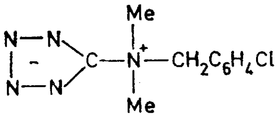
Tetrazole Studies. Part III.[1] Crystal Structure of 5-[(3-Chlorobenzyl)dimethylammonio]tetrazolide

By **Gerald B. Ansell**, Chemistry Division, Code 605, Research Department, Michelson Laboratory, Naval Weapons Center, China Lake, California 93555, U.S.A.

Crystals of the title compound (I) are monoclinic, space group $P2_1/a$, with $a = 16.277 \pm 0.008$, $b = 10.842 \pm 0.008$, $c = 6.407 \pm 0.004$ Å, $\beta = 98.81$°. The structure was solved by the symbolic addition procedure from 879 observed reflections, measured by diffractometer, and refined by full-matrix least-squares to R 0.060. The compound has an ylide structure with a positively charged quaternary nitrogen atom, the tetrazole ring carrying an equalizing overall negative charge. There are no significant changes in bond lengths within this negatively charged tetrazole ring, compared with those previously measured in uncharged rings.

THIS series of tetrazoles are being studied for reasons described previously.[1,2] The title compound (I) is of additional interest since it was one of three isomers separated after the monobenzylation of sodium 5-dimethylaminotetrazole [3] and appeared to have an ylide structure. A preliminary report of the structure has been published.[4]



(I)

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[1] Part II, G. B. Ansell, *J.C.S. Perkin II* 1973, 2036.

[2] G. B. Ansell, *J.C.S. Dalton*, 1973, 371.

[3] L. Huff, D. M. Forkey, D. W. Moore, and R. A. Henry, *J. Org. Chem.*, 1970, **35**, 2074.

[4] G. B. Ansell, *Chem. Comm.*, 1970, 684.

EXPERIMENTAL

Crystal dimensions were measured on a General Electric XRD 5 single-crystal orienter by use of Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ peaks at room temperature. Errors quoted are estimated from the observed deviations of individual values from their mean.

Crystal Data.—$C_{10}H_{12}ClN_5$, $M = 237.5$. Monoclinic, $a = 16.277 \pm 0.008$, $b = 10.842 \pm 0.008$, $c = 6.407 \pm 0.004$ Å, $\beta = 98.81 \pm 0.08°$, $U = 1\,117.3$ Å^3, $D_m = 1.32$ (compressed pellet), $Z = 4$, $D_c = 1.41$, $F(000) = 496$. Space group $P2_1/a$ from systematic absences: $h0l$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$ with each molecule occupying equivalent positions $\pm (x, y, z;\ 1/2 + x,\ 1/2 - y,\ z)$. Cu-$K_{\alpha1}$ ($\lambda = 1.540\,50$ Å) and Cu-$K_{\alpha2}$ radiation ($\lambda = 1.544\,34$ Å); μ(Cu-K_α) = 29.3 cm^{-1}.

Intensities were collected from two crystals on an automated General Electric diffractometer equipped with pulse-height selection and a scintillation counter. Both crystals were mounted along the b axis. From the first ($0.008 \times 0.011 \times 0.010$ mm^3) most intensities $2\theta < 100°$ were collected, and from the second ($0.043 \times 0.086 \times 0.157$ mm^3) mainly data for which $100° < 2\theta < 110°$. Total intensities T_c, were measured by the moving-crystal moving-counter 2θ scan method, with stationary-crystal–stationary-counter background counts (B_1, B_2) taken at the beginning and end of each scan. The integrated intensity, I, was obtained by subtracting the appropriate background from T_c; Lorentz and polarization corrections were applied to I. Equivalent intensities were averaged. 879 Reflections having a net average $I > 1.5\sigma_{av}$ (where $\sigma^2 = T_c +$ total background) were considered observed and used in the subsequent structure determination. 527 Reflections were considered to be statistically unreliable.

TABLE 1

Final atomic co-ordinates ($\times 10^4$) expressed as fractions of the unit cell with estimated standard deviations in parentheses. Hydrogen atom positions were not refined

	x	*y*	*z*
Cl	4 823(1)	3 739(2)	7 294(3)
C(1)	4 601(4)	2 519(5)	8 911(11)
C(2)	5 024(4)	2 461(6)	10 979(12)
C(3)	4 826(4)	1 518(7)	12 227(11)
C(4)	4 218(4)	633(6)	11 501(10)
C(5)	3 830(4)	718(5)	9 407(10)
C(6)	4 003(4)	1 666(6)	8 106(10)
C(7)	3 211(4)	−270(5)	8 543(9)
C(8)	2 053(4)	1 167(5)	7 308(8)
C(9)	1 766(4)	−1 001(5)	7 749(10)
C(10)	2 165(4)	324(6)	10 858(9)
N(1)	2 302(3)	80(4)	8 618(7)
N(2)	1 965(4)	1 093(5)	5 257(7)
N(3)	1 770(4)	2 260(5)	4 638(8)
N(4)	1 760(4)	2 956(5)	6 282(9)
N(5)	1 949(4)	2 265(4)	8 080(8)
H(1)	5 490	3 150	11 610
H(2)	5 140	1 410	13 730
H(3)	4 050	−100	12 580
H(4)	3 660	1 730	6 470
H(5)	3 260	−470	6 980
H(6)	3 340	−1 090	9 420
H(7)	2 410	1 170	11 310
H(8)	2 460	−330	11 870
H(9)	1 540	350	10 920
H(10)	1 150	−920	8 100
H(11)	2 050	−1 810	8 510
H(12)	1 710	−1 080	6 110

TABLE 2

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

(*a*) Bond lengths

Cl–C(1)	1.751(6)	N(4)–N(5)	1.370(7)
C(1)–C(2)	1.399(9)	N(5)–C(8)	1.309(7)
C(2)–C(3)	1.367(10)	H(1)–C(2)	1.10
C(3)–C(4)	1.405(9)	H(2)–C(3)	1.03
C(4)–C(5)	1.396(8)	H(3)–C(4)	1.12
C(5)–C(6)	1.379(8)	H(4)–C(6)	1.12
C(6)–C(1)	1.384(8)	H(5)–C(7)	1.04
C(5)–C(7)	1.515(8)	H(6)–C(7)	1.06
N(1)–C(7)	1.536(7)	H(7)–C(10)	1.02
N(1)–C(8)	1.467(8)	H(8)–C(10)	1.03
N(1)–C(9)	1.515(7)	H(9)–C(10)	1.02
N(1)–C(10)	1.510(7)	H(10)–C(9)	1.06
C(8)–N(2)	1.303(7)	H(11)–C(9)	1.07
N(2)–N(3)	1.349(7)	H(12)–C(9)	1.04
N(3)–N(4)	1.298(7)		

(*b*) Bond angles

Cl–C(1)–C(2)	118.6(5)	H(2)–C(3)–C(2)	120.5
C(1)–C(2)–C(3)	117.5(6)	H(2)–C(3)–C(4)	117.2
C(2)–C(3)–C(4)	122.3(7)	H(3)–C(4)–C(3)	120.6
C(3)–C(4)–C(5)	117.7(6)	H(3)–C(4)–C(5)	121.7
C(4)–C(5)–C(6)	121.8(6)	H(4)–C(6)–C(5)	119.9
C(5)–C(6)–C(1)	118.0(6)	H(4)–C(6)–C(1)	122.1
Cl–C(1)–C(6)	118.7(5)	H(5)–C(7)–H(6)	107.4
C(5)–C(7)–N(1)	113.8(5)	H(5)–C(7)–C(5)	110.8
C(7)–N(1)–C(8)	111.3(6)	H(5)–C(7)–N(1)	107.3
C(7)–N(1)–C(9)	107.5(4)	H(6)–C(7)–C(5)	109.5
C(7)–N(1)–C(10)	110.8(4)	H(6)–C(7)–N(1)	107.8
C(8)–N(1)–C(9)	108.5(6)	H(7)–C(10)–H(8)	108.4
C(8)–N(1)–C(10)	109.6(6)	H(7)–C(10)–H(9)	108.1
C(9)–N(1)–C(10)	108.9(4)	H(7)–C(10)–N(1)	108.6
N(1)–C(8)–N(2)	120.4(5)	H(8)–C(10)–H(9)	111.4
N(1)–C(8)–N(5)	123.6(5)	H(8)–C(10)–N(1)	110.9
N(2)–C(8)–N(5)	115.9(5)	H(9)–C(10)–N(1)	109.5
C(8)–N(2)–N(3)	102.9(5)	H(10)–C(9)–H(11)	109.0
N(2)–N(3)–N(4)	109.7(5)	H(10)–C(9)–H(12)	106.3
N(3)–N(4)–N(5)	109.6(5)	H(10)–C(9)–N(1)	111.5
N(4)–N(5)–C(8)	101.8(5)	H(11)–C(9)–H(12)	110.8
H(1)–C(2)–C(1)	122.1	H(11)–C(9)–N(1)	106.3
H(1)–C(2)–C(3)	120.3	H(12)–C(9)–N(1)	112.9

Solution and Refinement.—The phases of 74 reflections with E values >1.3 were assigned by symbolic addition with the programs FAME MAGIC LINK SYMPL.[5] The Fourier map based on these yielded enough information about the location of all carbon, nitrogen, and chlorine atoms for the structure to be solved. Isotropic full-matrix refinement [6] proceeded smoothly to R 0.11. At this stage methylene and benzene hydrogen positions were calculated by assuming tetrahedral or trigonal configuration around the respective carbon atoms. The inclusion of these (B 5.0 Å^2) in the least-squares calculation lowered R to 0.072. Methyl hydrogen atoms were then located from a

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[5] R. B. K. Dewar, A. L. Stone, E. B. Fleisher, personal communication.

[6] W. R. Busing, K. O. Martin, and H. A. Levy, 'A Fortran Crystallographic Least Squares Program,' Report ORNL TM 305, Oak Ridge National Laboratory, Tennessee, 1962; modified by W. C. Hamilton.

difference-Fourier map and were adjusted to give better tetrahedral configurations around C(9) and C(10). The effect of including these additional hydrogen atoms in subsequent anisotropic refinement lowered R to 0.060 and R' to 0.062 [where $R' = \sqrt{\Sigma w(|F_o| - |F_c|)^2}/\sqrt{\Sigma wF_o^2}$]. Refinement was considered complete when shifts in any parameter were $\leqslant 1/3\sigma$. During the last cycles of refinement a weighting scheme was chosen such that for $F < 12.5$ $\sqrt{w} = F_o/12.5$, for $F_o > 30$ $\sqrt{w} = 30/F_o$, and for $12.5 < F_o < 30$ $\sqrt{w} = 1$. This gave similar values for average $w\Delta^2$ values for ranges of F_o. Final atomic coordinates are listed in Table 1, and bond lengths and angles in Table 2. Thermal parameters, thermal ellipsoid amplitudes and orientations, and final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21283 (6 pp., 1 microfiche). Statistically unreliable values of F_o are listed with $F_o = 0$. Figure 1 shows configuration, thermal vibrations, and atom labelling, and Figure 2 the molecular packing.[7]

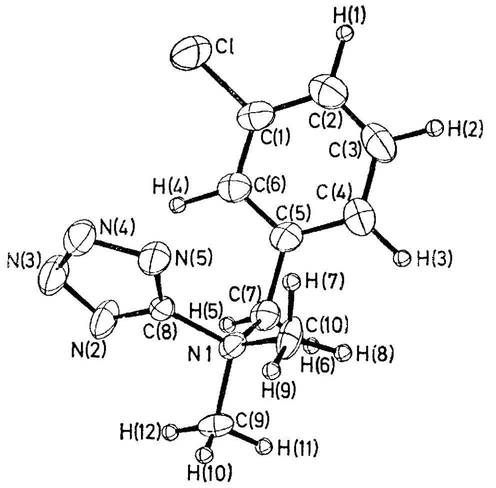

FIGURE 1 Atomic labelling and thermal ellipsoids shown with 35% probability

DISCUSSION

The ylide structure with an overall negative charge on the tetrazole ring and a positively charged quaternary nitrogen as originally suggested by Henry *et al.*[3] is confirmed.

The tetrazole ring is planar, no atom deviating from the mean plane through the five constituent atoms by >0.006 Å. All bond lengths are in excellent agreement with those of similar mono-substituted tetrazoles,[8,9] where various resonance forms were described as contributing to a ring having an overall negative charge. This overall negative charge seems to make no appreciable difference to the bond lengths, within this tetrazole ring and all known tetrazole structures discussed in Part II of this series.[1] N(1)–C(7), N(1)–C(9), N(1)–C(10) distances of (1.536, 1.515, and 1.510 Å) are in good agreement with accepted single N–C bond values. The significantly shorter N(1)–C(8) (1.467 Å) is indicative of partial double-bonding. Bond lengths and angles found in the benzyl grouping are in good agreement with previously found values. Atoms C(2), C(5), C(7), N(1), and C(9) are almost coplanar, deviating by <0.03 Å from the mean plane through them. The mean planes through the tetrazole and benzene rings make angles of 96 and 97° with this plane, and 51° with each other. There are no unusually short intramolecular distances.

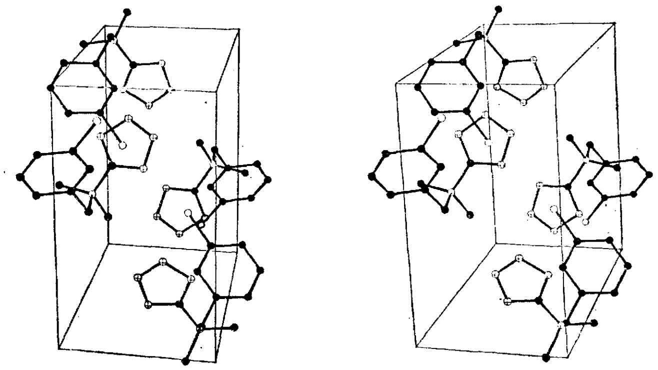

FIGURE 2 Molecular packing. The c axis is horizontal, b axis vertical, a axis away from viewer and rotated 20° about axis c and $-20°$ about axis b. Open circles are chlorine, closed circles carbon, and circle with cross nitrogen

I thank Dr. R. A. Henry for the crystal sample and for useful discussions.

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[7] C. K. Johnson, 'A Thermal Ellipsoid Plot Program for Crystal Structure Illustrations,' ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Tennessee, 1965.

[8] J. H. Bryden, *Acta Cryst.*, 1958, **11**, 31.

[9] G. J. Palenik, *Acta Cryst.*, 1963, **16**, 596.