The Crystal Structures of the α and β Forms of DL-Methionine

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Synopsis. The crystal structures of the α and β forms of DL-methionine have been refined by block-diagonal least-squares calculations using three-dimensional X-ray data to R=0.118 and 0.088 respectively. The structures of both the forms are essentially the same as those previously reported by Mathieson (*Acta Crystallogr.*, **5**, 332 (1952)).

Mathieson1) has determined the crystal structures of the α and β forms of DL-methionine, $C_5H_{11}NO_2S$, from two-dimensional X-ray data. Recently, Taniguchi *et al.*2) found that crystals of the β form undergo a reversible solid phase transformation at about 326 K to the α form accompanied with characteristic diffuse scattering during the transformation. In the course of their X-ray study of the phase transformation, it seemed that the structures given by Mathieson1) were too deficient in accuracy to interpret quantitatively the diffuse scattering patterns. Therefore, in this paper, we deal with a reexamination of the structures of the α and β forms.

Experimental

Plate-like crystals elongated along the b axis were obtained from aqueous solutions at room temperature. Weissenberg photographs showed that all the crystals examined were β form, but they gave diffraction patterns showing various degrees of streaking along the reciprocal-lattice rows parallel to c*. Therefore a crystal showing very weak streaks was selected for the data collection. A crystal of the α form with no streaking could be obtained from that of the β form by heating in a stream of hot air through the transition point, the crystal being kept at 333 K (±2 K) during X-ray exposure. Note that a few crystals of the α form obtained in this way did not transform to the β form even at room temperature but they were all poor in quality. Cell dimensions of the β form were determined from photographs taken with a Buerger back-reflection Weissenberg camera, and those of the α form were determined by examining double-exposure Weissenberg and oscillation photographs taken with the same crystal at room temperature (β form) and 333 K (α form). Crystal data obtained are: α form at 333 K, a=9.89(2), b=4.70(2), c=16.74(3) Å, β=102.3(7)°, space group $P2_1/a$, Z=4; β form at 293 K, a=9.912(5), b=4.700 (7), c=33.13(2) Å, β=106.3(3)°, I2/a, Z=8.

Intensities of 1310 independent reflections for the α form at 333 K and 1494 reflections for the β form at 293 K were collected on equi-inclination Weissenberg photographs for k=0 to 3 (α form) and for k=0 to 4 (β form). The intensities were measured visually and corrected for Lorentz and polarization factors. No correction for absorption was made.

The structures of the α and β forms given by Mathieson1) were refined by block-diagonal least-squares calculations3) with unit weights. The H atoms for both forms were included in the least-squares calculations with fixed positional parameters deduced from the geometry of the molecules and fixed isotropic thermal parameters (U=0.057 and 0.044 Å^2 for the α and β forms respectively). At a later stage of refinement, the positions of the H atoms for both forms were confirmed from difference syntheses except those of terminal methyl groups. The final R values for the α and

TABLE 1. ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) FOR NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS

The numbering of the atoms is the same as that given by Mathieson.1) The anisotropic thermal parameters are of the form: $\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
α Form at 333 K									
O (1)	−57 (3)	−523 (10)	3756 (3)	18 (2)	26 (3)	68 (2)	5 (2)	10 (2)	2 (2)
O (2)	1722 (4)	−3212 (9)	4352 (2)	32 (2)	15 (3)	38 (2)	1 (2)	9 (1)	7 (2)
N	3586 (4)	571 (11)	4077 (2)	18 (2)	25 (4)	34 (2)	−5 (2)	5 (1)	−3 (2)
C (1)	1217 (4)	−1147 (13)	3934 (3)	21 (2)	8 (4)	38 (2)	1 (2)	9 (2)	−5 (2)
C (2)	2176 (4)	671 (13)	3553 (3)	17 (2)	26 (4)	31 (2)	0 (2)	4 (2)	−1 (2)
C (3)	2212 (6)	−574 (17)	2701 (3)	33 (3)	59 (6)	32 (2)	−5 (3)	8 (2)	5 (3)
C (4)	3158 (8)	1000 (21)	2262 (4)	64 (4)	92 (8)	49 (3)	−14 (5)	27 (3)	−5 (4)
S	3248 (3)	−573 (7)	1291 (1)	90 (1)	116 (2)	46 (1)	−2 (2)	34 (1)	−16 (1)
C (5)	1536 (11)	200 (39)	724 (6)	96 (7)	239 (18)	63 (5)	16 (10)	7 (5)	15 (9)
β Form at 293 K									
O (1)	−2687 (2)	2065 (6)	1867 (1)	14 (1)	26 (2)	49 (2)	3 (1)	14 (1)	3 (1)
O (2)	−874 (3)	−756 (6)	2165 (1)	25 (1)	21 (2)	26 (1)	2 (1)	12 (1)	7 (1)
N	995 (3)	2967 (7)	2025 (1)	11 (1)	24 (2)	20 (1)	−5 (1)	6 (1)	−2 (1)
C (1)	−1422 (3)	1327 (7)	1950 (1)	16 (2)	11 (2)	22 (1)	2 (1)	11 (1)	−3 (1)
C (2)	−483 (3)	3078 (7)	1749 (1)	15 (2)	10 (2)	22 (1)	2 (1)	7 (1)	0 (1)
C (3)	−576 (4)	1865 (9)	1315 (1)	26 (2)	27 (2)	20 (2)	−5 (2)	11 (1)	−3 (1)
C (4)	412 (5)	3219 (10)	1096 (1)	49 (3)	34 (3)	30 (2)	−10 (2)	23 (2)	−2 (2)
S	153 (2)	1575 (4)	587 (0)	76 (1)	69 (1)	27 (1)	−27 (1)	32 (1)	−18 (1)
C (5)	1526 (6)	3238 (17)	420 (2)	65 (4)	98 (5)	43 (3)	−10 (4)	34 (3)	−3 (3)

Table 2. Bond lengths and angles and torsion angles

	α Form	β Form
Bond lengths (l/Å)		
C (1)-O (1)	1.265 (7)	1.255 (5)
C (1)-O (2)	1.238 (7)	1.242 (4)
C (2)-N	1.481 (8)	1.492 (5)
C (1)-C (2)	1.514 (9)	1.528 (5)
C (2)-C (3)	1.549 (10)	1.525 (5)
C (3)-C (4)	1.503 (13)	1.514 (6)
C (4)-S	1.806 (11)	1.805 (5)
C (5)-S	1.792 (19)	1.788 (8)
Bond angles (ϕ/°)		
O (1)-C (1)-O (2)	125.2 (6)	126.3 (3)
O (1)-C (1)-C (2)	116.9 (5)	116.7 (3)
O (2)-C (1)-C (2)	117.8 (5)	116.9 (3)
C (1)-C (2)-N	109.2 (5)	109.1 (3)
C (3)-C (2)-N	109.2 (5)	110.6 (3)
C (1)-C (2)-C (3)	108.3 (5)	109.0 (3)
C (2)-C (3)-C (4)	113.8 (7)	114.8 (3)
C (3)-C (4)-S	113.2 (7)	109.1 (3)
C (4)-S-C (5)	99.8 (7)	100.5 (3)
Torsion angles (ϕ/°)		
O (2)-C (1)-C (2)-N	−29.3	−31.0
N-C (2)-C (3)-C (4)	300.2	305.6
C (1)-C (2)-C (3)-C (4)	181.4	185.6
C (2)-C (3)-C (4)-S	177.4	180.7
C (3)-C (4)-S-C (5)	68.9	185.6

β forms were 0.118 and 0.088 respectively. Positional and thermal parameters are given in Table 1.[4] Bond lengths and angles and torsion angles are given in Table 2. All computations were made on a NEAC 2200-700 computer of the Computation Center of Osaka University.

Discussion

The structures of both the α and β forms are essentially the same as those given by Mathieson.[1] No significant difference between the molecules of the α and β forms is observed in bond lengths and angles except for the torsion angles C(3)–C(4)–S–C(5) (68.9 and 185.6° for the α and β forms respectively), which define the conformation of the terminal C(5) atom to the C(3) atom as *gauche* in the α form and *trans* in the β form.

A fundamental difference between the crystal structures of the α and β forms lies in the arrangements of layers along the c axis. The α form consists of a single-layer unit, P, with a stacking sequence $PPP\ldots$, while the β form consists of a double-layer unit, $Q\overline{Q}$, with a sequence $Q\overline{Q}Q\overline{Q}\ldots$, where $\overline{Q}$ is related to Q by the translation $(\mathbf{a}+\mathbf{b})/2$. The structures of layers P and Q are very similar to each other except for the positions of the terminal methyl groups; both P and Q layers consist of molecules connected by three types of NH···O hydrogen bonds (2.83, 2.80, and 2.77 Å in layer P and 2.82, 2.80, and 2.79 Å in layer Q). The closest interlayer contacts are C(5)···C(5) of 3.46 and 3.81 Å for the α and β forms respectively.

By comparing the structures of the two forms, the major change of the structure occurring on the phase transformation from the β to α forms may be explained in terms of the translation $(\mathbf{a}+\mathbf{b})/2$ of every second layer accompanied with the repositioning of the terminal methyl groups from *trans* to *gauche* to the C(3) atoms. A similar structural change can be seen on the phase transformation of DL-α-aminobutyric acid from the A to D forms.[5]

References

1) A. McL. Mathieson, *Acta Crystallogr.*, **5**, 332 (1952).

2) T. Taniguchi, Y. Takaki, and K. Sakurai, to be published.

3) T. Ashida, HBLS-V, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University (1973), pp. 55—61.

4) The structure factor tables are kept at the Office of the Chemical Society of Japan (Document No. 8011).

5) K. Nakata, Y. Takaki, and K. Sakurai, *Acta Crystallogr.*, in press.