

Tetrazole Studies. Part II.¹ Crystal Structure of 5-Bromotetrazole

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The structure of the title compound has been established by X-ray crystallography from diffractometer data. Crystals are monoclinic, space group $P2_1/m$, cell dimensions $a = 4.935(5)$, $b = 6.279(5)$, $c = 7.446(5)$, $\beta = 116.8(\pm 0.2)$. 316 Statistically reliable reflections were refined to R 0.045. Within the limits of experimental error the molecule appears to possess m -symmetry. Ring bond distances are: C–N 1.290 and 1.351, N–N 1.283–1.347 Å. The ring hydrogen could not be located, nor were hydrogen positions indicated by short $N \cdots N$ intermolecular contacts or approximately tetrahedral angles at the corresponding nitrogens. Ring distances clearly indicate the tetrazole ring to be a resonance hybrid. The planar molecules form sheets stacked along the b axis with a perpendicular spacing of $1/2 b$ (3.14 Å). Data were also refined in space group $P2_1$ to R 0.044 and the resulting model did not vary significantly from that obtained using space group $P2_1/m$.

TETRAZOLES are good π -electron donors and form complexes with transition metals.¹⁻⁶ They may also create a certain type of physiological activity by affecting the nervous system.⁷

An X-ray crystal structure analysis has been performed on 5-bromotetrazole since it is one of the less-polar tetrazoles and is not hydrated. Although we were not expecting to locate the ring hydrogen directly, in a molecule where bromine constitutes *ca.* 50% of the electronic content, we wished to establish evidence for ring hydrogen localisation from markedly differing N–N and C–N bond lengths within the ring, or from the positions of strong $N \cdots NH$ hydrogen bonds holding the tetrazole rings in a two- or three-dimensional lattice. Since this compound is one of a series being examined by Raman spectroscopy⁸ a knowledge of the space-group, molecules per unit cell, and molecular geometry with respect to the general crystal morphology was required in order to assign lattice vibrations.

EXPERIMENTAL

Cell dimensions were measured on a General Electric single-crystal orienter by use of $Cu-K\alpha_1$ and $Cu-K\alpha_2$ ($\lambda = 1.54040$ and 1.54434 Å) peaks at room temperature. Errors were estimated from the observed deviations of individual values from their means.

Crystal Data.— $CHBrN_4$, $M = 149$. Monoclinic, $a = 4.935(5)$, $b = 6.279(5)$, $c = 7.446(5)$ Å, $\beta = 116.8(1^\circ)$, (insufficient sample for measurement of D_m), $Z = 2$, $D_c = 2.40$. $\mu(Cu-K\alpha) = 128.0$ cm⁻¹. Space group $P2_1/m$ (No. 11) with the two molecules occupying special positions of m -symmetry at $(x, 1/4, z)$; $(\bar{x}, 3/4, \bar{z})$, or $P2_1$ (No. 4) with the two molecules occupying the general equivalent positions (x, y, z) ; $(x, 1/2 + y, z)$, from systematic absences $0k0$ for $k = 2n + 1$. In both cases b was unique.

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Intensity data were measured for a crystal with an approximated octagonal cross-section with radii perpendicular to the faces of 0.0041, 0.00450, 0.0050, 0.0050 cm and of length 0.014 cm. The crystal was mounted along 101^* . All possible total intensities (T_c) were measured for $0 < 2\theta \leq 120^\circ$ on the automated $1/4$ circle General Electric diffractometer equipped with a scintillation counter and pulse-height selection. The moving-crystal, moving-counter 2θ -scan method was used for measuring T_c (2θ scan = 3.66° at 4° min⁻¹). Stationary-crystal, stationary-counter background counts of 20 s (B_1, B_2) were made at the beginning and end of the 2θ scan. The integrated intensity I was calculated as $I = T_c - (B_1 + B_2) 1.83 \times 0.75$. Structure factors were obtained by application of the usual Lorentz and polarisation corrections. Equivalent reflections were averaged after each had been corrected for absorption.⁹ 325 Averaged reflections were measured, of which 319 had an average net count $> 1.0 \sigma_{av}$ ($\sigma = [T_c + (B_1 + B_2)]^{1/2}$) and were considered statistically significant. Only these were used in the subsequent structure refinements and Fourier syntheses.

Solution and Refinement of the Structure based on Space Group $P2_1/m$.—It is already well established that the tetrazole ring is planar.^{1,3-6,10-17} It was thus assumed that the molecules occupy the position of m -symmetry in space group $P2_1/m$. The x and y co-ordinates of the bromine atom were found by solution of a three-dimensional Patterson diagram and the remainder of the molecule (excluding hydrogen) was located by the usual Fourier¹⁸ and least-squares procedures.¹⁹ Full-matrix anisotropic refinement yielded a final R of 0.045 and a weighted value R' of 0.049. During the last cycle of refinement, shifts for all 36 positional and thermal parameters varied were $< 0.2\sigma$. A weighing scheme was chosen such that for values of $F_o < 5 \sqrt{w} = F_o/5$, for $5 < F_o < 15 \sqrt{w} = 1$, and $F_o > 15 \sqrt{w} = 15/F_o$. This results in 105 reflections with $F_o \leq 10$ having average $w\Delta^2$ values smaller than those of the remainder, which

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TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) with estimated standard deviations ($\text{\AA} \times 10^4$) in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Br	2163(14)	2500	4426(11)
C	4203(108)	2500	7192(100)
N(1)	7116(93)	2500	8234(88)
N(2)	7564(100)	2500	10154(83)
N(3)	5058(107)	2500	10284(87)
N(4)	2803(99)	2500	8389(88)

TABLE 2

Final thermal parameters ($\times 10$) with their estimated standard deviation in parentheses

	β_{11}	β_{22}	β_{33}	β_{13}
Br	4887(63)	2463(36)	705(20)	235(30)
C	2920(570)	1501(315)	880(206)	740(292)
N(1)	2741(473)	2271(305)	976(182)	507(240)
N(2)	3212(510)	3010(334)	542(169)	173(251)
N(3)	4006(547)	2516(323)	659(182)	479(256)
N(4)	3718(529)	2423(318)	753(181)	1(263)

For all atoms, $\beta_{12} = \beta_{23} = 0$. The temperature factor is of the form $B = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2(hk\beta_{12} + hl\beta_{13} + hl\beta_{23})$.

TABLE 3

Amplitudes of thermal vibration (\AA) along the principal axes of vibration ellipsoids. The direction of each principal axis is specified by the angles which it makes with the crystallographic axes *a*, *b*, and *c*

	\AA	<i>a</i>	<i>b</i>	<i>c</i>
Br	0.124	84.8	90.0	31.9
	0.222	90.0	0.0	90.0
	0.246	5.2	90.0	121.9
C	0.138	103.9	90.0	12.8
	0.171	13.9	90.0	102.8
	0.173	90.0	0.0	90.0
N(1)	0.145	75.0	90.0	41.7
	0.178	15.0	90.0	131.7
	0.212	90.0	0.0	90.0
N(2)	0.108	83.4	90.0	33.4
	0.200	6.6	90.0	123.4
	0.245	90.0	0.0	90.0
N(3)	0.121	91.0	90.0	25.8
	0.212	1.0	90.0	115.8
	0.224	90.0	0.0	90.0
N(4)	0.122	76.5	90.0	40.3
	0.220	90.0	0.0	90.0
	0.228	13.5	90.0	130.3

TABLE 4

Bond lengths and angles. The standard deviations for each atom were taken as the root-mean-square of $\sigma(x)$ and $\sigma(z)$. The standard deviation of bond lengths and angles were calculated from the formula given by G. A. Jeffrey and D. W. J. Cruickshank, *Quart. Rev.*, 1953, 7, 335

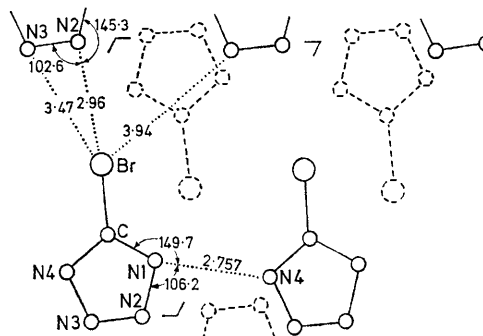
(a) Bond distances (\AA)			
Br-C	1.840(10)	N(2)-N(3)	1.283(13)
C-N(1)	1.290(13)	N(3)-N(4)	1.347(13)
N(1)-N(2)	1.345(13)	N(4)-C	1.351(14)
(b) Bond angles (deg.)			
Br-C-N(1)	125.0(8)	N(3)-N(4)-C	105.3(9)
C-N(1)-N(2)	104.2(9)	N(4)-C-N(1)	111.4(9)
N(1)-N(2)-N(3)	112.2(9)	Br-C-N(4)	123.6(8)
N(2)-N(3)-N(4)	106.9(9)		

have fairly similar average $w\Delta^2$ values for increasing ranges of F_o . The 002 and 101 reflections were omitted from the

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

final least-squares calculations since they appeared to suffer from extinction. The 203 reflection was also excluded since for some inexplicable reason it gave a large Δ value which distorted the average $w\Delta^2$ values for the range in which it fell. The six weak reflections gave small F_o values. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20788 (3 pp.).* A difference-Fourier synthesis was featureless, and gave no indication of the hydrogen position.

Final atomic co-ordinates are given in Table 1, thermal parameters in Table 2, thermal amplitudes and vibrations in Table 3, bond lengths and angles in Table 4, and molecular packing and closest intermolecular distances in the Figure.



The packing of the molecules as viewed down the *b* axis. Closest intermolecular contacts are shown

DISCUSSION

The planar tetrazole rings lie in sheets perpendicular to the *b* axis, separated by 3.14 \AA , a distance large enough to preclude any interaction between the sheets. Within the molecules the C-N (1.290 and 1.351 \AA) and N-N values (1.345, 1.283, and 1.347 \AA) are all shorter than those normally found for single bonds, and suggest the existence of considerable electron delocalisation as reported for other tetrazole systems.^{1,3-6,10-17} They correspond closely with those of previous determinations, listed in Table 5, which compares tetrazole rings with a variety of substituents at different ring sites, some coordinated to metals and even (*c*) an ylide configuration. There is a general tendency for N(2)-N(3) to be shorter than N(1)-N(2) and N(3)-N(4). Compound (*n*) appears to be the only one in which the tetrazole bond lengths differ markedly from those of the remaining compounds listed. This is no doubt due to the strongly electron-withdrawing nature of the CF_3 group in this compound. There are fairly short intermolecular³ distances between N(1) \cdots N(4) 2.757 and N(2) \cdots Br 2.960 \AA (Figure). However there does not seem to be evidence for hydrogen bonding since the angles at N(1) and N(2) indicate that hydrogen would have to be considerably displaced from the closest line of contact. Within the limits of this determination there is then little evidence for hydrogen ring localisation and the structure appears to have the following resonance forms:

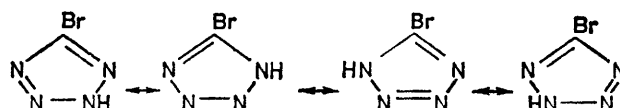


TABLE 5
Bond distances (Å) and angles (deg.) in various tetrazole derivatives

Compd.	C-N(1)	N(1)-N(2)	N(2)-N(3)	N(3)-N(4)	N(4)-C	N(4)-C- N(1)	C-N(1)- N(2)	N(1)-N(2)- N(3)	N(2)-N(3)- N(4)	N(3)-N(4)- C
(a)	1.290(13)	1.345(13)	1.283(13)	1.347(13)	1.351(14)	111.4(9)	104.2(9)	112.2(9)	106.9(9)	105.3(9)
(b)	1.337(15)	1.349(13)	1.313(16)	1.351(17)	1.326(17)	109.4(1.2)	107.5(1.2)	107.1(1.2)	110.2(1.2)	106.0(1.2)
(c)	1.30(2)	1.35(2)	1.31(2)	1.37(2)	1.31(20)	115(2)	103(2)	109(2)	110(2)	102(2)
(d)	1.36(2)	1.36(6)	1.26(2)	1.37(2)	1.33(2)	103(1.5)	112(1.5)	105(1.5)	109(2)	109(2)
(e)	1.30(2)	1.34(2)	1.29(2)	1.33(2)	1.30(2)	109(2)	109(2)	106(2)	111(2)	106(1)
(f)	1.34(4)	1.38(5)	1.28(5)	1.39(4)	1.33(5)	109(6)	108(6)	107(6)	109(6)	108(6)
(g)	1.329(15)	1.381(15)	1.255(15)	1.373(15)	1.321(15)	109.8(7)	106.4(7)	107.6(7)	111.1(7)	105.0(7)
(h)	1.329(3)	1.348(2)	1.310(2)	1.348(2)	1.329(3)	112.5(2)	104.3(2)	109.5(2)	109.5(2)	104.3(2)
(i)	1.318(6)	1.356(8)	1.295(7)	1.346(6)	1.302(8)	113.2	103.4	109.6	109.0	104.8
(j)	1.32(2)	1.34(2)	1.29(2)	1.32(2)	1.35(2)	112	101	114	107	106
(k)	1.38	1.35	1.30	1.31	1.36	106	110	103	117	104
(l)	1.360(4)	1.318(3)	1.313(4)	1.318(3)	1.360(4)	112.2(2)	103.7(3)	110.2(3)	110.2(3)	103.7(3)
(m)	1.321(20)	1.370(20)	1.290(20)	1.357(10)	1.327(4)	109(1)	109(1)	106(10)	112(1)	105(1)
(n)	1.314(20)	1.372(20)	1.291(20)	1.346(20)	1.323(20)	107(1)	107(1)	109(1)	107(1)	110(1)
(n)	1.372(24)	1.425(17)	1.119(17)	1.482(20)	1.413(22)	110.0(2)	106.0(2)	107(2)	119(2)	97.0(2)

(a) 5-Bromotetrazole; (b) *cis*-Bis[dimethyl(phenyl)phosphine]bis-(5-methyltetrazolato)palladium(II), ref. 1; (c) 5-(3-Chlorobenzyl-dimethylammonium)tetrazolate, ref. 10; (d) Tetrakis-(1-isopropyltetrazol-5-ato)aurate(III) anion, ref. 3; (e) Dichlorobis-(1-methyltetrazole)zinc(II), ref. 4; (f) Pentamethyltetrazole ICI, ref. 11; (g) 5-Aminotetrazole monohydrate, ref. 12; (h) Sodium tetrazolate monohydrate, ref. 13; (i) Hydrazinium-5-aminotetrazolate, ref. 14; (j) 2-Methyl-5-aminotetrazole, ref. 15; (k) 1,3-Dimethyl-5-aminotetrazole, ref. 16; (l) Anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide, ref. 17; (m) Bis[nitratobis(pentamethylene-tetrazole)silver(I)], ref. 5; (n) Bis-2-(5-perfluoromethyltetrazolato)- μ -1,2-bis(diphenylphosphino)ethane-bis-[1,2-bis(diphenylphosphino)ethane]dicopper(I), ref. 6.

On the basis of molecular geometry, anisotropic thermal motion is reasonable.

Refinement based on Space Group P2₁.—When the structure was refined in this space group final *R* and *R'* values were 0.044 and 0.047. There were no significant changes in any of the bond lengths or thermal motions. As expected, the estimated errors in the *b* direction were considerably higher than those in *a* or *c*,

and it is felt that the model obtained from the *P2₁/m* refinement more accurately represents the structure.

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