (1)	7776 (3)	−188 (1)
C(11)	9413 (2)	9548 (3)	1394 (2)
C(12)	10254 (2)	9609 (3)	2426 (2)
C(13)	10264 (1)	8012 (3)	3047 (1)
C(14)	10323 (1)	6409 (3)	2458 (1)
C(15)	10557 (2)	4900 (4)	3189 (2)
C(16)	11169 (2)	5749 (4)	4218 (2)
C(17)	11177 (1)	7729 (3)	4031 (1)
C(18)	9362 (2)	7946 (5)	3256 (2)
C(19)	7527 (2)	8110 (5)	27 (2)
C(20)	11313 (2)	8819 (4)	4959 (1)
C(21)	11363 (2)	10771 (4)	4809 (2)
C(22)	12217 (2)	8237 (4)	5830 (2)
C(23)	12291 (2)	7573 (4)	6684 (2)
C(24)	13206 (2)	6966 (4)	7517 (1)
C(25)	13471 (2)	7998 (5)	8491 (2)
C(26)	14470 (2)	7517 (7)	9264 (2)
C(27)	13406 (2)	9942 (6)	8330 (2)
C(28)	13159 (2)	5019 (5)	7682 (2)
C(1')	6164 (1)	8220 (3)	−4944 (2)
C(2')	5753 (2)	9651 (3)	−5584 (2)
C(3')	5196 (1)	9427 (3)	−6605 (2)
C(4')	5046 (1)	7781 (4)	−6982 (1)
C(5')	5434 (2)	6333 (3)	−6388 (2)
C(6')	5980 (2)	6544 (3)	−5382 (2)
N(1)	5858 (1)	11407 (3)	−5226 (1)
N(2)	4466 (1)	7551 (4)	−8057 (1)
N(3)	6703 (2)	8422 (3)	−3956 (1)
N(4)	6971 (1)	6982 (3)	−3329 (1)
O(1)	6376 (1)	11719 (3)	−4344 (1)
O(2)	5423 (1)	12563 (3)	−5818 (1)
O(3)	4240 (1)	8849 (4)	−8592 (1)
O(4)	4242 (2)	6070 (4)	−8369 (1)

Discussion

Fig. 1 shows a perspective view of a single molecule; Fig. 2 depicts the molecular packing viewed along **b**. Both show that the plane of the 2,4-dinitrophenyl-hydrazone moiety is approximately parallel to that of the steroid nucleus, and that the C_9H_{17} side chain is fully extended. The overall molecular dimensions are as expected and are reflected in the following means: $C_{sp^3}-C_{sp^3} = 1.533$; $C_{sp^3}-C_{sp^2} = 1.508$; $C_{sp^2}-C_{sp^2} = 1.317$; $C_{ar}-C_{ar} = 1.389$; N—O $= 1.225$ Å.

Ring *B*, containing the Δ^7 bond, adopts a half-chair conformation with torsion angles (Table 5) very close to those obtained from energy-minimization calculations (Bucourt & Hainaut, 1965). The mean torsion angle $[\bar{\omega} = 31.2 (4)°]$ is close to the value of

Table 3. *Bond lengths* (Å)

C(1)–C(2)	1·535 (5)	C(1)–C(10)	1·534 (5)
C(2)–C(3)	1·503 (6)	C(3)–N(4)	1·274 (4)
C(3)–C(4)	1·503 (5)	C(5)–C(6)	1·527 (6)
C(4)–C(5)	1·528 (4)	C(6)–C(7)	1·504 (5)
C(5)–C(10)	1·534 (5)	C(8)–C(9)	1·516 (5)
C(7)–C(8)	1·323 (4)	C(9)–C(10)	1·555 (4)
C(8)–C(14)	1·515 (4)	C(10)–C(19)	1·539 (6)
C(9)–C(11)	1·539 (5)	C(12)–C(13)	1·523 (6)
C(11)–C(12)	1·531 (5)	C(13)–C(17)	1·556 (4)
C(13)–C(14)	1·526 (5)	C(14)–C(15)	1·517 (5)
C(13)–C(18)	1·539 (6)	C(16)–C(17)	1·543 (6)
C(15)–C(16)	1·553 (5)	C(20)–C(21)	1·520 (6)
C(17)–C(20)	1·536 (5)	C(22)–C(23)	1·312 (4)
C(20)–C(22)	1·514 (5)	C(24)–C(25)	1·534 (6)
C(23)–C(24)	1·504 (5)	C(25)–C(26)	1·528 (6)
C(24)–C(28)	1·519 (7)	C(1')–C(2')	1·412 (4)
C(25)–C(27)	1·506 (8)	C(1')–C(6')	1·412 (4)
C(1')–N(3)	1·348 (3)	C(2')–N(1)	1·430 (4)
C(2')–C(3')	1·394 (4)	C(4')–C(3')	1·359 (5)
C(3')–C(4')	1·359 (5)	C(4')–N(2)	1·466 (3)
C(4')–C(5')	1·384 (4)	N(1)–O(1)	1·230 (3)
C(5')–C(6')	1·372 (4)	N(2)–O(3)	1·224 (4)
N(1)–O(2)	1·226 (4)	N(3)–N(4)	1·386 (4)
N(2)–O(4)	1·219 (5)		

Table 5. *Intra-annular torsion angles* (°)

Ring A		Ring B		
Bond	ω(obs)	Bond	ω(obs)	ω(theor)*
1–2	−50·7 (4)	5–6	−47·5 (4)	−45
2–3	35·0 (4)	6–7	15·0 (5)	15
3–4	−32·1 (4)	7–8	1·7 (5)	0
4–5	43·3 (4)	8–9	14·4 (5)	15
5–10	−56·1 (4)	9–10	−45·5 (4)	−45
10–1	60·8 (4)	10–5	63·1 (4)	62

Ring C		Ring D	
Bond	ω(obs)	Bond	ω(obs)
8–9	−41·9 (4)	13–14	45·4 (4)
9–11	44·1 (4)	14–15	−31·6 (4)
11–12	−53·8 (4)	15–16	4·9 (4)
12–13	58·2 (4)	16–17	22·7 (4)
13–14	−58·5 (4)	17–13	−41·0 (4)
14–8	51·6 (5)		

* Theoretical values of Bucourt & Hainaut (1965).
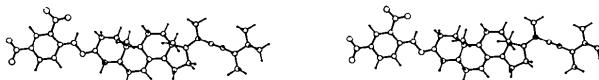
Fig. 1. Stereoscopic view of a single molecule of (I).

Table 4. *Bond angles* (°)

C(1)–C(10)–C(19)	110·2 (3)	C(2)–C(3)–C(4)	117·7 (3)
C(2)–C(3)–N(4)	125·7 (3)	C(3)–C(2)–C(1)	113·0 (3)
C(3)–N(4)–N(3)	115·4 (3)	C(4)–C(3)–N(4)	116·3 (3)
C(4)–C(5)–C(6)	109·9 (3)	C(5)–C(4)–C(3)	116·4 (3)
C(5)–C(6)–C(7)	111·9 (3)	C(5)–C(10)–C(1)	107·2 (3)
C(5)–C(10)–C(19)	111·5 (3)	C(8)–C(7)–C(6)	123·6 (3)
C(8)–C(9)–C(10)	112·6 (3)	C(8)–C(9)–C(11)	112·2 (3)
C(8)–C(14)–C(13)	114·6 (3)	C(8)–C(14)–C(15)	119·9 (3)
C(9)–C(8)–C(7)	122·8 (3)	C(9)–C(10)–C(1)	108·5 (3)
C(9)–C(10)–C(5)	108·2 (3)	C(9)–C(10)–C(19)	111·1 (3)
C(9)–C(11)–C(12)	115·0 (3)	C(10)–C(1)–C(2)	113·3 (3)
C(10)–C(5)–C(4)	113·2 (3)	C(10)–C(5)–C(6)	110·8 (3)
C(11)–C(9)–C(10)	112·8 (3)	C(12)–C(13)–C(17)	116·7 (3)
C(12)–C(13)–C(18)	111·0 (3)	C(13)–C(12)–C(11)	111·3 (3)
C(13)–C(14)–C(15)	105·4 (3)	C(13)–C(17)–C(16)	103·4 (3)
C(13)–C(17)–C(20)	119·1 (3)	C(14)–C(8)–C(7)	123·1 (3)
C(14)–C(8)–C(9)	113·9 (3)	C(14)–C(13)–C(12)	107·3 (3)
C(14)–C(13)–C(17)	99·9 (3)	C(14)–C(13)–C(18)	110·8 (3)
C(14)–C(15)–C(16)	103·8 (3)	C(16)–C(17)–C(20)	112·7 (3)
C(17)–C(13)–C(18)	110·6 (3)	C(17)–C(16)–C(15)	106·6 (3)
C(17)–C(20)–C(21)	113·8 (3)	C(17)–C(20)–C(22)	109·2 (3)
C(20)–C(22)–C(23)	127·4 (3)	C(22)–C(20)–C(21)	109·2 (3)
C(22)–C(23)–C(24)	125·3 (3)	C(24)–C(25)–C(26)	111·4 (4)
C(24)–C(25)–C(27)	112·9 (3)	C(25)–C(24)–C(23)	113·3 (3)
C(25)–C(24)–C(28)	111·8 (3)	C(27)–C(25)–C(26)	109·7 (4)
C(28)–C(24)–C(23)	110·1 (3)	C(1')–C(2')–C(3')	121·7 (3)
C(1')–C(2')–N(1)	122·4 (3)	C(1')–N(3)–N(4)	120·2 (3)
C(1')–C(6')–C(5')	121·0 (3)	C(2')–N(1)–O(1)	119·6 (3)
C(2')–N(1)–O(2)	118·3 (3)	C(3')–C(2')–N(1)	115·9 (3)
C(3')–C(4')–N(2)	118·3 (3)	C(4')–C(3')–C(2')	118·5 (3)
C(4')–N(2)–O(3)	118·4 (3)	C(4')–N(2)–O(4)	117·8 (3)
C(5')–C(4')–C(3')	122·2 (3)	C(5')–C(4')–N(2)	119·5 (3)
C(6')–C(1')–C(2')	117·0 (3)	C(6')–C(1')–N(3)	120·8 (3)
C(6')–C(5')–C(4')	119·6 (3)	N(3)–C(1')–C(2')	122·2 (3)
O(1)–N(1)–O(2)	122·0 (3)	C(3)–N(2)–O(4)	123·7 (3)
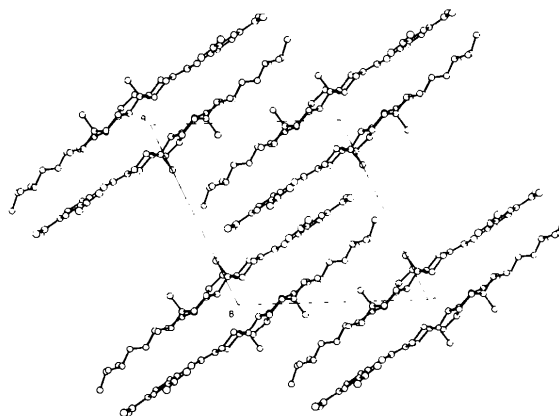
Fig. 2. Molecular packing in (I) viewed along **b**.

30·3° predicted for free cyclohexene, while the asymmetry parameter $\Delta C_2^{5,10}$ (Duax & Norton, 1975) is 1·5°. These figures are very similar to those obtained for ergosta-7,22-dien-3β-yl p-toluenesulphonate (Taylor, Watson & Smith, 1976), where (for two independent molecules) $\bar{\omega} = 32·5, 30·1°$ and $\Delta C_2^{5,10} = 3·5, 2·5°$. The Δ^7 bond in the present study does, however, show some significant (>10σ) deviations from planarity (Table 6).

The C ring adopts a slightly flattened chair conformation (Table 5); $\bar{\omega} = 51·4$ (4)° compared with 55·9° for free cyclohexane (Geise, Buys & Mijlhoff, 1971)

and 55·8° from energy minimization (Bucourt & Hainaut, 1965). The flattening occurs in the area of C(8)—C(9)—C(11), with compensatory puckering in the area of C(12)—C(13)—C(14). The ring is highly asymmetric; the only asymmetry parameter (Duax & Norton, 1975) which approaches zero is $\Delta C_s^9 = 3 \cdot 1°$. Comparable, but less accurate, torsion angles were obtained for the 3β-toluenesulphonate (Taylor, Watson & Smith, 1976).

The five-membered D ring, with values of φ_m and Δ (Altona, Geise & Romers, 1968) of 46·3 and 22·0°, approximates a 13β-envelope conformation. These pseudorotation parameters differ somewhat from those obtained for the 3β-toluenesulphonate (Taylor, Watson & Smith, 1976) where φ_m, $\Delta = 50 \cdot 6, 17°$ and 45·2, 11° for the two independent molecules.

The A ring adopts a severely distorted and flattened chair conformation (Table 5). The $\bar{\omega}$ value is 46·3 (4)°.

Table 6. *Details of some mean planes in the molecule*

Equations of planes, in the form $aX + bY + cZ + d = 0$, refer to orthogonal axes. Atomic deviations are in Å $\times$ 10³.

Plane 1: Δ^7 bond
$a = -0 \cdot 6885, b = 0 \cdot 2826, c = 0 \cdot 6679, d = -10 \cdot 4836$.
C(6) −39 (4), C(7) 39 (3), C(8) 40 (4), C(9) 1 (3), C(14) −39 (3).

Plane 2: benzene ring of 2,4-DNP group
$a = 0 \cdot 8182, b = 0 \cdot 0736, c = 0 \cdot 5702, d = 13 \cdot 8822$.
C(1') 2 (3), C(2') −1 (3), C(3') 1 (3), C(4') −2 (3), C(5') 4 (3), C(6') −3 (3), N(3)* −1 (3), N(1)* −43 (4), N(2)* 10 (4).

Plane 3: 2-nitro group of 2,4-DNP
$a = 0 \cdot 7786, b = 0 \cdot 1242, c = 0 \cdot 6151, d = 14 \cdot 4682$.
C(2') 0 (3), N(1) 0 (3), O(1) 0 (3), O(2) 0 (3).

Plane 4: 4-nitro group of 2,4-DNP
$a = 0 \cdot 8344, b = 0 \cdot 0822, c = 0 \cdot 5450, d = 12 \cdot 7248$.
C(4') 1 (3), N(2) −3 (3), O(3) 1 (3), O(4) 1 (3).

Dihedral angles: 2–3, 4·5; 2–4, 9·1; 3–4, 12·9°.

* Not included in mean-plane calculation.

Table 7. *Intermolecular contacts* <3·6 Å

E.s.d.'s are in the range 0·006–0·010 Å.

The first atom is at x,y,z. The symmetry code for the second atom is:

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

C(5')—O(2ⁱᵛ)	3·109		C(5')—O(1ⁱⁱⁱ)	3·382
C(1')—O(2ⁱⁱⁱ)	3·114		C(2)—O(4ⁱⁱ)	3·400
C(6')—O(2ⁱᵛ)	3·163		C(26)—O(3ᵛ)	3·461
C(4)—O(3ⁱⁱⁱ)	3·176		C(6')—O(1ⁱⁱⁱ)	3·474
N(3)—O(2ⁱⁱⁱ)	3·211		C(1')—N(1ⁱⁱⁱ)	3·504
C(6')—N(1ⁱⁱⁱ)	3·295		C(3')—C(28ⁱ)	3·520
N(4)—O(2ⁱⁱⁱ)	3·388		C(4')—O(1ⁱⁱⁱ)	3·568
C(6')—O(2ⁱⁱⁱ)	3·390			

and only two torsion angles [about C(1)—C(10) and C(5)—C(10)] exceed the free cyclohexane value of 55·9° (Geise, Buys & Mijlhoff, 1971). Distortion of the ring from ideal symmetry is evidenced by large asymmetry parameters (Duax & Norton, 1975), $\Delta C_s^2 = 20 \cdot 3°$ and $\Delta C_2^{1,2} = 24 \cdot 9°$. The minimum parameters are $\Delta C_s^3 = 5 \cdot 3°$ and $\Delta C_2^{1,10} = 7 \cdot 0°$. Comparison with our earlier work (Guy, Allen, Kennard & Sheldrick, 1977) and the known relative rate of 2-condensation of benzaldehyde with 5α-ergosta-7,22-dien-3-one (Barton, McCapra, May & Thudium, 1960) indicate that the asymmetry about the C(1)···C(4) mirror is some 8–10 times greater than expected.

Of the nine relevant molecules cited in our earlier paper (Guy, Allen, Kennard & Sheldrick, 1977) only one, 17β-toluenesulphonyloxy-5α-androstan-3-one (de Graaff & Romers, 1974), failed to fit the general pattern. Here the A ring was anomalously flat ($\bar{\omega} = 48 \cdot 4°$), the asymmetry about the C(1)···C(4) mirror was unexpectedly large, and other asymmetry parameters had high values. De Graaff & Romers (1974) concluded, from valence-force-field calculations, that these conformational anomalies were due to crystal packing forces. Such an explanation appears valid for the present structure, where the packing (Fig. 2, Table 7) is dominated by the 2,4-dinitrophenylhydrazone (2,4-DNP) moiety. A grouping formed by the 2,4-DNP and C(1), C(2), C(3) of the A ring has close intermolecular contacts (Table 7) with an identical grouping in a molecule related by the 2_1 axis at $\frac{1}{2},y,\frac{1}{2}$, and also with the C_9H_{17} side chain in a molecule related by the 2_1 axis at $0,y,0$. In particular the intermolecular proximity of the 4-nitro group to C(1), C(2), C(3) of the A ring appears to contribute to its anomalous conformation.

Bond lengths and angles in the 2,4-DNP compare well with published values (*e.g.* Warner, Lu, Myers, Dehaven & Jacobson, 1977; Potenza, Mastropaolo, Gallaher & Henderson, 1975). The planar C—NO$_2$ groups (Table 6) make angles of 4·5 and 9·1° with the phenyl ring. The near planarity of the 2,4-DNP is dictated by packing requirements noted above.

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Neutron Diffraction Study of Quinolinic Acid Recrystallized from D₂O: Evaluation of Temperature and Isotope Effects in the Structure*

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Abstract

The structure of quinolinic acid recrystallized from D₂O (2,3-pyridinedicarboxylic acid; $C_7H_3D_2NO_4$) has been refined based on neutron diffraction data measured at four temperatures: 35, 80, 100 and 298 K. The principal temperature dependence in cell constants is observed for the *b* axis, which is perpendicular to the molecular planes. The refined thermal parameters have been extrapolated by a least-squares procedure, to yield values for $T = 0$ K which provide estimates of the combined effects of static disorder and zero-point motion. The D atom shifts toward the midpoint of the short intramolecular O···O hydrogen bond when the crystal is cooled, just as was found in an earlier study to occur for the H atom in the undeuterated material. At 100 and 298 K, the D atom is displaced significantly further from the bond midpoint than is the H atom at the same temperature. The magnitude of this isotope effect appears to be independent of temperature. The exchangeable protons in the crystal have not been completely replaced by D; refinement of the D scattering lengths indicates the presence of approximately 2·7% H attached to N(1) and 4·4% H in the short hydrogen bond. The N scattering length has been refined to yield a value of 0·921 (2) × 10⁻¹¹ mm.

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Introduction

The general features of the crystal structure of quinolinic acid with a very short asymmetric intramolecular hydrogen bond have been elucidated from X-ray photographic data by Takusagawa, Hirotsu & Shimada (1973). Positions of the H atoms, including that in the short hydrogen bond, O···O 2·398 (3) Å, have been confirmed by neutron diffraction techniques at room temperature by Kvick, Koetzle, Thomas & Takusagawa (1974). Recently we have studied effects of temperature on the crystal structure (Takusagawa & Koetzle, 1978) and have observed a shift of the H atom toward the midpoint of the O···O hydrogen bond upon cooling the crystal to 100 K. We have now refined the structure of quinolinic acid based on neutron diffraction data collected with a sample recrystallized from D₂O. Measurements were made at 35, 80, 100 and 298 K, in an attempt to confirm the temperature effects observed in the undeuterated material and in order to elucidate the relationship between temperature and the