Tautomerism of Diazidopyrimidines. Molecular Structure of 2,4-Diazido-5-iodopyrimidine

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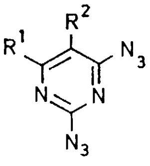
The molecular structure of the title compound has been determined by single-crystal *X*-ray analysis. Crystals are monoclinic, a = 11.08(1), b = 4.823(5), c = 15.86(1) Å, β = 92.1(1)°, Z = 4, space group $P2_1/n$. The structure was determined by Patterson and electron-density methods and refined by full-matrix least-squares methods to R 0.046 for 1 170 independent reflections. The compound exists in the diazido-form rather than as one of the potential tetrazolo tautomers.

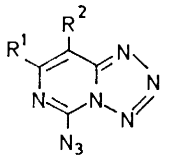
SOME confusion exists as to the preferred tautomeric forms of the diazidopyrimidines. It has been suggested [1] that contrary to general belief [2-5] 2,4-diazidopyrimidines exist predominantly in the 5-azidotetrazolo[1,5-*a*]pyrimidine form (Ic) with the isomeric 5-azidotetrazolo[1,5-*c*]pyrimidine form (Ib) as a likely minor constituent.

The 2,4-diazido-6-methylpyrimidine–5-azido-7-methyltetrazolo[1,5-*a*]pyrimidine tautomerism [(Ia) $\rightleftharpoons$ (Ic); R^1 = Me, R^2 = H] has been investigated and on the evidence of ^1H n.m.r. data it was concluded that (Ic) was the predominant form with *ca.* 10% of the 5-azido-8-methyltetrazolo[1,5-*c*]pyrimidine tautomer (Ib; R^1 = Me, R^2 = H) also present. Earlier work [2] on the same system, based on chemical and u.v. data, indicated that the diazido form (Ia) was preferred.

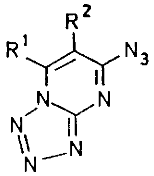
In the course of work on aspects of pyrimidine chemistry, we carried out the reaction of sodium azide with 2,4-dichloro-5-iodopyrimidine in aqueous ethanol. A product was isolated in which both chlorine atoms had been replaced by azide groupings. This compound can potentially exist in five tautomeric forms (Ia—e; R^1 = H, R^2 = I). The i.r. spectrum (KBr disc) showed a strong azide absorption [6] at 2 130 cm^{-1} and only weak absorption at 1 000—1 100 cm^{-1} where a tetrazolo-system would be expected.[7] In order to resolve the form in which the compound exists, a single-crystal *X*-ray study was undertaken.



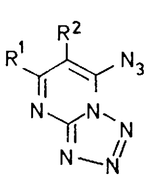
(Ia)



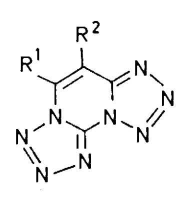
(Ib)



(Ic)



(Id)



(Ie)

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EXPERIMENTAL

Preparation.—2,4-*Diazido*-5-*iodopyrimidine*. A mixture of 2,4-dichloro-5-iodopyrimidine [8] (1.37 g, 5 × 10^{-3} mol) and sodium azide (0.70 g, 1.08 × 10^{-2} mol) was heated under reflux for 45 min in aqueous ethanol (1 : 1 v/v; 50 cm^3). The solution was cooled in an ice-bath, and the colourless crystals obtained were recrystallised from light petroleum (b.p. 40—60°) to give 2,4-*diazido*-5-*iodopyrimidine* (72%) m.p. 86 °C (decomp.) (Found: C, 16.65; H, 0.35; N, 39.35; C_4HIN_8 requires C, 16.70; H, 0.35; N, 38.90%).

Crystal Data.—C_4HN_8I, $M = 288.0$. *Monoclinic*, $a = 11.08(1)$, $b = 4.823(5)$, $c = 15.86(1)$ Å, $\beta = 92.10(1)°$, $U = 847.0$ Å^3, $D_m = 2.19$, $Z = 4$, $D_c = 2.26$ g cm^{-3}, $F(000) = 536$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 37.1 cm^{-1}. Space group $P2_1/n$ (a non-standard setting of C_{2h}^5, No. 14) from systematic absences.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances			
I–C(1)	2.08(1)	C(4)–N(2)	1.32(1)
C(1)–C(2)	1.40(1)	C(4)–N(3)	1.40(1)
C(1)–C(4)	1.42(1)	N(3)–N(4)	1.28(1)
C(2)–N(1)	1.33(1)	N(4)–N(5)	1.11(1)
C(3)–N(1)	1.35(1)	N(6)–N(7)	1.24(1)
C(3)–N(2)	1.35(1)	N(7)–N(8)	1.13(1)
C(3)–N(6)	1.41(1)		

(*b*) Angles			
I–C(1)–C(2)	121(1)	C(1)–C(4)–N(3)	120(1)
I–C(1)–C(4)	122(1)	N(2)–C(4)–N(3)	118(1)
C(2)–C(1)–C(4)	117(1)	C(2)–N(1)–C(3)	115(1)
C(1)–C(2)–N(1)	123(1)	C(3)–N(2)–C(4)	116(1)
N(1)–C(3)–N(2)	128(1)	C(4)–N(3)–N(4)	113(1)
N(1)–C(3)–N(6)	119(1)	N(3)–N(4)–N(5)	174(1)
N(2)–C(3)–N(6)	113(1)	C(3)–N(6)–N(7)	114(1)
C(1)–C(4)–N(2)	122(1)	N(6)–N(7)–N(8)	172(1)

Intensities were measured on a Stöe–Stadi 2 diffractometer by use of the background–ω scan–background technique, giving 1 170 independent reflections having $I/\sigma(I) \geqslant 3$. Lorentz and polarization factors were applied but no absorption correction was made.

Structure Analysis.—The position of the iodine atom was readily determined from the three-dimensional Patterson function, and the carbon and nitrogen atoms were located on a difference electron-density map. The structure was refined by full-matrix least-squares methods, finally with all atoms given anisotropic thermal parameters. The scattering factors of ref. 9 were used, those of iodine being corrected for real and imaginary components of the anomalous dispersion. The function minimised was $\Sigma\, w(F_o - F_c)^2$; w was adjusted to give best constancy of average values of $w(F_o - F_c)^2$, the final scheme being $\sqrt{w} = 1$ when $|F_o| \leqslant 45$, $\sqrt{w} = 45/|F_o|$ when $|F_o| > 45$. The final R for the 1 170 observed reflections was 0.046. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21782 (11 pp., 1 microfiche).* Positional and thermal parameters are given in Table 1, bond lengths and valency angles are in Table 2.

TABLE 1

Final positional parameters (fractional × 10^4) and anisotropic thermal parameters,* with standard deviations in parentheses

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
I	7 723(1)	−1 980(1)	−1 510(1)	92(1)	453(4)	28(1)	−9(1)	6(1)	−8(1)
N(1)	8 837(5)	3 453(14)	0 560(4)	56(5)	398(37)	31(3)	−16(10)	9(3)	7(8)
N(2)	7 095(5)	0 957(14)	1 026(4)	61(5)	350(35)	31(2)	−15(10)	8(3)	5(7)
N(3)	6 129(6)	−2 448(15)	0 181(4)	70(5)	414(40)	34(3)	−42(11)	7(3)	−5(7)
N(4)	5 477(6)	−2 701(15)	0 827(4)	67(5)	406(41)	37(3)	−43(12)	3(3)	8(8)
N(5)	4 858(7)	−3 097(18)	1 350(5)	92(7)	616(47)	50(4)	−85(15)	18(4)	4(11)
N(6)	7 990(6)	4 278(16)	1 899(4)	87(6)	408(38)	36(3)	−64(13)	18(3)	−33(8)
N(7)	8 820(7)	5 974(17)	2 002(4)	88(7)	476(43)	31(3)	−26(15)	15(3)	−28(9)
N(8)	9 534(8)	7 579(20)	2 186(5)	112(8)	697(58)	49(4)	−86(17)	17(4)	−62(11)
C(1)	7 850(6)	0 083(16)	−0 346(4)	61(6)	354(44)	24(3)	9(12)	5(3)	9(8)
C(2)	8 746(6)	2 063(18)	−0 169(5)	57(5)	421(43)	32(3)	5(13)	9(3)	18(9)
C(3)	7 989(6)	2 847(17)	1 117(4)	57(6)	309(40)	32(3)	2(12)	8(3)	2(8)
C(4)	7 035(6)	−0 432(17)	0 303(4)	51(5)	357(38)	26(3)	4(12)	3(3)	17(8)

* In the form exp $-\ 10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

DISCUSSION

The preferred tautomer is found (Figure) to be the diazido-form (Ia). The pyrimidine ring is effectively planar (Table 3) and the mean C–C and C–N bond lengths [1.41(1) and 1.34(1) Å] are as expected [10] for a nitrogen heteroaromatic system. The ring bond angles are similar to those found in 5-bromo-4,6-diaminopyrimidine.[11] The C–I bond length is in agreement with that

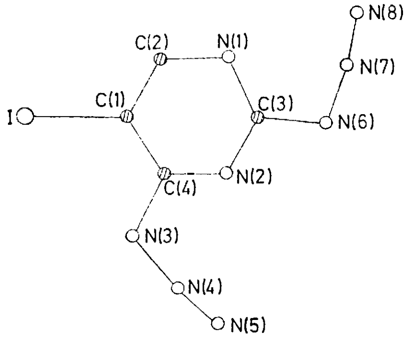

FIGURE 1

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

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for other aromatic iodo-compounds.[10] The ring substituents lie slightly out of the best pyrimidine mean plane, the deviations being given in Table 3. Both azide chains are non-linear and the N–N–N angles [174(1) and 172(1)°] are significantly different from 180° but lie within the range of values found for other azides.[10] The mean C–N–N angle (113.5°) is similar to that found [12] in 1-azido-4-nitrobenzene. As expected from bonding considerations the two N–N distances within each azide group differ significantly (mean 1.26 and 1.12 Å).

TABLE 3

Equation of least-squares plane through pyrimidine ring, referred to orthogonal axes. Distances of ring atoms and substituents from plane in Å

$$0.588\,53X - 0.708\,23Y + 0.389\,93Z - 4.901 = 0$$

Ring: C(1) −0.011, C(2) 0.001, C(3) −0.011, C(4) 0.012, N(1) 0.010, N(2) −0.001

Substituents: I −0.069, N(3) 0.039, N(4) 0.077, N(5) 0.114, N(6) −0.042, N(7) −0.020, N(8) 0.005

Since a tetrazolo-ring is electron-withdrawing and an azido-group electron-rich,[13] it has been suggested [14] that the tetrazolo-forms are destabilised by electron-withdrawing substituents in the ring, the tautomeric azido-form being favoured. In the title compound (Ia; $R^1 =$ H, $R^2 =$ I) it seems likely that it is the electron-withdrawing effect of the iodo-substituent which destabilises the possible tetrazolo-forms and outweighs the influence of the 2- and 4-azido-groups which would be expected to stabilise the tetrazolo forms (Ib) and (Ic) respectively.

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