

The Crystal and Molecular Structure of 2-Methyl-5-[methyl(mesyl)amino]-2H-1,2,3-triazole-4-carbonitrile.* On the Geometry of the *N*-Mesyl Groups

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(Received 1 March 1977; accepted 2 April 1977)

$C_6H_9N_5O_2S$ is orthorhombic, space group *Pbca*, with $a = 7.333$ (4), $b = 16.040$ (2), $c = 16.825$ (3) Å, $Z = 8$. The structure was refined to $R = 0.073$ for 1030 observed reflexions. The endocyclic methyl group is attached to N(2). The geometrical features of the *N*-mesyl groups as revealed in different crystal structures are discussed.

Introduction

Kálmán, Párkányi, Schawartz & Simon (1976) pointed out that the position of the endocyclic H atom in 5-mesylamino-2H-1,2,3-triazole-4-carbonitrile monohydrate (I) differs from those found in the analogous 5-tosylamino-1H-1,2,3-triazole-4-carbonitrile† and in some other 4,5-disubstituted 1H-1,2,3-triazoles {e.g. 5-amino-4-carbamoyl-1H-1,2,3-triazole (Kálmán, Simon, Schawartz & Horváth, 1974), tetrachlorobis[2-(5-amino-4-carboxamidinium)-1H-1,2,3-triazole]-copper monohydrate (Purnell, Shepherd & Hodgson, 1975) and 5-amino-4-ethoxycarbonyl-1H-1,2,3-triazole (Párkányi, Kálmán, Argay & Schawartz, 1977)}. In order to obtain a better view of this unusual 2H-tautomerism of (I), X-ray analysis of its dimethyl derivative (II) was performed.

Experimental

Colourless crystals of (II) (m.p. 105°C) were prepared from (I). Two equivalents of sodium methylate were added to one equivalent of (I) dissolved in methanol. The white disodium salt obtained was suspended in acetone and methylated with CH_3I .

Crystal data

$C_6H_9N_5O_2S$; $M_r = 215.2$, orthorhombic; $a = 7.333$ (4), $b = 16.040$ (2), $c = 16.825$ (3) Å, $V = 1978.98$ Å³; $D_c = 1.444$, $D_m = 1.440$ g cm⁻³; $Z = 8$, $F(000) = 896$, $\mu[\lambda(Cu K\alpha) = 1.5418 \text{ Å}] = 26.8$ cm⁻¹; space group *Pbca*.

* Dedicated to Professor A. Albert (Canberra) on his 70th birthday.

† Unpublished results of Hoge & Fischer, referred to in Stadler, Auschütz, Regitz, Keller, Van Assche & Fleury (1975).

Intensities of 1567 independent reflexions were collected on a Stoe semi-automatic two-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation (Kálmán, Simon, Schawartz & Horváth, 1974). After data reduction 537 reflexions with $|F| - 5\sigma(F) < 0$ were taken as unobserved. No absorption correction was made. The phase problem for 278 reflexions ($E \geq 1.20$) was solved with *SHELX* (Sheldrick, 1975), giving $R = 0.38$ for the non-hydrogen atoms. Prior to the refinement, all H atoms were generated with staggered methyl groups assumed, and with C–H constrained to 1.08 Å. These moieties were refined as rigid groups. Blocked full-matrix refinement for the non-hydrogen atoms gave a final R of 0.073 [$R_c = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.099$] for the observed reflexions ($R_{tot} = 0.109$ for all 1567 reflexions). The weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 3.0619 and 0.00118 respectively. A bonded-H-atom scattering factor was employed (Stewart,

Table 1. Fractional coordinates ($\times 10^4$)

Estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
S	−838 (2)	3854 (1)	1657 (1)
O(1)	−1612 (7)	3050 (3)	1756 (3)
O(2)	−145 (7)	4290 (4)	2321 (2)
N(1)	420 (7)	3651 (3)	−380 (3)
N(2)	80 (7)	3024 (4)	−869 (3)
N(3)	−93 (7)	2283 (3)	−533 (3)
N(4)	884 (6)	3741 (3)	1029 (3)
N(5)	332 (10)	1225 (4)	1237 (5)
C(1)	192 (8)	2443 (4)	247 (4)
C(2)	507 (7)	3290 (4)	335 (3)
C(3)	−2438 (9)	4487 (4)	1175 (4)
C(4)	243 (10)	1775 (5)	799 (5)
C(5)	−82 (10)	3158 (6)	−1726 (4)
C(6)	2132 (9)	4457 (4)	940 (4)

Table 4. Comparison of bond lengths and angles involving nitrogen in compounds I, II and A, B

In (B) there are two molecules per asymmetric unit; the numbers given are mean values, X = H or iso-C ₃ H ₇ .					
	(I)	(II)		(I)	(II)
S—N(4)	1.641 (2) Å	1.657 (5) Å	S—N—C	124.3 (1)°	116.0 (4)°
S—O(mean)	1.429 (2)	1.416 (5)	S—N—X	115	116.1 (5)
N(4)—C(2)	1.379 (3)	1.402 (7)	C—N—X	117	116.9 (5)
	(A)	(B)		(A)	(B)
S—N	1.629 (5) Å	1.628 (5) Å	S—N—C	121.4 (3)°	118.9 (3)°
N—C ϕ	1.439 (8)	1.442 (8)	S—N—X	—	120.1 (5)
			C—N—X	—	120.1 (4)

The entering exocyclic methyl group alters significantly the electronic structure of the S—N(4)—C(2) moiety and the conformation of the molecule. In (I) the plane of the S—N(4)—C(2) moiety is nearly parallel to the triazole ring (Fig. 2a) which provides an increased C(2)—N(4) interaction indicated by a strong multiple bond (1.379 Å). S and N(1) are *cis*. Presumably this is why the S—N(4)—C(2) angle is so large (124.3°). The methylation twisted the *N*-mesyl group around C(2)—N(4) by 124° (Fig. 2b) and diminished the S—N(4)—C(2) angle by 8.3°. Simultaneously, the nitrile group is considerably bent out of the best plane of the triazole ring [$\Delta_{C(4)} = 0.089$, $\Delta_{N(5)} = 0.199$ Å]. The weakened interaction between the triazole ring and the mesylamino group [compare Fig. 2(a) with Fig. 2(b)] resulted in the lengthening of S—N(4) and N(4)—C(2) (Table 4). The bond angles at N(4) indicate increased sp^3 character relative to (I). No similar $sp^2 \rightarrow sp^3$ shift was found between *p*-methoxybenzenesulphon-*p*-anisidide (A) and *p*-methoxybenzenesulphon-*N*-isopropyl-*p*-anisidide (B) (Pokrywiczki, Weeks & Duax 1973a, b) presumably because of the originally weak *N*-phenyl interaction in (A) (*cf.* torsion angle S—N—C ϕ_1 —C ϕ_2 = 75.2°).

The geometry of the *N*-mesyl group

The lengthening of the S—N bond in (II) is accompanied by a decrease in the S—O distances (Table 4). This phenomenon had not been observed previously; the structure of the *N*-mesyl moiety, apart from in (I) and (II), has been studied only in a few cases (Klug, 1968, 1970; Attig & Mootz, 1975; Gadret, Goursole, Leger, Colleter & Carpy, 1976). One of the first studies of the *N*-mesyl group (Kálmán, 1967) was in *S,S*-dimethyl-*N*-methylsulphonylsulphilimine (hereinafter: DMMS).^{*} Its parameters could be compared only with a few MeSO₂ groups (Wheatley, 1954; Bullough & Wheatley, 1957) and with those of some sulphonamides (Alléaume & Decap, 1965a, b; O'Connor & Maslen, 1965): therefore it was thought that '... the strength of the S—O $d\pi$ bond of the SO₂ groups is not weakened significantly by the strong S^{VI}—N $d\pi$ bond belonging to the same S atom, and, at the same time, the formation of a strong S^{VI}—N $d\pi$ bond is not hindered by the presence of the SO₂ group ...' which resulted in the conclusion that the *N*-mesyl

^{*} Prior to DMMS only the structure of methanesulphonamide was known, determined by Vorontsova (1966) without refinement.

Table 5. A comparison of some *N*-mesyl-group dimensions

Distances in Å, angles in degrees.

Note	S—N	S—O	S—C	N—C	N—S	N—H	O—S—O	O—S—N	O—S—C	N—S—C	S—N—C	S—N—S
<i>a</i>	1.657 (5)	1.419 (5)	1.750 (7)	1.402 (7)	—	—	120.1 (3)	106.5 (3)	108.7 (3)	106.2 (3)	116.0 (4)	—
		1.413 (5)	—	1.476 (8)	—	—	—	106.3 (3)	108.2 (3)	—	116.1 (5)	—
<i>b</i>	1.645 (1)	1.427 (1)	1.746 (1)	—	1.645 (1)	0.89	119.1 (1)	107.8 (1)	108.9 (1)	105.9 (1)	—	125.0 (1)
		1.428 (1)	—	—	—	—	—	104.9 (1)	109.4 (1)	—	—	—
<i>c</i>	1.641 (2)	1.429 (2)	1.747 (3)	1.379 (3)	—	0.93	118.5 (1)	108.8 (1)	108.8 (1)	105.9 (1)	124.3 (1)	—
		1.428 (2)	—	—	—	—	—	104.3 (1)	109.9 (1)	—	—	—
<i>d</i>	1.633 (2)	1.443 (2)	1.746 (2)	1.438 (3)	—	0.80	118.6 (1)	107.7 (1)	108.6 (1)	105.3 (2)	120.1 (3)	—
		1.425 (2)	—	—	—	—	—	105.3 (1)	108.4 (1)	—	—	—
<i>e</i>	1.633 (3)	1.426 (3)	1.742 (5)	1.444 (5)	—	0.88	119.1 (1)	107.7 (1)	108.4 (1)	107.2 (1)	118.8 (1)	—
		1.422 (3)	—	—	—	—	—	105.0 (1)	108.7 (1)	—	—	—
<i>f</i>	1.617 (6)	1.435 (6)	1.736 (6)	1.451 (10)	—	0.84	119.2 (3)	106.6 (3)	107.0 (3)	109.8 (3)	119.3 (3)	—
		1.447 (6)	—	—	—	—	—	105.9 (3)	108.2 (3)	—	—	—
<i>g</i>	1.602 (2)	1.437 (2)	1.753 (3)	—	1.626 (2)	—	116.1 (1)	114.2 (1)	106.0 (2)	106.9 (2)	—	115.4 (1)
		1.431 (2)	—	—	—	—	—	105.4 (1)	107.2 (2)	—	—	—

(a) Present work. (b) Bis(methanesulphonyl)imide.H₂O (Attig & Mootz, 1975). (c) 5-Mesylamino-2*H*-1,2,3-triazole-4-carbonitrile.H₂O (Kálmán, Párkányi, Schawartz & Simon, 1976). (d) Methanesulphonanilide (Klug, 1968). (e) *p*-(Hydroxy-1-isopropylamino-2-ethyl)methanesulphonanilide.HCl (Gadret *et al.*, 1976). (f) 2'-Hydroxymethanesulphonanilide (Klug, 1970). (g) *S,S*-Dimethyl-*N*-methylsulphonylsulphilimine (DMMS) (a refined structure with diffractometer data; Kálmán, Párkányi, Náray-Szabó & Kucsman, 1977).

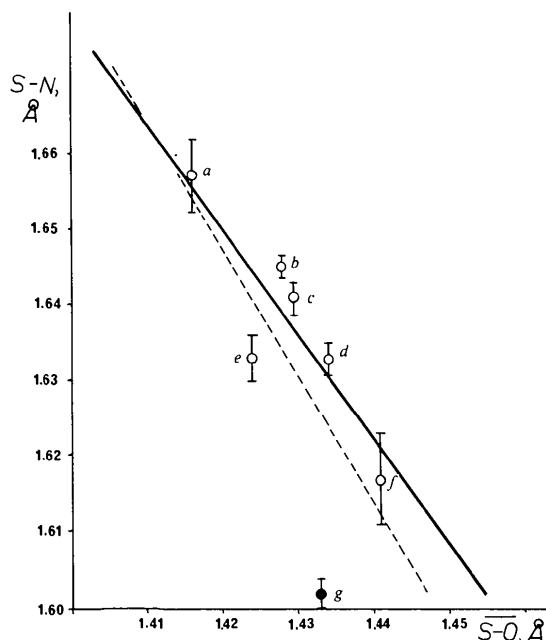


Fig. 3. Observed S—N distances plotted against the mean S—O lengths. The dotted line is described by the equation: $(S-N) = -1.727(S-O) + 4.102$, obtained for the seven *N*-mesyl groups each of which is referenced by the same letter as in Table 5. The full line represents the equation: $(S-N) = -1.394(S-O) + 3.630$ derived for the six mesylamino moieties.

group could not be regarded as subject to Jaffe's (1954) competition theory (Kucsman, Kálmán & Kapovits, 1967).

The determination of further *N*-sulphonyl (in each case RSO_2 was tosyl) sulphilimines (Cook, Glick, Rigau & Johnson, 1971; Kálmán, Duffin & Kucsman, 1971; Cameron, Hair & Morris, 1971, 1973; Kálmán & Sasvári, 1972) did not help to elucidate this question.* Thus it has remained unanswered whether the strong S—O (*d-p*) π bonds in the $R-SO_2-N$ tetrahedra, as in the tetrahedral oxyanions (Cruickshank, 1961; Kálmán, 1971), could (and to

* These works aimed mainly at clarifying the effect of the N coordination on the S—N(*d-p*) π multiple bonds in sulphilimines.

what extent) buffer the changes in the S—N lengths. The parameters of the *N*-mesyl groups listed in Table 5 permit an analysis of this question.*

The graph of the observed S—N lengths against the mean S—O distances depicted in Fig. 3 shows an inverse correlation. A linear regression analysis carried out for the seven *N*-mesyl groups resulted in the equation $(S-N) = -1.727(S-O) + 4.102$ (dotted line) with a low correlation coefficient ($r = 0.761$). The S—N distance in DMMSS (Kálmán, Párkányi, Náray-Szabó & Kucsman, 1977) displays the greatest deviation. A second analysis from which DMMSS was omitted gave a significantly better correlation coefficient of 0.881, and the deviation of the point belonging to DMMSS became even more pronounced ($\Delta = 0.03$ Å) from the full line representing the new equation: $(S-N) = -1.394(S-O) + 3.630$. This may be understood if the character of the N atom is taken into account. DMMSS, unlike the other compounds, has a mesylimino group. The lone pair of the di-coordinated N atom, as in other *N*-sulphonylsulphilimines (Kálmán, Duffin & Kucsman, 1971; Kálmán & Sasvári, 1972; Cameron, Hair & Morris, 1971, 1973; Kálmán, 1974), is partially delocalized towards S^{VI} forming, in general, stronger S—N bonds than those formed by tri-coordinated N atoms.

The S—C(sp^3) distances, which are notably influenced by the thermal motion, seem to be less dependent on the variation of the S—N and S—O lengths. In addition to these, the averages of the four (chemically three different) bond lengths, as in the tetrahedral oxyanions (Kálmán, 1971), are nearly identical, especially if librationaly corrected *N*-mesyl groups are compared (Table 6). These observations suggest that the *N*-mesyl groups bounded by irregular tetrahedra can be regarded as subject to Jaffe's (1954) competition theory with a restriction that only chemically similar (*i.e.* mesylamino) groups are comparable. The six mesylamino tetrahedra can be characterized by the mean values given in Table 7. The effect of the stronger

* An independent study of the geometry of the *N*-tosyl moieties containing di- and tri-coordinate N atoms is in progress (Kálmán & Párkányi, 1977).

Table 6. Librationally corrected bond lengths for some *N*-mesyl groups

Each of the *N*-mesyl groups is referenced by the same letter as in Table 5. Corrected data for (b) were taken from Attig & Mootz (1975). Bond lengths for both (c) and (g) were corrected as for (II) (Table 3).

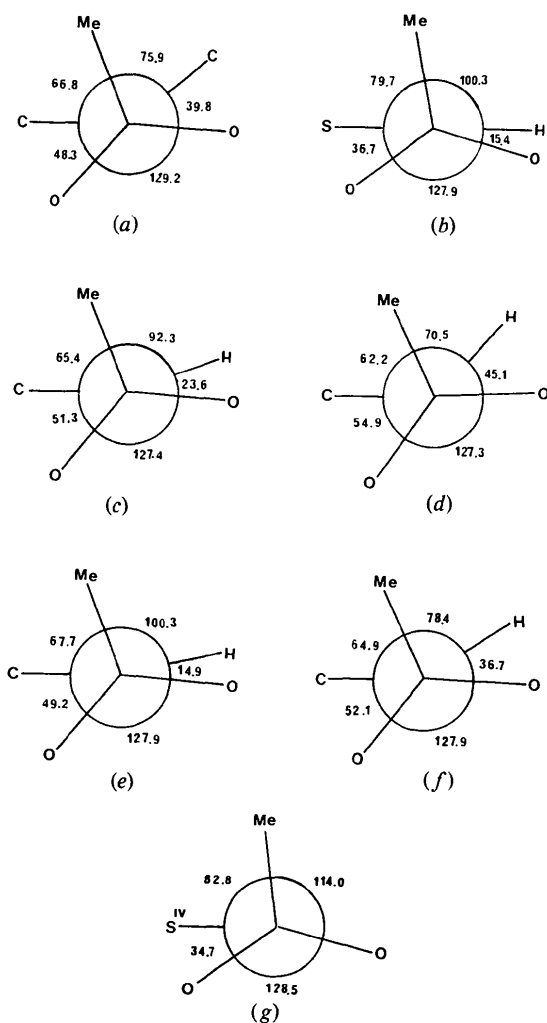
Note in Table 5	S—N	S—O(mean)	S—C	$\Sigma(S-X)$	$\langle S-X \rangle$
a	1.662 Å	1.422 Å	1.756 Å	6.26 Å	1.57 Å
b	1.652	1.437	1.756	6.28	1.57
c	1.644	1.434	1.756	6.27	1.57
g	1.610	1.450	1.766	6.28	1.57

Table 7. Mean bond lengths and angles of the six mesylamino tetrahedra

S—N	1.64 Å	O—S—O	119°
S—O	1.43	O—S—N	106
S—C	1.75	O—S—C	109
⟨S—X⟩	1.56	N—S—C	107

Table 8. SNH/SNC dihedral angles and C—N—S—C (methyl) torsion angles for four of the compounds referenced in Table 5

Note in Table 5	SNH/SNC dihedral angle	C—N—S—C(methyl) torsion angle
<i>e</i>	167.8°	67.7°
<i>c</i>	157.7	65.7
<i>f</i>	143.3	64.9
<i>d</i>	132.7	62.2

Fig. 4. Newman projections along the S—N bonds for the seven *N*-mesyl groups, each of which is referenced by the same letter (*a*–*g*) as in Table 5.

S—N bond in DMMSS on the bond angles will be discussed elsewhere (Kálmán & Párkányi, 1977).

The Newman projections (Fig. 4) show that the spatial arrangements of the *N*-mesyl groups relative to the other moieties to which they are linked by stronger or weaker N—C or N—S multiple bonds are similar. The mean C—N—S—C(methyl) torsion angle for five compounds containing N atoms with flattened trigonal pyramidal configuration (Fig. 4*a–e*) is 65.3°. As can be seen from Table 8, for the secondary mesylamines, the greatest C—N—S—C(methyl) torsion angle belongs to the least pyramidal S—N(H)C moiety. In DMMSS (*g* in Table 5) and bis(methanesulphonyl)imide (*b* in Table 5) where N has nearly perfect sp^2 hybridization (the SNH/SNS dihedral angle is 180°) the mean S—N—S—C(methyl) torsion angle is somewhat greater (81.3°). Apart from these slight differences the conformation of the *N*-mesyl groups in the crystalline state can be regarded as being unaffected by intermolecular forces.

References

- ALLÉAUME, M. & DECAP, J. (1965*a*). *Acta Cryst.* **18**, 731–736.
 ALLÉAUME, M. & DECAP, J. (1965*b*). *Acta Cryst.* **19**, 934–938.
 ATTIG, R. & MOOTZ, D. (1975). *Acta Cryst.* **B31**, 1212–1214.
 BULLOUGH, R. K. & WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 233–237.
 CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1971). *Chem. Commun.* pp. 918–919.
 CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1973). *J. Chem. Soc. Perkin II*, pp. 1951–1954.
 COOK, R. E., GLICK, M. D., RIGAU, J. J. & JOHNSON, C. R. (1971). *J. Amer. Chem. Soc.* **93**, 924–928.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
 GADRET, M., GOURSOLLE, M., LEGER, J. M., COLLETER, J. C. & CARPY, A. (1976). *Acta Cryst.* **B32**, 2757–2761.
 JAFFE, H. H. (1954). *J. Phys. Chem.* **58**, 185–190.
 KÁLMÁN, A. (1967). *Acta Cryst.* **22**, 501–507.
 KÁLMÁN, A. (1971). *J. Chem. Soc. (A)*, pp. 1857–1859.
 KÁLMÁN, A. (1974). Thesis, Degree of Doctor in Chemical Sciences (DSc), MTA, Budapest.
 KÁLMÁN, A., DUFFIN, B. & KUCSMAN, Á. (1971). *Acta Cryst.* **B27**, 586–594.
 KÁLMÁN, A. & PÁRKÁNYI, L. (1977). To be published.
 KÁLMÁN, A., PÁRKÁNYI, L., NÁRAY-SZABÓ, G. & KUCSMAN, Á. (1977). To be published.
 KÁLMÁN, A., PÁRKÁNYI, L., SCHAWARTZ, J. & SIMON, K. (1976). *Acta Cryst.* **B32**, 2245–2247.
 KÁLMÁN, A. & SASVÁRI, K. (1972). *Cryst. Struct. Commun.* **1**, 243–246.
 KÁLMÁN, A., SIMON, K., SCHAWARTZ, J. & HORVÁTH, G. (1974). *J. Chem. Soc. Perkin II*, pp. 1849–1852.

- KLUG, H. P. (1968). *Acta Cryst.* B24, 792–802.
 KLUG, H. P. (1970). *Acta Cryst.* B26, 1268–1275.
 KUCSMAN, Á., KÁLMÁN, A. & KAPOVITS, I. (1967). *Acta Chim. Hung.* 53, 97–104.
 O'CONNOR, B. H. & MASLEN, E. N. (1965). *Acta Cryst.* 18, 363–366.
 PÁRKÁNYI, L., KÁLMÁN, A., ARGAY, GY. & SCHAWARTZ, J. (1977). *Acta Cryst.* B33, 3102–3106.
 POKRYWIECZKI, S., WEEKS, C. M. & DUAX, W. L. (1973a). *Cryst. Struct. Commun.* 2, 63–66.
 POKRYWIECZKI, S., WEEKS, C. M. & DUAX, W. L. (1973b). *Cryst. Struct. Commun.* 2, 67–72.
 PURNELL, L. G., SHEPHERD, J. C. & HODGSON, D. J. (1975). *J. Amer. Chem. Soc.* 97, 2376–2380.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.
 SHELDRIK, G. M. (1975). The *SHELX* crystal structure calculation program. Univ. of Cambridge, England.
 STADLER, D., AUSCHÜTZ, W., REGITZ, M., KELLER, G., VAN ASSCHE, D. & FLEURY, J.-P. (1975). *Liebigs. Ann.* pp. 2159–2168.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
 VORONTSOVA, L. G. (1966). *Zh. Strukt. Khim.* 7, 280–283.
 WHEATLEY, P. J. (1954). *Acta Cryst.* 7, 68–72.

Acta Cryst. (1977). B33, 3102–3106

The Crystal and Molecular Structure of 5-Amino-4-ethoxycarbonyl-1*H*-1,2,3-triazole, C₅H₈N₄O₂*

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(Received 1 March 1977; accepted 2 April 1977)

C₅H₈N₄O₂ is monoclinic, space group $P2_1/c$, with $a = 10.667$ (2), $b = 6.287$ (2), $c = 10.881$ (2) Å, $\beta = 94.39$ (10)°, $Z = 4$. The structure was refined to $R = 0.085$ for 1281 observed reflexions. The tautomerism of the 1,2,3-triazoles can be characterized by the bond angles in the five-membered rings. The hydrogen bonding formed in the presence of the ethoxycarbonyl group is compared with that in related compounds.

Introduction

A minor by-product was isolated from the mother liquor of ethyl ethoxycarbonylacetimidate.HCl by ammonolysis (Pinner, 1895). It was identified as 1-ethoxycarbonylacetamidine.HCl (m.p. 110°C). This compound, like 1-carbamoylacetamidine, reacts with sulphonyl azide [Schawartz, Hornyák (née Hátori) & Szüts, 1970], and gives a sulphur-free colourless substance (m.p. 170°C). The X-ray analysis corroborated the predicted 1*H*-1,2,3-triazole structure.

Experimental

A crystal of 0.1 mm maximum dimension was mounted on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a graphite monochromator. Cell constants were determined by least squares from the setting angles of 15 reflexions.

* Dedicated to Professor A. Albert (Canberra) on his 70th birthday.

Crystal data

C₅H₈N₄O₂; $M_r = 156.1$, monoclinic; $a = 10.667$ (2), $b = 6.287$ (2), $c = 10.881$ (2) Å, $\beta = 94.39$ (10)°; $V = 727.58$ Å³; $D_c = 1.424$, $D_m = 1.42$ g cm⁻³, $Z = 4$. $F(000) = 328$, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 0.74$ cm⁻¹, space group $P2_1/c$.

During data collection (Mo $K\alpha$ radiation) the intensities of 98 reflexions were lower than a preset limit and these were omitted from the measurement. 1301 reflexions were retained in the final set, 1281 of which had $|F| - 4.5\sigma(F) > 0$ and were taken as observed. No absorption correction was performed.

The structure was solved with *SHELX* (Sheldrick, 1975) from 246 normalized structure factors ($E \geq 1.20$) giving $R = 0.38$ for the non-hydrogen atoms. Prior to the refinement, all H atoms, except those linked to N atoms, were generated with a staggered methyl group assumed and with C–H constrained to 1.08 Å. Blocked full-matrix least-squares refinement for the non-hydrogen atoms gave a final R of 0.085 [$R_G = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.099$] for the observed reflexions ($R_{\text{tot}} = 0.089$ for all 1301 reflexions). The weights