Crystal and Molecular Structure of Bis(quinoline)bromine Perchlorate

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The crystal structure of the title compound has been determined by single-crystal *X*-ray methods (2 739 reflections) and refined to *R* 0.075 by use of rigid-body methods. Crystals are monoclinic, space-group *Ca* [non-standard] with $a = 17.061(1)$, $b = 30.803(2)$, $c = 6.837(1)$ Å, $\gamma = 90.18(1)°$, $Z = 8$. The principal features are the cations. Each of two independent ions has a Br^+ ion co-ordinated linearly by two quinoline molecules with Br–N 2.10—2.18 Å. The coplanar quinoline molecules are related by approximate centres of symmetry at Br.

THE ability to form stable cations when co-ordinated is one of the most unusual aspects of the chemistry of iodine and to a lesser extent of bromine and chlorine. The structures of only two such species have previously been determined, both with iodine as central atom, containing the $[(\text{pyridine})_2I]^+$ and the $[(\text{thiourea})_2I]^+$ ions.[1,2] We report the structure of the first bromine-containing cation to be examined, bis(quinoline)bromine perchlorate, $[(\text{qu})_2Br][ClO_4]$.

EXPERIMENTAL

The preparation, by the reaction of bromine with a solution of silver perchlorate and quinoline in chloroform, produces monoclinic and triclinic crystal forms. Only the first has been investigated in detail.

Crystal Data.—$BrC_{18}H_{14}N_2ClO_4$, $M = 317.4$, Monoclinic, $a = 17.629(1)$, $b = 17.606(1)$, $c = 6.837(1)$ Å, $\gamma = 122.28(1)°$ for a primitive cell; a *C*-centred, pseudo-orthorhombic cell was found more convenient, with $a = 17.061(1)$, $b = 30.803(2)$, $c = 6.837(1)$ Å, $\gamma = 90.18(1)°$. $U = 3\,592.5$ Å^3, $Z = 8$, $D_c = 1.17$, $F(000) = 1\,760$. $\mu(\text{Cu-}K_\alpha) = 45.6$ cm^{-1}.

All further data refer to the pseudo-orthorhombic cell. The crystal habit is tabular, developed along *a* and *b* and, because of the pseudosymmetry, twinning is common. The extinctions $00l$ absent when $l \neq 2n$, $hk0$ absent when $h \neq 2n$ (and $k \neq 2n$) appeared to indicate space group $C2_1/a$, with one molecule as the asymmetric unit, but the structure determination showed the correct space group to be *Ca*, with two independent molecules in the asymmetric unit. The glide plane was placed at $z = \frac{1}{4}$ to permit comparison of $C2_1/a$ and *Ca*; in the latter space group the symmetry-equivalent positions are then $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0) + [x, y, z]$, $[\frac{1}{2} + x, y, \frac{1}{2} - z]$.

[1] O. Hassel and H. Hope, *Acta Chem. Scand.*, 1961, **15**, 407.

[2] G. H.-Y. Lin and H. Hope, *Acta Cryst.*, 1972, **B28**, 643.

The cell constants of the triclinic form are: $a = 8.39$, $b = 8.34$, $c = 15.29$ Å, $\alpha = 102.8$, $\beta = 98.2$, $\gamma = 114.20°$, $U = 789$ Å^3, $Z = 2$, $D_c = 1.34$.

Originally, data were collected by Weissenberg photographic methods with visual estimation of intensities (1 183 reflections),[3] and were used for structure solution. A more extensive data set was collected later with a Picker FACS 1 four-circle diffractometer (Cu-K_α radiation, $\lambda = 1.5418$ Å, graphite monochromator, $2\theta_{max.}$ 120°). Because of crystal decomposition, three crystals were used, changed after each had decomposed by *ca.* 5% to minimise the anisotropy of decomposition. The data were rescaled (linearly with time), corrected for Lorentz and polarisation factors and for absorption (by integration on a linear grid). 2 739 reflections were considered observed having $I/\sigma(I) > 3.0$. Cell constants were determined by least-squares fitting of the reflecting positions of 12 reflections on the diffractometer.

TABLE 1

Atomic co-ordinates ($\times 10^4$), and anisotropic *($\times 10^3$) and isotropic ($\times 10$) temperature factors, with standard deviations in parentheses

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Br(1)	88	−1 245	7 308(4)	4.76(11)	0.81(2)	25.77(60)	0.00(20)	−1.40(50)	−0.68(8)
Br(2)	245.3(9)	1 264.9(4)	2 692(3)	5.36(13)	0.93(3)	20.89(51)	0.56(20)	−1.79(45)	−0.33(9)
Cl(1)	2 571(3)	1 300(2)	6 461(11)	3.04(17)	1.16(7)	56.9(24)	−3.6(7)	−2.9(13)	−1.1(2)
Cl(2)	2 733(4)	3 739(2)	3 635(10)	4.50(23)	0.85(5)	55.8(22)	3.0(6)	0.5(14)	−0.2(2)
O(11)	2 897(10)	1 528(5)	8 085(22)	21(2)	5.5(6)	102(13)	−24(5)	−54(8)	12(2)
O(12)	3 185(8)	1 173(5)	5 171(23)	9(1)	4.8(4)	91(10)	14(4)	17(6)	1(1)
O(13)	2 038(9)	1 576(5)	5 450(22)	15(2)	3.7(4)	78(9)	−11(3)	−39(7)	6(1)
O(14)	2 166(9)	925(4)	7 144(28)	11(1)	2.0(2)	117(16)	−11(3)	26(6)	−7(1)
O(21)	2 193(9)	3 977(5)	4 803(20)	10(1)	2.9(3)	47(6)	3(2)	−2(4)	5(1)
O(22)	3 070(9)	3 401(5)	4 778(20)	12(1)	2.6(3)	95(9)	16(3)	30(5)	7(1)
O(23)	3 336(7)	4 023(5)	2 959(28)	14(1)	5.4(6)	106(13)	20(4)	−20(6)	−10(2)
O(24)	2 332(10)	3 556(5)	2 002(22)	15(3)	5.8(6)	101(13)	−26(4)	−31(10)	−7(2)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
N(11)	5 754(4)	3 188(2)	6 963(15)	45(3)	N(31)	−4 097(4)	−4 307(2)	−7 563(15)	38(3)
C(11)	6 528(4)	3 230(3)	7 008(15)	45(3)	C(31)	−3 329(5)	−4 249(3)	−7 746(15)	53(3)
C(12)	7 001(3)	2 866(3)	7 037(18)	61(4)	C(32)	−2 835(4)	−4 602(3)	−7 891(17)	72(4)
C(13)	6 663(3)	2 463(3)	7 018(19)	58(4)	C(33)	−3 144(4)	−5 011(3)	−7 844(18)	57(4)
C(14)	5 841(3)	2 416(2)	6 969(13)	39(3)	C(34)	−3 958(4)	−5 076(2)	−7 650(12)	50(3)
C(15)	5 378(3)	2 795(2)	6 941(11)	41(4)	C(35)	−4 444(3)	−4 707(2)	−7 506(11)	49(4)
C(16)	5 451(5)	2 011(2)	6 947(19)	68(5)	C(36)	−4 319(6)	−5 489(2)	−7 590(19)	73(6)
C(17)	4 636(5)	2 981(2)	6 898(18)	66(4)	C(37)	−5 128(6)	−5 537(3)	−7 360(20)	69(5)
C(18)	4 186(3)	2 362(3)	6 871(18)	50(3)	C(38)	−5 601(4)	−5 166(4)	−7 255(20)	70(6)
C(19)	4 536(3)	2 765(3)	6 891(17)	46(3)	C(39)	−5 280(3)	−4 756(3)	−7 306(19)	53(4)
H(11)	6 783(6)	3 549(3)	7 023(20)	60	H(31)	−3 097(6)	−3 933(3)	−7 782(21)	60
H(12)	7 613(3)	2 899(4)	7 073(24)	60	H(32)	−2 228(4)	−4 555(4)	−8 035(24)	60
H(13)	7 019(4)	2 186(3)	7 039(28)	60	H(33)	−2 770(5)	−5 281(3)	−7 953(27)	60
H(16)	5 784(6)	1 725(2)	6 967(27)	60	H(36)	−3 969(7)	−5 768(2)	−7 694(27)	60
H(17)	4 360(6)	1 676(3)	6 882(23)	60	H(37)	−5 382(8)	−5 848(3)	−7 355(26)	60
H(18)	3 572(4)	2 340(4)	6 835(24)	60	H(38)	−6 211(5)	−5 202(5)	−7 109(27)	60
H(19)	4 193(4)	3 047(3)	6 871(25)	60	H(39)	−5 641(4)	−4 481(4)	−7 199(27)	60
N(21)	−584(4)	−654(2)	−2 149(15)	58(4)	N(41)	−5 387(5)	−3 139(2)	−6 967(15)	41(3)
C(21)	−1 340(5)	−726(2)	−1 814(16)	58(4)	C(41)	−6 155(5)	−3 212(3)	−6 927(16)	65(5)
C(22)	−1 849(4)	−381(3)	−1 584(16)	58(3)	C(42)	−6 673(4)	−2 868(3)	−6 878(18)	58(4)
C(23)	−1 566(3)	337(3)	−1 703(15)	59(4)	C(43)	−6 387(3)	−2 453(3)	−6 872(18)	63(4)
C(24)	−764(3)	112(2)	−2 058(11)	53(4)	C(44)	−5 574(3)	−2 373(2)	−6 915(12)	53(4)
C(25)	−263(3)	−249(2)	−2 285(10)	36(3)	C(45)	−5 063(3)	−2 733(2)	−6 964(11)	44(4)
C(26)	−429(5)	531(2)	−2 200(16)	46(3)	C(46)	−5 236(4)	−1 954(2)	−6 912(15)	42(3)
C(27)	368(5)	592(2)	−2 552(17)	58(5)	C(47)	−4 427(5)	−1 892(2)	−6 955(14)	42(3)
C(28)	856(4)	229(3)	−2 774(16)	49(4)	C(48)	−3 929(3)	−2 254(3)	−7 003(16)	50(3)
C(29)	561(3)	−186(3)	−2 649(16)	51(4)	C(49)	−4 227(3)	−2 670(2)	−7 009(16)	43(3)
H(21)	−1 553(6)	−1 045(3)	−1 725(21)	60	H(41)	−6 369(6)	−3 532(3)	−6 932(20)	60
H(22)	−2 447(4)	−437(4)	−1 319(21)	60	H(42)	−7 280(4)	−2 925(4)	−6 846(24)	60
H(23)	−1 950(4)	297(3)	−1 529(22)	60	H(43)	−6 779(4)	−2 191(3)	−6 835(26)	60
H(26)	−791(6)	804(2)	−2 035(23)	60	H(46)	−5 605(6)	−1 682(2)	−6 875(23)	60
H(27)	602(6)	907(3)	−2 615(22)	60	H(47)	−4 191(6)	−1 567(2)	−6 952(19)	60
H(28)	1 457(4)	275(4)	−3 040(22)	60	H(48)	−3 320(4)	−2 207(4)	−7 036(22)	60
H(29)	932(4)	−455(3)	−2 818(22)	60	H(49)	−3 849(4)	−2 938(3)	−7 046(24)	60

* In the form exp $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{23}kl + 2\beta_{13}hl + 2\beta_{12}hk)\}$.

Structure Determination.—A sharpened Patterson synthesis shows Br $\cdots$ Br vectors and a clear image of two quinoline molecules in a plane (perpendicular to c) around each Br $\cdots$ Br vector. It appeared to be consistent with space group $C2_1/a$ with one independent bromine atom close to 0.12,0.25,0, but exhaustive attempts to refine the bromine and ring atoms failed to reduce $R <$ *ca.* 0.35.

The existence of the second modification of the compound suggested an alternative approach. We have frequently observed that when two modifications are found, one is centrosymmetric and the other not. Therefore, assuming that the triclinic form has space group $P\bar{1}$, noncentrosymmetric space groups were considered for the monoclinic form. Of the systematic absences, that associated with the screw axis could most easily arise by accident, and so space group *Ca* was examined. This idea received some support from further examination of the Patterson synthesis. The Br $\cdots$ Br vector at $0,0,\frac{1}{2}$ was elongated, and the Br $\cdots$ Cl

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[3] R. S. Nyholm, P. Pauling, G. B. Robertson, and J. Dollimore, University College London, Final Technical Report 1, 1963.

vectors were very diffuse, both facts suggesting that they consisted of overlapped vectors. The independent bromine atoms must still be related approximately as x, y, z and $-x$, $-y$, z with the main deviation in x ($+0.01$). Two cycles of least-squares refinement with the bromine atoms shifted off the pseudocentre by this amount, and including the chlorine atoms, gave R 0.28.

The light atoms were then located by Fourier syntheses. Least-squares refinement proved very slow to converge (with both data sets) and the final results had high standard deviations on atomic positions. This was almost certainly due to a combination of the pseudosymmetry with high thermal motion of the perchlorate groups. To avoid this, for the final refinement, rigid bodies were used for both perchlorate and quinoline groups, with anisotropic temperature factors for bromine, chlorine, and oxygen. The weighting scheme $w = 1$ for $F < 150$, $w = (150/F)^2$ for $F > 150$ was used and was shown to be satisfactory by an analysis of deviations. This gave a final R of 0.075, identical to that in the unconstrained refinement, and the standard deviations were improved. Before the final refinement, to include the effect of anomalous dispersion, test refinements were made to check the handedness of the three crystals. This revealed that crystals (2) and (3) were of opposite hand to crystal (1), and all their values were therefore replaced by $\bar{h}\bar{k}\bar{l}$. Final refinement was with the program BAYLS, a least-squares program developed by N. A. Bailey and converted to FORTRAN (by N. W. A.). A variety of programs was used at earlier stages. Final atomic co-ordinates and temperature factors are in Table 1.

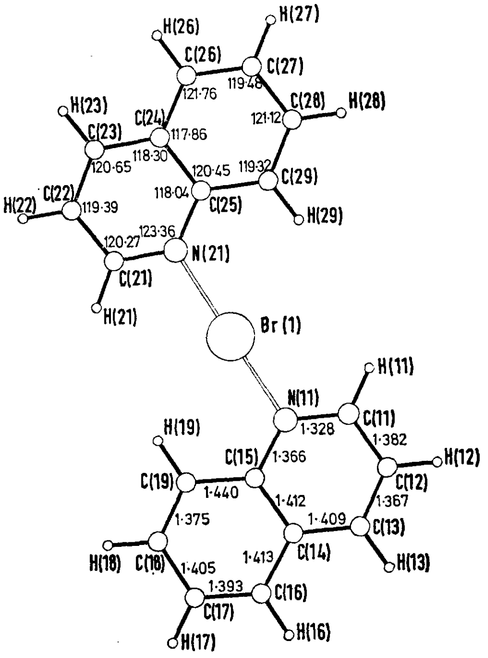

FIGURE 1 One cation, viewed normal to the ring planes. Bond lengths and angles shown for the quinoline molecules were those used to specify them as rigid bodies; in addition they were taken as planar, with C–H 1.05 Å and each C–H bond bisecting the corresponding C–C–N or C–C–C angle. Br(2) is similarly linked to the molecules, whose atoms have 3 and 4 as the first digits of their numbers

For the group atoms the positional standard deviations were calculated from the errors in the six group parameters taking into account their correlations with each other. They are thus valid at the normal level of approximation for the calculations of bond parameters involving atoms not in the same group. Figure 1 gives the atomic numbering, and the bond lengths and angles used to define the rigid quinoline groups. These were taken from the quinolinium ion in quinolinium perchlorate, the only available comparable structure.[4] This should be a reasonably good model, only exchanging $N \rightarrow H^+$ for $N \rightarrow Br^+$, and certainly accurate to within the errors of the unconstrained refinement. For the perchlorate ions, the Cl–O distance was taken as 1.425 Å, allowing for some rotational shrinkage;[5] Cl(1) is linked to O(11)—O(14) and Cl(2) to O(21)—O(24). Table 2 lists independent bond lengths and angles, and Table 3 gives information on molecular planes. Final structure factors are listed in Supplementary Publication No. SUP 21500 (21 pp., 1 microfiche).* Scattering factors were from ref. 6.

TABLE 2

Independent distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances			
Br(1)–N(11)	2.100(6)	Br(2)–N(31)	2.099(7)
Br(1)–N(21)	2.185(7)	Br(2)–N(41)	2.145(7)
(*b*) Angles			
N(11)–Br(1)–N(21)	176.6(4)	N(31)–Br(2)–N(41)	177.5(3)
C(11)–N(11)–Br(1)	117.2(5)	C(31)–N(31)–Br(2)	115.0(5)
C(21)–N(21)–Br(1)	113.8(5)	C(41)–N(41)–Br(2)	110.9(5)

TABLE 3

Equations of mean planes in orthogonal (Å) co-ordinates with axes $X = a$, $Y = b$, Z perpendicular, with deviations (Å) of the bromine atoms in square brackets

Plane (1): Quinoline (1)

$$-0.0237X + 0.0002Y + 0.9997Z = 4.50$$

[Br(1) 0.26]

Plane (2): Quinoline (2)

$$0.1749X - 0.0027Y + 0.9846Z = 6.56$$

[Br(1) 0.16]

Plane (3): Quinoline (3)

$$0.0971X - 0.0147Y + 0.9951Z = 1.77$$

[Br(2) 0.04]

Plane (4): Quinoline (4)

$$0.0231X - 0.0120Y + 0.9997Z = 1.98$$

[Br(2) 0.19]

Angles (°) between planes: (2)–(1) 11.4, (4)–(3) 4.2

RESULTS AND DISCUSSION

The structure determination confirms the expected ionic composition. There are two independent $[(qu)_2Br]^+$ ions which are almost identical (Figure 1). Each has a linear N–Br–N arrangement with the two almost coplanar quinoline groups related by an approximate centre of symmetry at the bromine atom. The mean Br–N distance is 2.13 Å, but each molecule contains a longer and a shorter bond (means 2.165 and 2.100 Å).

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[4] G. B. Robertson and A. Robson, unpublished work.

[5] D. Cruickshank *J. Chem. Soc.*, 1961, 5486.

[6] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

The difference between these is highly significant: the smaller pair of values show no difference, while the 3σ differences of the larger pair from their mean are probably not significant. The asymmetry is unexpected because both the I^+ species are exactly symmetrical; it might be considered an artifact were it not that it has appeared also in the refinement with individual atoms and in that of the photographic data set. It can perhaps be compared with the asymmetrical I_3^-, Br_3^-, and similar ions.[7] The bond distance can be compared with that of S–I of 2.629(1) in $[(\text{thiourea})_2I]^+$.[2] Allowing 0.34 Å for the difference between atomic radii of S and N and 0.19 Å for that between I and Br gives a predicted value of 2.10 Å, close to that observed; however, the distance is clearly longer than the sum of the covalent radii of N and Br (1.94 Å).[8] The reported distance in $[(\text{py})_2I]^+$ is much shorter, 2.16 (10)Å, but the accuracy is too low for this difference to be meaningful.[1]

The geometry can be rationalised by two views. Following the Nyholm–Gillespie approach, there is a ten-electron system with sp^3d hybrid orbitals forming a trigonal bipyramid in which the ligands occupy the apices. On the three-centre model, there is overlap between two ligand σ-orbitals and one bromine orbital (say p_z), with two electron pairs occupying the three molecular orbitals. In fact, these two models are not contradictory, but merely represent the extremes of a continuum in which the d-orbital participation in bonding orbital varies from zero to 50%. Using a simple model (Figure 2) involving only bromine p_z and d_{z^2}, the d_{z^2} orbital interacts only with the non-bonding three-centre orbital. The effect of increasing overlap, as the d_{z^2} orbital energy is lowered, is to convert this non-bonding orbital into a bonding orbital, as its proportion of d character increases. Similarly, the character of the second antibonding orbital changes from pure d_{z^2} to a mixed σ–d_{z^2}. The precise position in the continuum of $[(\text{qu})_2\text{Br}]^+$ must be uncertain, but in view of the modest electron attracting power of nitrogen, less rather than more d-orbital involvement is likely.

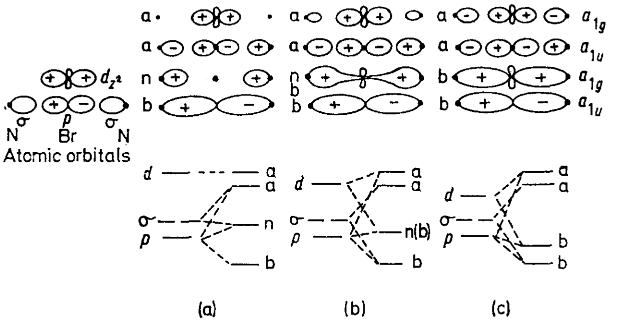

FIGURE 2 Schematic representation of the bonding of a linear three-atom system as the d-orbital energy changes from (a) high with no bond involvement, through (b) an intermediate state, to (c) low with full involvement. The upper diagrams show the spatial distribution of the orbitals, the lower their energies. Orbitals are labelled b (bonding), n (non-bonding), and a (antibonding), and the symmetry labels for $C_{\infty v}$ are also given

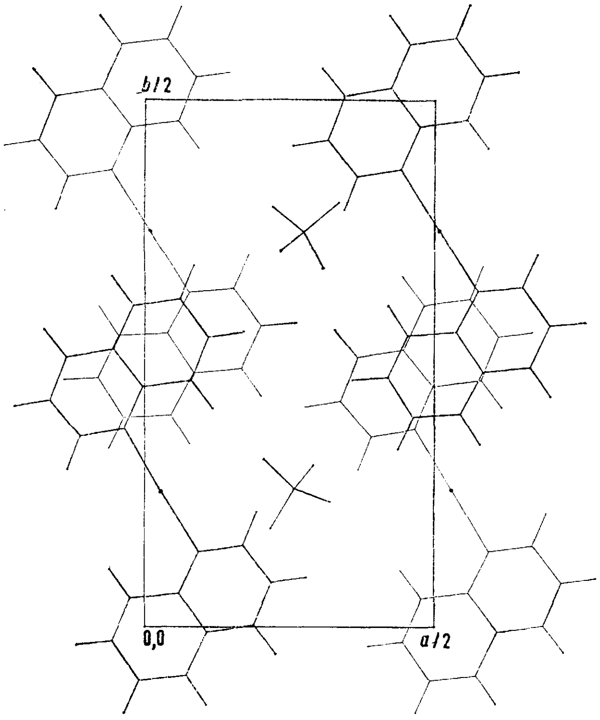

FIGURE 3 Packing diagram, projected down c

One further aspect of the bonding is significant. The virtual coplanarity of the two quinoline molecules donating to each bromine suggests that π interactions may be important, involving donation from quinoline π-orbitals to bromine d-orbitals, or perhaps from bromine p-orbitals to quinoline π^* orbitals.

Molecular Packing.—This is shown in Figure 3. The planar $[(\text{qu})_2\text{Br}]^+$ ions are almost perpendicular to z; four of them lie near $z = \frac{1}{4}$ and four near $z = \frac{3}{4}$. The overlapping of the quinoline rings with a separation of *ca.* 3.5 Å is probably due to charge-transfer interactions. The perchlorate groups are centred at about $z = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$, and $\frac{7}{8}$, filling interstices in the cation framework; their oxygen atoms have very high thermal parameters, but are not disordered.

We thank Dr. R. G. Tonkyn for the preparation of the original crystals.

[5/514 *Received*, 17*th March*, 1975]

[7] J. E. Davies and E. K. Nunn, *Chem. Comm.*, 1969, 1274.

[8] F. A. Cotton and G. H. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, New York, 1972, p. 117.