X-Ray Analysis of 6-Ethoxycarbonyl-4-ethylpyrazolo[1,5-*a*]pyrimidin-7(4*H*)-one and 6-Ethoxycarbonyl-4-ethyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one

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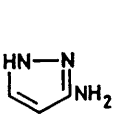
The product obtained by treating 6-ethoxycarbonyl-7-hydroxypyrazolo[1,5-*a*]pyrimidine (2a) with ethyl iodide is shown by *X*-ray analysis to be 6-ethoxycarbonyl-4-ethylpyrazolo[1,5-*a*]pyrimidin-7(4*H*)-one (3a). When 3-amino-1,2,4-triazole (5a) was cyclised with diethyl ethoxymethylenemalonate the product was shown to have the structure (2b), rather than (6), by an *X*-ray analysis of its *N*-ethyl derivative, 6-ethoxycarbonyl-4-ethyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (3d). Carbon-13 chemical shift values in the above and related compounds have been assigned.

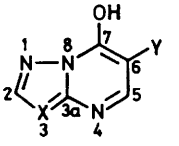
As part of a continuing programme on semi-synthetic penicillins we decided to prepare a series of heterobicyclic acids characterised by the presence of a bridgehead nitrogen atom. An additional requirement that we imposed was the presence in the heterobicyclic acid of an oxygen function on the ring carbon atom *ortho* to the carboxy-group. This paper describes the preparation of certain pyrazolo[1,5-*a*]pyrimidines and 1,2,4-triazolo[1,5-*a*]pyrimidines that satisfied our requirements and establishes unequivocally their structures.

3-Aminopyrazole (1) was condensed as described with diethyl ethoxymethylenemalonate to give the pyrazolo-[1,5-*a*]pyrimidine (2a).[1] Compound (2a) offers three sites for potential alkylation; two at nitrogen and one at oxygen, but literature evidence suggests that in general hydroxyazaindolizines are alkylated at ring nitrogen atoms.[2] Alkylation of (2a) with ethyl iodide in DMF with potassium carbonate as base was stated to give a 66% yield of the pyrazolo[1,5-*a*]pyrimidone (3a).[3] We repeated this reaction to obtain (3a), with properties very similar to those reported. While literature precedent suggested that the structure for (3a) was correctly assigned the spectroscopic data for this compound were also consistent with the isomeric structure (4). An *X*-ray analysis confirmed unequivocally that the correct structure was represented by (3a).

The 1,2,4-triazolo[1,5-*a*]pyrimidine (2b) was described by Allen as the product of cyclisation of 3-amino-1,2,4-triazole (5a) with diethyl ethoxymethylenemalonate.[4] However, experimental details were not provided and the evidence for assigning structure (2b), rather than the isomeric (6), to the reaction product appeared to rely mainly on the interpretation of u.v. spectral data. We condensed 3-amino-1,2,4-triazole (5a) with diethyl ethoxymethylenemalonate in refluxing glacial acetic acid and obtained a product with u.v. absorption data, $\lambda_{max.}$ 264 (ε 8 630) and 297 (ε 15 200) compared with Allen's reported values for (2b) of 248 (ε 5 100) and 291 (ε 9 000). The i.r. spectrum of this product showed a maximum of 1 720 cm^{-1}, attributed to the ester group, but no absorption that could be assigned to an amide carbonyl group [observed at 1 690 cm^{-1} in (3d) and 1 670 cm^{-1} in (7b)]. This suggested that the product was correctly represented by the enol form (2b) rather than the keto-form (3b). The enol form (2b) was also supported by the ^1H n.m.r. spectrum which showed two one-proton singlets. The assignment of the downfield singlet at δ 8.85 to the C(5) proton, see structure (2) for numbering system, and the upfield singlet at δ 8.56 to the triazole proton at C(2) was made from a study of the reported n.m.r. data for related compounds

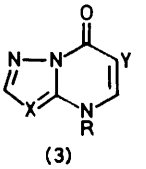


(1)

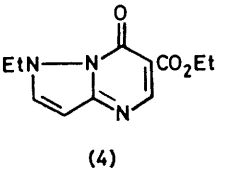


(2)

a; X = C, Y = CO_2Et
b; X = N, Y = CO_2Et
c; X = C, Y = H
d; X = N, Y = H
e; X = N, Y = CO_2H



(3)

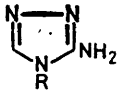


(4)

a; X = C, R = Et, Y = CO_2Et
b; X = N, R = H, Y = CO_2Et
c; X = N, R = Et, Y = H
d; Y = N, R = Et, Y = CO_2Et

incorporating the triazole ring system.[5-7] However, while these spectroscopic data for the cyclised product supported the enol structure (2b), rather than tautomeric forms such as (3b), they did not rule out the alternative structure (6). In order to resolve this point we reacted the cyclisation product with an excess of alkyl iodide.

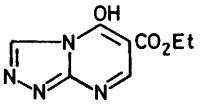
7-Hydroxy-1,2,4-triazolo[1,5-*a*]pyrimidines offer four sites for potential alkylation; three at nitrogen, and one at oxygen. Previous work has shown that alkylation occurs preferentially at N(4) in the six-membered ring together with some attack at N(3) in the triazole ring.[5,8] Thus, Sprickett observed that 7-hydroxy-1,2,4-triazolo[1,5-*a*]pyrimidine (2d), when treated with



(5)

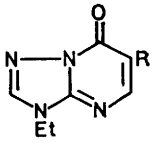
a; R = H

b; R = Et



(6)

ethyl iodide in dimethylformamide (DMF) gave the N(4)-ethyl compound (3c) as the major product, together with a small amount of N(3)-substituted derivative (7a).[5] Treatment of the cyclisation product (2b) or (6), with an excess of ethyl iodide in DMF–HMPT afforded as the major product the crystalline N(4)-ethyl derivative (3d), m.p. 136 °C, whose structure was confirmed by *X*-ray analysis. The minor product was



(7)

a; R = H

b; R = CO_2Et

identified as the N(3)-ethyl compound (7b), m.p. 161 °C, on the basis of its spectroscopic properties and identity of melting point to that reported by Sprickett for (7b), which he prepared unambiguously from the cyclisation of 3-amino-4-ethyl-1,2,4-triazole (5b) with diethyl ethoxymethylenemalonate.[5] Hence, the major product of the cyclisation of 3-amino-1,2,4-triazole (5a) with diethyl ethoxymethylenemalonate is correctly formulated as (2b). The ester (2b) was readily hydrolysed in acidic media, but not basic, to the free acid (2e).

The use of ^{13}C n.m.r. to determine the molecular structure of azaindolizines has been reported.[9,10] The work of Dea and his co-workers was of particular interest in the present context since they used ^{13}C n.m.r. to determine the site of glycosidation of certain triazolo-[1,5-*a*]pyrimidines.[10] The assignments of carbon resonances in compounds (3a), (2b), (3d), and (7b) are listed in Table 1.

In the case of the pyrazolo[1,5-*a*]pyrimidine (3a) the ester carbonyl was readily identified at 163.5 p.p.m. Of the three remaining quaternary carbons the downfield singlet at 152.5 p.p.m. was assigned to the C(7) carbonyl, the singlet at 141.4 p.p.m. to C(3a) and that at δ 99.2 to C(6). The carbon doublet in the proton-coupled ^{13}C n.m.r. spectrum at 91.5 p.p.m. was assigned to C(3) and, of the two remaining doublets, that at δ 143.4 was assigned to C(2) on the basis of a value of 142.8 p.p.m. for this carbon reported by Dea for a closely related N(4)-ribofuranoside derivative of (2c).

Compound (2b) exhibited two weak singlets in the ^{13}C n.m.r. spectrum at 152.8 and 150.3 p.p.m. The former was assumed to be due to C(7) rather than C(3a) since the C(7) carbonyl is invariably downfield of C(3a). The carbon doublet in the hydrogen-coupled spectrum at δ 151.4 was assigned to the triazole ring carbon, again based on the work of Dea who reported a value of 151.6 p.p.m. for this carbon in a closely related N(4)-ribofuranoside derivative of (2d). The assignments of the two remaining carbons, C(5) and C(6), readily followed. The assignment of the carbon doublet at 152.2 p.p.m. to C(2) in the ^{13}C n.m.r. spectrum of compound (3d) and the doublet at 149.0 p.p.m. to C(5) was made on the assumption that N(4)-alkylation of (2b) would have little effect on the triazole proton at C(2). The singlets at 150.9 p.p.m. and 150.2 p.p.m. were assigned to C(7) and C(3a) respectively by noting their relative intensities compared with the corresponding resonances in compound (2b) and from the assumption that the C(7) carbonyl would be downfield of C(3a).

TABLE 1

^{13}C Chemical shift data for compounds (3a) (2b), (3d), and (7b) [a]

Carbon atom [b]	(3a)	(2b)	(3d)	(7b)
2	143.4	151.4	152.2	158.9
3	91.5			
5	147.8	147.8	149.0	143.2
6	99.2	102.8	102.9	105.4
7	152.5	152.8	150.9	150.4
3a	141.4	150.3	150.2	143.2
Ester CO	163.5	163.1	162.8	164.2

[a] P.p.m. downfield from $SiMe_4$; solvent $(CD_3)_2SO$. [b] See structure (2) for numbering system.

In the case of compound (7b) the singlets at δ 150.4 and 143.2 p.p.m. were assigned to C(7) and C(3a) respectively. The doublet at 158.9 p.p.m. was assigned to C(2) rather than C(5) since it was assumed that C(2) would be affected more than C(5) by alkylation at N(3). The assignment of C(5) to the remaining doublet at 143.2 p.p.m. followed. These assignments for C(2) and C(5) contrast with those made by Dea for a N(3)-ribofuranoside derivative of (2d), where the C(2) carbon had a shift of 140.8 p.p.m. and C(5) a value of 153.3 p.p.m.

EXPERIMENTAL

M.p.s were measured on a Büchi apparatus and are uncorrected. U.v. data were obtained on a Pye–Unicam SP 1800 spectrophotometer. ^1H N.m.r. data were recorded at 90 MHz on a Perkin-Elmer R32 instrument with $SiMe_4$ as internal standard. I.r. measurements were made on a Perkin-Elmer 457 grating spectrophotometer. Mass spectra were obtained at 70 eV using an AEI MS9 instrument operating at 8 kV. ^{13}C Measurements were obtained on a Varian CFT20 spectrometer with $SiMe_4$ as internal standard. Merck Kieselgel H (type 60) was used for column chromatography; for analytical and preparative thin-layer

purposes, pre-coated Merck Kieselgel 60 F 284 plates were used. Chloroform with 0—2% methanol was used for elution.

6-*Ethoxycarbonyl*-7-*hydroxy*-1,2,4-*triazolo*[1,5-a]*pyrimidine* (2b).—3-Amino-1,2,4-triazole (5a) (8.41 g, 100 mmol) and diethyl ethoxymethylenemalonate (24.0 g, 110 mmol) in glacial acetic acid (150 ml) were refluxed together for 6 h. The reaction mixture was cooled, filtered, and the crystalline precipitate washed with water and dried (8.2 g, 36.6%), m.p. 256—257 °C, $\nu_{max.}$ (KBr) 3 450br, 1 720, 1 620, and 1 580 cm^{-1}; $\lambda_{max.}$ (EtOH) 264 (ε 8 630) and 297 (ε 15 200) nm; δ_H (Me_2SO) 12.8 (1 H, s, OH), 8.85 (1 H, s, 5-H), 8.56 (1 H, s, 2-H), 4.38 (2 H, q, OCH_2), and 1.34 (3 H, t, CH_3) (Found: C, 46.0; H, 3.95; N, 27.3. $C_8H_8N_4O_3$ requires C, 46.16; H, 3.87; N, 26.91%).

6-*Carboxy*-7-*hydroxy*-1,2,4-*triazolo*[1,5-a]*pyrimidine* (2e).— 6-Ethoxycarbonyl-7-hydroxy-1,2,4-triazolo[1,5-*a*]pyrimidine (2b), (5.2 g, 25 mmol) was heated in 2N-hydrochloric acid (40 ml) under reflux for 5 h, cooled, and filtered to give the *product* (2e), 3.30 g (67%), m.p. 296 °C (decomp.), $\nu_{max.}$ (KBr) 3 400br, 1 720br, and 1 580 cm^{-1}; $\lambda_{max.}$ ($NaHCO_3$) 264 (ε 10 940) and 293 (ε 14 900); δ_H (NaOD) 8.75 (1 H, s, 5-H) and 8.31 (1 H, s, 2-H) (Found: C, 40.25; H, 2.35; N, 30.95. $C_6H_4N_3O_3$ requires C, 40.01; H, 2.24; N, 31.10%).

6-*Ethoxycarbonyl*-4-*ethyl*-1,2,4-*triazolo*[1,5-a]*pyrimidin*-7(4H)-*one* (3d).— 6-Ethoxycarbonyl-7-hydroxy-1,2,4-triazolo[1,5-*a*]pyrimidine (2b), (2.08 g, 10 mmol) potassium carbonate (1.38 g, 10 mmol), and ethyl iodide (1.60 ml, 15 mmol) were heated at 80 °C for 4 h in dry dimethylformamide (20 ml) and hexamethylphosphoric triamide (20 ml). The solution was cooled, the volume reduced under vacuum and, after dilution with a large volume of water, extracted with ethyl acetate. After washing and drying, the ethyl acetate extract was evaporated to give a crude oil which was chromatographed on silica.

The major component was identified as (3d), 1.28 g (54.2%), m.p. 136—137 °C, $\nu_{max.}$ (KBr) 3 400br, 1 715, 1 690, 1 610, and 1 570 cm^{-1}; $\lambda_{max.}$ (EtOH) 252 (8 920) and 290 nm (ε 12 800); δ_H ($CDCl_3$) 8.62 (1 H, s, 5-H), 8.10 (1 H, s, 2-H), 4.42 (2 H, q, OCH_2), 4.32 (2 H, q, NCH_2), 1.62 (3 H, t, CH_3), and 1.39 (3 H, t, CH_3) (Found: C, 50.75; H, 5.25; N, 23.65. $C_{10}H_{12}N_4O_3$ requires C, 50.84; H, 5.12; N, 23.73%).

The minor component eluted was identified as 6-ethoxycarbonyl-3-ethyl-1,2,4-triazolo[1,5-*a*]pyramidin-7(4*H*)-one (7b), (0.12 g, 5%), m.p. 160—161 °C, $\nu_{max.}$ (KBr) 1 740, 1 670, and 1 590 cm^{-1}; $\lambda_{max.}$ (EtOH) 253 (ε 6 780) and 303 nm (ε 15 370); δ_H ($CDCl_3$) 8.81 (1 H, s, 5-H), 8.34 (1 H, s, 2-H), 4.37 (2 H, q, NCH_2), 4.26 (2 H, q, OCH_2), 1.56 (3 H, t, CH_3), and 1.42 (3 H, t, CH_3); *m/e* (relative intensity) 236 ($M^{+\bullet}$ 10).

Crystal Structure Determination of the Pyrimidone (3a).—*Crystal data.* $C_{11}H_{13}N_3O_3$, $M = 235.2$. Monoclinic, $a = 5.080(2)$, $b = 15.581(3)$, $c = 14.199(3)$ Å, $\beta = 90.1(1)°$, $U = 1\,123.9$ Å^3, $D_c = 1.39$, $Z = 4$, $D_m = 1.37$ g cm^{-3}, $F(000) = 496$. Space group $P2_1/n$ from systematic absences; Mo-K_α radiation (graphite monochromator) $\lambda = 0.710\,69$ Å, $\mu = 1.12$ cm^{-1}.

The cell parameters were initially found from oscillation and Weissenberg photographs and then refined by least-squares from the setting angles of 23 reflections on a Hilger-Watt four-circle diffractometer. Reflections were scanned ($\omega - 2\theta$ mode) for $\theta \leqslant 25°$. Of the 1 966 observable reflections scanned, 980 had a net count of $\geqslant 3°$ and were deemed observed and used in the refinement. Lorentz and polarisation, but not absorption corrections, were applied.

The structure was solved automatically using the centrosymmetric direct methods routine of SHEL-X.[11] Refinement was carried out by full-matrix least-squares methods, at first isotropically and then anisotropically. The terminal carbon atom of the ester group had large thermal parameters and its position is not well defined. This thermal disorder possibly accounts for the rather short C–C distance in this ethyl group. After two cycles of anisotropic refinement a difference-map revealed all the hydrogen atoms except those on the disordered methyl group. Subsequently, hydrogens at calculated positions were included in the computations but their parameters were not refined. Finally a weighting scheme of the form $w = 1.0/A(0)\cdot T(O)\cdot x + A(1)\cdot T(1)\cdot x + A(2)\cdot T(2)\cdot x + A(3)\cdot T(3)\cdot x$ where $A(0) - A(3)$ are the coefficients for a Chebyshev series in $T(I)\cdot x$ with $x = F_o/F_o(\max)$ was applied. The coefficients used were $A(0) = 1\,315$, $A(1) = 3.3$, $A(2) = -19.1$, and $A(3) = -11.7$. At convergence the maximum shift/standard deviation (excluding the methyl of the ethoxy group) was 0.12, and of the ill-defined methyl group 0.7. The final conventional R value was 6.8%.

A diagram of the molecule showing bond lengths and angles, with standard deviations in parentheses, is illustrated in Figure 1 which also shows the crystallographic

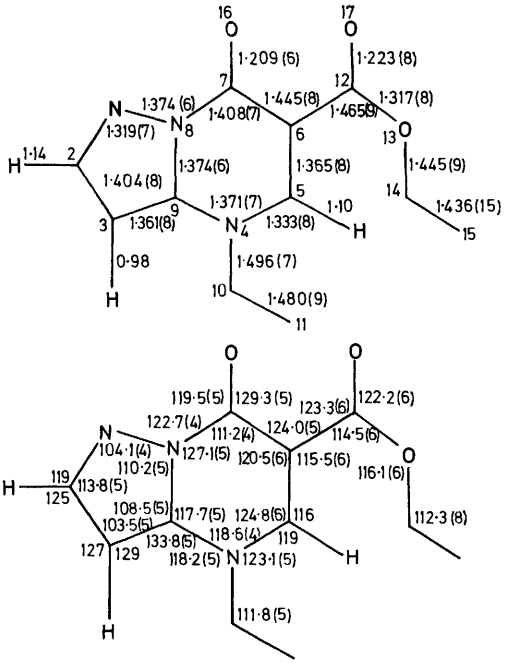


FIGURE 1 Bond lengths (Å) and angles (°) of compound (3a) with standard deviations in parentheses

numbering. Analysis of the data indicates the fused ring system to be planar within experimental error and this can be seen from Figure 2 which represents a perspective view of the molecule.

Except for SHEL-X, crystallographic calculations were done using the Oxford CRYSTALS package.[12] The drawing was prepared using PLUTO.[13] Table 2 lists the fractional co-ordinates of the atoms. The thermal parameters of the non-hydrogen atoms and a listing of observed

and calculated structure factors are available in Supplementary Publication No. SUP 22670 (28 pp.).*

Crystal Structure Determination of the Pyrimidone (3d).—*Crystal data*. $C_{12}H_{12}N_4O_3$, M = 236.2. Orthorhombic, a = 14.476(2), b = 8.489(2), c = 18.889(3) Å, U = 232 1 Å^3,

TABLE 2

Fractional co-ordinates (× 10^4) with standard deviations in parentheses of compound (3a)

Atom	x/a	y/b	z/c
N(1)	2 744(11)	2 987(3)	1 403(3)
C(2)	3 928(13)	3 254(4)	630(4)
C(3)	2 930(13)	2 885(4)	−198(4)
N(4)	−758(9)	1 815(3)	−317(3)
C(5)	−2 395(12)	1 355(4)	214(4)
C(6)	−2 535(11)	1 400(4)	1 173(4)
C(7)	−813(11)	1 968(4)	1 692(4)
N(8)	879(9)	2 418(3)	1 083(3)
C(9)	995(11)	2 354(4)	118(3)
C(10)	−661(12)	1 744(4)	−1 367(4)
C(11)	1 253(14)	1 087(5)	−1 679(5)
C(12)	−4 533(13)	853(4)	1 611(5)
O(13)	−4 415(11)	821(3)	2 538(4)
C(14)	−6 351(21)	284(6)	2 995(6)
C(15)	−6 776(31)	526(8)	3 958(10)
O(16)	−674(9)	2 089(3)	2 531(3)
O(17)	−6 178(9)	452(3)	1 161(4)
H(2)	5 196	3 860	661
H(3)	3 446	3 016	−847
H(5)	−3 701	883	−123

D_c = 1.35, Z = 8, D_m = 1.35 g cm^{-3}, $F(000)$ = 992. Space group *Pbca* (from systematic absences); Mo-K_α radiation (graphite monochromator) λ = 0.710 69 Å, μ = 1.1 cm^{-1}.

The cell parameters were initially found from oscillation and Weissenberg photographs and were then refined from

TABLE 3

Fractional co-ordinates (× 10^4) for compound (3d) with standard deviations in parentheses

Atom	x/a	y/b	z/c
N(1)	8 989(2)	7 879(4)	4 711(2)
C(2)	9 205(2)	8 893(5)	4 208(2)
N(3)	10 122(2)	9 193(4)	4 105(2)
N(4)	11 399(2)	8 086(3)	4 755(2)
C(5)	11 615(2)	7 147(5)	5 302(2)
C(6)	10 984(2)	6 336(4)	5 694(2)
C(7)	10 008(2)	6 417(5)	5 532(2)
N(8)	9 847(2)	7 481(4)	4 967(2)
C(9)	10 488(2)	8 282(4)	4 593(2)
C(10)	12 105(3)	8 925(5)	4 328(2)
C(11)	12 253(3)	8 159(6)	3 618(2)
C(12)	11 370(3)	5 340(5)	6 264(2)
O(13)	10 746(2)	4 651(3)	6 657(1)
C(14)	11 085(3)	3 689(6)	7 243(2)
C(15)	10 266(4)	2 969(6)	7 586(2)
O(16)	9 363(2)	5 724(4)	5 798(1)
O(17)	12 187(2)	5 207(5)	6 363(2)
H(2)	8 709	9 410	3 908
H(5)	12 295	7 038	5 435

the setting angles of 23 reflections measured on a Hilger-Watt four-circle diffractometer. Reflections were measured for $\theta \leqslant 25°$ ($\omega - 2\theta$ scan mode) and intensities were deemed observed if $I \geqslant 3\sigma(I)$. Lorentz and polarisation corrections were made. 2 041 Reflections were scanned of which 1 154 were observed and used in the refinement.

The structure was solved routinely using MULTAN,[14] all the non-hydrogen atoms being shown in the first E-map.

* See Notice to Authors No. 7, in *J.C.S. Perkin I*, 1979, Index issue, for details of the supplementary publications scheme.

During the early stages of isotropic refinement the temperature factors clearly indicated an arrangement of carbon and nitrogen atoms as shown in Figures 3 and 4. This arrangement was confirmed when, after several cycles of anisotropic refinement, a difference-map showed a peak in

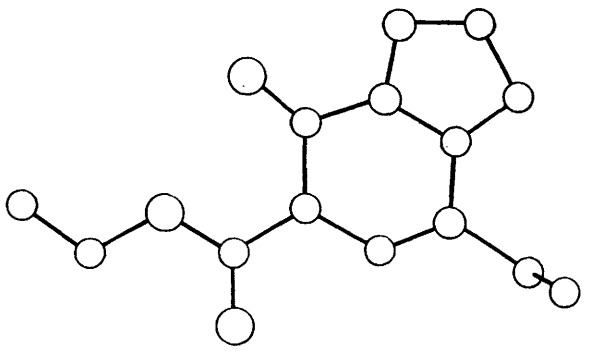


FIGURE 2 Perspective drawing of compound (3a)

the correct position for a hydrogen attached to the supposed carbon atom and no peaks near the supposed nitrogen atoms. All the hydrogens of the molecule were located from this map and final refinement was by full-matrix least-squares with heavier atoms anisotropic and hydrogen atoms included but not refined. The weighting scheme used in the

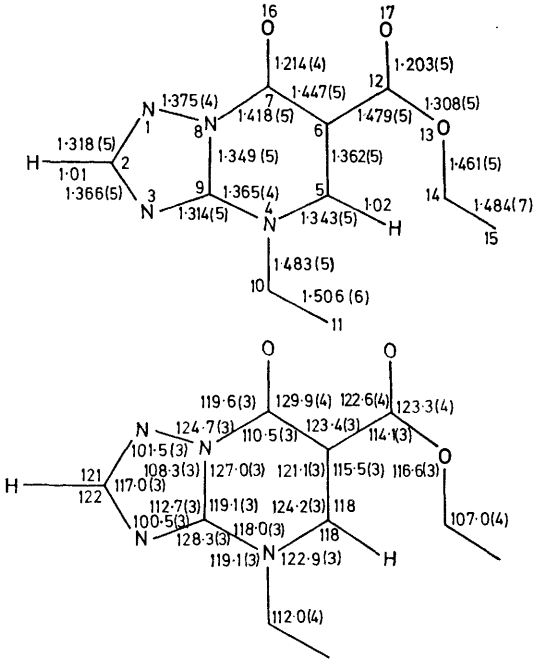


FIGURE 3 Bond lengths (Å) and angles (°) of compound (3d) with standard deviations in parentheses

final stages of refinement was of the form $w = 1/\{1 + [(F_o - A)/B]^2\}$ with A = 12.0 and B = 15.0. The maximum shift/standard deviation at convergence was 0.04 and R was 5.2%.

Figure 3 shows the bond lengths and angles of (3d) with standard deviations in parentheses and also indicates the crystallographic numbering. Figure 4 is a perspective drawing of the molecule which calculation shows to have a planar fused ring system. Apart from MULTAN, crystal-

lographic computations were done using the Oxford CRYSTALS package,[12] and the drawing was prepared using PLUTO.[13] Table 3 gives the fractional co-ordinates of the

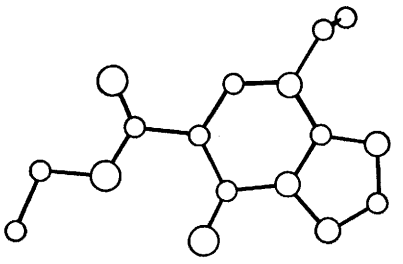


FIGURE 4 Perspective drawing of compound (3d)

atoms. The thermal parameters of the non-hydrogen atoms and a listing of observed and calculated structure factors are available in Supplementary Publication No. SUP 22670 (28 pp.).

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