

of 0.003 Å. The dihedral angle between the planes is 1.1°. Similar bends have been found for TTF molecules and are listed in Table 2 for the compounds compared there.

There are no intermolecular contacts less than the sums of the van der Waals radii. A stereoscopic view (Johnson, 1971) of the packing is given in Fig. 2. The molecules pack on edge in sheets [the (100) mirror planes]. The plane-to-plane separation is 3.88 Å but the molecular overlap is minimal, and the prominent feature appears to be that each thione S is surrounded by three C(2)=C(2') bonds at 3.44, 3.90, and 5.20 Å.

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Structure of 3-Bromopyridinium Perchlorate Hemihydrate

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Abstract. C₅H₅BrN⁺.ClO₄⁻.½H₂O, monoclinic, *P*2₁/*n* (*P*2₁/*c* in standard setting), *a* = 12.181 (2), *b* = 8.085 (3), *c* = 18.973 (2) Å, β = 103.66 (1)°, *V* = 1816.15 Å³, *Z* = 8, *D_m* (flotation) = 1.89, *D_c* = 1.94 Mg m⁻³. The structure was solved using the heavy-atom technique and refined by the full-matrix least-squares method to a final *R*(*F*) value of 5.7%. The 3-bromopyridinium cations are linked in pairs by means of N–H···O hydrogen bonds to a bridging H₂O molecule [N···O distances are 2.89 (2) and 2.80 (2) Å].

Introduction. The 3-bromopyridine (BrPy)–perchloric acid system has already been investigated by DTA, IR spectroscopy and X-ray diffraction (Belin & Pichvai, 1978). Both 1:1 and 2:1 adducts have been charac-

terized; the latter displays a homoconjugated cation (BrPy.H.PyBr)⁺ with non-symmetrical NHN hydrogen bonding.

The present research was initiated to determine whether the 3-bromopyridine–perchloric acid–water ternary system would also lead to bromopyridinium homoconjugated cations or to heterocations (BrPy.H.OH₂)⁺ including water molecules. So far no evidence of a higher hydrate has been found in the system.

The title compound was synthesized from BrPy and commercial (≈ 70%) perchloric acid and then recrystallized in a water–acetone solution to yield large, flat, plate-shaped crystals.

A crystal of dimensions 0.45 × 0.20 × 0.40 mm was selected under polarizing microscope and mounted

in a 0.5 mm diameter Lindemann-glass capillary using silicon grease. Preliminary Weissenberg photographs showed the crystal to belong to the monoclinic system. Lattice constants were determined by least-squares refinement of the angular positions of 25 reflections collected and centered on an Enraf-Nonius CAD-4 four-circle automatic diffractometer. Integrated diffraction intensities were collected at room temperature (298 K) in the range $0^\circ < 2\theta < 50^\circ$ within the two octants $\bar{h}, \bar{k}, \bar{l}$ and h, k, l using graphite-monochromatized Mo $K\alpha$ radiation. (The profile analysis of a few low-angle reflections indicated that an $\omega\text{-}\frac{4}{3}\theta$ scan method was the most appropriate for data collection.) During data collection the intensities of three standard reflections were checked after every 35 reflections and no substantial loss in intensity was observed. The data were corrected for background, Lorentz-polarization and absorption effects. The final data set consisted of 2866 independent reflections of which 1318 with $I > 3\sigma(I)$ were used in the refinement.

The structure was solved in the centrosymmetric space group $P2_1/n$ using conventional Patterson, Fourier and least-squares refinement techniques. Scattering factors for neutral atoms and corrections for anomalous-dispersion effects for Br and Cl atoms were taken from *International Tables for X-ray Crystallography* (1974). The Br and Cl atoms were readily located from the Patterson map. An electron density synthesis based on phases calculated from their positions revealed all the non-hydrogen atoms of the ring, as well as the perchlorate O atoms. Refinement of these positions and isotropic temperature parameters by block-diagonal least squares gave a conventional R factor ($\sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.17.

At this stage an electron density difference map indicated the presence of a single residual peak of $5 \text{ e } \text{\AA}^{-3}$ which was attributed to the O atom of the water molecule. Refinements were conducted using the full-matrix least-squares technique minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_{\text{count}}^2(F)^2/4(F)^2 + (0.01F)^2$ with anisotropic thermal parameters for all atoms ($R = 0.066$). A subsequent Fourier difference synthesis clearly indicated the presence of all H atoms except those of the water molecule. These H atoms were refined with isotropic thermal parameters of 5 \AA^2 . The positions of the water H atoms were difficult to calculate reliably so they were deleted from the model. The final agreement factors were $R(F) = 0.055$ and $R_w(F) = 0.057$. The goodness-of-fit defined as $[\sum w(|F_o| - |F_c|)^2 / (N - M)]^{1/2}$, where N is the number of observations (1318) and M the number of parameters varied (262), is 1.33.

In the final cycle of refinement, the shift/e.s.d. values in the Br and Cl parameters were ≤ 0.08 in positions and ≤ 0.1 in temperature factors, while the changes in light atoms were ≤ 0.2 ; the final electron density difference map was flat except for a very few areas with

Table 1. *Final positional parameters*

| | x | y | z |
|-------|------------|-------------|-------------|
| BrA | 0.1940 (1) | 0.3646 (2) | 0.27649 (8) |
| BrB | 0.4836 (1) | 0.3083 (2) | 0.58106 (8) |
| ClA | 0.8777 (3) | 0.4496 (5) | 0.2985 (2) |
| ClB | 0.2814 (3) | 0.3885 (4) | 0.0506 (2) |
| O(1)B | 0.3242 (8) | 0.5366 (11) | 0.0865 (5) |
| O(2)B | 0.169 (1) | 0.440 (2) | 0.0196 (8) |
| O(3)B | 0.322 (2) | 0.346 (2) | 0.9966 (9) |
| O(4)B | 0.266 (1) | 0.263 (1) | 0.0972 (6) |
| O(1)A | 0.8652 (8) | 0.356 (1) | 0.3590 (5) |
| O(2)A | 0.9263 (8) | 0.357 (1) | 0.2510 (5) |
| O(3)A | 0.7716 (8) | 0.508 (2) | 0.2605 (6) |
| O(4)A | 0.9517 (9) | 0.582 (1) | 0.3244 (5) |
| OW | 0.5589 (8) | 0.515 (2) | 0.1437 (8) |
| C(2)A | 0.412 (1) | 0.400 (2) | 0.2566 (6) |
| C(3)A | 0.3517 (9) | 0.329 (2) | 0.2996 (7) |
| C(4)A | 0.398 (1) | 0.231 (2) | 0.3582 (7) |
| C(5)A | 0.512 (2) | 0.209 (2) | 0.3731 (7) |
| C(6)A | 0.579 (1) | 0.279 (2) | 0.3342 (9) |
| NA | 0.526 (1) | 0.375 (2) | 0.2775 (7) |
| C(2)B | 0.263 (1) | 0.224 (2) | 0.5899 (6) |
| C(3)B | 0.3214 (9) | 0.321 (2) | 0.5534 (6) |
| C(4)B | 0.270 (1) | 0.423 (1) | 0.4966 (7) |
| C(5)B | 0.153 (1) | 0.417 (2) | 0.4755 (7) |
| C(6)B | 0.094 (1) | 0.316 (2) | 0.5102 (8) |
| NB | 0.149 (1) | 0.222 (1) | 0.5660 (7) |
| H(1)A | 0.537 (13) | 0.398 (20) | 0.242 (7) |
| H(2)A | 0.380 (9) | 0.497 (15) | 0.217 (6) |
| H(4)A | 0.340 (9) | 0.169 (14) | 0.392 (6) |
| H(5)A | 0.540 (11) | 0.159 (17) | 0.408 (6) |
| H(6)A | 0.672 (10) | 0.286 (15) | 0.347 (6) |
| H(1)B | 0.133 (12) | 0.153 (18) | 0.588 (8) |
| H(2)B | 0.298 (9) | 0.139 (14) | 0.640 (6) |
| H(4)B | 0.314 (8) | 0.510 (15) | 0.458 (6) |
| H(5)B | 0.103 (9) | 0.483 (15) | 0.433 (6) |
| H(6)B | 0.017 (10) | 0.289 (15) | 0.510 (7) |

a background $\leq 0.7 \text{ e } \text{\AA}^{-3}$ around the perchlorate O atoms (see below).

The crystallographic programs used were *DRF* (a modification of the Zalkin Fourier program), *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinements, and *ORFFE* (Busing, Martin & Levy, 1964) for molecular geometry and error functions, and *ORTEP II* (Johnson, 1971) as the thermal-ellipsoid program for molecular plots.

Discussion. Final atomic parameters with their estimated standard deviations are listed in Table 1.*

Bond distances and angles for the two independent 3-bromopyridinium cations are given in Fig. 1. Corresponding C-N, C-C and C-Br distances in the two cations are not significantly different (within a 3σ limit). The C-H bond lengths average 1.07 (6) and N-H, 0.75 (10) Å.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34809 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

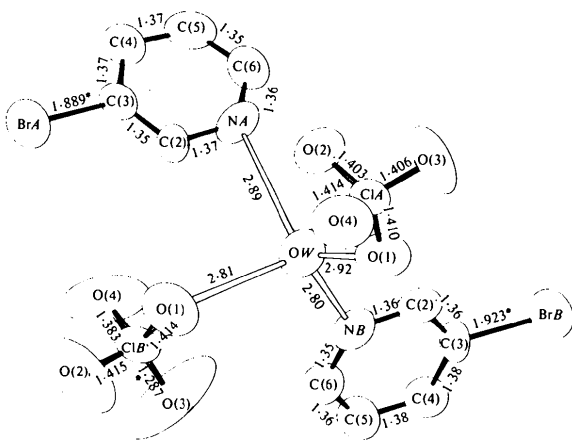


Fig. 1. Environment of a water molecule viewed along c . Interatomic distances are in Å; mean standard deviations are 0.02 Å for C–C and C–N, 0.011 Å for C–Br and 0.009 Å for Cl–O bond lengths. Distances on the figure have not been corrected for thermal motion; corrected values are 1.912 for C(3)–BrA, 1.938 for C(3)–BrB and 1.480 Å for ClB–O(3). Atomic positions correspond to x, y, z for OW, ring A and perchlorate B, and to the symmetry positions $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ for ring B and $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ for perchlorate A.

The mean planes of the C atoms in the pyridine rings are described by the equations $0.2789X - 6.5167Y - 11.0063Z = -5.3339$ for ring A and $2.5614X - 5.9938Y - 12.6921Z = -8.1407$ for ring B. The Br atoms are significantly out of the planes of the pyridine rings by 0.157 (1) Å for BrB and 0.032 (1) Å for BrA.

There are two non-equivalent nearly linear (168°) hydrogen bonds between the pyridine rings and the water molecule: $NA \cdots OW = 2.89$ (2) and $NB \cdots OW = 2.80$ (2) Å; it should be noted that another oxygen contact $NA \cdots O(4)A^i = 3.110$ (18) Å, with (i) = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$, does not correspond to a hydrogen bond

since the angle $NA-H(1)A \cdots O(4)A^i$ is 102° , and $H(1)A \cdots O(4)A^i = 2.87$ Å.

The water achieves its tetrahedral environment with the perchlorate oxygens O(1)A and O(1)B through hydrogen bonding; there is also another contact, $OW \cdots O(3)A = 2.986$ (14) Å. The dihedral angle between the two pyridine rings in the environment of the water molecule is 77.6° .

The perchlorate anions exhibit the expected tetrahedral geometry. However perchlorate B displays a feature often found in ClO_4^- ions: large vibrational thermal motion or orientational disorder. It is of interest that O(1)B, which is involved in hydrogen bonding with the water molecule, has the smallest temperature factor. The three highest residual electron density peaks detected in the final difference Fourier map together with O(1)B form a tetrahedral environment around ClB and show a slight amount of orientational disorder (10%) of perchlorate B around the ClB–O(1)B axis.

The atomic coordinates for the predominant orientation have been refined and are given in Table 1. The second orientation was judged not to be worth subsequent refinement.

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Structure de l'Acide Dibenzylpyruvique

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(Reçu le 7 février 1979, accepté le 12 octobre 1979)

Abstract. $C_{17}H_{16}O_3$, $M_r = 268.3$, monoclinic, $P2_1/c$, $a = 9.199$ (3), $b = 6.097$ (2), $c = 26.69$ (1) Å, $\beta = 100.20$ (5) $^\circ$, $Z = 4$, $V = 1479$ Å³, $d_m = 1.12$ (4), $d_x = 1.16$ Mg m⁻³. The structure was refined to $R = 0.047$ with 2185 reflexions measured at room temperature with an automatic diffractometer. The molecules form

centrosymmetric dimers by hydrogen bonding between carboxylic groups.

Introduction. Les α céto-acides $R-CO-COOH$ participent au métabolisme des amino-acides et des glucides. Ceci explique l'intérêt que présentent ces © 1980 International Union of Crystallography