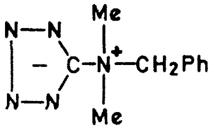
The Crystal Structure of a New 5-Tetrazole Ylide

By GERALD B. ANSELL

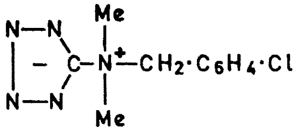
(*Chemistry Division, Research Department, Naval Weapons Center, China Lake, California* 93555)

Summary One of the products formed by the monoalkylation of sodium 5-dimethylaminotetrazole with 3-chlorobenzyl chloride has been positively identified as an ylide.

HENRY *et al.*[1] have described the monobenzylation of sodium 5-dimethylaminotetrazole. They obtained three products. Two are the 1- and 2-benzyl-isomers and the third is a water-soluble compound with a melting point of 205° (as compared with 78° and 95° for the other two). On the basis of n.m.r. and i.r. evidence they suggest the third product is a novel ylide (I).[1] An *X*-ray crystal structure determination of the compound 5-(3-chlorobenzyldimethylammonium) tetrazolate (II) has been carried out to verify their findings.



(I)



(II)

Flattened colourless prisms of the material were found to have cell dimensions $a = 16·272$, $b = 10·842$, $c = 6·407$ Å, $\beta = 98·810°$, space group $P2_1/a$, $D_{\rm m} = 1·32$ g cm^{-3} (measured from a compressed pellet which usually gives a figure up to 10% lower than by flotation),[2] $D_{\rm c} = 1·41$ g cm^{-3} for $Z = 4$.

647 observed reflections were collected using Ni-filtered Cu-K_α radiation on a diffractometer equipped with a scintillation counter. The phases of 74 reflections with *E* values greater than 1·3 were assigned by symbolic addition using the programs—FAME–MAGIC–LINK–SYMPL.[3] The Fourier based on these yielded enough information about the location of all carbon, nitrogen, and chlorine atoms to solve the structure. Isotropic full-matrix least-squares refinement of these atoms proceeded smoothly to $R = 0·11$. At this stage methylene and benzene hydrogen positions were calculated by assuming tetrahedral or trigonal configurations around the respective carbon atoms. The inclusion of these ($B = 5·0$ Å^{-2}) and anisotropic refinement for C, N, and Cl lowered R to 0·072. Methyl hydrogens were then found from a difference Fourier. These were adjusted slightly to give better tetrahedral configuration around C(9) and C(10) (Figure). The effect of adding these 6 hydrogens and further anisotropic refinement of non-hydrogen atoms was to lower R to 0·056. The Figure shows the molecular configuration of the compound and all important bond lengths at $R = 0·056$. Those within the tetrazole ring are in good agreement with similar mono-substituted tetrazoles studied by Bryden[4] and Palenik[5] where various resonance forms were described as contributing to a ring having an overall negative charge. This gives additional confirmation to the ylide structure suggested by Henry *et al.*[1] The $N^+(1)$–C(7), $N^+(1)$–C(9), $N^+(1)$–C(10) bonds of 1·53, 1·53, 1·51 Å are longer than ordinary N–C distances (1·47),[6,7] but several long N^+–C(sp^3) bonds have been reported.[8–10] A 1·47 Å bond was found between the tetrazole carbon [C(8)] and the quaternary nitrogen [N(1)].

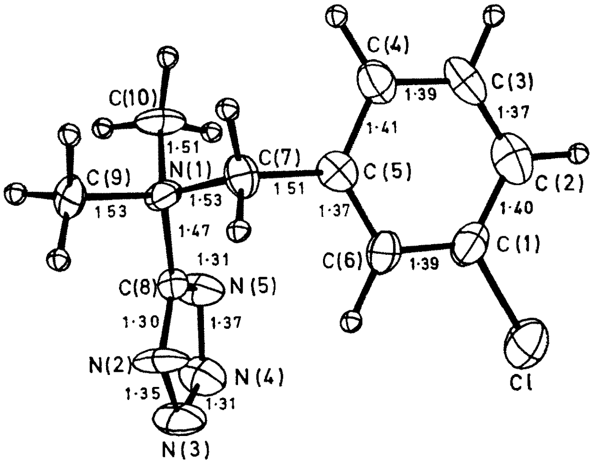


FIGURE. *The molecule as seen by looking down the* c *axis and then rotating −20° about the* a *axis.* $\sigma = 0·01$ Å *for* C(1)–Cl *and* 0·02 Å *for all other bonds involving* C *and* N.

Atoms C(5), C(7), C(9), and N(1) are almost coplanar, each atom deviating less than 0·02 Å from the mean plane through the 4 atoms. It is noteworthy that the best planes through the benzene and tetrazole rings are equally inclined (96·2° and 97·0°) to this plane. The benzene and tetrazole rings have an interplanar angle of 51·5°. The C(6) · · · C(8) distance of 3·17 Å is the shortest C–C contact between the benzene and tetrazole rings. However, the angle C(6)–H[C(6)]–C(8) (98·5°) seems to preclude the possibility of hydrogen bonding with C(8).

I thank Dr. R. A. Henry for the sample of 5-(3-chlorobenzyldimethylammonium) tetrazolate and a preprint of reference 1.

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