

## Structure of Propionamide at 123 K\*

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**Abstract.** C<sub>3</sub>H<sub>7</sub>NO, monoclinic,  $P2_1/c$ ,  $a = 8.728$  (4),  $b = 5.734$  (6),  $c = 9.790$  (4) Å,  $\beta = 115.74$  (5)° at 123 K,  $D_m$  (293 K) = 1.046,  $D_x = 1.100$  Mg m<sup>-3</sup>,  $Z = 4$ ;  $R = 0.084$ ,  $R_w = 0.098$  for 394 reflections. The molecules are planar and form dimers.

**Introduction.** The cell parameters of propionamide have been reported as  $a = 9.76$ ,  $b = 5.78$ ,  $c = 8.97$  Å,  $\beta = 113.5^\circ$ , space group  $P2_1/a$  (Turner & Lingafelter, 1955). Adler, Ballantine, Ranganathan & Davis (1964) found that propionamide undergoes radiolysis in the presence of oxygen. Adler & Petropoulos (1965) showed by using ESR spectra that when propionamide irradiated at 77 K loses a hydrogen and forms the radical CH<sub>3</sub>CHCONH<sub>2</sub>, the radical of type CH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub> is also formed. The  $G$  value for hydrogen is 0.44, independent of temperature between 77 and 323 K. Therefore, even at low temperatures some H atoms of propionamide are affected by radiation. If the temperature is increased to about 148 K during or after irradiation, oxygen diffusing into the crystal causes chain reactions and therefore further crystal damage.

In order to avoid structural damage, the structure of propionamide was determined at 123 K.

Propionamide obtained from Eastman Kodak was recrystallized twice from chloroform and dried in a vacuum desiccator (m.p.  $353.7 \pm 0.5$  K).

Single crystals were grown as platelets from benzene–acetone solution by slow evaporation of solvent (propionamide is very soluble in acetone, but almost insoluble in benzene).

The crystal platelets showed parallel extinction between crossed polars. The only pronounced cleavage was parallel to **b**. A crystal  $0.2 \times 0.3 \times 0.1$  mm was

cut from a platelet, sealed in a glass capillary, and oriented along **b**.

The space group and approximate cell parameters were obtained from precession and Weissenberg photographs.

Intensity data at 123 K were collected on a General Electric single-crystal orienter (equipped with a Cu tube and scintillation counter) by the  $\theta$ – $2\theta$  scan method. Precise cell parameters were determined at three different temperatures by least squares from 12 reflections well distributed in reciprocal space. The results are given in Table 1.

The main features of the low-temperature system (Usanmaz, 1974) are similar to those described by Post & Fankuchen (1951).

From the permitted 750 reflections with  $8 < 2\theta < 125^\circ$  the intensities of 394 unique reflections were measured. The intensities of the other reflections were almost zero, or could not be differentiated from the background. The background was counted on each side of the peak for 10 s with stationary crystal and detector. The scan range was  $3^\circ$ . The large number of unobserved reflections was presumably due to the small size of the crystal and radiation damage.

The intensities were corrected for Lorentz and polarization factors. An overall isotropic temperature factor ( $B = 2.95$  Å<sup>2</sup>) and scale factor were calculated from a Wilson (1942) plot. Propionamide and acrylamide are isomorphous; therefore, the refined fractional coordinates of the heavier atoms (C, O, N) of acrylamide (Usanmaz, 1974) were used as starting coordinates in least-squares refinement.

Table 1. Propionamide cell parameters (e.s.d.'s in parentheses)

Temperature (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	Volume (Å <sup>3</sup> )
123	8.728 (4)	5.734 (6)	9.790 (4)	115.74 (5)	441.5
163	8.840 (6)	5.757 (8)	9.791 (5)	115.57 (6)	449.5
203	8.670 (6)	5.755 (7)	9.810 (4)	113.79 (6)	447.2

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Table 2. Fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and thermal parameters [ $\times 10^4$ , anisotropic for C, N, O; isotropic ( $\text{\AA}^2$ ) for H] with e.s.d.'s in parentheses

	x	y	z	B
O	1347 (6)	2369 (7)	1190 (4)	*
N	1071 (7)	1274 (10)	-1117 (5)	*
C(1)	1689 (7)	2667 (10)	84 (5)	*
C(2)	2851 (13)	4542 (14)	90 (9)	*
C(3)	3332 (11)	6283 (12)	1355 (9)	*
H(1)	17 (8)	-2 (11)	-117 (6)	1.8 (1.2)
H(2)	125 (7)	182 (10)	-192 (7)	1.5 (1.3)
H(3)	384 (10)	373 (14)	19 (8)	4.0 (2.0)
H(5)	225 (8)	727 (12)	126 (6)	2.1 (1.3)
H(6)	387 (12)	578 (16)	233 (10)	5.2 (2.3)
H(7)	464 (18)	571 (23)	140 (14)	10.6 (4.2)

\* Anisotropic temperature factors in the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ :

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O	306 (12)	334 (16)	105 (5)	-44 (11)	139 (7)	-20 (7)
N	259 (13)	328 (20)	93 (6)	34 (13)	117 (8)	13 (9)
C(1)	208 (13)	282 (20)	98 (7)	22 (16)	96 (8)	5 (10)
C(2)	250 (19)	433 (35)	142 (11)	99 (21)	115 (13)	-46 (14)
C(3)	252 (21)	294 (27)	170 (12)	13 (19)	94 (14)	-11 (14)

The function minimized in the least-squares refinement was  $|wF_o^2 - |F_c|^2|^2$ , where  $w = 1/\sigma^2(F_o)^2$  with  $\sigma^2(F_o)^2 = \sigma_{\text{count}}^2(F_o)^2 + (0.05F_o^2)^2$  and  $\sigma_{\text{count}}^2$  is based on counting statistics.  $R$  reduced to 0.22 with isotropic and 0.15 with anisotropic temperature factors.

The positions of the H atoms were located after many trials from difference Fourier computations and their coordinates and isotropic temperature factors refined in the least-squares calculations. The radicals that were expected to form after irradiation are  $\text{CH}_2\text{CH}_2\text{CONH}_2$  or  $\text{CH}_3\dot{\text{C}}\text{HCONH}_2$ . Therefore, the H atoms bonded to C(2) and also the methyl H atoms would not be well defined. This was observed for H(4) and H(7). The positions of these H atoms are then in doubt.\* The final  $R = 0.084$  and  $R_w = 0.098$ .†

Fractional coordinates are listed in Table 2.

**Discussion.** A schematic diagram of the molecular dimer with the labelling of the atoms and nonbonded distances is shown in Fig. 1. The molecule is planar, but the H atoms connected to C(2) and C(3) are in a tetrahedral configuration.

\* The coordinates of H(7) could be determined with sufficient accuracy to warrant publication, but those of H(4) have not been included. The approximate position of H(4) is, however, indicated in Fig. 2.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36341 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A stereoscopic drawing of the molecule, with 50% probability vibrational ellipsoids, is shown in Fig. 2, and a perspective view of one unit cell is shown in Fig. 3.

Bond lengths and angles are in Table 3. The C=O length (1.254  $\text{\AA}$ ) is longer than usual (1.23  $\text{\AA}$ ) and the C-N length (1.326  $\text{\AA}$ ) is shorter than usual (1.47  $\text{\AA}$ ), indicating resonance of the form:

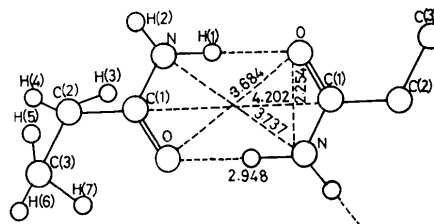
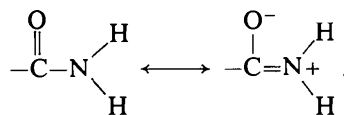


Fig. 1. Schematic diagram of the molecular dimer. (Distances are in  $\text{\AA}$ .)

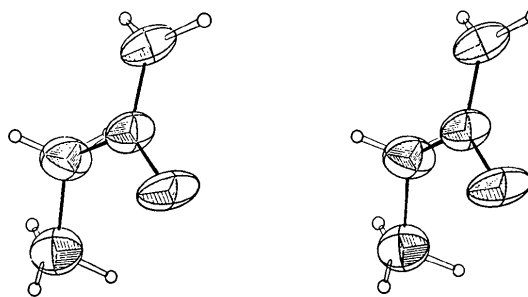


Fig. 2. The structure of the propionamide molecule (thermal ellipsoids are at the 50% probability level).

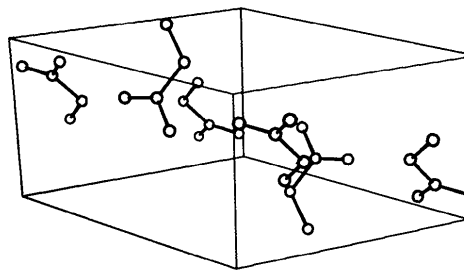


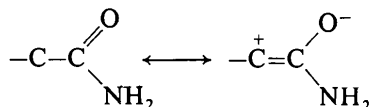
Fig. 3. Packing of the molecules in the unit cell with H atoms omitted.

Table 3. Bond distances (Å) with e.s.d.'s in parentheses and bond angles (°) (e.s.d.'s 0.1–0.2° for non-hydrogen and 1.0–2.3° for H atoms)

C(1)–O	1.254 (9)	O–C(1)–N	121.7
C(1)–N	1.326 (10)	O–C(1)–C(2)	121.1
C(1)–C(2)	1.476 (18)	N–C(1)–C(2)	117.2
C(2)–C(3)	1.502 (6)	C(1)–C(2)–C(3)	115.6
N–H(1)	1.07 (10)	H(1)–N–H(2)	127
N–H(2)	0.92 (8)	C(1)–N–H(1)	118
C(2)–H(3)	0.95 (12)	C(1)–N–H(2)	113
C(3)–H(5)	1.07 (10)	C(1)–C(2)–H(3)	104
C(3)–H(6)	0.91 (10)	C(3)–C(2)–H(3)	109
C(3)–H(7)	1.17 (11)	C(2)–C(3)–H(5)	111
		C(2)–C(3)–H(6)	119
		C(2)–C(3)–H(7)	77

The presence of this resonance in amides, imides, amino acids, peptides and proteins (Robertson, 1953) affects their chemical behaviour.

The C(1)–C(2) (1.476 Å) and C(2)–C(3) lengths (1.502 Å) are shorter than usual (1.54 Å), indicating that the following type of resonance also occurs:



The fact that the C(1)–C(2)–C(3) bond angle (115.6°) is larger than tetrahedral also suggests the above resonance.

The unusually large standard deviations in positional and thermal parameters of the H atoms are the expected results of radiation damage. From ESR results, it is possible to identify the free-radical type, but it is not possible to decide which H atoms are lost upon irradiation (Adler & Petropoulos, 1965). However, the structure analysis shows clearly that H(4) and H(7) are responsible for the free-radical formation. This result is very important for the understanding of the solid-state behaviour of this type of compound. The H atoms which contribute to hydrogen bonding are not affected by radiation, and thus have good parameters and e.s.d.'s.

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### Structure of 7 $\alpha$ -Methyl-4-androstene-3,17-dione

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**Abstract.** C<sub>20</sub>H<sub>28</sub>O<sub>2</sub>,  $M_r = 300.2$ ,  $D_m = 1.21$ ,  $D_c = 1.21$  Mg m<sup>-3</sup>, orthorhombic,  $P2_12_12_1$ ,  $Z = 4$ ,  $a = 6.424$  (2),  $b = 9.466$  (2),  $c = 27.008$  (6) Å,  $U = 1642.4$  Å<sup>3</sup>,  $\mu(\text{Mo } K\alpha) = 0.041$  mm<sup>-1</sup>. Final  $R = 3.8\%$  for 1452 reflexions. Ring A adopts a 1 $\alpha$ -sofa conformation and rings B and C are observed as chair conformations. Ring D adopts an envelope conformation with C(14) at the flap.

**Introduction.** In an attempt to explain the antifertility activity of RMI 12,936 (Cox, Mkandawire & Mallinson, 1981), various possible metabolites have been examined. 7 $\alpha$ -Methyl-4-androstene-3,17-dione was prepared from 7 $\alpha$ -methyltestosterone (Cox & Sim, 1982) by oxidation with sodium dichromate/acetic acid. Crystallographic data were obtained from an Enraf-Nonius CAD-4 automated diffractometer using mono-