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PAPER

Diiodoacetylene: compact, strong ditopic halogen bond donor†

Catherine Perkins,‡ Stefano Libri, Harry Adams and Lee Brammer*

Diiodoacetylene, C_2I_2, is the smallest ditopic halogen bond donor other than I_2 or other dihalogens. A convenient synthesis of diiodoacetylene from the common Sonagashira coupling reagent $Me_3SiC{\equiv}CH$, is described. The halogen-bonded adducts of C_2I_2 with dimethylformamide (DMF), pyrazine (pyz) and 1,4-diazabicyclooctane (dabco) have been characterised by X-ray crystallography. All adopt 1D halogen-bonded chains linked *via* short C–I···O [I···O 2.834(4)–2.888(4) Å; C–I···O > 170°] or C–I···N [I···N 2.715(3)–2.832(7) Å; C–I···N > 175°] interactions. Attempts to synthesise the adduct of C_2I_2 with hexamethylenetetramine (hmta) resulted in isolation and crystallographic characterisation of the adduct of C_2I_4·hmta, indicating decomposition of C_2I_2 to yield C_2I_4 in solution. The adduct comprises two independent C_2I_4 molecules that act, respectively, as tetratopic and ditopic halogen bond donors forming C–I···N interactions [I···N 2.948(7)–2.999(8) Å; C–I···N > 165°], occupying three of the four nitrogen sites on htma. The remaining nitrogen sites engage in N···C(π) interactions directed orthogonal to the plane of the ditopic C_2I_4 molecules. Separate surveys of halogen bonds formed by diiodo(poly)alkynes $I(C{\equiv}C)_nI$ ($n = 1$–3) and by C_2I_4 molecules indicate that C–I···N halogen bonds are shorter, when normalised for van der Waals radii, and, by inference, stronger than halogen bonds involving other acceptor groups, and demonstrates that C_{sp}–I···N halogen bonds are generally shorter C_{sp^2}–I···N halogen bonds.

Introduction

Haloalkynes have a well-established role in synthetic organic chemistry,[1] but their application in supramolecular chemistry is less well developed despite a long history. Haloalkynes can form halogen bonds,[2] in this context involving the attractive inter-action of a C–I group with a Lewis base. More generally, the study of halogen bonds has expanded dramatically over the past 10 years,[3] resulting in applications in areas such as conducting materials,[4] liquid crystals,[5] anion recognition[6] and even structural biology.[7] Halogen-bonded adducts of 1-iodoalkynes with Lewis bases were first reported many decades ago,[8] but the ability of iodoalkynes to act as halogen bond donors in solution was clearly established by Laurence and coworkers some 30 years ago using IR spectroscopy.[9] Their study further showed that the change in stretching frequency $\Delta\nu_{C–I}$ upon halogen-bonded adduct formation can be correlated to the halogen bond enthalpy. Thus, iodoalkynes form strong halogen bonds with a variety of Lewis bases, although are not as strong halogen bond donors as ICN, I_2 and the interhalogens IBr and ICl,

which remain the strongest halogen bond donors quantified to date.

Diiodoacetylene can be viewed as one of a family of the simplest linear ditopic halogen bond donors $I–(C{\equiv}C)_n–I$, members of which are known for $0 \leq n \leq 4$,[10] and for which halogen-bonded adducts have been characterised for $n \leq 3$. A large number of halogen-bonded adducts and networks are known for I_2 ($n = 0$), including halogen bonds to nitrogen heterocycles[11] and as part of polyiodide anions and networks.[12] Very few studies of halogen bonding have been undertaken for the longer diiodopolyalkynes ($n \geq 2$). Indeed all have been reported by Goroff and coworkers, who have described adducts of $I–(C{\equiv}C)_2–I$ (8 structures), $I–(C{\equiv}C)_3–I$ (3 structures).[10,13] Diiodo-acetylene itself has been crystallographically charac-terised and forms a network of T-shaped C–I···π halogen bonds[14] in an analogous manner to the C–H···π hydrogen-bonded network in acetylene.[15] Halogen-bonded adducts of diiodoacetylene have been reported (13 structures) with oxygen bases,[16] a sulphur base,[17] a selenium base[17] and most commonly with halide ions.[18] Here we report a convenient synthesis of diiodoacetylene and its halogen-bond adducts with nitrogen and oxygen bases (pyrazine, dabco and DMF). We further report its ease of decomposition to yield tetraiodoethylene and the subsequent formation of the C_2I_4·hmta (**4**) adduct from one such decomposition. Halogen bond donors and acceptors are shown in Scheme 1.

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK. E-mail: lee.brammer@sheffield.ac.uk

‡ Current address: Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK.
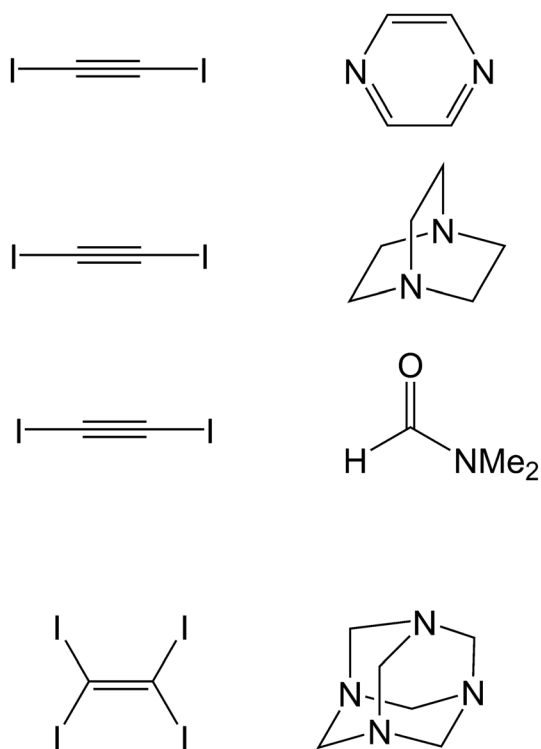
Scheme 1 Halogen bond donors (left) and acceptors (right) used in adduct formation.

Experimental

General

All reagents were purchased from Fluorochem Ltd., Alfa Aesar or Lancaster Synthesis Inc. and used as received.

Synthesis

1,2-diiodoacetylene, C_2I_2. *N*-iodosuccinamide (NIS) (1.395 g, 6 mmol) and $AgNO_3$ (0.086 g, 0.5 mmol) were dried under vacuum for 10 mins. Trimethylsilylacetylene (TMSA) (0.5 mL, 5.1 mmol) followed by DMF (10 mL) was added to a mixture of the two reactants and allowed to stir for 30 mins. After this time GC-MS analysis showed the presence of 1,2-diiodoacetylene (5.29 mins) and 1-iodo-2-(trimethylsilyl)acetylene (4.35 mins), indicating that the monoiodo(silyl)alkyne intermediate could not be isolated by this method. After a further 30 mins of reaction only 1,2-diiodoacetylene was present (*i.e.* 100% conversion by GC-MS). The reaction mixture was then filtered, the product extracted with diethyl ether, dried with $MgSO_4$ and the solvent removed *in vacuo*. Although C_2I_2 can be handled as solid, it has been shown to decompose explosively at temperatures between 80 and 130 °C or due to shock.[19] Thus, the compound was not isolated and was stored in CH_2Cl_2 solution as a precaution.

Crystal syntheses

C_2I_2·pyz (1). C_2I_2 (5 mg, 0.018 mmol) was dissolved in CH_2Cl_2 (*ca.* 2 mL) and pyrazine (1.4 mg, 0.018 mmol) was dissolved in EtOH (*ca.* 2 mL). The latter solution was layered on the former with a buffer layer of CH_2Cl_2 (*ca.* 1 mL). Large yellow block crystals of **1** suitable for single crystal X-ray diffraction were obtained after 3 days (4.2 mg, 0.012 mmol, 65.2% yield). Calcd: C 20.13%, H 1.13%, N 7.83%, I 70.91%. Found: C 20.17%, H 0.92%, N 7.73%, I 67.68%.

C_2I_2·dabco (2). C_2I_2 (5 mg, 0.018 mmol) was dissolved in CH_2Cl_2 (*ca.* 2 mL) and dabco (2.2 mg, 0.018 mmol) was dissolved in EtOH (*ca.* 2 mL). The latter solution was layered on the former with a buffer layer of CH_2Cl_2 (*ca.* 1 mL). Large yellow block crystals of **2** suitable for single crystal X-ray diffraction were obtained after 3 days (6.0 mg, 0.0154 mmol, 85.5% yield).

C_2I_2·DMF (3). C_2I_2 (5 mg, 0.018 mmol) was dissolved in CH_2Cl_2 (*ca.* 1 mL). Slow evaporation over 3 days yielded yellow block crystals that were suitable for single crystal X-ray diffraction of the C_2I_2·DMF adduct (**3**), indicating that DMF had not been fully removed from the previously synthesised C_2I_2.

C_2I_4·hmta (4). C_2I_2 (5 mg, 0.018 mmol) was dissolved in CH_2Cl_2 (*ca.* 2 mL) and hexamethylenetetramine (hmta) (1.2 mg, 0.009 mmol) was dissolved in EtOH (*ca.* 2 mL). The latter solution was layered on the former with a buffer layer of CH_2Cl_2 (*ca.* 1 mL). Small yellow plate crystals of **4** suitable for single crystal X-ray diffraction were obtained after 3 days. The product was not phase pure.

X-ray crystallography

X-Ray data for compounds **1–4** were collected on a Bruker APEX II diffractometer using graphite-monochromated Mo-Kα radiation. Low temperature data collections were undertaken using either an Oxford Cryosystems Cobra or N-HeliX low temperature device. Intensity data were indexed and integrated using the APEX II suite of programs.[20] Details of the crystal, data collection and refinement parameters are summarized in Table 1. Data were corrected for absorption using empirical methods (SADABS) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[21] The structures were solved by direct methods and refined by full-matrix least squares on weighted F^2 values for all reflections using either the SHELXTL program[22] or SHELXL *via* the OLEX-2 suite of crystallographic programs.[23] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, refined using idealized geometries (riding model), and assigned fixed isotropic displacement parameters. In the crystal structure of **1**, both molecules are situated at centres of inversion, whereas in the crystal structure of **2** both molecules are situated on mirror planes. The crystal structure of **4** exhibits rotational disorder about two separate axes for one of the two independent C_2I_4 molecules (see ESI† for more details). The crystal structure of **4** has been reported previously at 296 K.[24] Although the unit cell reported is very similar to that observed in our 120 K study, the space group *C2/m* was used rather than *P2₁/c* in the present study. Rotational disorder of the C_2I_4 molecule was reported about only one axis.

Results

The synthesis of diiodoacetylene was first reported in 1865, involving the reaction of silver acetylide with iodine in ether.[25] A

Table 1 Data collection, structure solution and refinement parameters for **1–4**

	$C_2I_2 \cdot$pyz (**1**)	$C_2I_2 \cdot$dabco (**2**)	$C_2I_2 \cdot$DMF (**3**)	$C_2I_4 \cdot$hmta (**4**)
Crystal colour	yellow	yellow	yellow	yellow
Crystal size/mm	$0.02 \times 0.05 \times 0.29$	$0.03 \times 0.021 \times 0.012$	$0.015 \times 0.01 \times 0.008$	$0.43 \times 0.28 \times 0.19$
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group, Z	$P\bar{1}$, 1	$P2_1/m$, 2	$P2_1/n$, 4	$P2_1/c$, 4
a/Å	4.2383(6)	6.5418(2)	5.575(3)	15.9274(7)
b/Å	7.3655(10)	8.2834(3)	14.420(7)	11.0145(4)
c/Å	7.8486(10)	10.3370(3)	11.901(6)	8.7574(4)
α (°)	113.047(4)	90.00	90.00	90.00
β (°)	99.614(4)	101.233(2)	103.109(8)	92.800(2)
γ (°)	93.365(4)	90.00	90.00	90.00
V/Å^3	220.20(5)	549.41(3)	931.8(8)	1534.5(1)
Density/Mg m^{-3}	2.699	2.357	2.501	2.908
T/K	293	120	120	120
μ/mm^{-1}	7.071	5.678	6.686	8.106
θ range/°	2.88 to 27.49	3.18 to 27.49	3.33 to 25.68	2.25 to 27.52
Reflections collected	3429	4640	5749	15 754
Independent reflections (R_{int})	1004 (0.0216)	1345 (0.0236)	1726 (0.0369)	3358 (0.0356)
Reflections used in refinement, n	1004	1345	1726	3358
L.S. parameters, p	46	67	84	176
Restraints, r	0	0	0	51
$R_1(F)$,^{a} I > 2.0σ(I)	0.0401	0.0268	0.0304	0.0491
w$R_2(F^2)$,^{a} all data	0.1307	0.0433	0.0864	0.0952
$S(F^2)$,^{a} all data	1.234	1.033	1.031	1.208

^{a} $R_1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; w$R_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$; $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{1/2}$.

number of other syntheses have since been reported.[19,26] Here we report a convenient synthesis from the reagent trimethylsilylacetylene (TMSA), commonly deployed when linking two arenes *via* an alkyne bridge using two consecutive Sonogashira coupling reactions.[27] Iodination of TMSA using N-iodosuccinamide and AgNO$_3$ yields diiodoacetylene as the sole product after 1 h, consistent with contemporary methods for direct halogenation of protected alkynes.[10,28] Adducts $C_2I_2 \cdot$pyz (**1**) and $C_2I_2 \cdot$dabco (**2**) were prepared by layering solutions of the two components, whereas crystals of $C_2I_2 \cdot$DMF (**3**) were obtained upon recrystallisation of diiodoacetylene from CH_2Cl_2, adduct formation arsing from a small amount of residual DMF remaining from the original synthesis of diiodoacetylene. Attempts to prepare adducts of C_2I_2 with hexamethylenetetramine (hmta) resulted in decomposition of C_2I_2 to liberate iodine resulting in conversion of residual C_2I_2 to tetraiodoethylene, C_2I_4.[29] In our study we were able to isolate the adduct $C_2I_4 \cdot$hmta (**4**).

The crystal structures of adducts **1** and **2** are shown in Fig. 1. Combination of linear ditopic halogen bond donor (C_2I_2) and acceptor in both cases results in a parallel linear assemblies propagated by C–I⋯N halogen bonds (I⋯N 2.832(7) Å; C–I⋯ N 175.3(3)° in **1**; I⋯N 2.715(3), 2.719(4) Å; C–I⋯N 178.2(2), 178.7(2)° in **2**). Interactions between neighbouring halogen-bonded chains include C–H⋯π hydrogen bonds between pyrazine or dabco and the π-bond of the alkynes. The crystal structure of **3** comprises zigzag chains in which the carbonyl oxygen acts as a bifurcated halogen bond acceptor (Fig. 2; I⋯O 2.834(4), 2.888(4) Å; C–I⋯O 170.7(2), 173.0(2)°) in a manner analogous to the well-established behaviour of carbonyl groups as hydrogen bond acceptors.[30] Parallel chains are linked *via* C–H⋯π hydrogen bonds involving the methyl hydrogen atoms of the DMF molecules to give a sheet; the sheets then stack in an antiparallel manner. The halogen bond geometry at the acceptor oxygen atom deviates from the 120° angles anticipated from the

lone pair directions (C=O⋯I 125.1(4), 145.4(4)°; I⋯O⋯I 89.4(1)°) presumably to accommodate other intermolecular interactions (notably C–H⋯π).

The crystal structure of $C_2I_4 \cdot$hmta (**4**) is shown in Fig. 3. Two independent C_2I_4 molecules, each of which has crystallographic inversion symmetry, link htma molecules *via* a C–I⋯N halogen-bonded network of corrugated sheets (Fig. 3a) that involves three of the four nitrogen atoms on each htma molecule (I⋯N 2.948(7), 2.997(8), 2.999(8) Å; C–I⋯N 166.6(3), 169.2(3), 170.9(3)°). The fourth nitrogen atom interacts orthogonal to the C_2I_4 plane with the molecule that participates in only two C–I⋯N halogen bonds (Fig. 3b). The nitrogen lone pair is directed approximately at one of the two alkene carbon atoms
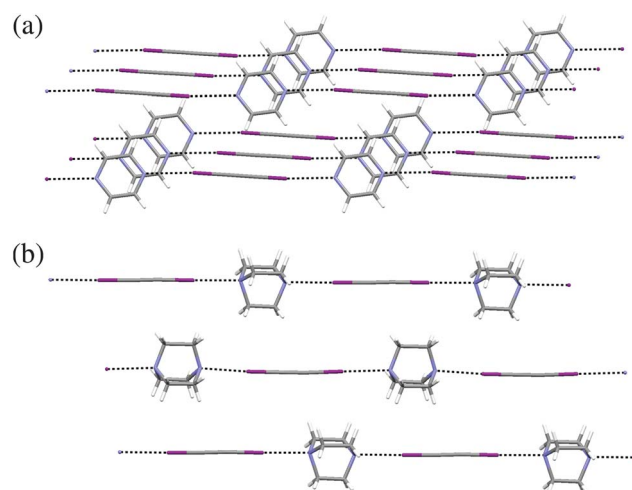
(a)

(b)

Fig. 1 Linear halogen-bonded assemblies of (a) $C_2I_2 \cdot$pyz (**1**) and (b) $C_2I_2 \cdot$dabco (**2**). C–I⋯N halogen bonds are shown as dashed lines. C–H⋯π hydrogen bonds between chains are not shown.
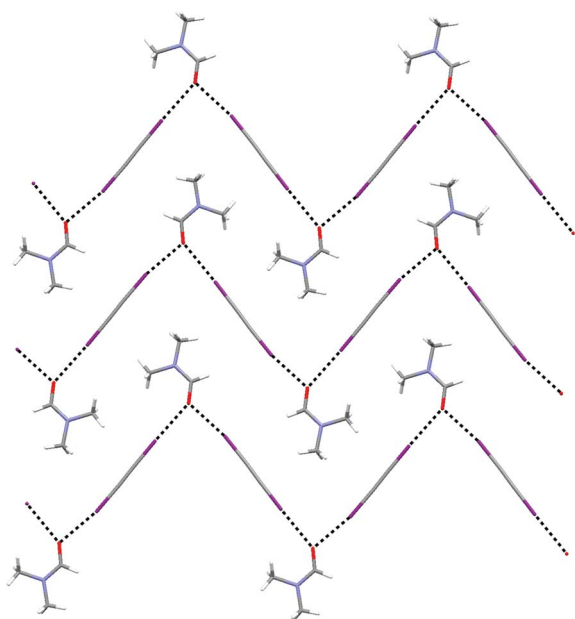
Fig. 2 Zigzag halogen-bonded assemblies of $C_2I_2 \cdot$DMF. C–I⋯O halogen bonds are shown as dashed lines. C–H⋯π hydrogen bonds between chains are not shown.
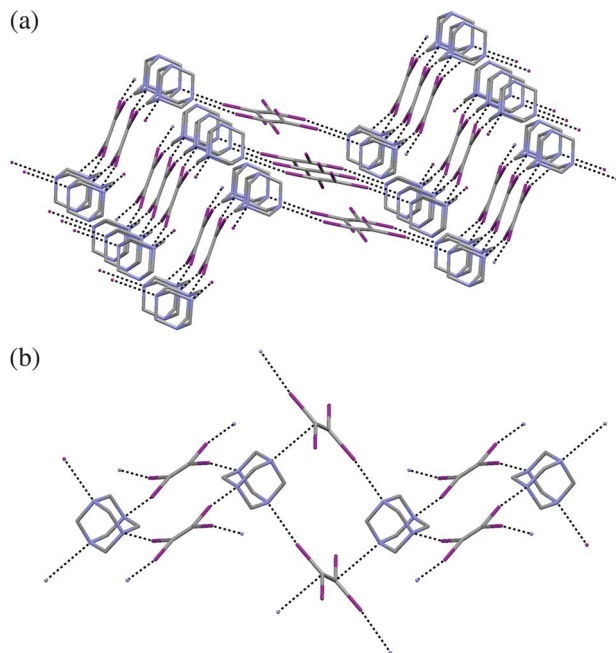
(a)

(b)

Fig. 3 Halogen-bonded assembly of $C_2I_4 \cdot$htma. (a) Showing corrugated layer structure propagated *via* C–I⋯N halogen bonds and (b) showing tetrahedral supramolecular coordination of htma *via* three C–I⋯N halogen bonds and an N⋯C(π) interaction. Hydrogen atoms are omitted for clarity. The C_2I_4 molecule that forms only two C–I⋯N halogen bonds is disordered (Fig. S1, ESI†).

(N⋯C 3.367(9) Å; N⋯C=C 89.2(5)°). One C_2I_4 molecule forms four C–I⋯N halogen bonds, while the other forms two. The latter alkene is both rotationally disordered about the normal to its molecular plane and rotationally disordered about the I⋯I vector involving the two halogen-bonded iodine atoms (Fig. S1,

ESI†). The two remaining iodine atoms, which do not participate in C–I⋯N halogen bonds, form C–I⋯I–C interactions with neighbouring molecules.

Discussion

Crystal structures of **2**, **3** and **4** show that diiodoacetylene forms short linear halogen bonds to both nitrogen and oxygen acceptor groups with normalised bond distances[31] as short as R_{IN} 0.80 (**1**), R_{IN} 0.77 (**2**) and R_{IO} 0.81 (**3**). These are among the shortest halogen bonds recorded for diiodo(poly)alkynes $I(C\equiv C)_nI$ (n = 1–3) which collectively form short halogen bonds across a variety of acceptor groups (Fig. 4). Most halogen bonds are close to linear in geometry (C–I⋯X ≥ 170°), with only a few exceptions.[32] There is no discernable difference between halogen bond geometries for the different polyalkynes. However, it is noticeable that halogen bonds to nitrogen are generally shorter and by inference stronger than those formed by other acceptor groups, the majority having R_{IN} ≤ 0.80. A qualitative ranking of halogen bond lengths based upon the data currently available for these diiodo(poly)alkynes is $R_{IN} < R_{IO} < R_{ICl} < R_{IBr} < R_{II} \leq R_{IS} \approx R_{ISe}$.

Decomposition of iodoalkynes to liberate iodine is well documented. Indeed the original impetus for the extensive work by Goroff and coworkers on diiodopolyalkynes was their ease of degradation to C_n species that might be used in construction of smaller all-carbon molecules than the most well known fullerenes (C_{60}, C_{70}, *etc*).[10] The degradation of diiodoacetylene to yield tetraiodoethylene has also previously been observed by Yamamoto, who reported a structure containing both C_2I_2 and C_2I_4 which resulted from such degradation.[18c] In our case the only iodine-containing product isolated and crystallographically characterised was the $C_2I_4 \cdot$htma adduct (**4**). In their original report of the structure of $C_2I_4 \cdot$htma, Pennington, Hanks and coworkers note that it is unusual to observe a C_2I_4 molecule that forms 4 C–I⋯N halogen bonds.[24] Indeed in 1 : 1 adducts with ditopic halogen bond acceptors such a 4,4-bipyridine and similar species the C_2I_4 acts as linear connector *via* two C–I⋯N halogen bonds involving *trans* iodine substituents. The two remaining iodine substituents usually form C–I⋯I–C interactions with neighbouring molecules. This is the case for the rotationally disordered C_2I_4 molecule in **4**. In a survey of 27 halogen-bonded C_2I_4 adducts identified in the CSD (Nov 2010, version 1.13), ten structures form two C–I⋯N halogen bonds and C–I⋯I–C interactions involving remaining iodines. Two further structures adopt similar patterns but with C–I⋯O or C–I⋯S halogen bonds instead of C–I⋯N. Eleven structures form halogen bonds with all four C–I groups, seven of these involving halide ions as the acceptor group. The remaining four structures form either three halogen bonds or adopt a pattern analogous to **4** in which one C_2I_4 molecule forms four halogen bonds and a second independent molecule forms only two. Full details are provided in Table S1, ESI†

The geometries of the halogen bonds formed in adducts of C_2I_4 are presented in Fig. 5. Type I C–I⋯I–C interactions are not included, but type II contacts (*i.e.* C–I⋯I(C) halogen bonds) are considered. Again it is clear that nitrogen atoms, principally in neutral heterocyclic molecules provide excellent halogen bond acceptor sites and often lead to short C–I⋯N interactions. However, discrimination between other types of acceptor groups is not apparent from the data. Halogen bonds involving C_2I_4 are
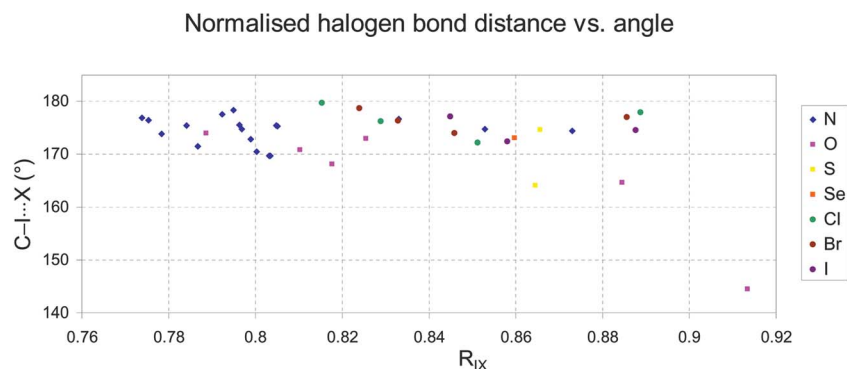
Normalised halogen bond distance vs. angle

Fig. 4 Plot of normalised halogen bond length[31] R_{IX} *vs.* C–I···X halogen bond angle (°) for ditopic halogen bond donors I(C≡C)$_n$I (n = 1–3). Halogen bond acceptor atoms (X) are distinguished by different coloured dots.

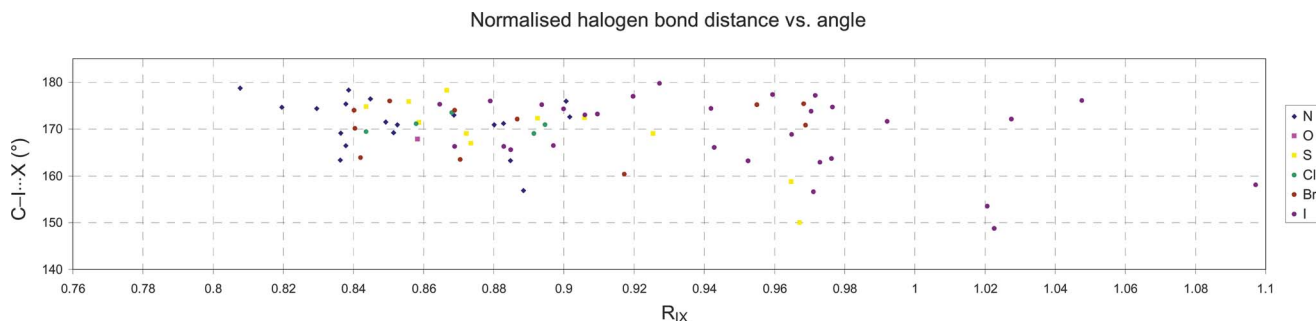Normalised halogen bond distance vs. angle

Fig. 5 Plot of normalised halogen bond length[31] R_{IX} *vs.* C–I···X halogen bond angle (°) for tetratopic halogen bond donors I$_2$C=CI$_2$. Halogen bond acceptor atoms (X) are distinguished by different coloured dots.

generally longer and, although mostly adopting geometries with C–I···X ≥ 160°, deviate further from linear geometries than those involving C$_2$I$_2$ (Fig. 4). This is consistent with the more electron-withdrawing nature of sp hybridised carbon atoms over sp^2 hybridised carbon which results the relative halogen bond strengths being C$_{sp}$–I···X > C$_{sp^2}$–I···X (X = acceptor group).

This behaviour parallels that of C$_{sp}$–H···X and C$_{sp^2}$–H···X hydrogen bonds.[33] With respect to the two molecules being studied, lengthening of the halogen bonds involving C$_2$I$_4$ may also result from as a compromise in the need to accommodate interactions with so many C–I groups in close proximity.

Conclusions

A facile synthesis and of diiodoacetylene and crystal structures of three new adducts with short C–I···N or C–I···O halogen bonds are reported. The degradation of C$_2$I$_2$ to liberate iodine and thereby generate tetraiodoethylene C$_2$I$_4$ is also documented, and has resulted in isolation of the adduct C$_2$I$_4$·htma. The crystal structure of this known adduct has been redetermined in a different space group. Comparison of halogen bond geometries of C$_2$I$_2$ with those of C$_2$I$_4$ across all reported crystal structures indicates that the C$_{sp}$–I group of the former results in shorter halogen bonds that are closer to linear geometry than those of the C$_{sp^2}$–I group of the latter.

Acknowledgements

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