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Imidazo[1,2-*b*]-*as*-triazine

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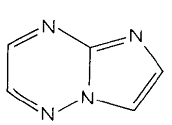
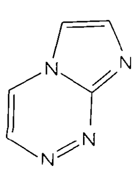
Abstract. $C_5H_4N_4$, $P2_1/n$, $Z = 4$, $a = 10{\cdot}661$ (4), $b = 13{\cdot}038$ (2), $c = 3{\cdot}816$ (2) Å, $\beta = 93{\cdot}29$ (2)°, $V = 529{\cdot}6$ Å^3, $R = 6{\cdot}3$% for 633 observed structure factors. Stacking in columns occurs along [001] with a plane-to-plane distance of 3·36 Å.

Introduction. Acid hydrolysis of 3-amino-*as*-triazine (Rykowski & van der Plas, 1976) resulted in an imidazo-*as*-triazine which, on the available spectroscopic evidence, could be either imidazo[1,2-*b*]-*as*-triazine (I) or imidazo[2,1-*c*]-*as*-triazine (II). In order to establish which was correct a crystal structure determination was undertaken.



(I)



(II)

633 independent intensities ($I > 2{\cdot}5\sigma$) were collected on a Nonius CAD-4 automatic diffractometer with graphite-monochromated Cu $K\alpha$ radiation and the θ–2θ scan method. No absorption correction was applied (crystal dimensions 0·25 × 0·3 × 0·3 mm). The structure was solved from an E^2 Patterson synthesis. From the peaks surrounding the origin the orientation of the six-membered ring could be obtained. There were several acceptable Patterson peaks that could represent the distance between the centres of two six-membered rings related by a centre of symmetry, each of these providing a possible set of coordinates for the atoms of the six-membered ring. The difference synthesis based on one of these sets contained indications for the three missing non-hydrogen atoms. In the refinement of the rough structure thus obtained all atoms were at first treated as C in isotropic least-squares calculations. Discrimination between N and C was then made on the basis of the resulting thermal parameters. At a later stage a difference synthesis clearly indicated four H atoms, the positions of which confirmed the assignment of C and N. The least-squares refinement, anisotropic for C and N and isotropic for H, converged to $R = 6{\cdot}3$% for the 633 observed structure factors. The final parameters are listed in Table 1.*

Discussion. The molecule as found is depicted in Fig. 1. Thus the reaction product is imidazo[1,2-*b*]-*as*-triazine (I). The bond distances and angles are indicated in Fig.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32075 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

1. In Table 2 the bond lengths are compared with the corresponding values in 5-(*p*-chlorophenyl)-1,2,4-triazine (Atwood, Krass & Paudler, 1974) and in imidazole (Martínez-Carrera, 1966). The only significant

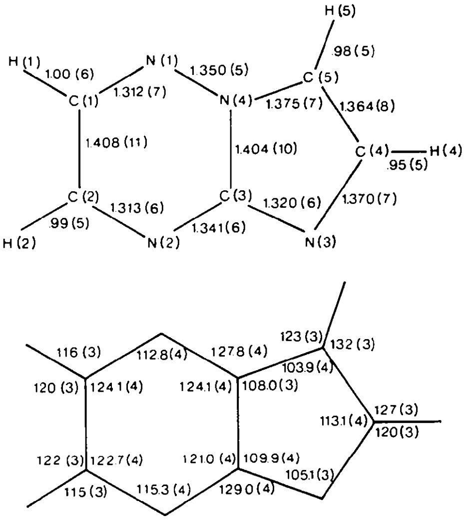

Fig. 1. Bond lengths and bond angles.

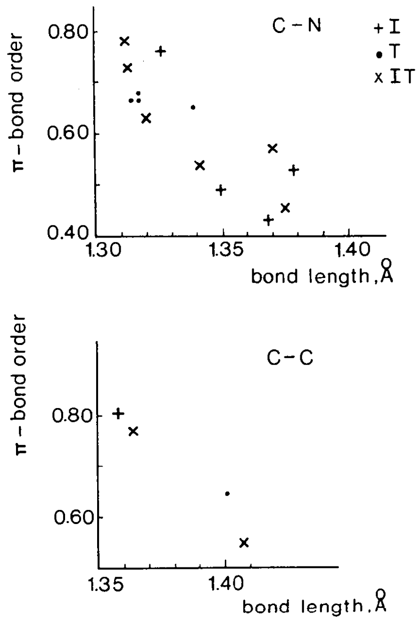

Fig. 2. LCAO π-bond orders *versus* bond lengths for imidazole (I), the triazole ring in 5-(*p*-chlorophenyl)-1,2,4-triazole (T) and imidazo[1,2-*b*]-*as*-triazine (IT).

Table 1. *Final parameters (standard deviations in parentheses)*

The form of the anisotropic temperature factor is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots 2hka^*b^*U_{12} + \cdots) \times 10^{-3}]$.

	x	y	z	$U_{11}(U_{\rm iso})$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·0177 (4)	0·1972 (4)	−0·0145 (13)	36 (3)	54 (3)	59 (3)	8 (3)	2 (3)	10 (3)
C(2)	0·1124 (4)	0·2608 (4)	0·1382 (12)	45 (3)	43 (3)	57 (3)	8 (3)	0 (3)	7 (3)
C(3)	0·2584 (4)	0·1478 (3)	−0·0111 (11)	29 (3)	39 (3)	42 (3)	−8 (2)	−3 (2)	5 (2)
C(4)	0·3422 (5)	0·0132 (4)	−0·2152 (13)	43 (3)	48 (3)	57 (3)	5 (3)	9 (3)	1 (3)
C(5)	0·2167 (5)	−0·0015 (4)	0·2889 (13)	52 (3)	40 (3)	51 (3)	−3 (3)	5 (3)	−6 (3)
N(1)	0·0390 (4)	0·1088 (4)	−0·1650 (11)	28 (2)	60 (3)	61 (3)	−6 (2)	−5 (2)	6 (2)
N(2)	0·2323 (4)	0·2377 (3)	0·1385 (10)	41 (3)	38 (3)	56 (3)	−2 (2)	−3 (2)	−1 (2)
N(3)	0·3687 (3)	0·1042 (3)	0·0475 (11)	28 (2)	47 (3)	62 (3)	0 (2)	0 (2)	0 (3)
N(4)	0·1623 (3)	0·0852 (3)	−0·1597 (9)	30 (2)	42 (2)	44 (3)	−6 (2)	0 (2)	6 (2)
H(1)	−0·073 (6)	0·214 (5)	0·019 (15)	0·06 (2)					
H(2)	0·093 (5)	0·327 (4)	0·252 (13)	0·03 (2)					
H(4)	0·409 (5)	−0·030 (4)	−0·281 (13)	0·03 (2)					
H(5)	0·171 (5)	−0·051 (5)	−0·440 (14)	0·06 (2)					

Table 2. *Experimental bond lengths* (Å) *and π-bond orders* (*b.o.*) *in imidazo*[1,2-*b*]-*as-triazine* (*IT*), 5-(*p-chlorophenyl*)-1,2,4-*triazine* (*T*) *and imidazole* (*I*)

	IT		T		I	
	Length	b.o.	Length	b.o.	Length	b.o.
C(1)–C(2)	1·41	0·55	1·40	0·65		
C(2)–N(2)	1·31	0·73	1·32	0·67		
N(2)–C(3)	1·34	0·54	1·34	0·65		
C(3)–N(4)	1·40	0·41	1·31	0·67		
N(4)–N(1)	1·35	0·40	1·34	0·65		
N(1)–C(1)	1·31	0·78	1·32	0·68		
C(3)–N(3)	1·32	0·63			1·33	0·76
N(3)–C(4)	1·37	0·57			1·38	0·53
C(4)–C(5)	1·36	0·77			1·36	0·81
C(5)–N(4)	1·38	0·45			1·37	0·43
N(4)–C(3)	1·40	0·41			1·35	0·49

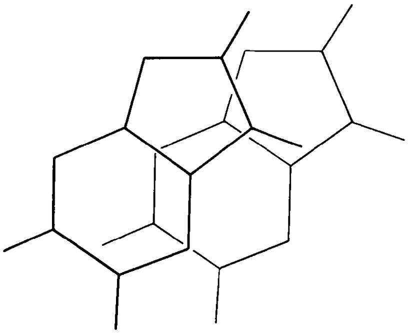

Fig. 3. Stacking of the molecules.

differences involve C(3)—N(4), which is considerably longer than in 5-(*p*-chlorophenyl)-1,2,4-triazine and imidazole. Simple LCAO calculations for imidazole, 1,2,4-triazine and the title compound with the parameters suggested by Streitwieser (1961) have been carried out and the resulting π-bond orders are listed in Table 2. There is a reasonable correlation between the bond lengths and the bond orders (Fig. 2); in particular, the relatively long C(3)—N(4) in the title compound is reflected in a low bond order.

The molecules are planar within the limits of accuracy and are stacked in tightly packed columns along [001], the distance between the planes of adjacent molecules being 3·36 Å. The stacking is indicated in Fig. 3. The packing of the columns is depicted in Fig. 4 in a projection of the structure along [001]. All contacts between the columns correspond to normal van der Waals distances.

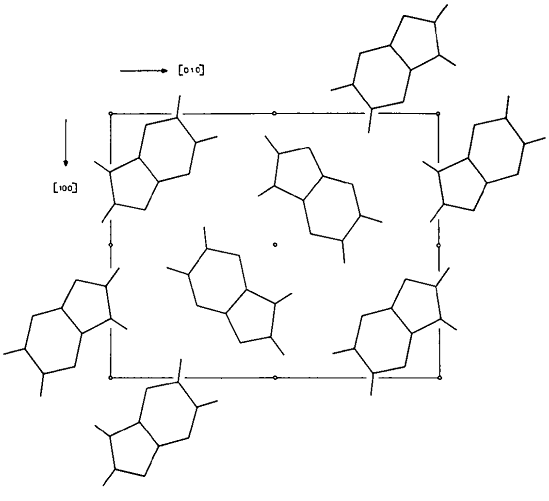

Fig. 4. Projection of the structure along [001].

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An Antitumor Agent, 2-(3,3-Dimethyl-1-triazeno)phenyl-1-carboxamide*

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Abstract. $C_9H_{12}ON_4$, monoclinic, $P2_1/c$, $a = 9{\cdot}444(5)$, $b = 7{\cdot}085(4)$, $c = 16{\cdot}005(7)$ Å, $\beta = 108{\cdot}08(4)°$, $Z = 4$, $D_x = 1{\cdot}257(1)$, $D_m = 1{\cdot}25(1)$ g cm^{-3}, at 23 °C. Its structure is similar to that of $C_6H_{11}ON_6$, a related antitumor agent reported earlier; both have an internal hydrogen bond.

Introduction. The sample was provided by Dr Corwin Hansch of Pomona College. Two distinct crystalline forms grew from the pure sample dissolved in toluene. The predominant form, which was orthorhombic, appeared to include a molecule of toluene in the asymmetric unit (according to its density, cell volume and mass-spectroscopy information). Investigation of the other (monoclinic) form suggested that it did not include the solvent molecule, and it was used for the structure determination.

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