Preparation and *X*-Ray Structure of the 8a-Azonia-3,4-diazaphenanthrene Cation

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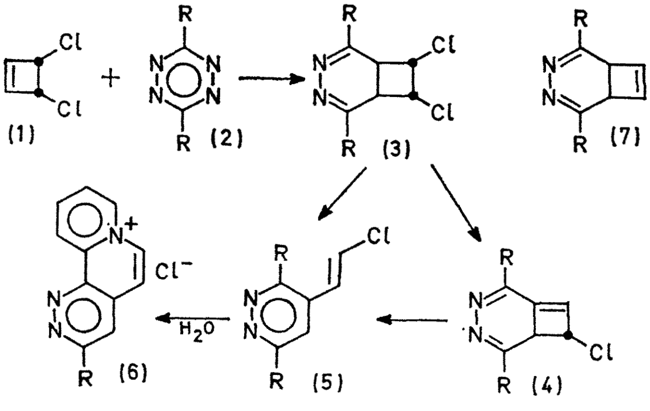
Summary *cis*-3,4-Dichlorocyclobutene reacts with 3,6-di-(2-pyridyl)-*s*-tetrazine in refluxing chlorobenzene to yield a new bridgehead nitrogen ring system, the 8a-azonia-3,4-diazaphenanthrene cation, the structure of which was confirmed by *X*-ray analysis.



R = (2-pyridyl)

THE (4 + 2)π cycloaddition of *cis*-3,4-dichlorocyclobutene (**1**) to 3,6-di(2-pyridyl)-*s*-tetrazine (**2**) (with concomitant elimination of nitrogen) was investigated as a potential synthesis of the 3,4-diazabicyclo[4,2,0]octa-2,4,7-triene (**7**) *via* the dichloro-compound (**3**). In practice, however, the product obtained from this reaction in boiling chlorobenzene was not compound (**3**) but one which exhibited properties typical of a quaternary ammonium salt.† This compound was shown by single-crystal *X*-ray analysis to be 2-(2-pyridyl)-8a-azonia-3,4-diazaphenanthrene chloride monohydrate (**6**) (yield 36%).

Crystals of $C_{16}H_{11}N_4Cl,H_2O$ (from MeOH) are monoclinic;

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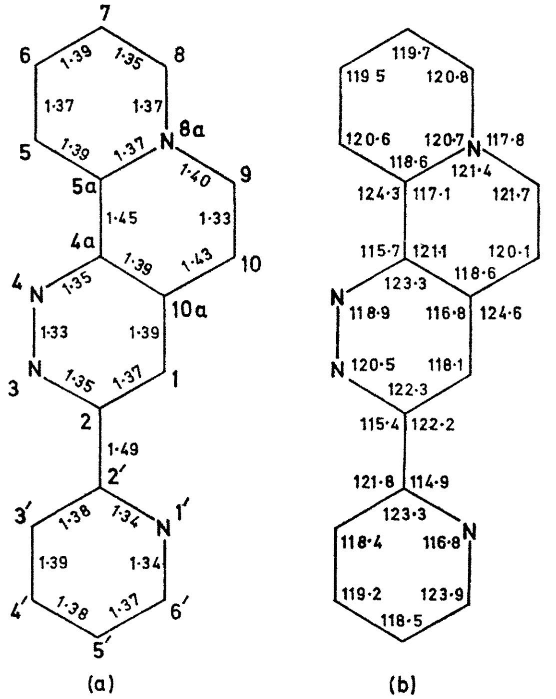
† Satisfactory analytical and spectral data were obtained.

$a = 7{\cdot}052$, $b = 8{\cdot}340$, $c = 24{\cdot}875$ Å, $\beta = 100{\cdot}5°$, space group $P2_1/c$, $Z = 4$. Two crystals, of approximate dimensions $0{\cdot}5 \times 0{\cdot}13 \times 0{\cdot}2$ and $0{\cdot}2 \times 0{\cdot}25 \times 0{\cdot}2$ mm were used to collect data around the *a* and *b* axes on an automatic computer-controlled Supper equi-inclination diffractometer. Intensities of 2590 reflections (1946 statistically significant) were measured using Cu-K_α radiation and converted to structure factors without correcting for absorption ($\mu = 24{\cdot}3$ cm^{-1}). The structure was solved by application of Sayre's equation[1] using a modified version of Long's program[2] followed by Fourier and difference syntheses and refined by full-matrix least-squares. Refinement with anisotropic temperature parameters for chlorine, oxygen, nitrogen, and carbon is in progress, *R* for the 'observed' reflections being 0·062 at the present stage. The hydrogen atoms of the 2-(2-pyridyl)-8a-azonia-3,4-diazaphenanthrene cation, in calculated positions, were included in the structure-factor calculation, but not in the least-squares refinement. Reasonable positions for the hydrogen atoms of the water molecule have been derived from difference maps.

Bond distances and angles of the cation skeleton, which are unlikely to change significantly on completion of the refinement, are given in the Figure. The pyridine ring, planar within experimental error, is almost coplanar with the mean plane through the 8a-azonia-3,4-diazaphenanthrene system, the angle between the two planes being 1·5°. The latter ring system is only approximately planar, individual atoms deviating by up to 0·08 Å from the mean plane, with angles between the planes of the three rings of 1·5—4°.

A possible mechanism for this conversion is outlined in the sequence (3)—(5). Initial formation of the expected adduct (3) may be followed either by 1,4-dehydrochlorination[3] and ring opening to give the vinylpyridazine (5), or a two-step reaction *via* the triene (4). The base-catalysed rearrangement of bromocyclo-octatetraene to β-bromostyrene[4] provides precedent for the conrotatory ring opening of (4) to (5). Nucleophilic addition followed by elimination of the remaining chlorine atom would lead to the observed product 3,6-Diphenyl-*s*-tetrazine did not react with *cis*-3,4-dichlorocyclobutene, even when heated in trichlorobenzene under reflux. This is in accord with the greater reactivity of the more electron-deficient 3,6-di(2-pyridyl)-*s*-tetrazine towards $(4 + 2)\pi$ cycloaddition reactions.



(a) (b)

FIGURE. (a) *Bond distances* (Å) *and* (b) *angles* (°) *in the* 2-(2-*pyridyl*)-8a-*azonia*-3,4-*diazaphenanthrene cation. Current average standard deviations are* 0·007 Å *for distances and* 0·4° *for angles.*

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