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4-Amino-3-(2-aminophenyl)-4*H*-1,2,4-triazole

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Abstract. $C_8H_9N_5$, orthorhombic, $P2_1ab$, $Z=4$, $a=8{\cdot}9724$ (4), $b=11{\cdot}3495$ (6), $c=8{\cdot}1436$ (3) Å, $V=829{\cdot}3$ Å^3. $R=4{\cdot}0\%$ for 692 observed structure factors. Angle of 43·0° between the two ring planes. Internal N–H···N bond of 2·89 Å.

Introduction. In connexion with the study of ring transformations occurring during hydrazinolysis and hydroxylaminolysis of diazines (for the latest paper in a series on this subject see van der Plas & Vollering, 1974) it was found that on reaction of 4-chloroquinazoline with hydrazine, ring contraction into an *N*-amino-3-(2-aminophenyl)-1,2,4-triazole takes place. When the work on the reaction was nearly completed the same ring contraction was reported by Bowie & Thomason (1972) who on chemical and spectroscopic evidence assumed the product to be 4-amino-3-(2-aminophenyl)-4*H*-1,2,4-triazole. This assignment is confirmed by the present crystal structure determination.

692 independent reflexions with $I<2\sigma(I)$ were collected on a Nonius AD3 automatic three-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation, discrimination and the θ–2θ scan method. No correction for absorption was made. After direct methods failed to produce a solution, the Patterson approach was tried. The probable orientation of the six-membered ring was derived from the peaks surrounding the origin of an E^2 synthesis. From a sixfold Patterson minimum function based on the relative positions of the ring atoms thus obtained, two possible locations of the benzene ring relative to the symmetry elements were derived. With the corresponding sets of coordinates for the ring atoms, structure factors and a difference synthesis were calculated. The difference synthesis based on the set of lower R contained indications for the remaining atoms. The rough model of the molecule thus obtained proved essentially correct and could be readily refined. The five-membered ring was at first refined by isotropic least squares with all atoms treated as C. On the basis of the resulting temperature parameters, discrimination between C and N was made. Anisotropic least-squares refinement with a Cruickshank (1961) weighting scheme converged to $R=7{\cdot}7\%$. Difference syntheses used to locate the H atoms indicated that the assignment of C and N had been only partially correct. After correction, and introduction of the H atoms with isotropic temperature parameters, R converged to 4·0%. The final parameters are listed in Table 1, bond lengths and angles in Fig. 1.*

Discussion. The triazole ring is planar within 0·004 Å with N(4) and C(3) at distances of 0·105 and 0·055 Å on the same side of the ring. The benzene ring is planar within 0·016 Å with N(5) and C(2) on opposite sides at distances of 0·075 and 0·070 Å. The angle between the planes of the two rings is 43·0°. The amino

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31556 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final parameters* ($\times 10^4$) (*standard deviations in parentheses*)

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	−2072 (5)	3161 (3)	−4777 (5)	36 (2)	42 (2)	40 (2)	2 (2)	−6 (2)	3 (2)
C(2)	−1010 (5)	2008 (3)	−2992 (4)	29 (2)	31 (2)	32 (2)	−3 (2)	4 (2)	−5 (2)
C(3)	−38 (4)	1562 (3)	−1678 (4)	33 (2)	31 (2)	32 (2)	−5 (2)	4 (2)	−1 (2)
C(4)	−762 (4)	499 (3)	−1892 (4)	39 (2)	27 (2)	33 (2)	−6 (2)	2 (2)	1 (2)
C(5)	1737 (5)	131 (3)	−645 (5)	41 (2)	29 (2)	45 (2)	2 (2)	1 (2)	7 (2)
C(6)	1878 (5)	781 (4)	786 (5)	48 (3)	40 (2)	38 (2)	−4 (2)	−10 (2)	12 (2)
C(7)	1070 (6)	1798 (4)	1029 (5)	68 (3)	40 (2)	37 (3)	−6 (2)	−10 (3)	0 (2)
C(8)	114 (5)	2182 (3)	−197 (5)	47 (2)	33 (2)	35 (4)	2 (2)	−5 (3)	−2 (4)
N(1)	−1094 (4)	3155 (2)	−3507 (4)	30 (2)	26 (2)	35 (2)	−1 (2)	0 (2)	3 (2)
N(2)	−2582 (4)	2102 (3)	−5041 (5)	42 (2)	44 (2)	40 (2)	−7 (2)	−8 (2)	3 (2)
N(3)	−1905 (4)	1367 (3)	−3898 (4)	42 (2)	38 (2)	38 (2)	−7 (2)	−7 (2)	−1 (2)
N(4)	−283 (4)	4171 (3)	−3043 (4)	41 (2)	24 (2)	49 (2)	−6 (2)	−3 (2)	−1 (2)
N(5)	586 (5)	−179 (3)	−3275 (4)	64 (2)	36 (2)	46 (2)	19 (2)	1 (2)	−12 (2)

Table 1 (*cont.*)

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	U ($\times 10^3$)
H(1)	−229 (6)	390 (4)	−534 (2)	5 (2)
H(2)	74 (1)	397 (5)	−304 (6)	9 (2)
H(3)	−65 (7)	444 (5)	−215 (6)	8 (2)
H(4)	223 (5)	−60 (4)	−76 (5)	4 (1)
H(5)	249 (5)	51 (4)	167 (5)	4 (1)
H(6)	107 (6)	221 (4)	201 (6)	8 (2)
H(7)	−52 (5)	289 (3)	−3 (5)	4 (2)
H(8)	−9 (6)	15 (4)	−420 (5)	5 (1)
H(9)	109 (5)	−81 (4)	−347 (5)	5 (2)

group of N(5) is planar and coplanar with the benzene ring. The amino group of N(4), however, is pyramidal and is apparently forced out of coplanarity by steric interaction with the benzene ring, especially H(7). The difference between the two amino groups is also reflected in the lengths of the bonds with which they are attached [C(4)–N(5) 1·373, N(1)–N(4) 1·415 Å]. That considerable strain is present is also apparent from the fact that in both rings the bonds carrying the

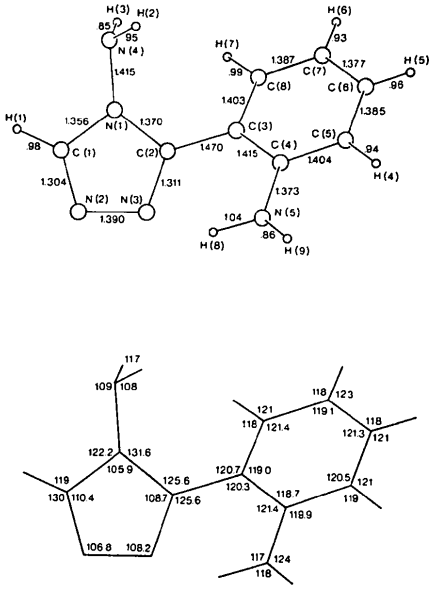

Fig. 1. Bond lengths and bond angles.

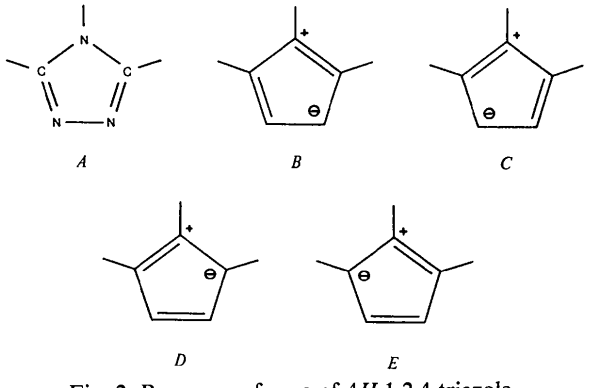

Fig. 2. Resonance forms of 4*H*-1,2,4-triazole.

amino groups are tilted out of the ring plane. In the triazole ring C(2)–N(1), C(1)–N(1) and N(2)–N(3) are relatively long and C(1)–N(2) and C(2)–N(3) relatively short, suggesting a preponderance of the neutral resonance form (*A* in Fig. 2). A satisfactory description of the bond lengths in the triazole ring is possible in terms of contributions from the 5 resonance forms of Fig. 2. Apparently there is little resonance interaction with the attached phenyl and amino groups as was already implied by their non-coplanarity with the triazole ring. With Pauling's (1948) formula for the relation between bond length r and double bond character x: $r=r_1-(r_1-r_2)3x/(3x+1)$, with r_2 the double bond length (1·24 for N–N and 1·28 Å for C–N) and r_1 the single bond length (1·47 Å for both N–N and C–N), one arrives at contributions of 42, 25, 19, 2 and 13% for the resonance forms *A*, *B*, *C*, *D* and *E*.

Dewar & Gleicher (1966) have published results of PPP and SPO calculations on 4*H*-1,2,4-triazole. Their calculated bond lengths are in reasonable agreement with our experimental results (Table 2). Our results are not directly comparable with those for 1,2,4-triazole itself which is 1*H*-1,2,4-triazole (Goldstein, Ladell & Abowitz, 1969) whilst our compound is a derivative of 4*H*-1,2,4-triazole. The bond lengths in the benzene ring vary slightly about an average of 1·395 Å, the accepted value for benzene. C(4)–N(5) is similar in length to the C–N bonds in comparable aniline derivatives. There is an intramolecular hydrogen bond of 2·89 Å between N(3) and N(5). This hydrogen bond together with the steric repulsion between the triazole and the benzene rings is responsible for the conformation of the molecule. N(5) is also involved in an intermolecular hydrogen bond with N(2) of the molecule generated by a 2_1 axis. Another weak hydrogen bond connects N(3) with N(4) of the molecule related by a glide plane. The dimensions of the 3 hydrogen bonds are given in Table 3. The packing is effected by the weak N–H···N hydrogen bonds and by normal van der Waals contacts.

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Table 2. *Comparison of calculated bond lengths (Dewar & Gleicher, 1966) with experimental values*

	PPP	SPO	Exp.
N(1)–C(1)	1·401 Å	1·401 Å	1·356 Å
C(1)–N(2)	1·283	1·286	1·304
N(2)–N(3)	1·362	1·361	1·390
N(3)–C(2)	1·283	1·286	1·311
C(2)–N(1)	1·401	1·401	1·370

Table 3. *Hydrogen bonds* (N–H···N)

	N–H	H···N	N···N	∠N–H···N
N(5)–H(8)···N(3)	1·0 Å	2·1 Å	2·89 Å	126°
N(5)–H(9)···N(2)	0·9	2·2	3·06	157
N(4)–H(2)···N(3)	0·9	2·3	3·17	162

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1,3,5(10)-Oestratrien-3,17α-diol

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Abstract. $C_{18}H_{24}O_2$, monoclinic, $P2_1$, $a=9{\cdot}148$ (5), $b=23{\cdot}292$ (10), $c=7{\cdot}235$ (5) Å, $\beta=98{\cdot}70$ (7)°, $Z=4$. The two independent molecules do not have exactly the same conformations. With a 17α substituent, the two *D* rings are almost in the half-chair conformation. In the crystal, the molecules are disposed

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal parameters for non-hydrogen atoms*

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3975 (6)	−3285 (2)	5184 (7)	184 (9)	17 (1)	176 (11)	−3 (5)	97 (15)	0 (6)
C(2)	3865 (6)	−3871 (2)	5506 (7)	190 (9)	17 (1)	216 (13)	−13 (5)	86 (17)	−20 (6)
C(3)	4060 (5)	−4076 (2)	7334 (6)	126 (7)	14 (1)	214 (11)	4 (4)	109 (14)	2 (5)
C(4)	4396 (5)	−3699 (2)	8778 (6)	114 (6)	15 (1)	183 (10)	9 (4)	90 (13)	5 (5)
C(5)	4527 (5)	−3107 (2)	8471 (6)	102 (6)	13 (1)	164 (10)	2 (4)	62 (12)	3 (5)
C(6)	4905 (6)	−2714 (2)	10162 (7)	149 (8)	15 (1)	161 (10)	−2 (4)	−4 (14)	0 (5)
C(7)	5421 (5)	−2123 (2)	9646 (6)	141 (8)	15 (1)	172 (10)	−7 (4)	−14 (14)	−4 (5)
C(8)	4370 (5)	−1883 (2)	7998 (6)	105 (6)	13 (1)	163 (9)	−6 (4)	63 (12)	−7 (5)
C(9)	4467 (5)	−2251 (2)	6264 (6)	115 (7)	15 (1)	168 (10)	−9 (4)	69 (13)	0 (5)
C(10)	4310 (5)	−2894 (2)	6642 (6)	115 (7)	14 (1)	174 (10)	1 (4)	82 (13)	0 (5)
C(11)	3362 (6)	−2032 (2)	4585 (7)	186 (9)	19 (1)	189 (12)	−19 (5)	−20 (16)	9 (6)
C(12)	3672 (6)	−1397 (2)	4154 (7)	191 (9)	19 (1)	213 (12)	−18 (5)	1 (17)	21 (6)
C(13)	3629 (5)	−1024 (2)	5858 (6)	108 (6)	16 (1)	214 (11)	−4 (4)	57 (13)	16 (5)
C(14)	4713 (5)	−1263 (2)	7509 (6)	113 (6)	13 (1)	177 (10)	−1 (4)	70 (12)	−1 (5)
C(15)	4795 (7)	−792 (2)	8983 (7)	217 (10)	16 (1)	229 (13)	3 (5)	120 (18)	−1 (6)
C(16)	4587 (6)	−225 (2)	7840 (8)	173 (9)	17 (1)	274 (14)	20 (5)	119 (18)	0 (6)
C(17)	4211 (5)	−404 (2)	5768 (7)	113 (7)	14 (1)	237 (12)	10 (4)	57 (14)	21 (6)
C(18)	2030 (6)	−981 (3)	6278 (9)	128 (9)	27 (2)	446 (20)	14 (6)	118 (21)	63 (9)
O(83)	3900 (4)	−4645 (1)	7757 (5)	190 (6)	14 (1)	221 (8)	0 (3)	141 (11)	−2 (4)
O(97)	5519 (3)	−374 (1)	4847 (4)	130 (5)	17 (1)	235 (8)	−7 (3)	80 (10)	25 (4)
C(51)	9849 (5)	−1846 (2)	9620 (6)	123 (7)	14 (1)	162 (10)	−6 (4)	14 (13)	−5 (5)
C(52)	9344 (5)	−1287 (2)	9336 (6)	129 (7)	13 (1)	189 (10)	−6 (4)	44 (13)	−26 (5)
C(53)	8657 (5)	−1127 (2)	7578 (6)	91 (6)	13 (1)	207 (11)	1 (4)	49 (12)	−2 (5)
C(54)	8474 (5)	−1526 (2)	6127 (6)	96 (6)	14 (1)	182 (10)	1 (4)	34 (12)	4 (5)
C(55)	8964 (5)	−2085 (2)	6417 (6)	103 (6)	14 (1)	155 (9)	2 (4)	53 (12)	−3 (5)
C(56)	8669 (6)	−2500 (2)	4808 (6)	173 (8)	16 (1)	161 (11)	15 (5)	50 (15)	4 (5)
C(57)	9405 (5)	−3081 (2)	5184 (6)	152 (8)	16 (1)	169 (10)	15 (4)	49 (14)	−8 (5)
C(58)	9287 (5)	−3285 (2)	7142 (6)	119 (6)	12 (1)	172 (10)	3 (4)	23 (13)	0 (5)
C(59)	10211 (5)	−2874 (2)	8559 (6)	90 (6)	13 (1)	156 (10)	−1 (4)	29 (11)	−4 (5)
C(60)	9674 (5)	−2259 (2)	8217 (6)	89 (6)	12 (1)	172 (10)	−4 (3)	63 (12)	−6 (5)
C(61)	10256 (5)	−3070 (2)	10598 (6)	141 (7)	15 (1)	161 (10)	10 (4)	14 (13)	−5 (5)
C(62)	10694 (5)	−3700 (2)	10903 (6)	127 (7)	16 (1)	173 (10)	13 (4)	46 (13)	3 (5)
C(63)	9716 (5)	−4088 (2)	9544 (6)	104 (6)	16 (1)	188 (11)	1 (4)	47 (13)	11 (5)
C(64)	9836 (5)	−3894 (2)	7546 (6)	125 (7)	14 (1)	179 (10)	0 (4)	24 (13)	−4 (5)
C(65)	9116 (7)	−4383 (2)	6316 (8)	239 (11)	16 (1)	265 (15)	0 (6)	−85 (20)	−11 (7)
C(66)	9584 (7)	−4925 (3)	7513 (9)	252 (12)	19 (1)	332 (17)	−9 (7)	−82 (23)	−14 (8)
C(67)	10152 (6)	−4726 (2)	9509 (7)	137 (8)	16 (1)	269 (13)	0 (4)	21 (16)	14 (6)
C(68)	8123 (6)	−4077 (3)	9973 (8)	130 (8)	25 (1)	348 (17)	6 (6)	151 (18)	49 (8)
O(33)	8135 (3)	−581 (1)	7179 (4)	131 (5)	13 (1)	235 (8)	5 (3)	11 (10)	−12 (4)
O(37)	11697 (4)	−4836 (1)	10064 (5)	129 (5)	17 (1)	236 (8)	16 (3)	80 (10)	25 (4)