# The Crystal and Molecular Structure of a New Heterocycle: 1,2-Dibromo-1,2-diphenyl-1,2-dihydroazeto[1,2-*a*]pyridinium Chlorate

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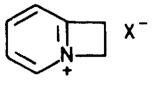
The structure of the title compound, representative of the hitherto unknown dihydroazeto[1,2-*a*]-pyridinium ring system, has been determined by a three-dimensional *X*-ray analysis. Orthorhombic crystals in space group *Fdd*2 have lattice parameters $a$ = 12.18(1), $b$ = 17.34(2), $c$ = 18.72(2) Å for $Z$ = 8. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R$ 0.0547 for 1 039 reflections. The molecular cation lies across a two-fold axis which gives rise to a disorder of the bridgehead atoms. The heterocycle has all its atoms nearly coplanar, with the four-membered ring trapezoidally distorted having the shortest and longest sides 1.37(2) and 1.59(2) Å, respectively.

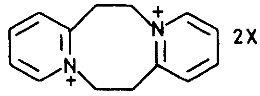
Various early reports [1,2] claim the preparation of 1,2-dihydroazeto[1,2-*a*]pyridinium salts (1) by the intramolecular cyclisation of 2-(2-halogenoalkyl)pyridines and by the action of hydrobromic acid on 2-vinylpyridine. This structural assignment for the products persisted even as late as 1954 [3] 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 dihydroazetopyridinium salts (8)—(12) have been reported [5] as the products of bromine oxidation of the respective 2-aminoimidazo[1,5-*a*]pyridinium salts (3)—(7), the reaction proceeding *via* an amino-nitrene intermediate with loss of nitrogen.

The assignment [5] of the 6 : 4 fused-ring structure to the products in preference to a tricyclic tetrahydrodipyridodiazocinium structure (2) was based partly on the assumption that nitrogen loss from the amino-nitrene with synchronous intramolecular cyclisation as shown was more likely than an intermolecular four-centre reaction following the nitrogen extrusion required for the formation of the tricyclic structure. Further evidence for the proposed structure was obtained by the isolation of phenyl 2-pyridylmethyl ketone following the hydrogenation and basification of (10).

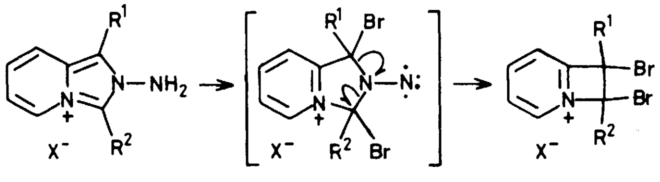
We sought to provide direct evidence for the formation of the 6 : 4 fused ring system in the compounds (9)—(12) and to secure molecular dimensions for the hitherto unknown dihydroazeto[1,2-*a*]pyridinium system. For the purpose of an *X*-ray study it was necessary to reduce the number of bromine atoms in the molecule and the diphenyl derivative (12) was prepared by the bromine oxidation of the corresponding *N*-amino-compound (7). This last compound was itself obtained from 1,3-diphenylimidazo[1,5-*a*]pyridine using a general procedure described elsewhere.[5] The perchlorate salt of (12) proved to be the most satisfactory for the present study, and a preliminary report has been published.[6]



(1)



(2)



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

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

## Experimental

Colourless crystals of the perchlorate salt of (12) obtained by recrystallisation from methanol–70% perchloric acid had m.p. 204.5 °C (Found: C, 44.4; H, 2.9; N, 2.8. $C_{19}H_{14}Br_2ClNO_4$ requires C, 44.3; H, 2.7; N, 2.7%).

*Crystal Data.*—Orthorhombic, $a$ = 12.18(1), $b$ = 17.34(2), $c$ = 18.72(2) Å, $D_m$ = 1.72 g cm$^{-3}$ (by flotation), $D_c$ = 1.73 g cm$^{-3}$, $Z$ = 8, $F(000)$ = 2.032, $\mu$ = 71.97 cm$^{-1}$ for Cu-$K_\alpha$ radiation, $\lambda$ = 1.5418 Å. Space group *Fdd*2. Equi-inclination Weissenberg photographs and the multiple film technique using Cu-$K_\alpha$ radiation on a crystal close to the optimum size (0.3 mm) were used for data collection. The intensities of 1 039 reflections on $a$-axis layers 0—10 inclusive were measured using an OPTRONICS P-1000 microdensitometer [7] and processed by the SHELX system [8] incorporating 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. Finally each of the aromatic hydrogen atoms was positioned on the median line through its bonded carbon atom and in the same plane as this carbon and its two linked neighbours assuming C–H as 1.08 Å.

## Results and Discussion

The final atomic co-ordinates together with their standard deviations are given in Table 1 and the interatomic distances and bond angles calculated from these co-ordinates are collected in Table 3. Structure factors are in Supplementary Publication No. SUP 23511 (6 pp.).† The atomic numbering scheme is shown in Figure 1 and the hydrogen atoms are

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† For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

**Table 1.** Fractional atomic co-ordinates and isotropic temperature factors with their estimated standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ | $10^4U_{iso}$ |
|---|---|---|---|---|
| Br(1) | 0.186 6(1) | −0.519 3(1) | 0.250 0(0) | † |
| C(1) | 0.035 9(9) | −0.538 3(5) | 0.284 6(6) | 390(21) |
| C(6) | 0.037 0(12) | −0.530 4(7) | 0.489 3(8) | 612(29) |
| H(6) | 0.064 2(12) | −0.554 4(7) | 0.539 5(8) | 900 |
| C(7) | 0.077 2(10) | −0.560 9(6) | 0.425 4(7) | 512(25) |
| H(7) | 0.108 7(10) | −0.586 0(6) | 0.474 0(7) | 900 |
| C/N(8) | 0.037 8(8) | −0.529 4(4) | 0.364 2(5) | 374(18) |
| C(11) | −0.007 1(8) | −0.612 5(6) | 0.254 2(6) | 461(24) |
| C(12) | −0.025 2(10) | −0.617 0(6) | 0.182 1(7) | 528(25) |
| H(12) | 0.000 6(10) | −0.570 4(6) | 0.147 8(7) | 900 |
| C(13) | −0.076 5(12) | −0.681 4(9) | 0.153 3(10) | 747(38) |
| H(13) | −0.098 2(12) | −0.682 7(9) | 0.097 4(10) | 900 |
| C(14) | −0.100 0(15) | −0.743 3(9) | 0.196 8(9) | 759(37) |
| H(14) | −0.136 3(15) | −0.794 7(9) | 0.174 2(9) | 900 |
| C(15) | −0.076 6(13) | −0.740 9(9) | 0.268 6(10) | 770(40) |
| H(15) | −0.092 2(13) | −0.790 4(9) | 0.302 1(10) | 900 |
| C(16) | −0.033 0(10) | −0.673 1(6) | 0.298 3(7) | 507(25) |
| H(16) | −0.019 8(10) | −0.668 7(6) | 0.355 2(7) | 900 |
| Cl(1) | 0.0(0) | 0.0(0) | 0.211 6(2) | † |
| O(1) | 0.019 7(17) | 0.060 6(10) | 0.258 2(14) | † |
| O(2) | −0.096 4(16) | 0.003 9(13) | 0.167 5(10) | † |

Temperature factors for hydrogen atoms were not refined.

† Indicates anisotropic temperature factor used. These are given in Table 2.

**Table 2.** Anisotropic temperature factors

| | $10^4U_{11}$ | $10^4U_{22}$ | $10^4U_{33}$ | $10^4U_{23}$ | $10^4U_{13}$ | $10^4U_{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 505(6) | 559(6) | 460(6) | 86(5) | −35(6) | 49(6) |
| Cl(1) | 527(10) | 517(16) | 538(21) | 0 | 0 | −95(16) |
| O(1) | 1 658(98) | 1 200(116) | 2 115(183) | 880(125) | −556(160) | −744(115) |
| O(2) | 1 351(60) | 1 771(116) | 932(93) | −664(99) | 146(95) | 5(106) |

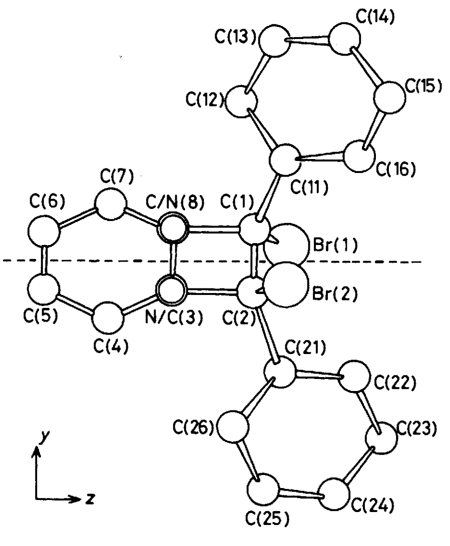

**Figure 1.** Molecular structure of the cation of the title compound viewed along the $x$-axis, showing the atom numbering system used in the analysis

numbered as the atoms to which they are attached. The molecular cation lies across a two-fold axis, satisfying the requirements of a crystal having eight molecules of relative molecular mass 515.5 in *Fdd*2 space-group symmetry. This results in a disorder of the bridgehead atoms C(8) and N(3) which are doubly labelled in Figure 1. All the atoms of the dihydroazeto[1,2-*a*]pyridinium ring system are nearly coplanar (Table

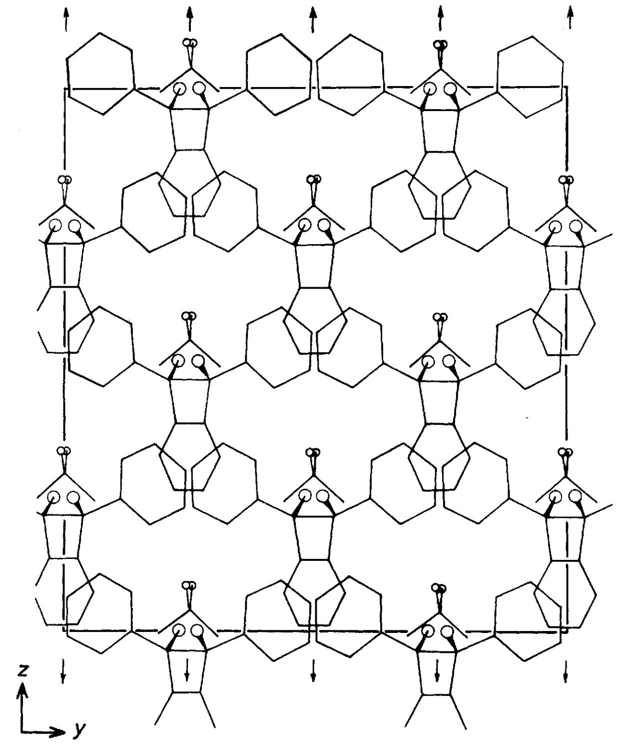

**Figure 2.** The molecular packing viewed along the $x$-axis. Large circles are bromine atoms; small circles are oxygen atoms included to give perspective

**Table 3.** Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonded distances

| | | | |
|---|---|---|---|
| C(1)-Br(1) | 1.975(10) | C(11)-C(12) | 1.370(16) |
| C(1)-C(2) | 1.590(19) | C(11)-C(16) | 1.375(16) |
| C(1)-C/N(8) | 1.498(13) | C(12)-C(13) | 1.388(19) |
| C(1)-C(11) | 1.500(14) | C(13)-C(14) | 1.378(23) |
| C(2)-N/C(3) | 1.498(13) | C(14)-C(15) | 1.375(24) |
| N/C(3)-C(4) | 1.356(15) | C(15)-C(16) | 1.404(19) |
| C(4)-C(5) | 1.398(19) | Cl(1)-O(1) | 1.387(15) |
| C(5)-C(6) | 1.386(26) | Cl(1)-O(2) | 1.437(18) |
| C(6)-C(7) | 1.398(19) | Cl(1)-O(3) | 1.387(15) |
| C(7)-C/N(8) | 1.356(15) | Cl(1)-O(4) | 1.437(18) |

(b) Interbond angles

Oxygen atoms O(1)/O(1A) and O(2)/O(2A) are related by a two-fold axis

| | |
|---|---|
| C(2)-C(1)-C/N(8) | 85.5(0.5) |
| C(1)-C/N(8)-N/C(3) | 93.8(0.5) |
| C(1)-C/N(8)-C(7) | 143.5(0.9) |
| N/C(3)-C/N(8)-C(7) | 122.4(0.6) |
| C(5)-C(6)-C(7) | 121.0(0.7) |
| C(6)-C(7)-C/N(8) | 116.5(1.0) |
| Br(1)-C(1)-C/N(8) | 107.1(0.7) |
| Br(1)-C(1)-C(2) | 111.8(0.8) |
| Br(1)-C(1)-C(11) | 110.0(0.7) |
| C(2)-C(1)-C(11) | 121.6(1.0) |
| C(1)-C(11)-C(12) | 118.7(1.0) |
| C(1)-C(11)-C(16) | 120.5(1.0) |
| C(11)-C(12)-C(13) | 120.1(1.2) |
| C(11)-C(16)-C(15) | 119.3(1.3) |
| C(12)-C(13)-C(14) | 119.4(1.6) |
| C(13)-C(14)-C(15) | 120.6(1.6) |
| C(14)-C(15)-C(16) | 119.5(1.5) |
| C(12)-C(11)-C(16) | 120.7(1.1) |
| O(1)-Cl(1)-O(2) | 117.8(1.4) |
| O(1)-Cl(1)-O(1A) | 102.1(1.6) |
| O(1)-Cl(1)-O(2A) | 104.8(1.0) |
| O(2)-Cl(1)-O(1A) | 104.8(1.0) |
| O(2)-Cl(1)-O(2A) | 109.8(1.6) |
| O(1A)-Cl(1)-O(2A) | 117.8(1.4) |

(c) Intermolecular non-bonded distances

| | | | |
|---|---|---|---|
| Cl · · · Cl | 7.07(1) | C(7) · · · C(14) | 3.55(2) |
| O(1) · · · O(2) | 4.68(2) | C(14) · · · C(14) | 3.66(2) |
| O(2) · · · C(6) | 3.44(2) | O(2) · · · Br | 3.09(1) |
| O(2) · · · C(7) | 3.48(2) | Br · · · Br | 4.59(1) |
| C(7) · · · C(15) | 3.71(2) | | |

4) and the phenyl groups lie in the expected *trans*-configuration requiring the bromine atoms to be likewise. The four-membered ring is trapezoidally distorted with two sides C(1)–C/N(8) and C(2)–N/C(3) equal, 1.50(1) Å, and the other two, C/N(8)–N/C(3), 1.37(2), and C(1)–C(2), 1.59(2) Å. The internal bond angles reflect a high degree of strain with C/N(8)–C(1)–C(2) compressed from the tetrahedral value to 85.5(5)° with the external bond angles correspondingly expanded to 121.6(10)° for C(2)–C(1)–C(11). The bridgehead atoms whose bonds are all in the same plane have angles ranging from 93.8(5)° for C(1)–C/N(8)–N/C(8) to 143.5(9)° for C(1)–C/N(8)–C(7), causing the pyridinium ring to become unsymmetrical although its bond lengths do not differ significantly from the mean value, 1.38(1) Å. We believe this to be the first report of a crystal structure on a azetopyridinium ring system and therefore no directly comparable data are available.

**Table 4.** Least-squares planes given in the form $lX' + mY' + nZ' = d$ where $X'$, $Y'$, and $Z'$ are co-ordinates in Å. Deviations (Å) of atoms from the planes are also given

Plane 1 Dihydroazeto[1,2-*a*]pyridinium ring system

$$-0.7483X - 0.6634Y + 0.0032Z = 5.726$$

X(1) 0.003, X′(1) 0.010, C(7) −0.003, C′(7) 0.003, C(6) 0.009, C′(6) −0.016, C(1) 0.122, C′(1) 0.105

Only the atoms of the six-membered ring were included in the calculation of the plane equation.

Plane 2 Phenyl ring

$$-0.9110X - 0.3817Y - 0.1564Z = -3.239$$

C(11) 0.008, C(12) −0.032, C(13) 0.026, C(14) 0.005, C(15) −0.029, C(16) 0.023

The chlorine atoms of the perchlorate anions lie on two-fold axes in planes [100], [200], and [400], with chlorine atom separations of 7.07 Å. The closest approach of oxygen atoms on neighbouring anions, O(1) of one to O(2) of another, is 4.68 Å. The heterocyclic cation lies across the two-fold axis and its bromine atoms lie in planes parallel to the [001] plane at $z = 0, \frac{1}{4}$, and $\frac{1}{2}$. The closest Br · · · Br approach is 4.59 Å, and there is a relatively short contact of 3.09 Å for Br · · · O(2). The closest contact between the anion and the cation on the same two-fold axis is O(2) · · · C(6), 3.44 Å, although an anion on a neighbouring axis also has a close contact, C(7) · · · O(2), 3.48 Å. Contacts between carbon atoms of the cations are made by C(7) · · · C(15) and C(7) · · · C(14), having values 3.71 and 3.55 Å, respectively. Figure 2 suggests possible short contacts between phenyl groups of neighbouring cations but the C(14) · · · C(14) distance is 3.66 Å, with a large contribution from the $x$ component.

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