Synthesis, structure and thermal decomposition of nitrogen–iodine charge-transfer complexes

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Dipyridylquinoxaline (dpq), 4-cyanopyridine (4-CNpy), 4,4′-bipyridine (4,4′-bpy) and quinoxaline form n→σ* charge-transfer complexes with iodine (I_2), in which the N · · · I distance [2.532(3) Å for dpq·I_2; 2.543(9) and 2.555(9) Å for 4-CNpy·I_2; 2.406(7) Å for 4,4′-bpy·2I_2; 2.92(1) and 2.95(1) Å for quinox·I_2] is shorter than the sum of the van der Waals radii for nitrogen (1.55 Å) and iodine (1.98 Å). Donation of electron density into the antibonding orbital of iodine weakens the I–I bond resulting in elongation relative to the value observed in elemental iodine (2.715 Å). Dpq, 4-CNpy and 4,4′-bpy form molecular adducts, while quinoxaline forms a polymeric species in which there are interactions at both ends of the I_2 molecule. The type of complex which forms depends on the nucleophilic character of the donor (and its corresponding effect of the I_2 molecule) and on the lattice energy of the complex. The strength of the N · · · I interaction in each of the reported complexes has been investigated by X-ray crystallographic analysis and vibrational spectroscopy (far-IR). All of the complexes undergo thermal decomposition involving loss of I_2, and their lattice energy, as a function of thermal stability, has been explored.

Introduction

In addition to their importance in refining our ideas about bonding theory, as exemplified by the extensive work of Mulliken,[1] charge-transfer complexes of iodine (I_2) with an assortment of n-donor molecules have proved useful in a variety of other areas. Triphenylphosphine and arsine·I_2 complexes have been used as oxidizing agents to produce metal complexes in which the metals are found to have unusually high oxidation states.[2] The conversion of methylpyridines into pyridine aldehydes as intermediates for the preparation of pyridine aldoximes and pyridine aldoxime methiodides involves the formation of a methylpyridine·I_2 complex.[3] The formation of triiodide anions in a polyamine polymer has been shown to occur *via* formation of a charge-transfer complex.[4] A purine·I_2 compound has been used as a model to investigate the role of n-donor interactions of purines and pyridines in the structure and reactivity of nucleic acids.[5] Continuing interest in charge-transfer complexes containing iodine is demonstrated by a number of recent articles reporting complexes with donor molecules containing phosphorus,[6,7] sulfur,[8] arsenic[7] and selenium.[8e,9] Complexes of iodine with nitrogen-based donor molecules are also well known and have been extensively studied.[10]

In all of these complexes the charge-transfer interaction consists of an n→σ* donation. We have utilized this interaction to prepare a variety of diazine·I_2 complexes in which N · · · I charge-transfer interactions at either end of both the donor and acceptor molecules result in the formation of extended chains.[11] We are interested in these compounds for the role that directed intermolecular N · · · I interactions might play in the rapidly growing field of crystal engineering. Similar to hydrogen bonding[12] and other attractive forces,[13] such interactions could be used to permit the rational design of co-crystals with interesting and useful properties.

Despite extensive investigation of these systems, however, reliable prediction of the structure of a given complex is still not possible. For example, the only solid product isolated from the reaction of pyridine with iodine, $[(py)_2I](I_7)$,[14] results from dissociation of the I_2 bond, yet 4-methylpyridine, a stronger n-donor which should lead to more extensive destabilization of the I_2 bond (thus favoring an ionic compound), forms a 1:1 adduct with iodine.[15] Acridine[16] and 2,2′-bipyridine[17] form more complicated structures in which the complexed iodine molecule exhibits amphoteric behavior, with one end of the I_2 molecule acting as a Lewis acid to the nitrogen donor and the other end serving as a Lewis base to a second I_2 molecule. This I · · · I interaction is fairly weak and occurs at both ends of the second I_2 molecule to bridge complexes into dimers for acridine and a polymeric chain for 2,2′-bipyridine. Similar weak interactions in pyrazine and its derivatives also occur at both ends of the I_2 molecule, but strong interactions at either end of an iodine molecule have never been observed, in spite of the fact that molecular dynamics simulations favor a 2:1 complex (py-I_2-py) in pyridine solution.[10d]

Linear relationships between pK_a values and stretching force constants[10e] or hyposochromic shifts in the visible band associated with I_2[10i] for pyridine·I_2 complexes suggests that the pK_a value of a given donor is a good indicator of the expected strength of the charge-transfer interaction.[18] Yet, other factors such as steric and packing interactions often come into play.

Through an integrated approach involving X-ray crystallography, thermal analysis, molecular modelling, and spectroscopic methods we are attempting to gain a better understanding of the factors which determine the strength and type of interactions to be expected for a given complex. We report here the synthesis, structure and characterization of a complex formed by dipyridylquinoxaline and I_2 (dpq·I_2) and related pyridyl, diazinyl and dipyridyl derivatives: 4-cyanopyridine (4-CNpy·I_2), 4,4′-bipyridine (4,4′-bpy·2I_2), and quinoxaline (quinox·I_2). The structural formulae of the donor molecules for these and related compounds are shown.

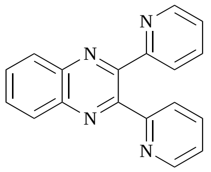
For all of these compounds, the nature of the N · · · I_2 interaction has also been investigated by a combination of vibrational spectroscopy and thermal analysis. The comparison of this information with the structural results will be useful to provide insight into the factors important for determining the relative nucleophilicities of various donor sites for complex formation and decomposition.

In the following paper[19] we present a practical application of charge-transfer interactions for crystal engineering. N · · · I

Table 1 Crystal data

	dpq·I_2	4-CNpy·I_2	4,4′-bpy·$2I_2$	quinox·I_2
Formula	$C_{18}H_{12}N_4I_2$	$C_6H_4N_2I_2$	$C_{10}H_8N_2I_4$	$C_8H_6N_2I_2$
Mw	538.12	357.91	663.78	383.95
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$Pbca$ (No. 61)
a/Å	8.1654(4)	7.641(2)	16.569(1)	21.559(6)
b/Å	9.5649(6)	7.912(3)	8.9795(8)	11.365(3)
c/Å	12.3619(6)	15.667(4)	13.261(1)	8.176(3)
α (°)	70.511(2)	86.93(2)		
β (°)	79.391(2)	87.57(2)	129.126(4)	
γ (°)	75.963(2)	81.88(2)		
V/Å^3	877.35(6)	935.7(5)	1530.5(2)	2003.2(9)
Z	2	4	4	8
D_c/g cm^{-3}	2.04	2.54	2.88	2.55
μ/mm^{-1}	3.59	6.66	8.12	6.23
Transmission coefficient	0.80/1.00	0.52/1.00	0.54/1.00	0.58/1.00
No. obsd data	2607[a]	1826[a]	956[b]	730[a]
$R(F_0)$[c]	0.028	0.035	0.022	0.040
$R_w(F_0)$[d]	0.041	0.045	0.029	0.048

[a] $[I > 3\sigma(I)]$. [b] $[I > 2\sigma(I)]$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.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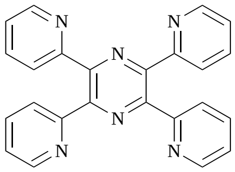
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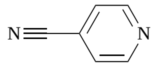
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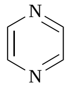
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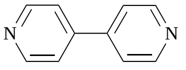
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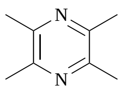
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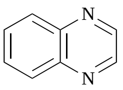
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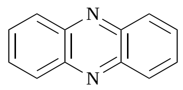
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interactions are utilized to prepare metastable complexes of tetrapyridylpyrazine (tpp) with iodine in two different stoichiometric ratios. Decomposition of the two complexes through loss of I_2 gives two different polymorphs of tpp. The feasibility of this phenomenon for separation and conversion of other polymorphic compounds is being actively investigated. A key point in identifying molecules suitable for this technique will be the nucleophilic character of possible donor sites, as this property (and the resulting structural motifs) will primarily determine the potential for complex formation and the ease of I_2 loss.

Experimental

General

Dipyridylquinoxaline was prepared by a method similar to that of Goodwin and Lyons, by the reaction of *o*-phenylenediamine and 2,2′-bipyridine in ethanol.[20] Quinoxaline, 4-cyanopyridine and 4,4′-bipyridine were purchased from Aldrich Chemical Co., and used as received. Iodine was purchased from Fisher Scientific Co., Fair Lawn, NJ, and was resublimed prior to use. Solvents were obtained from commercial houses and were dried and purified by standard techniques and stored over activated sieves. Far-IR spectra were obtained as Nujol mulls in sealed polyethylene bags on a Nicolet 20F spectrometer. Carbon, hydrogen and nitrogen analyses were performed by Atlantic Microlabs, Norcross GA, or (for 4,4′-bpy·$2I_2$) on a Perkin-Elmer 2400 Series II CHNS analyser.

X-Ray diffraction

Powder diffraction data were acquired on a Scintag XDS/2000 theta-theta diffractometer with Cu-Kα_1 radiation ($\lambda = 1.54060$ Å) and an intrinsic germanium solid-state detection system. Single crystal intensity data were measured at 21 ± 1 °C (−70 ± 1 °C for quinox·I_2 due to the higher volatility of this complex) with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using $\omega/2\theta$ scans (2θ max = 50°; for 4-CNpy·I_2, 2θ max = 45°) on either a refurbished (Crystal Logic of Los Angeles, CA) Syntex P2_1 diffractometer (dpq·I_2), a Nicolet R3m V diffractometer (4-CNpy·I_2), or a Rigaku AFC7R (18 kW) diffractometer (quinox·I_2 and 4,4′-bpy·$2I_2$). The data were corrected for Lorentz and polarization effects; the intensities of three reflections, remeasured periodically throughout data collection, varied by less than 2%, indicating no need for a decay correction (4-CNpy·I_2 exhibited a 21.2% decay; a linear correction was applied to the data for this compound). An absorption correction, based on azimuthal scans of several intense reflections, was applied to the data for each compound. For all compounds, the structure was solved by direct methods and refined by using full-matrix least-squares techniques. all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were either refined with isotropic thermal parameters (dpq·I_2 and 4,4′-bpy·$2I_2$) or were included at idealized positions ($d_{C-H} = 0.96$ Å) with a refined isotropic group thermal parameter [$U_H = 0.10(2)$ Å^2 for 4-CNpy·I_2 and $U_H = 0.06(2)$ Å^2 for quinox·I_2]. 4,4′-Bpy·$2I_2$ possesses crystallographic twofold symmetry [the midpoint of the bond joining the pyridyl rings is coincident with a twofold axis at (1/2, 0, 1)]; the formula units of the other complexes (two per asymmetric unit for 4-CNpy·I_2) occupy general positions within their unit cells. Structure solution, refinement and the calculation of derived results were performed with the SHELXTL[21] package of computer programs. Neutral atom scattering factors and the real and imaginary anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*, Vol. IV.[22] Relevant crystallographic data are given in Table 1.†

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† Atomic coordinates, distances and angles and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) (Reference No. 188/98). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC should give the full literature citation and reference number.

Table 2 Selected bond distances (Å) and angles (°)[a]

dpq·I_2		4-CNpy·I_2		4,4′-bpy·2I_2		quinox·I_2	
Distances/Å							
I(1)–I(2)	2.759(1)	I(1)–I(2)	2.749(2)	I(1)–I(2)	2.797(1)	I(1)–I(2)	2.724(1)
		I(3)–I(4)	2.745(2)				
I(1)–N(3)	2.532(3)	I(1)–N(1)	2.555(9)	I(1)–N(1)	2.406(7)	I(1)–N(1)	2.95(1)
		I(3)–N(3)	2.543(9)			I(2)–N(2a)	2.92(1)
Angles (°)							
I(2)–I(1)–N(3)	173.8(1)	I(2)–I(1)–N(1)	175.5(2)	I(2)–I(1)–N(1)	177.8(1)	I(2)–I(1)–N(1)	178.8(3)
		I(4)–I(3)–N(3)	175.5(2)			I(1)–I(2)–N(2a)	175.8(3)
I(1)–N(3)–C(9)	125.5(3)	I(1)–N(1)–C(1)	126.0(8)	I(1)–N(1)–C(1)	120.6(5)	I(1)–N(1)–C(8)	121(1)
I(1)–N(3)–C(10)	116.1(3)	I(1)–N(1)–C(5)	115.9(7)	I(1)–N(1)–C(5)	121.8(5)	I(1)–N(1)–C(1)	116(1)
		I(3)–N(3)–C(7)	127.7(8)			C(3)–N(2)–I(2b)	123(1)
		I(3)–N(3)–C(11)	116.3(6)			C(2)–N(2)–I(2b)	121(1)
C(1)–N(1)–C(8)	117.8(4)			C(1)–N(1)–C(5)	117.5(7)	C(1)–N(1)–C(8)	123(1)
C(2)–N(2)–C(3)	118.4(4)					C(2)–N(2)–C(3)	116(1)
C(9)–N(3)–C(10)	117.8(4)	C(1)–N(1)–C(5)	118(1)				
C(14)–N(4)–C(15)	117.1(5)	C(7)–N(3)–C(11)	116(1)				

[a] Atoms labelled with a lower-case character were generated by the following symmetry operation: a: *x*, 1 + *y*, *z*; b: *x*, −1 + *y*, *z*.

Thermal analysis

Thermal gravimetric analyses were performed on a Perkin-Elmer Series 7 analyser with the TGA7 software package (version 2.20). The samples had a mass of approximately 10 mg each and all calculations were performed on data represented as percent loss of starting mass. For onset calculations, the samples were heated at a constant rate of 5 °C min^{-1} from 25 °C until all of the material had evaporated. Mass loss and onset calculations were performed by standard methods.

Synthesis

Solid state synthesis. All of the complexes can be formed by simply mixing the solid reactants in a closed vial; the reactions typically go to completion in 2–3 d, as verified by powder diffraction. However, the products obtained are in the form of microcrystalline powders. In order to obtain X-ray quality crystals, the reactions were also run in solution.

Synthesis of dpq·I_2. Dpq·I_2 is formed by the reaction of stoichiometric amounts of I_2 and dpq in a dry non-protic solvent of low polarity, such as hexane, toluene or *m*-xylene. When ethanol is used as the solvent a complex mixture of polyiodide salts is formed in addition to dpq·I_2.[23] In a typical reaction 0.100 g (0.35 mmol) of dpq and 0.090 g (0.35 mmol) of I_2 were dissolved in *m*-xylene (50 ml); slow evaporation of solvent yielded 0.138 g (0.26 mmol) of reddish-brown crystals of dpq·I_2 (73.0% yield). X-Ray quality crystals could also be grown by diffusion of iodine vapor into a *m*-xylene solution of dpq. For dpq·I_2: far IR ν/cm^{-1}(Nujol) 592 (m), 576 (w), 549 (s), 436 (w), 171 (s), 112 (m). Calc. for $C_{18}H_{12}N_4I_2$: C, 40.17; N, 10.41; H, 2.25%. Found: C, 42.42; N, 10.69; H, 2.42% [the observed deviation in these values is presumably due to loss of ~3% (by mass) I_2 from the sample prior to analysis].

Synthesis of 4-CNpy·I_2. 4-CNpy·I_2 is formed by the reaction of stoichiometric amounts of I_2 and 4-CNpy in ethanol (95%). In a typical reaction 0.101 g (0.97 mmol) of 4-CNpy and 0.252 g (0.99 mmol) of I_2 were dissolved in ethanol (50 ml); slow evaporation of solvent yielded 0.329 g (0.92 mmol) of reddish-brown crystals of 4-CNpy·I_2 (94.8% yield). For 4-CNpy·I_2: far IR ν/cm^{-1}(Nujol) 557 (s), 468 (s), 176 (s), 127 (w). Calc. for $C_6H_4N_2I_2$: C, 20.14; N, 7.83; H, 1.13%. Found: C, 20.25; N, 7.88; H, 1.17%.

Synthesis of 4,4′-bpy·2I_2. 4,4′-bpy·2I_2 is formed by the reaction of stoichiometric amounts of I_2 and 4,4′-bpy in ethanol (95%). In a typical reaction 0.143 g (0.92 mmol) of 4,4′-bpy and 0.501 g (1.97 mmol) of I_2 were dissolved in ethanol (50 ml); slow evaporation of solvent yielded 0.541 g (0.82 mmol) of reddish-brown crystals of 4,4′-bpy·2I_2 (89.0% yield). For 4,4′-bpy·2I_2: far IR ν/cm^{-1}(Nujol) 627 (s), 566 (w), 484 (w), 154 (s). Calc. for $C_{10}H_8N_2I_4$: C, 18.09; N, 4.22; H, 1.21%. Found: C, 18.22; N, 4.13; H, 1.18%.

Table 3 N···I and I–I distances of related charge-transfer complexes

Compound	*d* (N···I)/Å	*d* (I–I)/Å	Ref.
Trimethylamine·I_2	2.27	2.83	27*a*
4-Picoline·I_2	2.31	2.83	15
Hexamethylcyclotriphosphazene·I_2	2.417(7)	2.823(1)	27*b*
$Ph_3PNSiMe_3$·I_2	2.432(4)	2.8332(8)	27*c*
Hexamethylenetetraamine·I_2	2.439(8)	2.830(1)	27*d*
Hexamethylenetetraamine·2I_2	2.496(5)	2.791(1)	27*d*
	2.498(5)	2.771(2)	
Hexamethylenetetraamine·3I_2	2.593(6)	2.746(1)	27*e*
9-Cyclohexyladenine·I_2	2.520(3)	2.764(1)	5
Pyrazine·I_2	2.817(1)	2.733(1)	11
Phenazine·I_2	2.982(1)	2.726(1)	27*f*
	3.092(1)		
Tetramethylpyrazine·I_2	3.072(1)	2.722(1)	11
Dipyridylquinoxaline·I_2	2.532(3)	2.759(1)	[a]
4-Cyanopyridine·I_2	2.543(9)	2.745(2)	[a]
	2.555(9)	2.749(2)	
4,4′-Bipyridine·2I_2	2.406(7)	2.797(1)	[a]
Quinoxaline·I_2	2.92(2)	2.724(1)	[a]
	2.95(2)		
Tetrapyridylpyrazine·2I_2	2.562(8)	2.750(1)	19

[a] This paper.

Synthesis of quinox·I_2. Quinox·I_2 is formed by the reaction of stoichiometric amounts of I_2 and quinox in ethanol (95%). In a typical reaction 0.110 g (0.85 mmol) of quinox and 0.243 g (0.96 mmol) of I_2 were dissolved in ethanol (50 ml); slow evaporation of solvent yielded 0.284 g (0.74 mmol) of dark-red crystals of quinox·I_2 (87.4% yield). For quinox·I_2: far IR ν/cm^{-1}(Nujol) 613 (w), 530 (w), 399 (m), 202 (s). Calc. for $C_8H_6N_2I_2$: C, 25.02; N, 7.30; H, 1.58%. Found: C, 25.07; N, 7.24; H, 1.64%.

Results

Structures

All of the compounds studied are $n\rightarrow\sigma^*$ charge-transfer complexes, in which the N···I distance is shorter than the sum of van der Waals radii for nitrogen (1.55 Å) and iodine (1.98 Å).[24] Donation of electron density into the antibonding orbital of iodine weakens the I–I bond resulting in elongation relative to the value observed in elemental iodine (2.715 Å).[25] Selected bond distances and angles for the four compounds are listed in Table 2. For comparison, Table 3 lists N···I and I–I distances for related charge-transfer complexes. References and metric

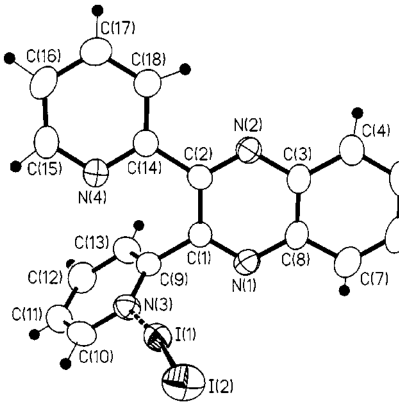

Fig. 1 Thermal ellipsoid plot (50% probability ellipsoids) of dpq·I_2

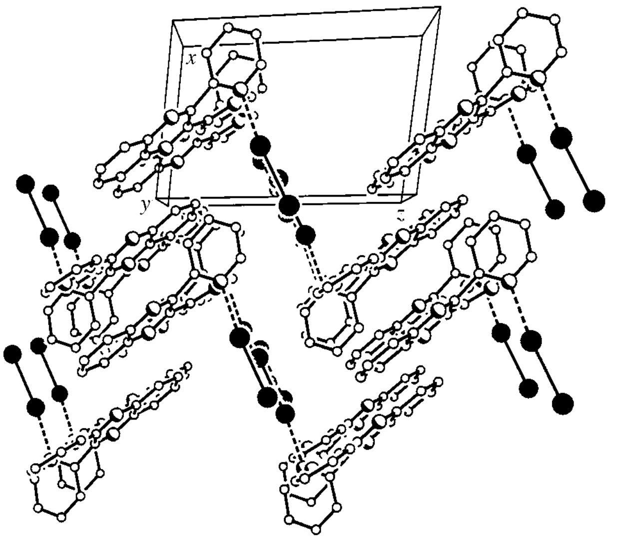

Fig. 2 Crystal packing viewed down the *b*-axis of dpq·I_2. (Iodine atoms are shown as solid circles; nitrogen atoms as partially shaded circles; carbon atoms as open circles; hydrogen atoms have been omitted for clarity).

parameters for many of the compounds mentioned below were obtained by searching the Cambridge Structural Database.[26]

dpq·I_2. Dipyridylquinoxaline forms a simple 1 : 1 charge-transfer complex with iodine (see Fig. 1). The N···I interaction [2.532(3) Å] is within the range observed for similar compounds (see Table 3). Complexation leads to an elongated I–I bond [2.759(1) Å], which is typical for these types of compounds, but has no apparent effect on the bonding within the donor molecule. The distances and angles within the dpq molecule are experimentally identical to those of the uncomplexed parent molecule[28] and to a dpq molecule included in the lattice of $[CuBr(dpq)_2]HSO_4$·dpq.[29]

The major effect of complexation is on the conformation of the pyridyl ring planes relative to the quinoxaline plane; the dihedral angle between the quinoxaline plane and the plane of the pyridine ring interacting with I_2 is 77.9°, while the uncomplexed pyridine ring makes a dihedral angle of 14.3° with the quinoxaline plane. The dihedral angle between the pyridyl ring plane and the diazine ring plane for the parent dpq molecule and the related compounds, tetrapyridylpyrazine (tpp)[30–32] and dipyridylpyrazine (dpp)[33] typically lies between 30 and 60°.

There are no extended interactions involving the opposite end of the I_2 molecule or any other donor sites of dpq. The dpq and I_2 molecules are associated into segregated regions, forming loose stacks running parallel to the *b*-axis of the unit cell (Fig. 2).

4-CNpy·I_2. The N···I distance in 4-CNpy·I_2 (Fig. 3) is slightly longer, and the I–I distance slightly shorter than in dpq·I_2, indicating a slightly weaker N···I interaction. Similar to dpq·I_2, complexation has no significant effect on the bonding within the donor molecule, as its bonding parameters agree with those of the parent molecule.[34] As with many nitriles,[35] including the parent molecule, the crystal packing of 4-CNpy·I_2 is influenced by self-association of the cyano group. There are two 4-cyanopyridine molecules in the asymmetric unit for 4-CNpy·I_2; for one of them there are no significant interactions involving the cyano groups, but for the other the –C≡N groups of a pair of molecules related by inversion symmetry are lined up in an antiparallel configuration with fairly short N···C contacts of 3.50(1) Å, as opposed to similar contacts of 3.620(6) Å observed in the parent compound.

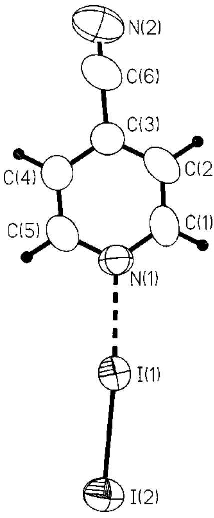

Fig. 3 Thermal ellipsoid plot (50% probability ellipsoids) of 4-CNpy·I_2 (molecule one is shown)

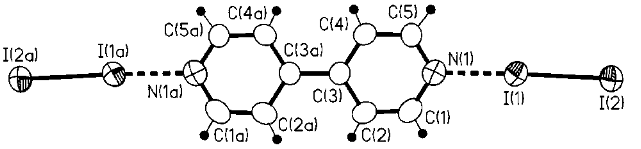

Fig. 4 Thermal ellipsoid plot (50% probability ellipsoids) of 4,4′-bpy·$2I_2$

4,4′-bpy·$2I_2$. 4,4′-Bpy·$2I_2$ (Fig. 4) forms a slightly stronger interaction to iodine than dpq·I_2; the N···I distance is shorter, and the I–I distance is longer. Although the structure of the parent compound has not been determined, the bonding distances and angles within the donor molecule agree well with those of a number of 4,4′-bpy molecules either complexed to metal atoms[36] or included as guest molecules in crystalline compounds.[37] The conformation of 4,4′-bpy, as defined by the dihedral angle between the two pyridine rings, can vary from a coplanar arrangement of the two planes to an orientation in which the ring planes are normal to each other. This is similar to biphenyl and derivatives, a class of compounds for which much work has been done.[38] The coplanar arrangement is often favored by crystal packing, but this conformation results in close contact between *ortho* hydrogen atoms. Although planar biphenyls were originally thought to be disordered, low-temperature studies now suggest that they are ordered.[38] 4,4′-Bpy molecules have also been observed in both planar[36b,d,37a] and nonplanar configurations with dihedral angles of 26.9–40.0°.[36,37b] The donor molecule in 4,4′-bpy·$2I_2$ falls into the latter category with a dihedral angle of 25.1°.

quinox·I_2. Quinox·I_2 (Fig. 5) forms a significantly weaker complex than any of the pyridyl derivatives. The N···I interaction is significantly longer and the I–I bond is nearly equivalent to that observed in elemental iodine. Quinoxaline however, with two equivalent donor sites, does form an extended chain

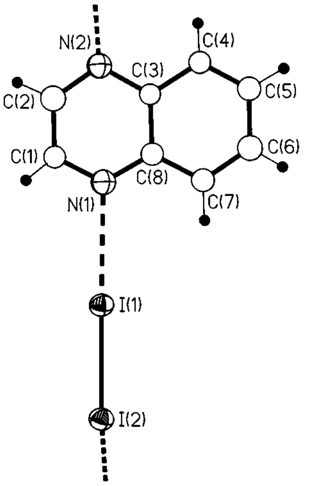

Fig. 5 Thermal ellipsoid plot (50% probability ellipsoids) of quinox·I_2

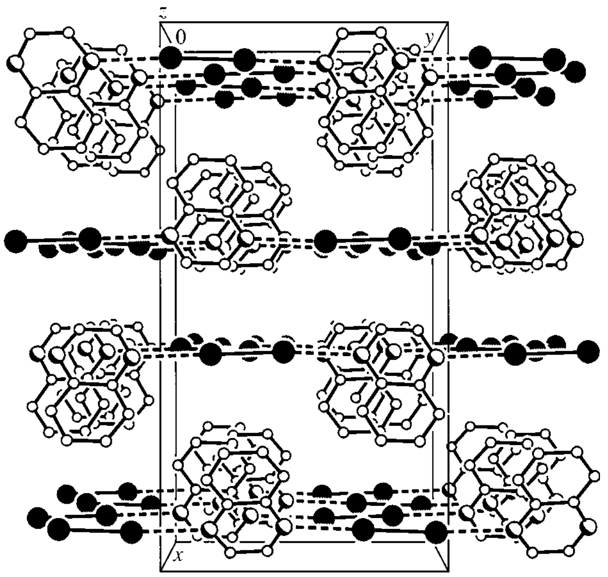

Fig. 6 Crystal packing viewed down the *c*-axis of quinox·I_2. (Iodine atoms are shown as solid circles; nitrogen atoms as partially shaded circles; carbon atoms as open circles; hydrogen atoms have been omitted for clarity).

structure with interactions occurring at both donor sites and at either end of the I_2 molecule (Fig. 6). The distances and angles within the donor agree well with quinoxaline molecules complexed to metal atoms in chain structures[39] or included as clathrates.[40] The chain structure is similar to that observed for I_2 complexes of pyrazine,[11] tetramethylpyrazine[11] and phenazine.[27f] The chains pack with the I_2 and quinox molecules segregated into separate stacks, also similar to the other diazine·I_2 complexes.

Thermal analysis

Thermal decomposition data for the reported compounds and related nitrogen heterocycle·I_2 charge-transfer complexes are given in Table 4. Pyrazine, tetramethylpyrazine, quinoxaline and I_2 have substantial vapor pressure at elevated temperatures, though their molecular complexes do not. As the complexes are heated to decomposition, there is a noticeable darkening of the solid, accompanied by evolution of iodine vapor. The decomposition of the pyrazine·I_2 polymer is above the melting point of pyrazine (54–56 °C), but volatilization of the heterocycle is so fast that no liquid is observed. Likewise, the fragmentation of the tmpz·I_2 and quinox·I_2 polymers and the 4-CNpy·I_2 adduct results in sublimation of the component molecules without melting. Decomposition of the complexes of iodine with less volatile donor molecules involves an initial loss of all or most of the I_2 followed by subsequent loss of the donor with continued heating.

Table 4 Thermal decomposition of nitrogen heterocycle·I_2 charge transfer complexes

Compound	Mass (Donor) (%)	Mass (I_2) (%)	Onset/°C	Mass loss (%)
dpq·I_2	48	52	106	46
			237	54
4-CNpy·I_2	29	71	105	100
quinox·I_2	34	66	99	100
4,4′-bpy·$2I_2$	24	76	163	77
tpp·I_2	60	40	102	40
tpp·$2I_2$	43	57	112	40
			163	12
pyz·I_2	24	76	101	100
tmpz·I_2	35	65	82	100
phenaz·I_2	41	59	131	65

Far-IR spectroscopy

All of the compounds exhibit a strong signal in the range 150–200 cm^{-1}, which is attributed to the I–I stretching vibration of complexed iodine.[41] The frequency of this vibration is lower than that for elemental I_2 (from Raman),[42] and is inversely related to the N···I contact distance in the complex. The sterically obstructed complexes, tmpz·I_2 and quinox·I_2 each exhibit signals at significantly higher frequency (202 cm^{-1}) than does pyz·I_2 (184 cm^{-1}), which has an unhindered N···I interaction. The signals observed for the complexes involving stronger donors, 4-CNpy·I_2, tpp·I_2, tpp·$2I_2$ and 4,4′-bpy·$2I_2$, shift to successively lower frequencies (176, 173, 172, 171 and 154 cm^{-1}, respectively), consistent with the increasingly strong N···I interactions.

Discussion

Pyridine donor ligands are uniformly stronger n-donors as is evidenced by their shorter N···I distances and greater elongation of the I–I bond. When there is a possibility of bonding to a pyrazinyl nitrogen as opposed to a pyridyl nitrogen, the latter is favored. The I–I stretching frequency of the complexed iodine is lower for the pyridyl donors than for the pyrazinyl donors. Finally, in the systems considered here, decomposition of the pyridyl·I_2 complexes generally occurs at higher temperatures than are observed for the pyrazinyl·I_2 complexes. All of these observations can be explained by the generally good agreement between the relative basicity of the donor and the expected strength of the charge transfer interaction. The electron-withdrawing power of a second nitrogen atom in the ring reduces the basicity of both pyrazinyl donor sites relative to a pyridyl donor. Increased base strength leads to stronger, therefore shorter N···I interactions and greater perturbation of the I_2 molecule. Elongation of the I–I bond, due to donation into a-σ^*-orbital of the acceptor molecule, is increased and the shift to lower frequency for the I–I stretching vibration is enhanced. The increased strength of the donor–acceptor bonding results in a more stable complex which requires greater thermal energy to disrupt. However, exceptions to this trend indicate that other factors are also important, and suggest that base strength is not an ideal predictor for determining the thermal stability of these charge transfer complexes.

One exception involves 4-cyanopyridine which is a relatively strong donor, as evidenced by fairly short N···I distances [2.543(9) and 2.555(9) Å; two molecules in the asymmetric unit] and correspondingly low frequency for I–I stretching (176 cm^{-1}) in 4-CNpy·I_2, but the onset of thermal decomposition is modest (105 °C) and more importantly all of the mass of the complex is lost in a single event. This indicates that the lattice energy of the complex is somewhat low, in spite of the fact that the complex itself is relatively stable. Another exception, phenaz$\cdot$$I_2$, has a higher decomposition temperature than most of the pyridyl donors, in spite of the fact that its pK_a value (1.2)[43] is lower. Conversely, its $N\cdots I$ distance is considerably longer than that found for pyz$\cdot$$I_2$, a complex with a much weaker donor (pK_a 0.65).[44] The high decomposition temperature is presumably due to the higher lattice energy of this complex which is attributed to more efficient packing of the large planar donor molecules. The increased length of the $N\cdots I$ interaction is probably the result of steric shielding of the donor sites by hydrogen atoms in the 1, 4, 5 and 8 positions of the phenazine ring. It should be noted, however, that this steric obstruction can be overcome with a stronger donor. We have found that acridine (pK_a of 5.60),[45] which possesses similar shielding hydrogen atoms about its donor, forms a very strong charge transfer bond with iodine [$N\cdots I$ distance of 2.442(4) Å].[16]

Tetramethylpyrazine, a stronger base than phenazine (pK_a of 3.55),[44] forms even weaker interactions to I_2 due to steric shielding of the lone-pair by bulkier methyl groups. This is reflected in a much lower decomposition temperature, a longer $N\cdots I$ distance and a shorter I–I bond. Quinoxaline, on the other hand is a weaker base (pK_a of 0.72)[43] than phenazine, yet forms a slightly stronger $N\cdots I$ interaction due to the less obstructed donor site. However, distortion of the $N\cdots I$ interaction in quinox$\cdot$$I_2$ away from an ideal trigonal planar arrangement to avoid the fused-ring hydrogen atom was much less than expected. This is presumably due to the strong directional nature of the $n\rightarrow\sigma^*$ interaction and/or possibly some overriding effect of other more important packing interactions. Consistent with this is the fact that while the base strength of quinoxaline is similar to that of pyrazine, it has a significantly weaker $N\cdots I$ interaction due to steric hindrance, but has nearly the same thermal decomposition temperature because of its higher lattice energy.

Increased donation into the σ^* orbital of the I_2 molecule results in elongation of the I–I bond, providing an additional indicator of donor strength. Yet, as with base strength, perturbation of the I–I bond is but one factor in determining the thermal stability of the complex. For example, the I_2 stretching vibrations for the two complexes formed between I_2 and tpp are virtually identical, yet they have very different thermal behavior. The 1:1 complex loses all of its iodine in a single event at 102 °C. The 1:2 complex, on the other hand loses approximately 70% of its iodine at a slightly higher temperature (112 °C), and then loses most of the remaining iodine in a series of small events starting at a temperature of about 163 °C, and continuing until all of the mass is lost at an elevated temperature (>250 °C).[19] At room temperature, tpp$\cdot$$I_2$ loses all of its iodine within 3 d (as verified by powder diffraction), while tpp$\cdot$2I_2 takes 2–3 weeks for the decomposition to go to completion. As the structure of tpp$\cdot$$I_2$ is unknown, we can only speculate, but the similarity of the far-IR spectra for the two compounds suggests that the nature of their $N\cdots I$ interactions must be essentially identical. This suggests that tpp$\cdot$$I_2$, like tpp$\cdot$2$I_2$, forms a simple donor–acceptor adduct, but that a pyridyl ring on only one side of the central pyrazine ring interacts with iodine, rather than one ring on either side as in tpp$\cdot$2I_2. The lower concentration of acceptor molecules and more open packing of the hydrocarbon portion of the molecule should lead to greater ease of diffusion of the I_2 molecules out of the solid, as is observed.

Like tpp$\cdot$$I_2$, dpq$\cdot$$I_2$ is a simple 1:1 adduct, with an $N\cdots I$ interaction on one side of the donor molecule and weaker hydrocarbon packing on the other side. Comparison of the structure of the dpq, with that of dpq$\cdot$$I_2$ should, therefore provide some insight into the mechanism of decomposition in tpp$\cdot$$I_2$.

The major effect of complexation in dpq$\cdot$$I_2$ is on the conformation of the pyridyl ring planes relative to the quinoxaline plane; the dihedral angle between the quinoxaline plane and the plane of the pyridine ring interacting with I_2 is 77.9°, while the uncomplexed pyridine ring makes a dihedral angle of 14.3° with the quinoxaline plane. The dihedral angle between the pyridyl ring plane and the diazine ring plane for the parent dpq molecule and the related compounds, tetrapyridylpyrazine (tpp)[30–32] and dipyridylpyrazine (dpp)[33] typically lies between 30 and 60°. However, the relative orientation of adjacent pyridyl rings with regard to position of the nitrogen atoms varies for the different compounds and for different forms within compounds. Tpp crystallizes in two polymorphic forms.[30,31] In one polymorph the nitrogen atoms of adjacent pyridyl rings lie on the same side of the pyrazine plane; one of the rings is inclined so that the nitrogen atom is oriented toward the interior of the molecule and the other is inclined toward the exterior (*endo*/*exo* conformation; see structure formulae for **1** and **2** in the following paper). In the other polymorph, the nitrogen atoms of adjacent pyridyl rings lie on opposite sides of the pyrazine plane, and both are inclined toward the interior of the molecule (*endo*/*endo*). In uncomplexed dpq the molecule has an *endo*/*endo* conformation, yet when included as a guest molecule in [CuBr(dpq)$_2$]$HSO_4$$\cdot$dpq it has an *endo*/*exo* conformation. Dpp has only been observed in one form, and has an *endo*/*endo* conformation.

Molecular modelling results on dpp[19] suggest that the *endo*/*endo* conformation is slightly more stable than the *endo*/*exo* conformation, and that conversion from one to the other goes through a transition state in which one pyridyl ring rotates to an orientation normal to the pyrazine plane and the other rotates to an orientation coplanar with the pyrazine ring, and with the nitrogen atom of this ring oriented in an *endo* fashion. The conformation of the donor molecule is similar to this transition state; the dihedral angle between the quinoxaline plane and the plane of the pyridine ring interacting with I_2 is 77.9°, while the uncomplexed pyridine ring makes a dihedral angle of 14.3° with the quinoxaline plane. Both pyridyl nitrogen atoms are oriented toward the interior of the molecule, so the conformation can be best described as intermediate between the transition state and the *endo*/*endo* form of uncomplexed dpq. As described above, the dpq and I_2 molecules are associated into segregated regions, forming loose stacks running parallel to the b-axis of the unit cell. When left in an open atmosphere, iodine slowly diffuses out of dpq$\cdot$$I_2$ leaving behind microcrystals of the uncomplexed form of dpq (verified by powder X-ray diffraction). Similar results have been obtained for tpp, but the two complexes, tpp$\cdot$$I_2$ and tpp$\cdot$2I_2, give different polymorphs upon loss of I_2, thereby allowing interconversion of the two polymorphic forms *via* decomposition of the charge transfer complexes.[19]

Conclusion

Aromatic nitrogen heterocycles form strong charge transfer complexes with iodine through an $n\rightarrow\sigma^*$ interaction. Depending on a variety of factors, such as steric, electronics and packing energies, several different types of complexes can form. Strong donors, such as dpq, 4-CNpy, 4,4′-bpy, and tpp form simple Lewis acid–Lewis base adducts. Weaker donors, such as quinox, pyz, tmpz and phenaz form polymeric species in which there are interactions at both ends of the I_2 molecule. This is presumably due more to lower perturbation of the I_2 molecule by the weaker donors than to the presence of two donor pairs, since many of the stronger donors just discussed have additional donor sites which are not utilized in their complexes with I_2. Although these diazinyl donors form weaker complexes, they can exhibit relatively high thermal stability due to the increased lattice energies of their polymeric structures. Not discussed in this paper is a third class of complex which involves strong donors, such as acridine[16] and 2,2′-bipyridine,[17] complexed to I_2 molecules which exhibit amphoteric behavior. In these complexes, one end of an I_2 molecule acts as an acceptor to the nitrogen-donor pair and the other end acts as a donor to a second I_2 molecule which, similar to the diazinyl polymeric complexes, interacts with a donor pair (in this case an iodine-donor atom) at either end to bridge the complex into an oligomeric structure. Details concerning this 'iodine sponge' behavior will be reported in due course.

Acknowledgements

We are grateful to the National Science Foundation (Chemical Instrumentation and EPSCoR to Clemson; ILI to Furman) and to the Duke Endowment of Furman University for support of the facilities utilized in this work.

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Paper 7/00203C
Received 8*th January* 1997
Accepted 12*th July* 1997