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Molecular Complexes of 1,4-Diazines with Iodine

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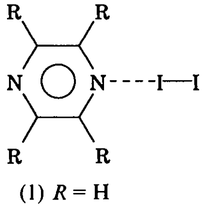
Abstract

The structure of a 1:1 pyrazine–iodine molecular complex has been determined at 203 K and that of a related complex, tetramethylpyrazine–iodine, at 203 and 294 K. Both structures consist of alternating linear chains of diazine and iodine molecules connected through an n–σ^* donor–acceptor interaction. The N···I distances are 2.817 (1) Å in the pyrazine–iodine complex, and 3.085 (1) and 3.072 (1) Å in the tetramethylpyrazine complex at 203 and 294 K respectively.

Comment

Structure determinations of the molecular complexes of iodine with pyrazine (1) and tetramethylpyrazine [(2*a*) at 203 K, (2*b*) at 294 K] were undertaken to investigate the effect of the methyl substituents on the strength of the N···I interaction.



(1) $R = \mathrm{H}$

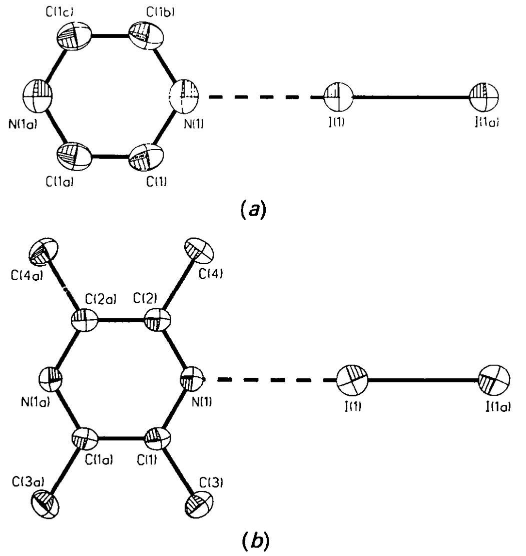
(2*a*), (2*b*) $R = \mathrm{CH_3}$

Pyrazine forms a weak complex with iodine, as revealed by the longer N···I distance and relatively minor perturbation of the iodine molecule [$d(\mathrm{I_2})$ = 2.733 (1) *versus* 2.715 Å for elemental iodine (van Bolhius, Koster & Migchelsen, 1967)] in (1) compared with other nitrogen–iodine complexes (Foster, 1969).

As electron donation by the methyl substituents increases the basicity of the N atoms of tetramethylpyrazine relative to those of pyrazine [pK_a (tetramethylpyrazine) = 3.55, pK_a (pyrazine) = 0.65 (Chia & Trimble, 1961)], tetramethylpyrazine might be expected to form a stronger complex with iodine. However, steric shielding of the functional group by the methyl substituents [similar to that responsible for a significant reduction in the nucleophilicity of tetramethylpyrazine relative to pyrazine (Pritchard & Siddiqui, 1972)] results in a somewhat weaker complex with longer N···I contacts and less perturbation of the iodine molecule [$d(\mathrm{I_2})$ = 2.718 (1) for (2*a*), 2.722 (1) Å for (2*b*)]. Further evidence for the N···I distance being sterically limited is provided by the negligible axial compression (parallel to the donor–acceptor chains) of the *b* axis upon cooling from 294 to 203 K (0.09% for *b versus* 0.43 for *a* and 0.99% for *c*).

The longer than expected N···I distances [2.982 (1) and 3.098 (1) Å] observed for a similar complex of phenazine [pK_a = 1.2 (Albert, Goldacre & Phillips, 1948)] with iodine (Uchida, 1967; Uchida & Kimura, 1984) are probably also the result of steric shielding, in this case involving the H atoms at the 1, 4, 5 and 8 positions of the fused ring system.

The complexes consist of chains of alternating diazine and iodine molecules which stack roughly



(*a*)

(*b*)

Fig. 1. Views showing the labelling of non-H atoms. Thermal ellipsoids are shown at 50% probability levels. (*a*) $\mathrm{C_4H_4N_2.I_2}$. Atoms labelled with lower-case characters are related to their origin atom by the following operations: I(1*a*) $1-x, y, -z$; N(1*a*) and C(1*a*) $-x, y, 1-z$; C(1*b*) $x, -y, z$; C(1*c*) $-x, -y, 1-z$. (*b*) $\mathrm{C_8H_{12}N_2.I_2}$ [(2*a*) shown]. The following symmetry operations apply: I(1*a*) $-x, y, \frac{1}{2}-z$; N(1*a*), C(1*a*), C(2*a*), C(3*a*) and C(4*a*) $1-x, y, \frac{1}{2}-z$.

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normal to the diazinyl ring planes parallel to the *c* axis to form segregated columns of donor and acceptor molecules (Fig. 2). Adjacent molecules in the donor and acceptor columns of (2) are offset in a zigzag fashion due to steric interaction between the methyl groups of neighboring molecules in the donor columns. However, there are no unusually close contacts between adjacent molecules within the columns for either complex.

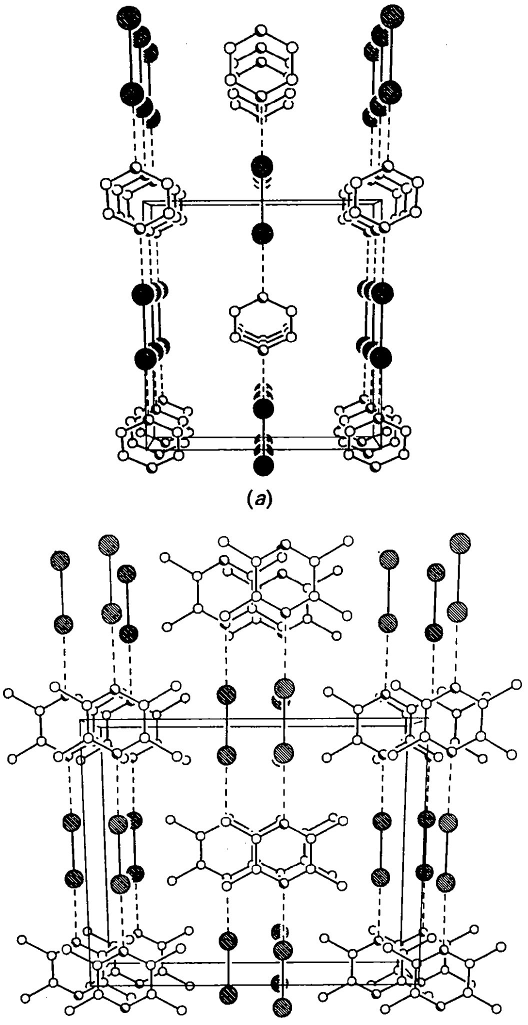

Fig. 2. Packing diagrams for (*a*) $C_4H_4N_2.I_2$ and (*b*) $C_8H_{12}N_2.I_2$ viewed down the *c* axis; *a* vertical; origin upper left, back.

The chains in (2*a*) and (2*b*) are approximately linear [I(1*a*)—I(1)···N(1) = 177.4 (1) for (2*a*), 177.7 (1)° for (2*b*); I(1)···N(1)···N(1*a*) = 175.4 (2) for (2*a*), 176.2 (2)° for (2*b*)] with the I atoms nearly coplanar with the diazine ring [deviations: I(1) = −0.23 for (2*a*), −0.21 Å for (2*b*); I(1*a*) = −0.32 for (2*a*), −0.28 Å for (2*b*)] as is generally observed for this type of complex (Foster, 1969). In (1), however, the I atoms lie significantly out of the diazine plane [deviations: I(1) = 0.52, I(1*a*) = 1.26 Å] (Fig. 3) resulting in non-linear chains [I(1*a*)—I(1)···N(1) = 175.2 (1), I(1)···N(1)···N(1*a*) = 169.4 (2)°]. The pyrazine and iodine molecules are tilted relative to the stacking axes of their respective columns by differing degrees (79.4 and 85.2° respectively) resulting in non-linearity of the chains. The observed tilting may facilitate better packing of the columns in a direction normal to the column stacking axis, as layers of alternating donor and acceptor columns joined by N···I interactions stack in this direction in an offset interlocking fashion.

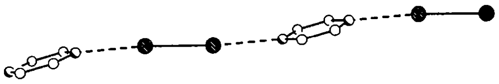

Fig. 3. Non-linear chain of (1).

Experimental

Complex (1)

Crystal data

$C_4H_4N_2.I_2$
M_r = 333.90
Monoclinic
$C2/m$
a = 9.671 (2) Å
b = 9.079 (3) Å
c = 4.466 (1) Å
β = 96.20 (2)°
V = 389.9 (2) Å^3
Z = 2
D_x = 2.84 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 28 reflections
θ = 15.5-29.7°
μ = 7.89 mm^{-1}
T = 203 K
Parallelepiped
0.36 × 0.27 × 0.24 mm
Red

Data collection

Nicolet *R*3*m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.74, $T_{\max}$ = 1.00
786 measured reflections
372 independent reflections
345 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.088
$\theta_{\max}$ = 25°
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 11$
$l = -6 \rightarrow 0$
3 standard reflections monitored every 97 reflections
intensity variation: 3%

Refinement

Refinement on F
Final R = 0.0472
wR = 0.0519
S = 1.19
345 reflections
23 parameters

H atoms not determined
$w = 1/[\sigma^2(F)+0.001(F^2)]$
$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 2.79 e Å^{-3}
$\Delta\rho_{\min}$ = −2.72 e Å^{-3}

Complex (2*a*)

Crystal data

$C_8H_{12}N_2.I_2$
M_r = 390.02

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$C2/c$
$a = 11.607$ (5) Å
$b = 13.751$ (5) Å
$c = 7.578$ (3) Å
$\beta = 108.54$ (3)°
$V = 1146.6$ (8) Å^3
$Z = 4$
$D_x = 2.26$ Mg m^{-3}

Cell parameters from 28 reflections
$\theta = 15.2$–$30.2°$
$\mu = 5.39$ mm^{-1}
$T = 203$ K
Parallelepiped
0.36 × 0.30 × 0.21 mm
Red

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.78$, $T_{\max} = 1.00$
1144 measured reflections
1047 independent reflections
944 observed reflections
$[I>3\sigma(I)]$

$R_{\rm int} = 0.037$
$\theta_{\max} = 25°$
$h = -14 \rightarrow 14$
$k = -17 \rightarrow 0$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 97 reflections intensity variation: 1%

Refinement

Refinement on F
Final $R = 0.0341$
$wR = 0.0471$
$S = 1.93$
944 reflections
55 parameters

H atoms not determined
$w = 1/[\sigma^2(F)+0.00035(F^2)]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}

Complex (2*b*)

Crystal data

$C_8H_{12}N_2.I_2$
$M_r = 390.02$
Monoclinic
$C2/c$
$a = 11.657$ (2) Å
$b = 13.763$ (3) Å
$c = 7.654$ (1) Å
$\beta = 108.06$ (1)°
$V = 1167.5$ (3) Å^3
$Z = 4$
$D_x = 2.22$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.071073$ Å
Cell parameters from 50 reflections
$\theta = 34.8$–$47.8°$
$\mu = 5.29$ mm^{-1}
$T = 294$ K
Parallelepiped
0.40 × 0.31 × 0.23 mm
Red

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.69$, $T_{\max} = 1.00$
1140 measured reflections
1043 independent reflections
927 observed reflections
$[I>3\sigma(I)]$

$R_{\rm int} = 0.019$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 97 reflections intensity variation: −5.5%

Refinement

Refinement on F
Final $R = 0.0482$
$wR = 0.0754$
$S = 1.51$
927 reflections
56 parameters

H atoms not included
$w = 1/[\sigma^2(F)+0.001(F^2)]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.86$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

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

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

	x	y	z	$U_{\rm eq}$
(1)				
I(1)	0.3697 (1)	0	0.0918 (1)	0.032 (1)
N(1)	0.1119 (10)	0	0.3312 (29)	0.038 (2)
C(1)	0.0549 (6)	0.1228 (6)	0.4165 (14)	0.039 (1)
(2*a*)				
I(1)	0.1165 (1)	0.4122 (1)	0.2473 (1)	0.039 (1)
N(1)	0.3848 (3)	0.4097 (3)	0.2597 (6)	0.029 (2)
C(1)	0.4405 (4)	0.4931 (3)	0.2534 (6)	0.027 (1)
C(2)	0.4406 (4)	0.3262 (3)	0.2546 (6)	0.027 (1)
C(3)	0.3744 (5)	0.5852 (4)	0.2617 (8)	0.038 (2)
C(4)	0.3733 (4)	0.2305 (4)	0.2589 (8)	0.042 (2)
(2*b*)				
I(1)	0.1162 (1)	0.4123 (1)	0.2475 (1)	0.058 (1)
N(1)	0.3820 (4)	0.4096 (4)	0.2579 (8)	0.044 (2)
C(1)	0.4399 (5)	0.4933 (4)	0.2539 (7)	0.037 (2)
C(2)	0.4405 (5)	0.3281 (4)	0.2546 (8)	0.037 (2)
C(3)	0.3722 (7)	0.5868 (5)	0.2589 (11)	0.058 (4)
C(4)	0.3735 (6)	0.2341 (6)	0.2574 (11)	0.058 (3)

Table 2. *Geometric parameters* (Å, °)

	(1)		(2*a*)	(2*b*)
I(1)—I(1*a*)	2.733 (1)	I(1)—I(1*a*)	2.718 (1)	2.722 (1)
I(1)—N(1)	2.817 (1)	I(1)—N(1)	3.085 (1)	3.072 (1)
N(1)—C(1)	1.318 (8)	N(1)—C(1)	1.325 (6)	1.340 (7)
		N(1)—C(2)	1.325 (6)	1.318 (7)
C(1)—C(1*a*)	1.362 (9)	C(1)—C(1*a*)	1.40 (1)	1.42 (1)
		C(2)—C(2*a*)	1.40 (1)	1.41 (1)
		C(1)—C(3)	1.492 (7)	1.516 (9)
		C(2)—C(4)	1.536 (7)	1.51 (1)
I(1*a*)—I(1)—N(1)	175.2 (1)	I(1*a*)—I(1)—N(1)	177.4 (1)	177.7 (1)
C(1)—N(1)—I(1)	121.6 (3)	C(1)—N(1)—I(1)	119.2 (2)	120.0 (2)
		C(2)—N(1)—I(1)	120.4 (2)	122.2 (2)
C(1)—N(1)—C(1*b*)	115.5 (5)	C(1)—N(1)—C(2)	120.0 (4)	117.7 (5)
N(1)—C(1)—C(1*a*)	122.2 (5)	N(1)—C(1)—C(1*a*)	120.0 (3)	120.7 (3)
		N(1)—C(2)—C(2*a*)	119.9 (3)	121.6 (4)
		N(1)—C(1)—C(3)	118.0 (4)	117.3 (6)
		N(1)—C(2)—C(4)	119.0 (4)	117.1 (6)
		C(3)—C(1)—C(1*a*)	121.9 (3)	121.9 (4)
		C(4)—C(2)—C(2*a*)	121.1 (3)	121.4 (4)

Complex (1) was obtained by the co-sublimation of equimolar quantities of pyrazine and iodine and complexes (2*a*) and (2*b*) by the slow evaporation of an equimolar solution of tetramethylpyrazine and iodine in ethanol.

The structures were solved by direct methods and refined by full-matrix least squares. Corrections were applied for Lorentz and polarization, linear decay (2*b*), and real and imaginary anomalous dispersion (Cromer, 1974). The isotropic extinction parameters for (1) and (2*b*) were calculated following a similar method to Larson (1970) using *SHELXTL* (Sheldrick, 1986). The extinction coefficients were 0.0020 (5) and 0.0018 (2) respectively. Atomic scattering factors were taken from Cromer & Waber (1974).

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Lists of structure factors and anisotropic thermal parameters, together with a thermal ellipsoid plot for (2*b*) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55352 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1008]

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Bis(5-chloro-2-hydroxy-1,3-xylyl)-18-crown-4

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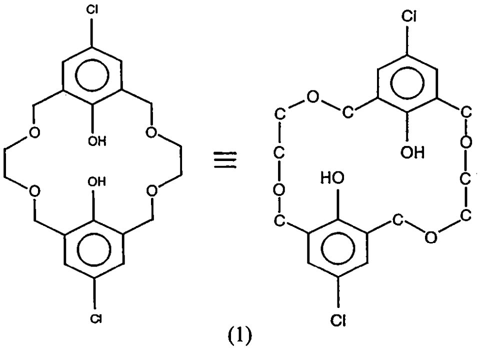
Abstract

The molecule lies about an inversion centre and the 18-membered macrocycle has a rectangular conformation dictated by a pair of O—H···O intramolecular hydrogen bonds between phenolic OH groups and proximal ether O atoms [O···O 2.735(3) Å].

Comment

Metacyclophanes with pendant functional groups have become important structures for studying aspects of host-guest chemistry such as the role of host preorganization and of synergism in ion binding between macrocyclic arrays and potential ligating groups. Substituted phenolic groups have been particularly useful in this regard either as single subunits in crown ether arrays or in multifunctional systems, the most important of the latter being the calixarenes. The phenolic groups provide convenient points of attachment for other functional groups. We have studied crown ethers with a single pendant phenolic group and have demonstrated synergism in binding of ammonia and primary amines (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985; Ferguson, Kaitner, Browne & McKervey, 1988). We have now extended our study of functional macrocycles to include crown ether systems with more than one phenolic unit and report here on the crystal and molecular structure of the 18-membered macrocycle (1) with two phenolic units.



(1)

Macrocycle (1) was synthesized from 2,6-bis(bromomethyl)-4-chlorophenol, which was first protected as its *o*-allyl ether. Cyclization with ethylene glycol and sodium hydride yielded a macrocycle which on deprotection using palladium on carbon in the presence of hydrochloric acid furnished crystals of (1).

The conformation of this centrosymmetric molecule (1) (Fig. 1) is determined by an intramolecular O—H···O hydrogen bond (and its inversion-centre-related one) between phenolic hydroxyl O(1) and proximal ether oxygen O(2) [O(1)···O(2) 2.735(3), O(1)—H 1.09, H···O(2) 1.82 Å, O(1)—H···O(2) 139°]. Similar hydrogen bonding was also found in 2-hydroxy-1,3-xylyl-18-crown-5 (2) and in 5-nitro-2-hydroxy-1,3-xylyl-18-crown-5 (3) (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985). As a result of the intramolecular O—H···O hydrogen bonding, the 18-membered macrocycle adopts an approximately rectangular conformation, with the aromatic ring plane inclined at 128.31(4)° to the best plane through the C and O atoms of the 18-membered ring, and with the hydroxyl oxygen O(1) lying in the plane of the aromatic ring. The macrocycle ring torsion angles are either near to *gauche*, or fully extended *trans* values.

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