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Structure of Bis(quinuclidine)iodine(I) Tetrafluoroborate

BY CAROLYN PRATT BROCK AND YIGANG FU

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, *USA*

AND LARRY K. BLAIR, PING CHEN AND MARK LOVELL

Department of Chemistry, Berea College, Berea, Kentucky 40404, *USA*

Abstract. $[(C_7H_{13}N)_2I]BF_4$, $M_r = 436.08$, cubic, $P2_13$, $a = 12.1355$ (6) Å, $V = 1787.2$ (4) Å^3, $Z = 4$, $D_x = 1.621$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 18.0$ cm^{-1}, $F(000) = 872$, $T = 295$ (1) K, $R = 0.029$ for 62 variables and the 371 reflections having $I > 3\sigma(I)$ and $4 < 2\theta < 60°$ [$(\sin\theta)/\lambda < 0.704$ Å^{-1}]. The structure is isostructural with that of bis(quinuclidine)bromine(I) tetrafluoroborate [Blair, Parris, Hii & Brock (1983). *J. Am. Chem. Soc.* **105**, 3649–3653]. Linear [(quinuclidine)$_2$I]$^+$ cations and discrete BF$_4^-$ anions are located on C_3 axes; the anions are disordered. The lengths of the two I—N bonds, 2.320 (3) and 2.267 (4) Å, differ by 0.053 (5) Å. The average I—N distance, 2.294 (5) Å, is typical of the average I—N distances found for similar complexes. The two quinuclidine cages are rotated by *ca* 30 (3)° with respect to each other. The cages themselves are twisted; the two N—C—C—C torsion angles are −6.0 (9) and 10.7 (10)°.

Introduction. This structure was determined as part of a study of bis(amine) complexes of Br^I and I^I. Bis-(quinuclidine)iodine(I) tetrafluoroborate was studied earlier by Pritzkow (1977; quoted by Hagedorn, Pritzkow & Jander, 1977), but nothing other than the average I—N distance, given as 2.29 (1) Å, seems to have been published.

Experimental. The title compound was synthesized by the same route as the analogous Br compound (Blair, Parris, Hii & Brock, 1983). Chunk-shaped, colorless crystal, 0.2–0.3 mm on a side, grown from acetonitrile used for data collection; data measured with an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator and operating in the ω–2θ mode; 20 reflections (θ range 12–14°) used to determine lattice parameters. Octant of data with *h, k, l* ≤ 17; correction for average intensity loss for three control reflections of −0.54% overall. Although the linear absorption coefficient (18.0 cm^{-1}) is not small, 360° ψ scans for eight reflections showed a maximum deviation of 1.5% from the average; no absorption correction was attempted.

The compound $[(C_7H_{13}N)_2X]BF_4$, $X = I$ (this work) appeared to be isostructural with the compound having $X = Br$ (Blair, Parris, Hii & Brock, 1983). The latter crystallizes in the cubic group $P2_13$ with the Br atoms on *xxx* positions very near the origin. Crystals of the I-containing compound are dark at all orientations when viewed between crossed polarizers, and have a cubic cell dimension 0.107 Å longer than found for the Br-containing crystals. The systematic absences (*h*00 for $h = 2n + 1$, and similarly for 0*k*0 and 00*l*) are consistent with the space groups $P2_13$ and $P4_232$; the two groups can be distinguished on the basis of the Laue symmetry. Averaging in $m\bar{3}$ of the 2921 observed intensities, which do not include any Friedel pairs, yielded 981 unique data; the R factor based on I for averaging is 0.029. Averaging in $m\bar{3}m$ yielded 449 reflections and an R factor of 0.071. We concluded that the space group is $P2_13$. Comparisons of the intensities of the 2196 reflections of mixed parity is even more convincing. These reflections are systematically weaker than the reflections with *h, k, l* all even or all odd because of the much smaller contribution of the I atom. Averaging of these weaker data in $m\bar{3}$ gave 732 unique reflections and an R factor of 0.096, while averaging in $m\bar{3}m$ gave 405 reflections and an R factor of 0.695. In $P2_13$, both ions are required to conform to crystallographic threefold rotation symmetry. If the space group had been $P4_232$, the required symmetry would have been 32.

This structure might have been very difficult to solve if coordinates for the analogous Br-containing crystal had not been available. The I atoms are located very near the origin and form a nearly face-centered array. They dominate the reflections for which $h + k$, $k + l$, and $h + l$ are all even, and contribute very little to the reflections having indices of mixed parity. The origin-removed sharpened Patterson is not very informative, even in retrospect; only the I···I and I···N vectors are identifiable. The locations of the I and N atoms do not provide enough phasing information to allow the remaining atoms to be located. In our hands, *DIRDIF* (Beurskens *et al.*, 1984) failed to find the solution. Even though the basic geometries of the ions and their approximate locations are known, it is not so simple to devise a satisfactory trial structure. As a result of the high symmetry, there are many stationary points which may separate a trial model from the correct solution. The rotations of the quinuclidine cages with respect to the cell axes and to each other must be determined, as must the senses and magnitudes of the twists of the cages. Since the Laue symmetry is $m\bar{3}$ rather than $m\bar{3}m$, the coordinates of the threefold axis may be x,x,x or $x,x,\bar{x}$ depending on how the axes have been labeled. An adequate description for the disordered BF_4^- ions must be found. We were probably fortunate to have done the Br-containing structure first, because the Br atom ($Z = 35$) is not as dominant as the I atom ($Z = 53$). Neither structure, however, was easy to solve. Both ultimately yielded to the method of trial and error. Group refinement techniques were invaluable in the early stages of structure solution and refinement.

In the final refinement cycles the BF_4^- ions were treated as rigid groups [$\bar{4}3m$ symmetry, $r(B-F) = 1.39$ Å]. Individual isotropic temperature factors were refined, except that the B values for the two B atoms, which are only 0.22 (3) Å apart, were held equal. The final value of the occupancy factor for the group containing B(1) is 0.541 (14). H atoms were idealized at a late point in the refinement and added as fixed contributions [$r(C-H) = 1.00$ Å, B_H 1.0 Å² larger than B_{eq} of the attached C atoms]. No correction for extinction was necessary. There are no significant differences between refinements of the two enantiomers. If the I atom [$x = y = z = -0.00102$ (5)] is moved to the other side of the origin, it shifts back to the original position during refinement. No other atom position is significantly affected.

Computer programs used have been described previously (Brock & Webster, 1976); scattering factors, including anomalous terms for the I atom, were taken from Cromer & Waber (1974). The final refinement was on F magnitudes with weights $w = 4I/[\sigma^2(I)]$, where [$\sigma^2(I)$] included a term $(0.02I)^2$; the maximum Δ/σ in the last cycle was 0.01. Agreement indices R, $wR = 0.029$, 0.034 for 62 variables and 371 reflections having $I > 3\sigma(I)$; error in an observation of unit

weight $= 2.52$ e. Agreement is better for the 249 more intense reflections having $h + k$, $h + l$, and $k + l$ even (R, $wR = 0.025$, 0.026; $\langle |F| \rangle = 54$ e) than it is for the 122 generally weaker reflections with indices of mixed parity (r, $wR = 0.052$, 0.055; $\langle |F| \rangle = 18$ e). For none of the 610 'weak' reflections excluded from the refinement is $||I_o| - |I_c|| > 3\sigma(I)$. The largest features in a final difference Fourier synthesis have heights $+0.94$ e Å^{-3} (near the BF_4^- ions) and -0.81 e Å^{-3} (near the I atom).

The molecular structure and the atom-numbering scheme are shown in Fig. 1. The packing diagram is indistinguishable from that published for the Br-containing compound (Blair, Parris, Hii & Brock, 1983). Atomic coordinates are listed in Table 1; bond lengths, bond angles, and some torsion angles are given in Table 2.*

Discussion. Perhaps the most surprising feature of the structure of [$(C_7H_{13}N)_2X$]BF_4, $X = I$ is its similarity to the structure of the compound with $X = Br$ (Blair, Parris, Hii & Brock, 1983). The average I—N bond length of 2.294 (5) Å is 0.16 Å longer than the average Br—N bond length of 2.138 (3) Å, but the 0.31 Å difference in 'length' between the two cations has few consequences for the crystal packing. The length of the body diagonal, with which the X—N vectors are collinear, increases by 0.184 (7) Å when X is changed from Br to I, only 59% of the increase that might have been expected. It might then be inferred that the crystal packing in the I-containing compound is 'tighter' than in the Br-containing compound, but additional structural evidence to support that assertion is lacking. The average value of B_{eq} for the non-hydrogen atoms of the cation is the same for the two structures. The disorder models for the anions are also very similar. The average B_{eq} for the B and F atoms in the I and Br structures are 7.9 and 9.4 Å², respectively, but the values are not
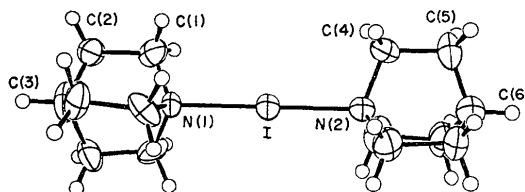
Fig. 1. Perspective drawing of the cation of bis(quinuclidine)-iodine(I) tetrafluoroborate. The shapes of the ellipsoids for the non-hydrogen atoms correspond to 50% probability contours of atomic displacement.

strictly comparable because the constraints used in the refinements were not the same.

The asymmetry of the N—X—N, X = I linkage is even greater than was observed for the Br compound. In the former the I—N bond lengths differ by 0·053 (5) Å; in the latter the Br—N bond lengths vary

Table 1. *Positional and displacement parameters for the atoms of bis(quinuclidine)iodine(I) tetrafluoroborate*

The equivalent displacement parameter is defined as $\frac{4}{3}\mathrm{Tr}(\beta\cdot\mathbf{G})$, where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

	x	y	z	$B_{eq}(\text{Å}^2)$
I	−0·00102 (5)	−0·00102	−0·00102	3·14 (2)
N(1)	0·1093 (5)	0·1093	0·1093	2·7 (2)
N(2)	−0·1089 (5)	−0·1089	−0·1089	2·9 (2)
C(1)	0·0506 (7)	0·2130 (7)	0·1364 (10)	4·3 (3)
C(2)	0·1140 (9)	0·2833 (9)	0·2203 (8)	4·5 (3)
C(3)	0·2291 (12)	0·2291	0·2291	5·9 (7)
C(4)	−0·0368 (8)	−0·1769 (8)	−0·1855 (8)	4·9 (3)
C(5)	−0·1107 (10)	−0·2456 (7)	−0·2647 (8)	5·1 (3)
C(6)	−0·2320 (10)	−0·2320	−0·2320	4·3 (6)
B(1)	0·4810 (8)	0·4810	0·4810	8·8 (9)
F(11)	0·5472 (8)	0·5472	0·5472	6·5 (6)
F(12)	0·3752 (9)	0·5250 (6)	0·4766 (9)	7·1 (4)
B(2)	0·4706 (11)	0·4706	0·4706	8·8
F(21)	0·4044 (11)	0·4044	0·4044	7·7 (7)
F(22)	0·4123 (9)	0·5645 (10)	0·5012 (17)	10·3 (6)

Table 2. *Bond lengths (Å), bond angles (°) and selected torsion angles (°) for bis(quinuclidine)iodine(I) tetrafluoroborate*

I—N(1)	2·320 (3)	I—N(2)	2·267 (4)
N(1)—C(1)	1·483 (10)	N(2)—C(4)	1·520 (9)
C(1)—C(2)	1·534 (14)	C(4)—C(5)	1·557 (13)
C(2)—C(3)	1·547 (14)	C(5)—C(6)	1·533 (13)
I—N(1)—C(1)	109·9 (4)	I—N(2)—C(4)	109·5 (5)
C(1)—N(1)—C(1)'	109·0 (4)	C(4)—N(2)—C(4)'	109·4 (4)
N(1)—C(1)—C(2)	112·2 (7)	N(2)—C(4)—C(5)	109·7 (8)
C(1)—C(2)—C(3)	105·2 (8)	C(4)—C(5)—C(6)	109·6 (8)
C(2)—C(3)—C(2)'	110·5 (9)	C(5)—C(6)—C(5)'	108·9 (7)
N(1)—C(1)—C(2)—C(3)	10·7 (10)	N(2)—C(4)—C(5)—C(6)	−6·0 (9)
C(1)—N(1)—C(3)—C(2)	6·5 (6)	C(4)—N(2)—C(6)—C(5)	−3·6 (6)
C(1)—N(1)—N(2)—C(4)	31·1 (6)	C(1)—N(1)—N(2)—C(5)	34·7 (6)
C(2)—N(1)—N(2)—C(4)	24·5 (6)	C(2)—N(1)—N(2)—C(5)	28·1 (5)

by 0·036 (3) Å. It is almost certain that the asymmetry is a crystal packing effect. The X—N bonds are long, weak and easily deformed along the direction of an asymmetric stretch. If the space group were $P4_232$, the cation would have 32 (D_3) rather than 3 (C_3) symmetry, and the two X—N bonds would be equivalent. The cation does conform roughly to D_3 symmetry, but atoms C(4) and C(5) are about 0·6 Å each from the positions generated by applying the required twofold rotation to atoms C(1) and C(2). In $P4_232$ the I atom and the center of the BF_4^- ions would be related by the translation $[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$. In the observed structure the I atom and the first BF_4^- ion are separated along $[x,x,x]$ by $x = 0·504$, but the I atom and the second BF_4^- ion are separated by only $x = 0·457$. In order to explain the asymmetry of the I—N bonds it must be assumed that the I atoms interact with neighboring species, probably the BF_4^- ions that are related by the approximate translations $[\frac{1}{2},0,0]$. Such interactions would have to extend over *ca* 6 Å, but the equatorial lone-pair electrons on the I atom can be expected to be sterically active over considerable distances.

The average I—N distance of 2·294 (5) Å determined for this structure is consistent with all distances known for species containing the N—I—N linkage (see Table 3). Most of the averages fall in the range 2·29–2·31 Å. The value of 2·16 (10) Å for $[(C_5H_5N)_2I]I_7$ (Hassel & Hope, 1961), although often cited, could be determined only roughly, and should probably be ignored. Another short value, 2·24 (2) Å (Osborn, 1972), corresponds to a structure in a thesis, which has never been published. The value of 2·27 Å corresponds to an ion, $[I(N_3)_2]^-$ (Hagedorn, Pritzkow & Jander, 1977), affected by important disorder. The larger values, 2·34 Å (Hartl, Bärnighausen & Jander, 1968) and especially 2·36 Å (Hartl & Ullrich, 1974), correspond to structures complicated by space-group ambiguities.

Many of the N—I—N groupings listed in Table 3 are nearly symmetrical, but others are very asymmetric. Nevertheless, the average I—N distance is nearly constant; as one bond is shortened, the other is lengthened. This pattern is very similar to that described

Table 3. I—N *distances (Å) in complexes containing linear* N—I—N *groupings*

Complex	d(I—N)		$\langle d$(I—N)$\rangle$	$\Delta[d$(I—N)]	Reference
[(Pyridine)$_2$I]$^+$	2·16 (10)		2·16	0	Hassel & Hope (1961)
[(3-Methylpyridine)$_2$I]$^+$	2·24 (2)		2·24	0	Osborn (1972)
[I(N$_3$)$_2$]$^-$	2·27		2·27	0	Müller, Dübgen & Dehnicke (1980)
[(Quinuclidine)$_2$I]$^+$	2·320 (3)	2·267 (4)	2·29	0·05	This work
[(2,4,6-Trimethyl-pyridine)$_2$I]$^+$	2·29 (1)	2·30 (1)	2·30	0·01	Brayer & James (1982)
(CH$_3$)$_3$NI	2·29 (1)		2·29	0	Hagedorn, Pritzkow & Jander (1977)
[(Hexamethylene-tetraamine)$_2$I]$^+$	2·30 (1)	2·30 (1)	2·30	0·00	Pritzkow (1975)
(2,2'-Bipyridine)-I$_2$(N$_3$)$_2$	2·442 (6)	2·185 (7)	2·31	0·26	Dörner, Dehnicke, Massa & Schmidt (1983)
	2·454 (6)	2·169 (7)	2·31	0·28	
NI$_3$.NH$_3$	2·30 (1)		2·30	0	Hartl, Bärnighausen & Jander (1968)
	2·14 (1)	2·53 (2)	2·34	0·39	
NI$_3$.pyridine	2·36 (4)		2·36	0	Hartl & Ullrich (1974)
	2·08 (6)	2·58 (5)	2·32	0·50	

by Bent (1968) for the I—I distances in the closely related I_3^- ions.

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N,N'-Diisopropyl-2,5-diphenyl-1,4-phenylenediamine

By JEAN-PAUL DECLERCQ AND MAURICE VAN MEERSSCHE

Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain, 1 place Louis Pasteur, B-1348 Louvain la Neuve, Belgium

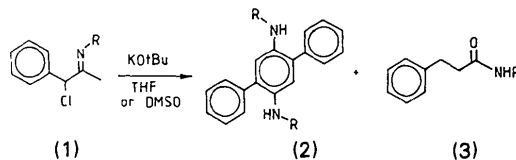AND NORBERT DE KIMPE* AND NICEAS SCHAMP

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure Links 653, B-9000 Gent, Belgium

Abstract. $C_{24}H_{28}N_2$, $M_r = 344.5$, triclinic, $P\bar{1}$, $a = 9.926$ (13), $b = 6.187$ (8), $c = 8.034$ (7) Å, $\alpha = 90.65$ (9), $\beta = 97.68$ (9), $\gamma = 100.48$ (10)°, $V = 480.5$ (9) Å^3, $Z = 1$, $D_x = 1.191$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.749$ cm^{-1}, $F(000) = 186$, $T = 291$ K, $R = 0.055$ for 907 observed reflections. As regards the relative conformation of the three rings, this molecule is rather different from *p*-terphenyl, but very similar to 2,5-diphenylhydroquinone.

Introduction. During investigation of the Favorskii rearrangement of various α-halogenated ketimines, a curious side reaction was observed (De Kimpe, Sulmon, Moëns, Schamp, Declercq & Van Meerssche, 1986). The reaction of α-chloroketimines (1) (*R* = iPr, cycloHex) with potassium *tert*-butoxide in tetrahydro-

furan or dimethyl sulfoxide afforded, besides minor amounts of the rearranged amide (3), condensation products (22–41%) which were identified as *N,N'*-dialkyl-2,5-diphenyl-*p*-phenylenediamines (2) (*R* = iPr, cycloHex). The mechanism was interpreted in terms of a double intramolecular nucleophilic substitution or a cyclocondensation of a zwitterionic Favorskii intermediate.

Both processes were followed by air oxidation of the resulting six-membered 1,4-diimine or the corresponding electron-rich cyclohexadienes. As mechanistic routes were also plausible for the formation of

* 'Onderzoeksleider' (Senior Research Associate) of the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek (National Fund for Scientific Research).