X-Ray Study of a New Heterocycle: The Crystal Structure of 1,2-Dibromo-1,2-diphenyl-1,2-dihydroazeto[1,2-*a*]pyridinium chlorate

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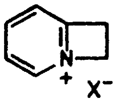
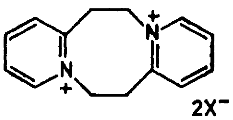
Summary Formation of the hitherto unknown dihydroazeto[1,2-*a*]pyridinium ring system obtained by bromine oxidation of 2-aminoimidazo[1,5-*a*]pyridinium salts is confirmed by single-crystal *X*-ray analysis.

The preparation of 1,2-dihydroazeto[1,2-*a*]pyridinium salts (**1**), by the intramolecular cyclisation of 2-(2-halogenoalkyl)pyridines and by the action of hydrobromic acid on 2-vinylpyridine, has been reported.[1,2] This structural assignment for the products persisted even as late as 1954,[3] but the compounds have since been shown[4] to be 6,7,13,14-tetrahydrodipyrido[1,2-*a*: 1,2-*e*]diazocinium salts (**2**). More recently the tetrasubstituted dihydroazeto-[1,2-*a*]pyridinium salts (**8**)—(**11**) have been reported[5] as the products obtained from bromine oxidation of the respective 2-aminoimidazo[1,5-*a*]pyridinium salts (**3**)—(**6**). Evidence for the assignment of the 6: 4 fused ring structure for the products, based on mechanistic and other considerations,[5] is supported by the present *X*-ray study on the salt (**12**) prepared by bromine oxidation of the *N*-amino-compound (**7**). The last compound was obtained from 1,3-diphenylimidazo[1,5-*a*]pyridine using a general procedure previously described.[5] The most suitable derivative for *X*-ray purposes was the perchlorate salt of (**12**) which recrystallised from methanol–70% perchloric acid (25: 1 v/v) at 60 °C with slow cooling as colourless distorted octahedral crystals, m.p. 204·5 °C (decomp.).

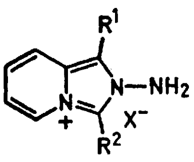
Crystal data: orthorhombic, space group *Fdd*2, a = 12·18(1), b = 17·34(2), c = 18·72(2) Å, D_m = 1·72 g cm^{-3}, D_c = 1·73 g cm^{-3} for Z = 8, μ(Cu-K_α) = 71·97 cm^{-1}. Equi-inclination Weissenberg photographs with Cu-K_α radiation of a-axis layers 0—10 inclusive afforded 1039 reflections which were measured using an OPTRONICS P-1000 microdensitometer,[6] and processed by the SHELX system,[7] which included an absorption correction. The structure was solved by the heavy-atom method. Full-matrix least-squares refinement with anisotropic temperature factors for bromine and the anion atoms gave R as 0·0547.†



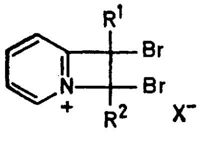
(1)



(2)



(3) R^1 = H, R^2 = H
(4) R^1 = H, R^2 = Ph
(5) R^1 = Ph, R^2 = H
(6) R^1 = H, R^2 = Me
(7) R^1 = Ph, R^2 = Ph



(8) R^1 = Br, R^2 = Br
(9) R^1 = Br, R^2 = Ph
(10) R^1 = Ph, R^2 = Br
(11) R^1 = Br, R^2 = Me
(12) R^1 = Ph, R^2 = Ph

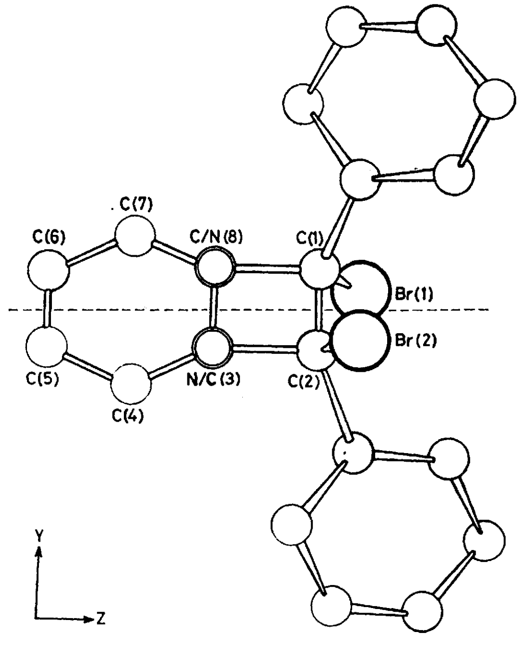


Figure. Molecular structure of the cation of the title compound, viewed along the a-axis.

The molecular structure is shown in the Figure. The molecular cation lies across a two-fold axis, satisfying the requirements of a crystal having 8 molecules of relative molecular mass 515·5 in *Fdd*2 space-group symmetry.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

This results in a disorder of the bridgehead atoms C(8) and N(3), which are doubly labelled in the Figure. All the atoms of the dihydroazeto[1,2-*a*]pyridinium ring system are nearly coplanar, and the angle between their least-squares plane and that of each of the planar phenyls is 113·8°. The phenyl groups lie in the expected *trans* configuration requiring the bromine atoms to be likewise. The four-membered ring is trapezoidally distorted, with C(8)–N(3) as the shortest side, 1·37(2) Å. The other two sides are C(8)–C(1), 1·50(1); C(1)–C(2), 1·59(2) Å and the enclosed angles are N(3)–C(8)–C(1), 93·8(5) and C(8)–C(1)–C(2), 85·5(5)°.

The authors believe this to be the first report of a crystal structure on an azetopyridinium ring system and no directly comparable data have been obtained by computer-assisted literature surveys.

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