The reaction of iodine with 9-methylacridine: formation of polyiodide salts and a charge-transfer complex

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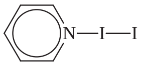
The reaction of iodine and 9-methylacridine in methylene chloride results not in the formation of a charge-transfer complex as with acridine, but in the iodine-rich salt $[ICH_2C_{13}H_8N–H]_4(I_8)(I_5)_2$, **8**, where a proton on the methyl group has been replaced by an iodine. In toluene, the reaction produces both a charge-transfer complex $ICH_2C_{13}H_8N–I_2$, **9**, and a salt $[CH_3–acridine(H)]_2(I_7)(I_5)$, **10**. Polyiodide salt formation can be explained by the availability of a facile reaction pathway from the aryl radical cation which results from initial oxidation by I_2.

Introduction

The interactions of I_2 with unsaturated nitrogen heterocycles are complex. Initially, lone pair electrons from the nitrogen are donated into a σ* I_2 antibonding orbital, leading to charge-transfer complexes (**1**). Early theoretical work by Mulliken[1] has led to detailed spectroscopic, thermodynamic and crystallographic studies on a number of such species.[2] These studies indicated that complexes of structure-type **1** are relatively delicate and are in equilibrium with other species, both in solution and in the solid state. For example, pyridine has been shown to dissociate into an ionic species (**2**)[3] and ultimately crystallize as a polyiodide salt of structure type **3**.[4]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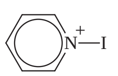
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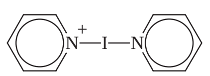
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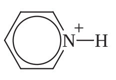
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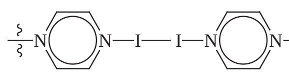
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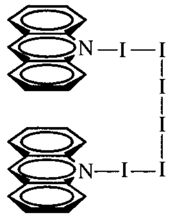
Other types of ionic species have also been observed. During the course of our investigations of I_2 as a solid state structure-controlling vector, we have often inadvertently prepared salts of type **4**, in which the iodine-rich counter ions condense into a variety of marvelous three-dimensional motifs. These structurally interesting salts are generally found as minor side products, formed by oxidation of the aromatic heterocycle to a radical cation followed by solvolysis or reaction with incipient moisture.[5] Polyiodide salts are of considerable current interest, with more than 300 entries in the crystallographic databases reported.[6] The most common salts are the triiodides, but compounds of much higher iodine content are known. Typically, these very iodine-rich complexes are best viewed as containing I_3^- ions loosely coordinated to iodine molecules.

The perturbation of the I–I bond by heterocycles can lead to other novel complexes. Certain diazines interact with both ends of the I_2, leading to extended structures of the type **5**.[7] Very recently, we have found that acridine (**6**) and 9-chloroacridine (**7**) form dimers in which the organic moieties are connected by I_6 chains.[8] These complexes, along with the polymer $[(2,2'\text{-bipyridine})_2I_6]_x$,[9] represent the only examples of structures containing neutral I_6 chains. Compounds **6** and **7** have some resemblance to the polyiodide salts discussed above, in that they may be thought of as acridine charge-transfer hosts of structure-type **1**, with entrapped I_2 guests.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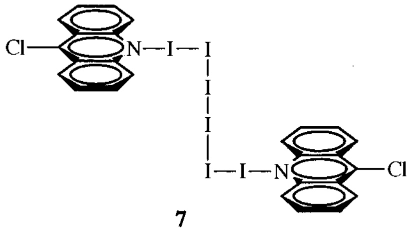
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We have taken advantage of the interaction of iodine and other simple Lewis acceptors with heterocycles to rationally design crystalline structures. The strength of the highly directional charge-transfer interaction can dominate the crystal packing, but the volatile acceptors can be relatively easily removed from the resulting solid.[10] We are very interested in the combination of electronic and steric energies required to form very iodine-rich species such as **6** and **7**. One strategy used in crystal engineering to probe the relationship of these energy parameters is to replace chlorine with a methyl group.[11] The groups occupy similar molar volumes (19.9 Å^3 *vs.* 23.5 Å^3, respectively), but have different electronic effects. Thus, while there are a number of isomorphous chloro- and methyl-substituted heterocycles known, there are also instances where the crystal packing of the two derivatives are very different.

The unique structures of complexes **6** and **7**, along with the biological importance of the acridine family of heterocycles, have prompted us to examine the reaction of 9-methylacridine with I_2. Here we report that 9-methylacridine does not form I_6 molecular complexes, but undergoes very facile halogenation at the benzylic position.

Experimental

General

Methylene chloride and toluene were obtained from commercial houses and were purified by distillation from CaH_2 (methylene chloride) or sodium–benzophenone (toluene) under argon just prior to use. 9-Methylacridine was obtained from

Table 1 Crystal data

	8	**9**	**10**
Formula	$C_{28}H_{22}N_2I_{11}$	$C_{17.5}H_{14}NI_3$	$C_{28}H_{24}N_2I_{12}$
FW	1782.44	619.00	1911.29
Cryst. size/mm	0.14 × 0.18 × 0.20	0.12 × 0.17 × 0.26	0.05 × 0.14 × 0.18
Cryst. system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	9.887(1)	12.986(2)	13.219(6)
b/Å	25.473(5)	15.562(3)	15.506(6)
c/Å	8.123(1)	9.759(2)	21.887(8)
α/°	91.49(1)	91.46(2)	
β/°	90.18(1)	101.43(2)	102.34(3)
γ/°	88.80(1)	68.00(1)	
V/Å^3	2044.7(5)	1789.8(7)	4383(2)
Z	2	4	4
D_{calc}/g cm^{-3}	2.89	2.30	2.90
μ/mm^{-1}	8.36	5.23	8.50
Transm. coeff.	0.45/1.00	0.35/1.00	0.43/1.00
No. obsd. data	6804[a]	5169[a]	3439[a]
$R(F_o)$[b]	0.039	0.032	0.057
$R_w(F_o)$[c]	0.055	0.048	0.068

[a] $(I > 2\sigma(I))$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.

Acros Chemical Company and used without further purification. Resublimed iodine was purchased from Fisher Scientific Company and used as received. Carbon, hydrogen and nitrogen analyses were obtained on a Perkin-Elmer 2400 Series II CHNS analyzer.

Thermal analysis

Thermal analyses were performed on a Perkin-Elmer Series TGA7 analyzer. Each sample had a mass of approximately 10 mg and was heated at 5 °C min^{-1} from 30 °C until the entire sample had evaporated. Mass loss and onset calculations were performed by standard methods.

X-Ray diffraction analysis

Single crystal intensity data for compounds **8**–**10** were measured at either 22 ± 1 °C (for **8**) or −90 ± 1 °C (for **9** and **10**) by using $\omega/2\theta$ scans ($2\theta_{max} = 50°$ for **8** and **9**, 45° for **10**) on a Rigaku AFC7R (18 kW rotating anode generator) diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). 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. An absorption correction, based on azimuthal (ψ) scans of several intense reflections, was applied to the data for each compound. The structures were 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 included (except for the methyl hydrogen atoms of **10**) at idealized positions ($d_{C-H} = 0.96$ Å; $d_{N-H} = 0.90$ Å) with a refined group thermal parameter ($U_H = 0.099(8)$ Å^2 for **8**; $U_H = 0.045(4)$ Å^2 for **9**; $U_H = 0.07(2)$ Å^2 for **10**). Structure solution, refinement and the calculation of derived results were performed with the SHELXTL-Plus[12] 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*.[13] Relevant crystallographic data are given in Table 1.

Powder diffraction was performed on a Scintag XDS/2000 theta–theta diffractometer with Cu-Kα radiation (λ = 1.54060 Å) and an intrinsic Germanium solid-state detection system.

Synthesis of 8

A solution of 9-methylacridine (100 mg, 0.52 mmol) was dissolved in 4.0 ml of methylene chloride and placed in a 25 mL beaker. Iodine (380 mg, 1.5 mmol) was added to the solution and the beaker was sealed with parafilm perforated with several small holes. The solvent (and excess iodine) was allowed to slowly evaporate. When the liquid volume had decreased by 90%, the remainder of the solvent was removed leaving large black tabular crystals of **8**. Isolated yield, 68%. Calc. for $C_{56}H_{44}N_4I_{22}$: C, 18.87; N, 1.57; H, 1.24. Found: C, 22.34; N, 1.78; H, 1.46% [the observed deviation in these values is presumably due to loss of ~5% (by mass) I_2 from the sample prior to analysis]. Powder diffraction data of the bulk product were compared to the predicted pattern calculated from the single crystal structure of **8** and were found to be nearly identical.

Synthesis of 9 and 10

Using the same procedure as for the synthesis of **8**, but using toluene as the solvent, a mixture of red parallelepiped crystals of **9** and dark red plates of **10** was isolated in approximately a 50/50 ratio. Yield of **9** + **10**, 87%. Elemental analysis data were not collected since the mixture components could neither be reliably separated nor homogeneously mixed without extensive loss of I_2. Powder diffraction data of the bulk product were compared to the predicted patterns calculated from the single crystal structures of **9** and **10** and were found to be nearly identical to a superposition of the two predicted patterns.

Results and discussion

Glusker and Miller reported that the reaction of 4-methylpyridine with I_2 resulted in the formation of two compounds.[14] The first of these was clearly a typical charge-transfer complex of type **1**, while the second was later shown, by X-ray diffraction, to be a salt of type **3**.[15] Spectroscopic studies on other methyl-substituted nitrogen aromatics seem to indicate that they initially form molecular complexes with I_2, much like their unsubstituted analogues.[16] It seemed, therefore, likely that the reaction of 9-methylacridine and I_2 in organic solvents would give a product of type **1**. Alternatively, the steric requirements of the heterocycle might allow the formation of an isomorph of compound **7**. Finally, products arising from a methylacridine radical cation might also be expected to compete with charge-transfer complex formation, since iodine has long been known to oxidize polycyclic aromatics to radical cations. For example, Tolbert and co-workers have examined the details of the iodine oxidation of 9-methylanthracene and related compounds in chloroform.[17] The radical cation was found to undergo both proton abstraction at the methyl group (followed by trapping

Table 2 Selected bond distances (Å) and angles (°) for **8**

Distances			
I(1)–C(14)	2.168(8)	I(2)–C(28)	2.157(9)
I(3)–I(4)	2.912(1)	I(4)–I(5)	2.938(1)
I(5)–I(6)	3.422(1)	I(5)–I(7a)	3.422(1)
I(6)–I(7)	2.741(1)	I(8)–I(9)	2.969(1)
I(9)–I(10)	2.872(1)	I(10)–I(11)	3.407(1)
I(11)–I(11b)	2.770(2)		
Angles			
I(3)–I(4)–I(5)	179.1(1)	I(4)–I(5)–I(6)	90.8(1)
I(4)–I(5)–I(7a)	90.9(1)	I(6)–I(5)–I(7)	160.8(1)
I(5)–I(6)–I(7)	177.0(1)	I(6)–I(7)–I(5c)	160.5(1)
I(8)–I(9)–I(10)	175.1(1)	I(9)–I(10)–I(11)	98.3(1)
I(10)–I(11)–I(11b)	172.6(1)	I(1)–C(14)–C(7)	108.1(5)
I(2)–C(28)–C(21)	109.5(6)		

Atoms labeled with a lower-case character were generated by the following symmetry operation: (a) $-1 + x, y, z$; (b) $2 - x, -y, 1 - z$; (c) $1 + x, y, z$.

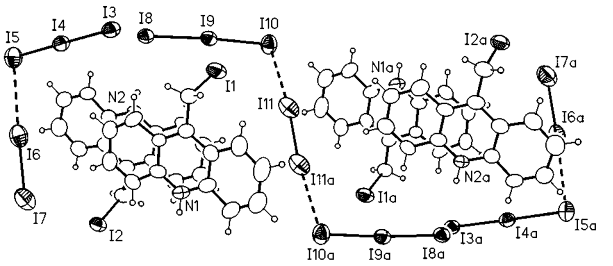

Fig. 1 Thermal ellipsoid plot (50% probability) of **8** showing a $[CH_2I–acridine(H)]_4(I_8)(I_5)_2$ unit.

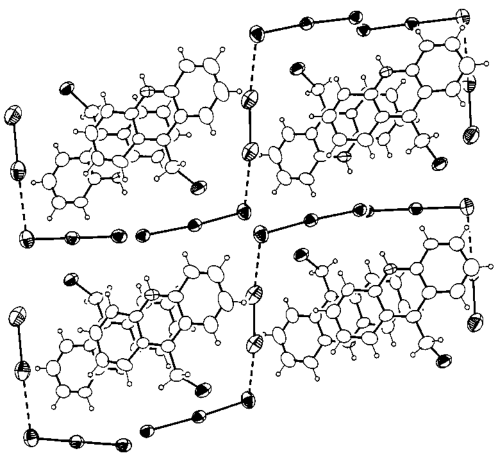

Fig. 2 Rectangular polyiodide tunnels in **8**.

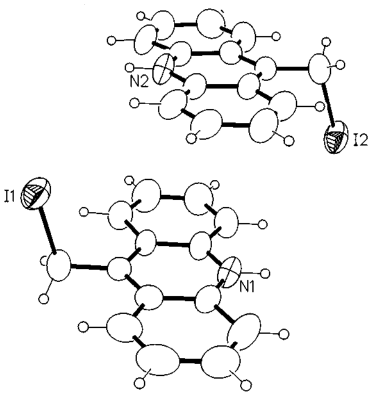

Fig. 3 Dimer of $[CH_2I–acridine(H)]^+$ cations in **8**.

with pyridine) and direct nucleophilic attack at the *meso* position. Other reactions, such as solvolysis, have also been observed under similar reaction conditions.

To minimize the possibility of side reactions, all experiments were performed in solvents freshly distilled from appropriate drying agents under argon. The effect of light on the reaction pathway was also examined, but found to be negligible. Slow evaporation of solvent from a methylene chloride solution of 9-methylacridine and I_2 resulted in a product which proved to be a salt with the general formula $[ICH_2C_{13}H_8N–H]_4(I_8)(I_5)_2$, (**8**). Polyiodide salts with an iodine/cation ratio of >3 are relatively rare, thus **8**, with a ratio of 4.5, is unusual. This compound displays a number of interesting structural features. There are four acridine cations in the unit cell, surrounded by four I_3^- counterions. Two of the counterions are weakly bound to an I_2, while the other two are bridged by an I_2 (Fig. 1). Selected bond distances and angles for compound **8** are shown in Table 2.

If the boundary between intra- and intermolecular I–I interaction distances is taken as 3.44 Å (80% of the sum of the van der Waals radii of two iodine atoms[18]) the anions in **8** can be described as an I_5^- ion (I3–I7) and as an I_8^{2-} ion (I8–I11 and I8b–I11b; second set generated by inversion symmetry about (*1 0 1/2*)). A weaker interaction between I_5^- anions related by translation along the *a*-axis (I5 ··· I7a = 3.860(1) Å) results in formation of a branched "comb-like" chain similar to that seen in tetramethylpyrazinium pentaiodide monohydrate.[5a] S-Shaped I_8^{2-} anions are interwoven between two branched chains (related to each other by inversion symmetry) to form rectangular tunnels (completed by translation along the *c*-axis) with I ··· I contact distances of 4.063(1)–4.192(1) Å (Fig. 2).

The two unique organic cations pack as a loosely associated dimeric structure (Fig. 3). The fused ring systems are essentially planar (mean deviations of 0.016 and 0.018 Å) and lie nearly parallel to one another (dihedral angle of 5.1°); the average interplanar spacing is 3.5(3) Å. The polyiodide tunnels are filled with dimeric pairs of organic cations which are related to each other by translation along the *c*-axis. Weak interactions consisting of N–H ··· I_{anion} and C–I ··· I_{anion} contacts (N ··· I range: 3.619(4)–3.939(4) Å; I ··· I range: 3.850(1)–3.982(1) Å) occur between the cations and anions.

The purity of the sample was established by X-ray powder diffraction of the bulk material. This was found to be nearly identical to the calculated pattern of **8**. Thermal gravimetric analysis showed that the solid evolves 42% of its mass in a sudden thermal event with an onset temperature of 146 °C. The remainder of the mass is lost in a series of ill-defined thermal events beginning at 281 °C. The first decomposition event is well above the temperature at which free I_2 would sublime, but below the vaporization temperature of methylacridine (190 °C). Iodine rich compounds such as this typically slowly lose I_2 at room temperature. We find that even with careful handling, approximately 5% of the total I_2 content is lost prior to the time elemental analysis can be obtained. Thus, the first thermal event is very close to the mass loss that would be expected if the polyiodide ions were decomposed to monoatomic I^- (expected mass loss, 49%). At much higher temperatures, other decomposition processes begin. These are completed by about 350 °C.

A particularly interesting feature of the structure is the fact that the methyl group has been iodinated. While radical chlorination and bromination of benzylic protons are common reactions, radical iodination is not, since direct abstraction of a benzylic proton is thermodynamically disfavored.[19] A simple ionic pathway is also unreasonable, since there is no strong base present which might be able to deprotonate the methylacridine.

There is some precedence for alkyl substituent iodination of nitrogen heterocycles. In 1970, Markovac and co-workers reported the conversion of 2-methylpyridines to aldehydes in hot I_2–DMSO.[20] This reaction was proposed to proceed *via* the corresponding iodomethanes, though the intermediates were not observed and the mechanism of their formation was not

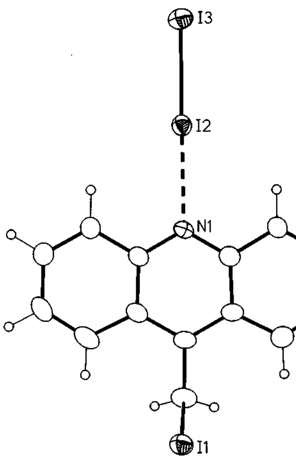

Fig. 4 Thermal ellipsoid plot (50% probability) of a CH_2–acridine·I_2 complex of **9**.

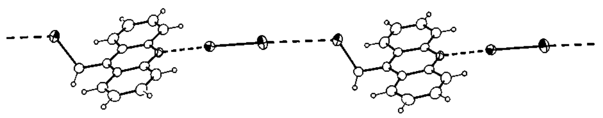

Fig. 5 Extended chain of CH_2–acridine·I_2 in **9**.

discussed. An explanation for both Markovac's results and our own can be found in the observation that methylarene radical cations are very powerful acids.[21] Thus, the formation of **8** can be understood to occur by a series of reactions in which the methylacridine is oxidized by iodine (eqn. (1)), deprotonated

$$\mathrm{CH_3{-}MA + I_2 \longrightarrow CH_3{-}MA^{\bullet +} + I_2^{\bullet -}} \tag{1}$$

by additional methylacridine (eqn. (2)), iodinated (eqn. (3))

$$\mathrm{CH_3{-}MA^{\bullet +} + CH_3{-}MA \longrightarrow CH_3{-}MA{-}H^+ + CH_2{=}MA^{\bullet}} \tag{2}$$

$$\mathrm{CH_2{=}MA^{\bullet} + I_2^{\bullet -} \longrightarrow ICH_2{-}MA + I^-} \tag{3}$$

and finally N-protonated by the methylacridinium ion (eqn. (4)).

$$\mathrm{ICH_2{-}MA} + \underset{\mathbf{10}}{\mathrm{CH_3{-}MA{-}H^+}} \rightleftharpoons \underset{\mathbf{8}}{\mathrm{ICH_2{-}MA{-}H^+}} + \mathrm{CH_3{-}MA} \tag{4}$$

Support for this mechanism comes from running the reaction in toluene. Again, the reaction was run in very dry solvent in the absence of oxygen and light. Two distinctly different materials were formed in approximately equivalent amounts. The first of these formed light orange crystals with a tabular habit, and was found to be that of a toluene solvate of the molecular complex **9** (Fig. 4). As in **8**, the methyl group has been iodinated.

The N···I distance in **9** is longer than that observed for the complex (acridine·I_2)$_2$·I_2, (**6**),[8] presumably due to electronic effects of the iodomethyl group, but is within the range observed for similar complexes of iodine with aromatic nitrogen donors.[10b] Weak I···I interactions from the terminal end of each I_2 to the iodomethyl substituent of an acridine molecule related by translation along the *ac*-diagonal (I1···I3 = 3.895(1) Å for molecule one; I4···I6 = 4.046(1) Å for molecule two) result in the formation of infinite chains (Fig. 5). The geometry of these I···I contacts suggests a weak n→σ* interaction from the methyl iodide donor to the I_2 acceptor.

Packing of the chains of **9** creates cages in which toluene molecules are weakly trapped (Fig. 6). At room temperature, these solvent molecules readily diffuse out of the crystal to leave a microcrystalline product. Since the production of **9** results in the liberation of one equivalent of HI, it is not surprising that the other compound isolated from the reaction was a polyiodide salt. Compound **10** has the formula [CH_3–acridine(H)]$_2$(I_7)(I_5), giving it an iodine/cation ratio of 6. This is a very iodine rich salt and, though not approaching the iodine content of the nonaiodides and greater, is quite rare.

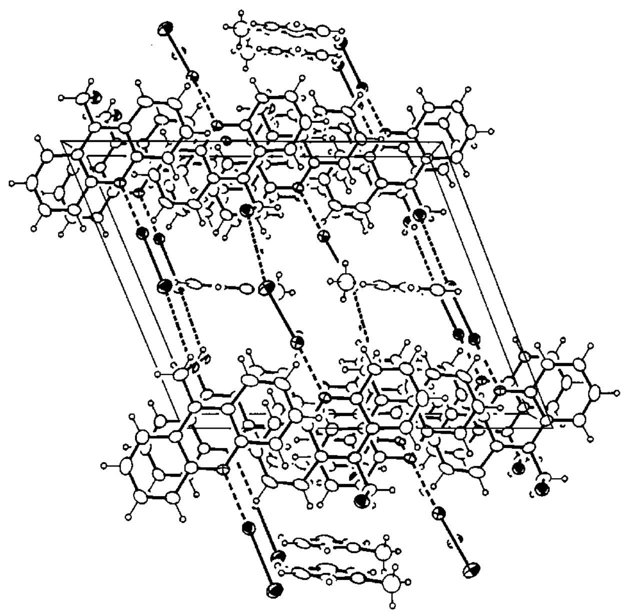

Fig. 6 Crystal packing in **9** showing entrapped toluene solvate molecules (origin is the upper, left, rear corner; $+x$ is down; $+y$ is to the right; and $+z$ is out).

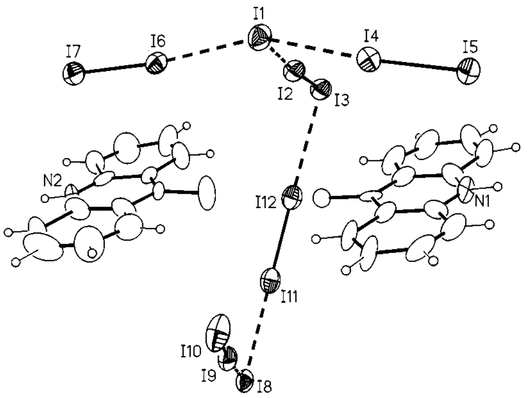

Fig. 7 Thermal ellipsoid plot (50% probability) of **10** showing an [acridine(H)]$_2$(I·3I_2)(I·2I_2) unit.

The structure of **10** consists of protonated methylacridine cations and a unique complex network of polyiodide anions (Fig. 7). The dominant structural feature is an extended branched chain of iodide anions and I_2 molecules. Four-coordinate iodine atoms (I1), with "seesaw" coordination and I–I distances ranging from 3.227(3)–3.419(3) Å, are linked by I_2 molecules (I2–I3) into a zigzag chain situated about a 2_1 screw axis parallel to the *b*-axis. Two iodine molecules (I4–I5 and I6–I7) extend from the chain. A V-shaped (I–2I_2) I_5^- anion (I8–I12) bridges the zigzag chain through weaker I···I interactions (I10···I1 = 4.099(3), I10···I2 = 3.836(3), I12···I3 = 3.540(3) Å) to complete a branched ribbon of polyiodide anions (Fig. 8).

The framework of the I_7^- zigzag chain is related to that of two other polyiodide structures that have been reported. The common feature in all of them is the iodide anion coordinated to four I_2 molecules in a distorted tetrahedral or seesaw geometry. In [$(C_5Me_5)_2Cr_2I_3$]$_2$ [I_{16}],[22] this feature is part of a discrete I_{16}^{2-} anion that is part of a complex layered network of cations and anions. Similar to **10**, the $I^-\cdots I_2$ contacts are grouped around 3.2–3.3 Å. The anion in [H_3O^+·18-crown-6][I_7^-] has an

Table 3 Selected bond distances (Å) and angles (°) for **9**

Distances			
I(1)–C(14)	2.174(6)	I(2)–I(3)	2.754(1)
I(2)–N(1)	2.659(5)	I(1)–I(3a)	3.895(1)
I(4)–C(28)	2.170(6)	I(5)–I(6)	2.746(1)
I(5)–N(2)	2.655(5)	I(4)–I(6b)	4.046(1)
Angles			
C(14)–I(1)–I(3a)	117.7(2)	I(3)–I(2)–N(1)	177.7(1)
I(2)–I(3)–I(1b)	176.8(1)	C(28)–I(4)–I(6b)	124.3(2)
I(6)–I(5)–N(2)	177.6(1)	I(5)–I(6)–I(4a)	160.6(1)
I(2)–N(1)–C(1)	121.0(3)	I(2)–N(1)–C(13)	119.2(3)
C(1)–N(1)–C(13)	119.5(5)	I(5)–N(2)–C(15)	121.3(3)
I(5)–N(2)–C(27)	118.9(3)	C(15)–N(2)–C(27)	119.7(5)
I(1)–C(14)–C(7)	109.6(4)	I(4)–C(28)–C(21)	109.6(4)

Atoms labeled with a lower-case character were generated by the following symmetry operation: (a) $1 + x, y, 1 + z$; (b) $-1 + x, y, -1 + z$.

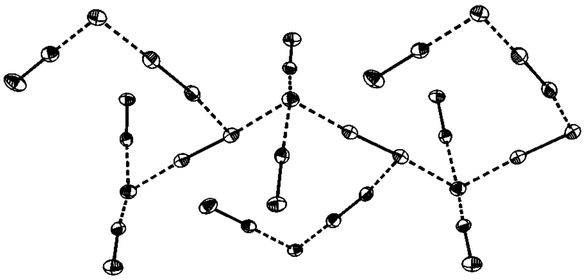

Fig. 8 Branched ribbon of polyiodide anions in **10**.

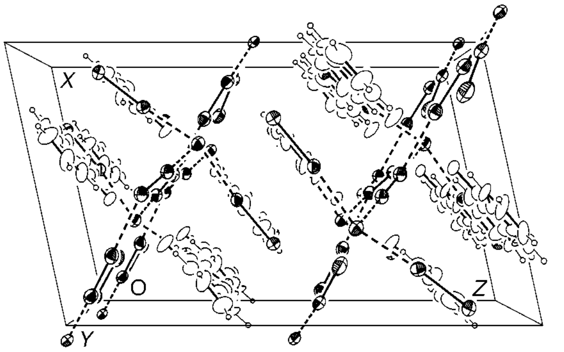

Fig. 9 Crystal packing in **10** (origin is the lower, left, rear corner; $+x$ is up; $+y$ is out; and $+z$ is to the right).

infinite sawhorse geometry consisting of an infinite branched chain of I^- anions and I_2 molecules.[23] The same basic building block of an I^- anion linked to four I_2 molecules with a seesaw geometry about the I^- is present in this compound as is seen in compound **10**. The major difference is that in the "sawhorse" structure the "legs" of the seesaw form the branches of the chain and propagation involves the "seat" I_2's as bridges. In **10**, the "seats" form the branches and propagation involves the "legs" as bridges. The organic cations pack within the branches of the anionic ribbon and serve to link the ribbons through weak N–H···I interactions to the center atom (I8) of the I_5^- anions (N1···I8 = 3.602(6), N2···I8 = 3.566(7) Å) to complete the crystal packing (Fig. 9). Selected bond distances and angles for compounds **9** and **10** are shown in Tables 3 and 4 respectively.

X-ray powder diffraction shows that the observed powder pattern of the product mixture is consistent with a superposition of the calculated patterns of **9** and **10** in approximately equal amounts. The formation of **10** strongly suggests that, in toluene at least, a mechanism similar to that shown in eqns. (1)–(4) is operational. Unlike the methylene chloride reaction, once an acridine abstracts a proton in toluene, it precipitates from the iodine-rich solution as a polyiodide salt, shutting down

Table 4 Selected bond distances (Å) and angles (°) for **10**

Distances			
I(1)–I(2)	3.255(3)	I(1)–I(4)	3.227(3)
I(1)–I(6)	3.268(3)	I(1)–I(3a)	3.419(3)
I(2)–I(3)	2.760(3)	I(3)–I(12)	3.540(3)
I(4)–I(5)	2.759(3)	I(6)–I(7)	2.739(3)
I(8)–I(9)	3.164(3)	I(8)–I(11)	3.256(3)
I(9)–I(10)	2.761(3)	I(11)–I(12)	2.745(3)
Angles			
I(2)–I(1)–I(4)	88.9(1)	I(2)–I(1)–I(6)	84.4(1)
I(4)–I(1)–I(6)	156.7(1)	I(2)–I(1)–I(3a)	108.0(1)
I(4)–I(1)–I(3a)	79.1(1)	I(6)–I(1)–I(3a)	81.8(1)
I(1)–I(2)–I(3)	175.8(1)	I(2)–I(3)–I(1b)	174.9(1)
I(2)–I(3)–I(12)	95.1(1)	I(1b)–I(3)–I(12)	79.8(1)
I(1)–I(4)–I(5)	175.5(1)	I(1)–I(6)–I(7)	173.8(1)
I(9)–I(8)–I(11)	82.3(1)	I(8)–I(9)–I(10)	175.2(1)
I(8)–I(11)–I(12)	177.9(1)	I(11)–I(12)–I(3)	170.3(1)

Atoms labeled with a lower-case character were generated by the following symmetry operation: (a) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (b) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

eqn. (4). The iodinated neutral species may undergo additional oxidation to a radical cation, but the rate of proton abstraction becomes insignificant due to steric hindrance.[17] In the absence of a viable competing pathway, the acridine crystallizes as the charge-transfer complex **9** as the solvent evaporates.

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