attributed to a difference in hydrophobicity, suggesting that the lipophilic side chain is probably more important for its hydrophobicity than for its shape. It is noteworthy that (3), which differs from (1) and (2) in the polar region, has the same lipophilic side chain as in (2) and is more active than (1). The order of activity in this series is (2) > (3) > (1).

The observed molecular structures and modeled conformational preferences provide suggestions of what is important to the active shape of these compounds, which include: (1) the pyrrolidine ring oriented at $\varphi_1 \approx \pm 100°$ and separated from rather than stacked over the central phenyl ring, and (2) the relative separation between the amine N atom and the central carbonyl O atom (which is more important than the relative orientation of these two groups). The combination of a model interaction consisting of a strong intermolecular hydrogen bond between the protonated amine and the anions, and a conserved orientation for the pyrrolidine ring relative to the phenyl ring found in the structures reported here and in the bis(pyrrolidinylmethyl) compounds (Glowka, Dargie & Codding, 1991) suggests that the pyrrolidine ring is a pharmacophoric group and its orientation relative to the phenyl ring is important to the activity of these class I agents. The flexible side chain attached to the central carbonyl C atom serves to increase the hydrophobicity of the molecule and thus increase in biology activity. Class I antiarrhythmic agents appear to have a distinct recognition requirement for shape and for the relative separation of functional groups, and a hydrophobicity requirement for transport to the binding site.

References

CAMPBELL, T. J. (1983a). *Cardiovasc. Res.* **17**, 344–352.
CAMPBELL, T. J. (1983b) *Br. J. Pharmacol.* **80**, 33–40.
CHORVAT, R. J. (1992). Personal correspondence.
CHORVAT, R. J., BLACK, L. A., RANADE, V. V., BARCELON-YANG, C., STOUT, D. M., BROWN, B. S., STAMPFLI, H. F. & QUON, C. Y. (1993). *J. Med. Chem.* **36**, 2494–2498.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
DEMPSEY, S. (1986). *MMS. The UCSD Molecular Modeling System.* Version 1.3. Univ. of California, San Diego, La Jolla, USA.
GLOWKA, M. L., DARGIE, R. L. & CODDING, P. W. (1991). *J. Med. Chem.* **34**, 2678–2684.
HARRISON, D. C. (1985). *Am. J. Cardiol.* **56**, 185–190.
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
MOHAMADI, F., RICHARDS, N. G. J., GUIDE, W. C., LISKAMP, M. L., CAUFIELD, C., CHANG, G., HENDRICKSON, T. & STILL, W. C. (1990). *J. Comput. Chem.* **11**, 440–467.
MORIGUCHI, I., KANADA, Y. & KOMATSU, K. (1976). *Chem. Pharm. Bull.* **24**(8), 1799–1806.
SHELDON, R. S., CANNON, N. J. & DUFF, H. J. (1987). *Circ. Res.* **61**, 492–497.
SHELDON, R. S., CANNON, N. J., NIES, A. S. & DUFF, H. J. (1988). *Mol. Pharmacol.* **33**, 327–331.
SHELDRICK, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
STEWART, J. M. (1976). *The XRAY76 System of Crystallographic Programs.* Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
ZAMPONI, G. W., DOYLE, D. D. & FRENCH, R. J. (1993). *Biophys. J.* **65**(1), 80–90.
ZAMPONI, G. W., SUI, X., CODDING, P. W. & FRENCH, R. J. (1993). *Biophys. J.* **65**(6), 2324–2334.

Tetramethylpyrazinium Polyiodides

ROSA D. BAILEY AND WILLIAM T. PENNINGTON

Department of Chemistry, Clemson University, Clemson, SC 29634–1905, USA

Abstract

(1): Tetramethylpyrazinium triiodide tetramethylpyrazine, $C_{12}H_{19}N_3I_3$, $M_r = 586.00$, triclinic, $P\bar{1}$, $a = 8.226(3)$, $b = 8.393(3)$, $c = 13.878(6)$ Å, $\alpha = 85.28(3)$, $\beta = 74.54(3)$, $\gamma = 87.96(3)°$, $V = 920.2(6)$ Å^3, $Z = 2$, $D_x = 2.12$ g cm^{-3}, $\lambda(\text{Mo}K\alpha) = 0.71073$ Å, $\mu = 50.9$ cm^{-1}, $F(000) = 542$, $T = 293 \pm 1$ K, $R = 0.033$ for 2476 unique observed reflections. (2): Tetramethylpyrazinium triiodide.0.5-methylhydroquinone.0.5methylquinone, $C_{15}H_{20}N_2O_2I_3$, $M_r = 641.03$, monoclinic, $P2_1/n$, $a = 7.679(2)$, $b = 12.520(4)$, $c = 10.774(3)$ Å, $\beta = 100.60(2)°$, $V = 1019.9(6)$ Å^3, $Z = 2$, $D_x = 2.09$ g cm^{-3}, $\lambda(\text{Mo}K\alpha) = 0.71073$ Å, $\mu = 46.0$ cm^{-1}, $F(000) = 598$, $T = 293 \pm 1$ K, $R = 0.086$ for 1267 unique observed reflections. (3): Tetramethylpyrazinium pentaiodide.hydrate, $C_8H_{15}N_2OI_5$, $M_r = 789.72$, triclinic, $P\bar{1}$,

$a = 8.206\,(1)$, $b = 9.228\,(2)$, $c = 13.936\,(2)$ Å,
$\alpha = 77.76\,(2)$, $\beta = 85.23\,(1)$, $\gamma = 65.88\,(1)°$,
$V = 941.2\,(3)$ Å^3, $Z = 2$, $D_x = 2.79\,\mathrm{g\,cm}^{-3}$,
$\lambda(\mathrm{Mo}\,K\alpha) = 0.71073$ Å, $\mu = 82.5\,\mathrm{cm}^{-1}$, $F(000) =$
700, $T = 293 \pm 1$ K, $R = 0.048$ for 2753 unique observed reflections. Crystallizes as integrated stacks of alternating organic cations and I_3^- anions. Pairs of stacks are bridged by neutral tetramethylpyrazine molecules through N—H···N hydrogen bonding. In (2), similar stacks of cations and I_3^- anions are formed, but are bridged in an extended fashion through hydrogen bonding by methylquinone (N—H···O) and methylhydroquinone (O—H···N) molecules. (3) crystallizes as a sheet structure with localized regions of monoprotonated cations bridged by water molecules into infinite hydrogen-bonded chains and polyiodide regions of branched chains of closely associated I_2 molecules and I_3^- anions.

Introduction

Polyhalide anions, particularly the polyiodides, have been the subject of considerable interest due to the high conductivity of many of their complexes (Bolton & Prasad, 1981; Coppens, Leung, Ortega, Young & Laporta, 1983), their ability to introduce partial oxidation into hydrocarbon donor molecules (Teitelbaum, Ruby & Marks, 1979; Lerner, Lyons, Tonge & Shriver, 1989) and to stabilize mixed-valence in metal complexes (Jircitano, Colton & Bowman Mertes, 1981), and to their rich and varied structural chemistry. A large number of polyiodide complexes have been structurally characterized (Tebbe, 1977; Coppens, 1982). The configuration of the polyiodide ion in these complexes may be linear or bent, and symmetric or asymmetric, depending on the nature of the counter cation and the packing environment (Hon, Mak & Trotter, 1982). Polyiodide ions range in size from I_3^- to I_{16}^{4-} (Herbstein & Kapon, 1979) and are found as either discrete molecular ions (Zhang, Wilson & Hendrickson, 1989), loosely associated ions (Leung, Boehme & Coppens, 1981) or close associations of I_2 molecules with I^- or I_3^- anions (Herbstein & Kapon, 1972; Jircitano, Colton & Bowman Mertes, 1981). Polyiodides have been broadly classified into the following four categories (Rossi, Marzilli & Kistenmacher, 1978): (1) large-cation polyiodides, such as bis(triphenylphosphin)iminium triiodide (Tebbe & Krauss, 1990); (2) clover phases consisting of a neutral organic/alkali-metal polyiodides, such as (benzophenone)$_9$(KI)$_2$I$_7$CHCl$_3$ (Leung, Boehme & Coppens, 1981); (3) protonated organic heterocycles with polyiodides, such as (1-methylcytosine)HI$_3$ (Rossi, Marzilli & Kistenmacher, 1978); (4) radical-cation polyiodides, such as (trimethylamine)(7,7,8,8-tetracyano-p-quinodimethane)(I$_3$)$_{1/3}$ (Coppens, Leung, Murphy, Tilborg, Epstein & Miller, 1980). Recently we investigated the reaction between iodine (I$_2$) and 1,4-diazines, pyrazine and tetramethylpyrazine, in which 1:1 molecular com-

plexes consisting of infinite chains of I$_2$ and diazine molecules are formed (Bailey, Buchanan & Pennington, 1992). As an extension of this work we report here the structures of several polyiodide complexes containing monoprotonated tetramethylpyrazinium cations: tetramethylpyrazinium triiodide (1), tetramethylpyrazinium triiodide.0.5methylhydroquinone.0.5methylquinone (2), tetramethylpyrazinium pentaiodide.hydrate (3). These structures fall into category (3) of the classification system described above.
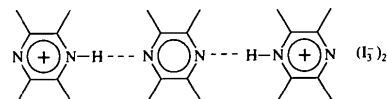
(1)
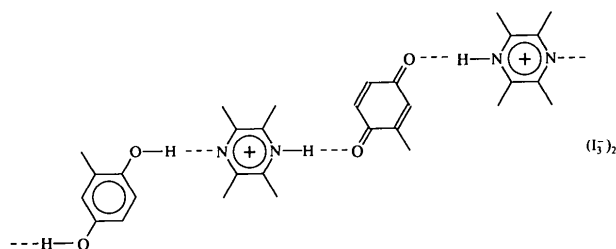
(2)
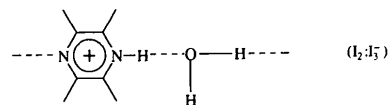
(3)

Experimental

Synthesis

(1) was prepared by reaction of stoichiometric amounts of tetramethylpyrazine, methylhydroquinone and iodine in dry acetonitrile. Data-quality crystals of (1) were obtained by recrystallization from a toluene/acetonitrile mixture (10:1). Crystals of (2) were formed as a minor product in the reaction described above. Compound (3) was formed in quantitative yield by reaction in ethanol of stoichiometric amounts of tetramethylpyrazine with hydrogen iodide (47% aqueous solution) and iodine.

Data collection, structure solution and refinement

All intensity data were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature (294 K) on a Nicolet R3mV diffractometer. The data were corrected for Lorentz and polarization effects and for real and imaginary anom-

alous dispersion effects (Cromer, 1974); the intensities of three reflections monitored every 97 measurements fluctuated within acceptable ranges ($\pm 2\%$), indicating no need for a decomposition correction. The correction for extinction, if applied, was based on the method of Larson (1970). The structures were solved by direct methods and refined (on F) by full-matrix least-squares techniques. The weighting scheme was based on counting statistics [$w = 1/(\sigma^2 F_o) + 0.0005 F_o^2$]. Structure solution, refinement and the calculation of derived results were performed using SHELXTL (Sheldrick, 1985); atomic scattering factors were those of Cromer & Waber (1974).

For (1), the asymmetric unit contains one monoprotonated tetramethylpyrazinium cation and one triiodide anion occupying general positions and half a neutral tetramethylpyrazine molecule situated about an inversion center at ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). All non-H atoms were refined with anisotropic thermal parameters. The pyrazinium H atom was refined isotropically. The methyl H atoms were placed in optimized difference Fourier positions ($d_{C-H} = 0.96$ Å) as a riding model contribution to the structure factor calculation; the methyl H atoms bonded to C(12) of the neutral molecule were disordered ($m = 0.50$) over two sets of positions related by rotation about the C—C_{Me} bond. A single group thermal parameter was refined for all the methyl H atoms [$U_{iso} = 0.099\,(7)$ Å^2].

For (2), the asymmetric unit contains one monoprotonated tetramethylpyrazinium cation disordered about an inversion center at ($\frac{1}{2},0,0$) and one triiodide anion situated about an inversion center at the origin. Methylquinone and methylhydroquinone molecules alternately occupy the same site and are both disordered about an inversion center at ($0,0,\frac{1}{2}$). All non-H atoms were refined anisotropically. The N—H and O—H H atoms (included at half-occupancy to account for the disorder of the cation and the half-occupancy of the methylhydroquinone molecules), phenyl H atoms and methyl H atoms [except for those of C(8), which is disordered over two sites related by inversion symmetry] were included at optimized difference Fourier positions ($d_{O-H} = 0.85$, $d_{N-H} = 0.90$ and $d_{C-H} = 0.96$ Å) and included in the structure factor calculation as for (1) [$U_{iso} = 0.11\,(3)$ Å^2]. The relatively high residual values obtained for this compound are presumably due to unresolved disorder in the structure.

The asymmetric unit of (3) contains two unique monoprotonated tetramethylpyrazinium cations, each of which is disordered about inversion centers [cation one at ($\frac{1}{2},0,\frac{1}{2}$); cation two at ($0,\frac{1}{2},0$)], an associated triiodide anion/iodine molecule and a water molecule. The non-H atoms were refined anisotropically. H atoms were included at optimized positions as for (1) and (2) [$U_{iso} = 0.12\,(2)$ Å^2]; the methyl H atoms of cation one were disordered over two sets of half-occupancy positions.

Results and discussion

Molecular structures with atomic numbering are shown in Fig. 1. Final atomic coordinates are given in Table 1 and selected distances and angles in Table 2.* (1) and (2) are columnar structures with stacks consisting of alternating organic cations and triiodide anions. (3) has a sheet structure with alternating layers of organic cations and polyiodide anions.

---

* Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
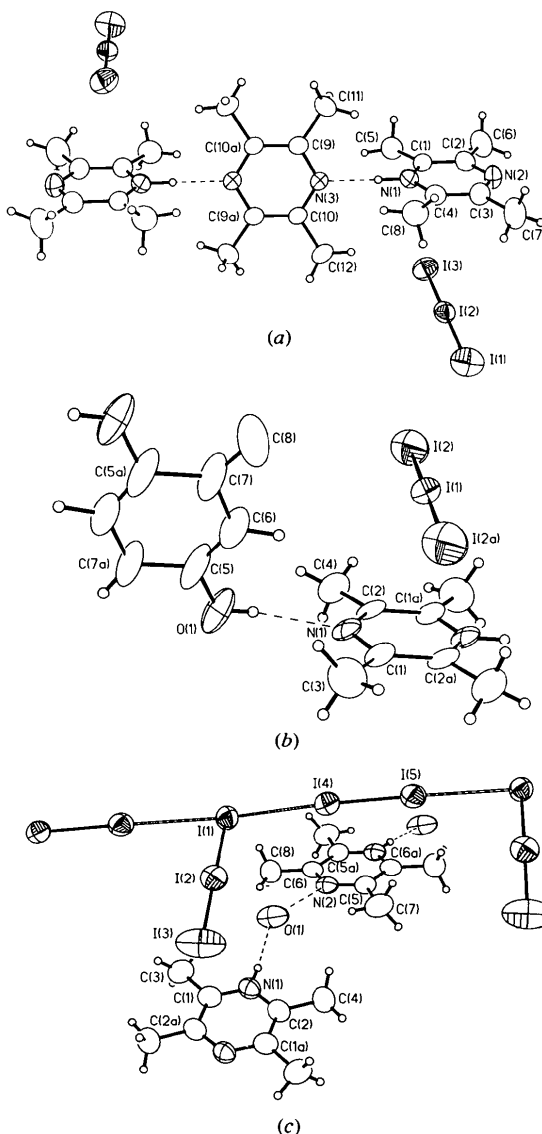

Fig. 1. Views showing the labeling of the non-H atoms. Thermal ellipsoids are shown at the 50% probability level for (a) (1), (b) (2) and (c) (3).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(1)				
I(1)	−0.2502 (1)	1.1759 (1)	0.6538 (1)	0.082 (1)
I(2)	−0.1607 (1)	0.8992 (1)	0.7808 (1)	0.051 (1)
I(3)	−0.0690 (1)	0.6344 (1)	0.9027 (1)	0.066 (1)
N(1)	0.3766 (5)	0.7967 (5)	0.7431 (3)	0.041 (2)
N(2)	0.2995 (6)	0.9832 (6)	0.8977 (4)	0.051 (2)
N(3)	0.4568 (5)	0.5975 (5)	0.5775 (3)	0.040 (1)
C(1)	0.3986 (6)	0.7358 (6)	0.8310 (4)	0.040 (2)
C(2)	0.3609 (7)	0.8358 (7)	0.9097 (4)	0.050 (2)
C(3)	0.2773 (7)	1.0380 (7)	0.8092 (4)	0.049 (2)
C(4)	0.3177 (7)	0.9453 (6)	0.7273 (4)	0.043 (2)
C(5)	0.4615 (8)	0.5679 (7)	0.8379 (5)	0.058 (2)
C(6)	0.3863 (10)	0.7817 (9)	1.0100 (5)	0.068 (3)
C(7)	0.2064 (10)	1.2041 (7)	0.8008 (6)	0.073 (3)
C(8)	0.3028 (8)	0.9978 (8)	0.6246 (5)	0.060 (2)
C(9)	0.6205 (6)	0.5796 (6)	0.5265 (4)	0.040 (2)
C(10)	0.3375 (6)	0.5205 (6)	0.5525 (4)	0.039 (2)
C(11)	0.7476 (7)	0.6679 (8)	0.5607 (5)	0.056 (2)
C(12)	0.1577 (7)	0.5484 (8)	0.6111 (5)	0.056 (2)
(2)				
I(1)	0.0	0.0	0.0	0.060 (1)
I(2)	0.0855 (2)	0.2262 (1)	0.0039 (1)	0.084 (1)
O(1)	0.3556 (17)	0.0176 (10)	−0.3996 (10)	0.074 (5)
N(1)	0.4647 (14)	0.0039 (10)	−0.1268 (10)	0.037 (4)
C(1)	0.4460 (16)	−0.0906 (13)	−0.0680 (11)	0.039 (5)
C(2)	0.5147 (16)	0.0916 (11)	−0.0640 (12)	0.034 (4)
C(3)	0.389 (2)	−0.1818 (14)	−0.1442 (14)	0.065 (6)
C(4)	0.534 (2)	0.1882 (14)	−0.1371 (14)	0.062 (6)
C(5)	0.178 (3)	0.0109 (13)	−0.4482 (13)	0.060 (6)
C(6)	0.053 (2)	0.0043 (12)	−0.3731 (13)	0.056 (6)
C(7)	−0.127 (3)	0.0007 (14)	−0.4191 (13)	0.064 (6)
C(8)*	−0.239 (4)	−0.015 (4)	−0.344 (3)	0.084 (17)
(3)				
I(1)	0.1019 (1)	−0.1409 (1)	0.1443 (1)	0.065 (1)
I(2)	0.1738 (1)	−0.2173 (1)	0.3686 (1)	0.067 (1)
I(3)	0.2556 (2)	−0.2771 (2)	0.5669 (1)	0.121 (1)
I(4)	−0.2636 (1)	0.1902 (1)	0.1538 (1)	0.065 (1)
I(5)	−0.5545 (1)	0.4795 (1)	0.1580 (1)	0.071 (1)
O(1)	0.2616 (13)	0.1335 (10)	0.2290 (6)	0.086 (5)
N(1)	0.4377 (10)	0.0534 (9)	0.4076 (5)	0.049 (3)
N(2)	0.0896 (10)	0.3839 (9)	0.0759 (6)	0.049 (3)
C(1)	0.5690 (12)	−0.0887 (12)	0.4297 (7)	0.050 (4)
C(2)	0.3652 (12)	0.1480 (11)	0.4741 (7)	0.050 (4)
C(3)	0.6438 (16)	−0.1840 (14)	0.3499 (8)	0.069 (5)
C(4)	0.2196 (14)	0.3107 (13)	0.4406 (9)	0.066 (5)
C(5)	−0.0498 (13)	0.5157 (11)	0.0937 (6)	0.047 (4)
C(6)	0.1465 (11)	0.3625 (11)	−0.0163 (6)	0.046 (4)
C(7)	−0.0945 (17)	0.5245 (16)	0.2003 (7)	0.072 (6)
C(8)	0.3047 (15)	0.2079 (14)	−0.0266 (9)	0.073 (5)

*This atom represents a half occupancy atom.

Structure of (1)

(1) consists of two monoprotonated tetramethylpyr-azinium cations bridged by a neutral tetramethylpyrazine molecule through N···H hydrogen bonding [N(1)···N(3)=2.874 (6), H(1)···N(3)=1.88(7) Å, N(1)—H(1)···N(3)=179 (6)°] and two discrete triio-dide anions. The trimer of tetramethylpyrazine moieties is situated about an inversion center $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ that relates the two anions. The I_3^- ion is linear and asymmetrical; the difference between the two I—I bond lengths (0.107 Å) is well within previously observed ranges. The larger ring angle at N(1) relative to those at N(2) and N(3), as

Table 2. *Selected geometric parameters* (Å, °)

(1)

I(1)—I(2)	2.990 (1)	I(2)—I(3)	2.883 (1)
N(1)—C(1)	1.338 (7)	N(1)—C(4)	1.344 (7)
N(2)—C(2)	1.334 (8)	N(2)—C(3)	1.332 (8)
N(3)—C(9)	1.354 (6)	N(3)—C(10)	1.328 (7)
C(1)—C(2)	1.394 (8)	C(1)—C(5)	1.489 (8)
C(2)—C(6)	1.494 (9)	C(3)—C(4)	1.391 (8)
C(3)—C(7)	1.500 (9)	C(4)—C(8)	1.493 (9)
C(9)—C(11)	1.499 (9)	C(9)—C(10^i)	1.398 (7)
C(10)—C(12)	1.506 (7)		
I(1)—I(2)—I(3)	179.1 (1)	C(1)—N(1)—C(4)	124.1 (5)
C(2)—N(2)—C(3)	120.1 (5)	C(9)—N(3)—C(10)	120.1 (4)
N(1)—C(1)—C(2)	117.0 (5)	N(1)—C(1)—C(5)	118.1 (5)
C(2)—C(1)—C(5)	124.8 (5)	N(2)—C(2)—C(1)	120.7 (6)
N(2)—C(2)—C(6)	117.8 (6)	C(1)—C(2)—C(6)	121.5 (5)
N(2)—C(3)—C(4)	121.6 (5)	N(2)—C(3)—C(7)	117.6 (6)
C(4)—C(3)—C(7)	120.9 (6)	N(1)—C(4)—C(3)	116.4 (5)
N(1)—C(4)—C(8)	118.1 (5)	C(3)—C(4)—C(8)	125.5 (5)
N(3)—C(9)—C(11)	116.8 (5)	N(3)—C(9)—C(10^i)	119.4 (5)
C(11)—C(9)—C(10^i)	123.8 (4)	N(3)—C(10)—C(12)	117.3 (5)
N(3)—C(10)—C(9^i)	120.5 (4)	C(12)—C(10)—C(9^i)	122.2 (5)

(2)

I(1)—I(2)	2.906 (2)	O(1)—C(5)	1.38 (2)
N(1)—C(1)	1.361 (19)	N(1)—C(2)	1.312 (17)
C(1)—C(3)	1.43 (2)	C(1)—C(2^{iii})	1.401 (17)
C(2)—C(4)	1.47 (2)	C(5)—C(6)	1.36 (3)
C(5)—C(7^{ii})	1.42 (2)	C(6)—C(7)	1.38 (3)
C(7)—C(8)	1.29 (4)		
C(1)—N(1)—C(2)	122.2 (11)	N(1)—C(1)—C(3)	118.3 (11)
N(1)—C(1)—C(2^{iii})	117.3 (12)	C(3)—C(1)—C(2^{iii})	124.4 (14)
N(1)—C(2)—C(4)	117.5 (12)	N(1)—C(2)—C(1^{iii})	120.5 (13)
C(4)—C(2)—C(1^{iii})	122.0 (13)	O(1)—C(5)—C(6)	122.2 (13)
O(1)—C(5)—C(7^{ii})	117.9 (16)	C(6)—C(5)—C(7^{ii})	119.6 (16)
C(5)—C(6)—C(7)	123.5 (14)	C(6)—C(7)—C(8)	120.6 (17)
C(6)—C(7)—C(5^{ii})	116.4 (17)	C(8)—C(7)—C(5^{ii})	121 (2)

(3)

I(1)—I(2)	3.106 (1)	I(2)—I(3)	2.785 (1)
I(1)—I(4)	3.311 (1)	I(1)—I(5^v)	3.463 (1)
I(4)—I(5)	2.768 (1)	N(1)—C(1)	1.306 (10)
N(1)—C(2)	1.343 (11)	N(2)—C(5)	1.339 (11)
N(2)—C(6)	1.356 (12)	C(1)—C(3)	1.500 (16)
C(1)—C(2^{iv})	1.398 (13)	C(2)—C(4)	1.493 (12)
C(5)—C(7)	1.512 (13)	C(5)—C(6^{vi})	1.399 (11)
C(6)—C(8)	1.512 (13)		
I(2)—I(1)—I(4)	93.8 (1)	I(2)—I(1)—I(5^v)	82.2 (1)
I(1)—I(2)—I(3)	176.1 (1)	I(1)—I(4)—I(5)	175.9 (1)
I(4)—I(5)—I(1^{vii})	174.2 (1)	C(1)—N(1)—C(2)	122.0 (8)
C(5)—N(2)—C(6)	122.6 (7)	N(1)—C(1)—C(3)	118.1 (8)
N(1)—C(1)—C(2^{iv})	119.8 (9)	C(3)—C(1)—C(2^{iv})	122.1 (8)
N(1)—C(2)—C(4)	117.9 (8)	N(1)—C(2)—C(1^{iv})	118.1 (7)
C(4)—C(2)—C(1^{iv})	124.0 (9)	N(2)—C(5)—C(7)	116.7 (7)
N(2)—C(5)—C(6^{vi})	120.6 (8)	C(7)—C(5)—C(6^{vi})	122.8 (8)
N(2)—C(6)—C(8)	117.5 (7)	N(2)—C(6)—C(5^{vi})	116.8 (7)
C(8)—C(6)—C(5^{vi})	125.7 (9)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, -y, -1 - z$; (iii) $1 - x, -y, -z$; (iv) $1 - x, -y, 1 - z$; (v) $1 + x, y - 1, z$; (vi) $-x, 1 - y, -z$; (vii) $x - 1, 1 + y, z$.

well as the successful refinement of the positional and thermal parameters of the pyrazinium proton, verify its placement, as opposed to a model consisting of two neutral diazines and one diprotonated cation. The crystal packing consists of integrated columns of alternating cations and anions which stack along the a-axis. Pairs of columns are bridged by neutral diazine molecules [Fig. 2(a)]; the best plane through the neutral diazine molecule makes a dihedral angle of 79.4 (9)° with that of the cation.

Structure of (2)

(2) is a disordered structure consisting of two monoprotonated tetramethylpyrazinium cations, one methylhydroquinone molecule and one methylquinone molecule (co-occupying the same site) and two I_3^- anions.* The cation is situated about an inversion center $(\frac{1}{2}, 0, 0)$; the ring angle at N is intermediate between those of the protonated and unprotonated N atoms of (1), suggesting that this is a monoprotonated cation disordered over the inversion center; however, the high degree of uncertainty in this value prevents an unambiguous interpretation. The methylquinone/methylhydroquinone molecules are also disordered across an

---

* An alternative model, suggested by a reviewer, consisting of a tetramethylpyrazine/methylhydroquinone chain structure with periodic protonation of the hydroquinone O atoms in positions *exo* to the chain cannot be ruled out. However, the lack of any hydrogen-bonding interactions *exo* to the chain, and the presumed weaker basicity of methylhydroquinone relative to tetramethylpyrazine, would seem to argue against this interpretation. Refinement problems encountered with this sample (as evidenced by the unusual thermal ellipsoids) are the result of the poor quality of the crystal used in this study, and our inability to grow a more suitable sample. These problems prevent an unambiguous interpretation of the disorder.
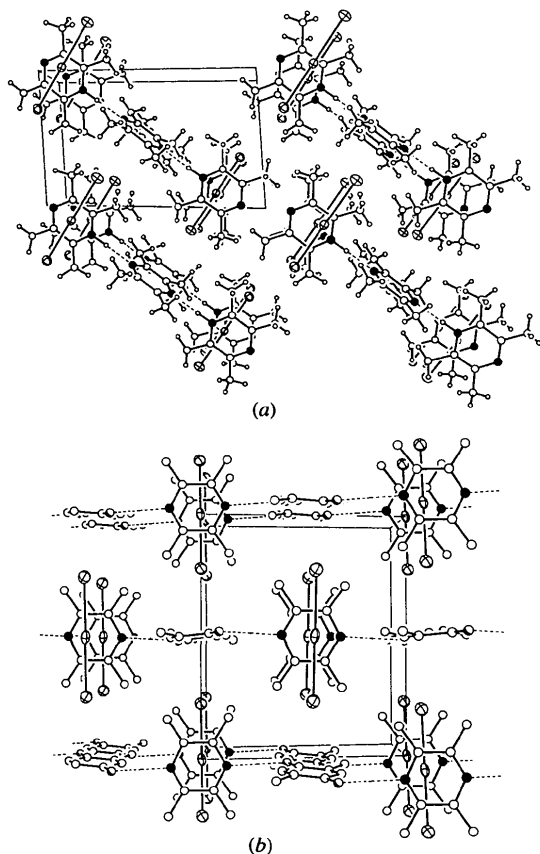

(a)

(b)

Fig. 2. Packing diagrams of (a) (1) and (b) (2) viewed down the a-axis. The origin in both figures is the upper left rear corner; positive z is to the right; positive y is down.

inversion center $(0, 0, \frac{1}{2})$. The cations and methylquinone/methylhydroquinone molecules are linked through hydrogen bonding $[O(1)\cdots N(1) = 2.92(1)\,\text{Å}]$ to form an infinite chain. The central iodine of the I_3^- ion lies on an inversion center at the origin resulting in a linear symmetrical anion, however, the principal axis of the thermal ellipsoid of the central atom is directed along the I—I bond direction, indicating that the apparent inversion symmetry is a consequence of disorder (see Hon, Mak & Trotter, 1982, for a similar disorder). The crystal packing in (2) is similar to that in (1), with integrated stacks of alternating cations and anions, however, in this stucture the stacks are linked by bridging methylquinone and methylhydroquinone molecules in an extended fashion [see Fig. 2(b)]. The dihedral angle between the best planes through the diazine cation and the methylquinone/methylhydroquinone molecules is 74 (2)°.

Structure of (3)

(3) crystallizes with two independent tetramethyl pyrazine cations per asymmetric unit, each of which is situated about an inversion center; the ring angles at the N atom for both cations are experimentally equivalent and are equal to the value observed for (2), indicating that both are monoprotonated cations disordered over the inversion centers. The cations are bridged through hydrogen bonding by a water molecule to form extended chains $[O(1)\cdots N(1) = 2.79(1); O(1)\cdots N(2) = 2.76(1)\,\text{Å}]$; the disorder in the cations requires that the H atoms of the water molecule are also disordered, such that the O atom $[O(1)]$ serves as a hydrogen-bonding donor to one of the N atoms and a hydrogen-bonding acceptor to the other. Using a cutoff of 3.30 Å (0.77 times the van der Waals contact between two I atoms; see Coppens, 1982) to distinguish between intramolecular *versus* intermolecular contacts in polyiodide complexes, the anionic portion of (3) is best described as unsymmetrical I_3^- ions closely associated with I_2 molecules. Unlike the zigzag chains typically seen in similar I_3^-/I_2 structures (Herbstein & Kapon, 1979; Gieren, Hubner, Lamm, Niedlein & Droste, 1985; Deplano, Trogu, Bigoli & Pellinghelli, 1987; Dong, Hwang, Schei, Peng & Yeh, 1989), (3) has an unusual structure in which only one end of the I_3^- ion is involved in interactions with I_2 molecules. The interactions occur from either end of the I_2 molecule; adjacent I_3^-/I_2 units are related by translation along the (1,0,1) direction, and the chains are approximately planar (mean deviation 0.07 Å). The resulting branched polyiodide chain is similar to that observed in (benzophenone)$_4$(LiI$_5$) (Leung, Boehme & Coppens, 1981). The polyiodide chains are associated into layers, parallel to the (1,1,0) plane; chains related by inversion symmetry across $(0, 0, \frac{1}{2})$ have the terminal ends of their I_3^- ions interwoven (see Fig. 3), resembling the packing observed for the I_{16}^{4-} anions in (theobromine)$_2$H$_2$I$_8$ (Herbstein & Kapon, 1979). There are no significantly close contacts

between these chains [shortest contact: $I(3)\cdots I(4') = 4.147\,(1)$ Å] or between the next nearest chain across the inversion center at the origin [shortest contact: $I(1)\cdots I(4'') = 4.315\,(1)$ Å]. Layers of polyiodide anions and water-bridged cations stack in an alternating fashion along the (1,1,0) direction to form a sheet structure (Fig. 4) similar to that found in (theobromine)$_2$H$_2$I$_8$ and (phenacetin)$_2$HI$_5$ (Herbstein & Kapon, 1979).

Concluding remarks

The alternating stacks of cations and anions formed in (1) and (2) contrasts with the segregated stacks formed in the neutral charge-transfer complex tetramethylpyrazine:I$_2$ (Bailey, Buchanan & Pennington, 1992). This packing feature is presumably due to the increased π-acidity of the aromatic heterocycle upon protonation and the increased donor properties of the triiodide anion relative to the neutral iodine molecule. Although the distances between the ions in the stacks [the deviation of the I atoms from the plane of pyrazinium ring is 3.53–3.92 Å for (1) and 3.74–3.75 Å for (2)] are too long to be indicative of strong interactions, they most certainly play a dominant role in the crystal packing. The unusual structure of the polyiodide chain in (3), in which one end of the triiodide anion is not involved in I$\cdots$I interactions,
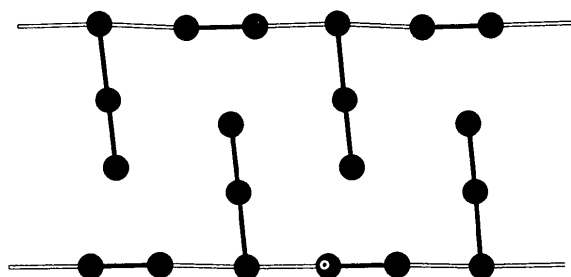

Fig. 3. Two interwoven branched polyiodide chains in (3).
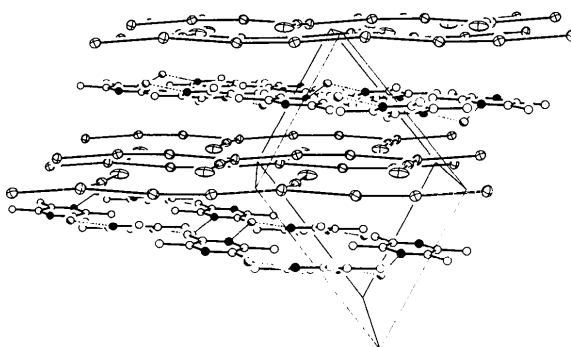

Fig. 4. Packing diagram of (3) showing the sheet structure. View is down the c-axis; the origin is the upper rear corner; positive x is down and to the left; positive y is down and to the right.

may also be related to this packing phenomenon. I(3) at the pendant end of the triiodide is positioned directly over the ring centroid of cation (1) at a distance of 3.782 (1) Å.

Among the most interesting physical properties of polyiodide complexes is their electrical behavior. (1) and (2), with alternating stacks of cations and anions, are expected to be insulators. (3), on the other hand, might be expected to exhibit interesting properties of a highly anisotropic nature due to its potential for ionic mobility within the layer. Investigation of the electrical properties of these and related compounds is currently underway.

References

BAILEY, R. D., BUCHANAN, M. L. & PENNINGTON, W. T. (1992). *Acta Cryst.* C48, 2259–2261.

BOLTON, B. A. & PRASAD, P. N. (1981). *Mol. Cryst. Liq. Cryst.* 76, 309–317.

COPPENS, P. (1982). *Extended Linear Chain Compounds*, edited by J. S. MILLER, Vol. I, ch. 7, pp. 333–356. New York: Plenum Press.

COPPENS, P., LEUNG, P., MURPHY, K. E., TILBORG, P. R., EPSTEIN, A. J. & MILLER, J. S. (1980). *Mol. Cryst. Liq. Cryst.* 61, 1–6.

COPPENS, P., LEUNG, P. C. W., ORTEGA, R., YOUNG, W. S. & LAPORTA, C. (1983). *J. Phys. Chem.* 87, 3355–3359.

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

DEPLANO, P., TROGU, E. F., BIGOLI, F. & PELLINGHELLI, M. A. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2407–2410.

DONG, T.-Y., HWANG, M.-Y., SCHEI, C.-C., PENG, S.-M. & YEH, S.-K. (1989). *J. Organomet. Chem.* 369, C33–C37.

GIEREN, A., HUBNER, T., LAMM, V., NEIDLEIN, R. & DROSTE, D. (1985). *Z. Anorg. Allg. Chem.* 523, 33–44.

HERBSTEIN, F. H. & KAPON, M. (1972). *Nature (London)*, 239, 153–154.

HERBSTEIN, F. H. & KAPON, M. (1979). *Philos. Trans. R. Soc. London*, 291, 199–218.

HON, P. K., MAK, T. C. W. & TROTTER, J. (1982). *Z. Kristallogr.* 158, 213–220.

JIRCITANO, A. J., COLTON, M. C. & BOWMAN MERTES, K. (1981). *Inorg. Chem.* 20, 890–896.

LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED. Munksgaard: Copenhagen.

LERNER, M. M., LYONS, L. J., TONGE, J. S. & SHRIVER, D. F. (1989). *Chem. Mat.* 1, 601–606.

LEUNG, P., BOEHME, R. F. & COPPENS, P. (1981). *Mol. Cryst. Liq. Cryst.* 78, 319–326.

ROSSI, M., MARZILLI, L. G. & KISTENMACHER, T. J. (1978). *Acta Cryst.* B34, 2030–2033.

SHELDRICK, G. M. (1985). *SHELXTL Users Manual*. Revision 5.1. Nicolet XRD Coporation, Madison, Wisconsin, USA.

TEBBE, K.-F. (1977). *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*, edited by A. L. RHEINGOLD, ch. 24, pp. 551–606. Amsterdam: Elsevier.

TEBBE, K.-F. & KRAUSS, N. (1990). *Acta Cryst.* C46, 878–880.

TEITELBAUM, R. C., RUBY, S. L. & MARKS, T. J. (1979). *J. Am. Chem. Soc.* 101, 7568–7573.

ZHANG, W., WILSON, S. R. & HENDRICKSON, D. N. (1989). *Inorg. Chem.* 28, 4160–4165.