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## *N*-Acetyl-DL-methionine, C<sub>7</sub>H<sub>13</sub>NO<sub>3</sub>S

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**Abstract.**  $M_r = 191.25$ , monoclinic,  $P2_1/c$ ,  $a = 5.882(1)$ ,  $b = 9.285(1)$ ,  $c = 21.934(3)$  Å,  $\beta = 124.88(5)^\circ$ ,  $V = 982.7(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.292$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.8$  cm<sup>-1</sup>,  $F(000) = 408$ ,  $T = 295$  K,  $R = 0.041$  for 2131 observed reflections. The peptide group is planar within about 0.03 Å. The carboxyl group, also approximately planar, exists in the un-ionized form, with N out of the plane by 0.536(1) Å. Bond lengths and angles are normal. Molecules are linked by N—H...O [2.953(2) Å] and O—H...O [2.550(2) Å] hydrogen bonds.

**Introduction.** Sulphur-centred radicals produced in crystals of *N*-acetyl-DL-methionine show well characterized thirteen-line hyperfine splitting in the ESR spectra and clear optical absorption bands (Kominami, Akasaka, Umegaki & Hatano, 1971; Kominami, 1972). The intensity ratios of these hyperfine lines are difficult to explain on the basis of a proposed radical structure. ENDOR (electron nuclear double resonance) measurements were made to establish the detailed electronic structures of these sulphur-centred radicals (Naito, Akasaka & Hatano, 1981), and to aid this study the crystal structure was determined by X-ray methods.

**Experimental.** Colourless crystals, 0.28 × 0.30 × 0.18 mm, CAD-4 diffractometer, graphite-

monochromatized Mo  $K\alpha$  radiation,  $\theta \leq 32.5^\circ$ ,  $\omega$ - $2\theta$  scan,  $\omega$ -scan width  $(0.70 + 0.35 \tan\theta)^\circ$  extended by 25% on either side of the peak for background measurement, horizontal aperture  $(2 + \tan\theta)$  mm, vertical aperture 4 mm. Cell parameters by least-squares fit to observed  $\sin^2\theta$  values for 25 centred reflections with  $15 < \theta < 21^\circ$ , absent reflections  $0k0$ ,  $k$  odd,  $h0l$ ,  $l$  odd ( $P2_1/c$ ); intensity and orientation checks for three standard reflections showed little ( $< \pm 0.9\%$ ) variation or decay throughout data collection. 3533 independent reflections ( $h -7$  to  $7$ ,  $k 0$  to  $14$ ,  $l 0$  to  $31$ ), 2131 (60.3%) with  $I \geq 3\sigma(I)$ ,  $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$ ,  $S$  = total peak count and  $B$  = time-averaged background, Lp corrections (no absorption corrections). Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares by *SHELX76* (Sheldrick, 1976), anisotropic, H atoms from a difference synthesis, isotropic; function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w = 1/\sigma^2(F)$ , three reflections with high  $F_c/F_o$  ratios, possibly due to extinction, removed; max. electron density in final difference map  $0.29$  e Å<sup>-3</sup>, final  $R = 0.041$ ,  $wR = 0.047$  for 2131 observed reflections, 161 variables,  $R = 0.079$  for all data;  $(\Delta/\sigma)_{\text{max}} = 0.04$ . Scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), local adaptations of standard computer programs *ORFFE* (Busing, Martin & Levy, 1964), *ORTEPII* (Johnson, 1976), and *PLUTO* (Motherwell & Clegg, 1978).

Table 1. Final positional (fractional  $\times 10^4$ , H  $\times 10^3$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

	x	y	z	$U_{eq}^*/U_{iso}$
S	4012.1 (13)	982.1 (5)	5605.5 (3)	72
C(1)	329 (4)	1291 (3)	2546 (1)	65
C(2)	-798 (3)	1582 (2)	2993 (1)	37
C(3)	-221 (2)	2762 (1)	4056 (1)	30
C(4)	-2763 (2)	3734 (1)	3648 (1)	32
C(5)	2079 (3)	3528 (2)	4764 (1)	39
C(6)	4619 (3)	2606 (2)	5274 (1)	52
C(7)	2599 (6)	1681 (4)	6081 (2)	86
N	756 (2)	2375 (1)	3605 (1)	34
O(1)	-3070 (2)	1121 (1)	2816 (1)	51
O(2)	-4356 (2)	3828 (1)	3826 (1)	50
O(3)	-2954 (2)	4484 (1)	3120 (1)	52
H1(C1)	214 (6)	148 (3)	279 (1)	75 (7)
H2(C1)	-56 (6)	61 (3)	222 (2)	86 (8)
H3(C1)	-19 (7)	206 (4)	224 (2)	120 (12)
H(C3)	-79 (4)	191 (2)	418 (1)	45 (4)
H1(C5)	128 (3)	383 (2)	501 (1)	34 (4)
H2(C5)	260 (4)	432 (2)	462 (1)	50 (5)
H1(C6)	599 (5)	327 (3)	570 (1)	75 (6)
H2(C6)	555 (5)	224 (3)	502 (2)	88 (7)
H1(C7)	70 (8)	217 (4)	571 (2)	125 (11)
H2(C7)	338 (8)	247 (4)	631 (2)	130 (13)
H3(C7)	257 (12)	87 (7)	635 (3)	215 (21)
H(N)	213 (4)	278 (2)	369 (1)	49 (5)
H(O3)	-444 (5)	502 (3)	287 (1)	76 (7)

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

C(1)–C(2)	1.489 (2)	C(4)–O(2)	1.207 (2)
C(2)–N	1.333 (2)	C(4)–O(3)	1.300 (2)
C(2)–O(1)	1.236 (2)	C(5)–C(6)	1.518 (3)
C(3)–C(4)	1.523 (2)	C(6)–S	1.796 (2)
C(3)–C(5)	1.531 (2)	C(7)–S	1.786 (3)
C(3)–N	1.445 (2)		
C(1)–C(2)–N	117.2 (1)	C(3)–C(4)–O(3)	113.4 (1)
C(1)–C(2)–O(1)	122.6 (1)	O(2)–C(4)–O(3)	124.2 (1)
N–C(2)–O(1)	120.2 (1)	C(3)–C(5)–C(6)	114.3 (1)
C(4)–C(3)–C(5)	108.8 (1)	C(5)–C(6)–S	115.6 (1)
C(4)–C(3)–N	112.7 (1)	C(2)–N–C(3)	121.0 (1)
C(5)–C(3)–N	110.1 (1)	C(6)–S–C(7)	101.4 (1)
C(3)–C(4)–O(2)	122.4 (1)		

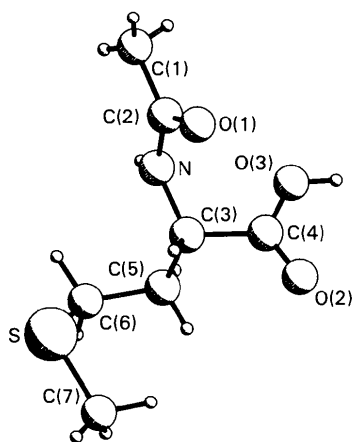


Fig. 1. View of the molecule of *N*-acetyl-DL-methionine, with the atom-numbering scheme.

**Discussion.** Final atomic parameters are in Table 1.\*

The conformation of the molecule (Fig. 1) can be described in terms of the torsion angles (notation of Lakshminarayanan, Sasisekharan & Ramachandran, 1967):  $\psi_2 = \text{N}-\text{C}(3)-\text{C}(4)-\text{O}(3) = -25.5 (2)$ ,  $\chi_1 = \text{N}-\text{C}(3)-\text{C}(5)-\text{C}(6) = -63.1 (2)$ ,  $\chi_2 = \text{C}(3)-\text{C}(5)-\text{C}(6)-\text{S} = -59.2 (2)$ ,  $\chi_3 = \text{C}(5)-\text{C}(6)-\text{S}-\text{C}(7) = -59.3 (2)^\circ$ . The peptide group, C(1), C(2), C(3), N, O(1), is planar within about 0.03  $\text{\AA}$ . The carboxyl group exists in the un-ionized form, with H bonded to O(3); the group is approximately planar, with N displaced from the plane by 0.536 (1)  $\text{\AA}$ .

Bond lengths and angles in the molecule (Table 2) are in general similar to those in related materials (Marsh & Donohue, 1967), *e.g.* in *N*-acetyl-DL-methionine dimethylamide and diethylamide (Aubry, Protas, Marraud & Neel, 1971; Aubry, Protas, Cung & Marraud, 1979). The average C–S bond length of 1.791 (2)  $\text{\AA}$  is slightly smaller than the sum of single-bond radii, 1.812  $\text{\AA}$  (Pauling, 1960), but in good agreement with previously observed values (Mathieson & Robertson, 1949). Outer bond lengths such as S–C(7) and C(2)–C(1) are possibly in error as a result of fairly large thermal librations.

Molecules are linked by N–H...O and O–H...O hydrogen bonds (Fig. 2). N–H(N) = 0.81 (2), H(N)...O(2)(1+x, y, z) = 2.14 (2), N...O(2) = 2.953 (2)  $\text{\AA}$ , N–H(N)...O(2) = 176 (2)°; O(3)–H(O3) = 0.87 (2), H(O3)...O(1)(-1-x, 1/2+y, 1/2-z) = 1.72 (3), O(3)...O(1) = 2.550 (2)  $\text{\AA}$ , O(3)–H(O3)...O(1) = 159 (3)°.

\* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42018 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

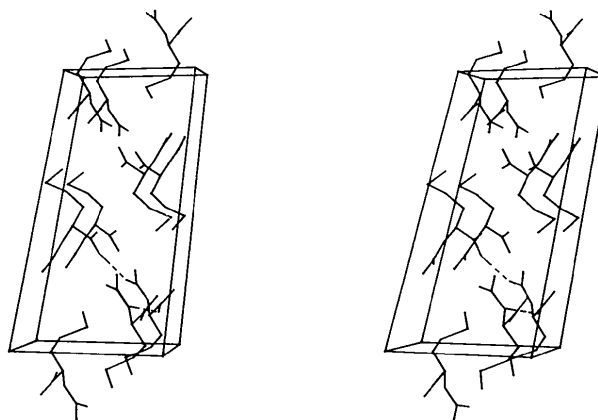


Fig. 2. Molecular packing of *N*-acetyl-DL-methionine (stereoview 15° from a, with b horizontal, c vertical). One example of each type of hydrogen bond is shown with broken lines.

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## Structure of 4,10-Dibenzyl-4,10-diazabicyclo[5.5.0]dodec-1(7)-ene Dihydrochloride, $C_{24}H_{32}N_2^+ \cdot 2Cl^-$

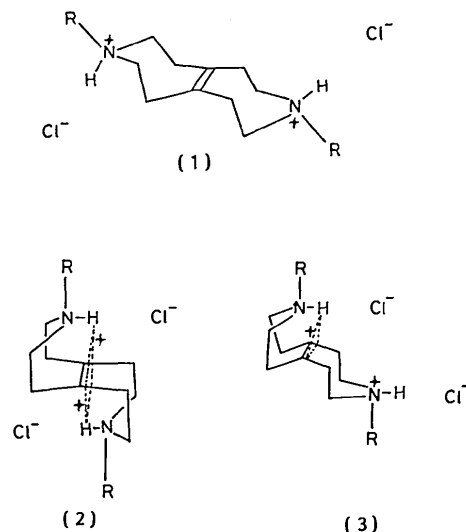
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**Abstract.**  $M_r = 419.44$ , orthorhombic,  $Pcab$ ,  $a = 12.737$  (2),  $b = 16.796$  (2),  $c = 10.364$  (1) Å,  $V = 2217.2$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.257$  Mg m<sup>-3</sup>, Cu Kα,  $\lambda = 1.5418$  Å,  $\mu = 2.75$  mm<sup>-1</sup>, m.p. 503–508 K decomposed,  $F(000) = 896$ ,  $T = 295$  K, final  $R = 0.040$  for 1618 non-zero reflections. The molecule has  $\bar{1}$  symmetry. The N atoms are protonated, and hydrogen-bonded to the Cl<sup>-</sup> ions [ $N^+ \cdots Cl^-$  3.064 (1),  $H \cdots Cl^-$  2.06 (2) Å,  $\angle N^+ - H \cdots Cl^-$  172 (2)°]. The seven-membered ring takes a chair-like conformation. The benzyl group is bonded equatorially to the ring.

**Introduction.** The title compound was assumed to take one of the conformations, (1), (2) or (3). The last two conformations would display a nonclassical interaction between the proton bonded to the N atom and the double bond. To ascertain whether or not such an interaction was present, the compound was synthesized (Kimura, 1984, unpublished). The structure (1) has been confirmed by the present X-ray crystallographic study.



R = CH<sub>2</sub>Ph