A Stable Carbene Iodine Adduct: Secondary Bonding in 1,3-Diethyl-2-iodo-4,5-dimethylimidazolium Iodide

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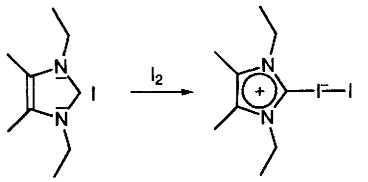
The stable carbene iodine adduct **2** is formed by the reaction of the imidazol-2-ylidene **1** with iodine; the X-ray structure of **2** is reported.

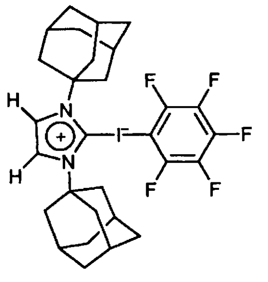
It is well known that iodine forms adducts with π- and σ-donors. With imidazol-2-ylidenes,[1,2] both types of interaction are feasible. In fact, experiment shows that 1,3-diethyl-4,5-dimethylimidazol-2-ylidene **1**[2] forms a stable adduct **2** with iodine,† the solid-state structure of which demonstrates clearly the σ interaction mode.

The molecular structure of **2** (Fig. 1)‡ may be considered as an isolated transition state which models the nucleophilic attack of the carbene on the iodine molecule. The hypervalency caused at the central iodine atom is revealed by its geometry [C(1)–I(1)–I(2) 176.0(1)°] and by the significant lengthening of the iodine–iodine bond [I(1)–I(2) 3.348(1) Å]. Consequently, the carbon–iodine distance [C(1)–I(1) 2.104(3) Å] is also slightly elongated by comparison with the structure of iodoarenes.[3] The geometry of the five membered ring (Fig. 1) shows only minor deviations from the uncoordinated imidazol-2-ylidene **1**.[4]

In the unit cell (Fig. 2), the molecules of **2** form dimers in which the terminal iodine atoms are situated near the line normal to the centre of the adjacent heterocyclic ring [$\mathrm{Imid_{centre}\cdots I(2)}$ 3.855(1) Å]. The intermolecular distance of



1 **2**



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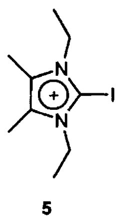
$\mathrm{Bu^t_3P^+}$—I—I

4



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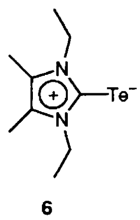

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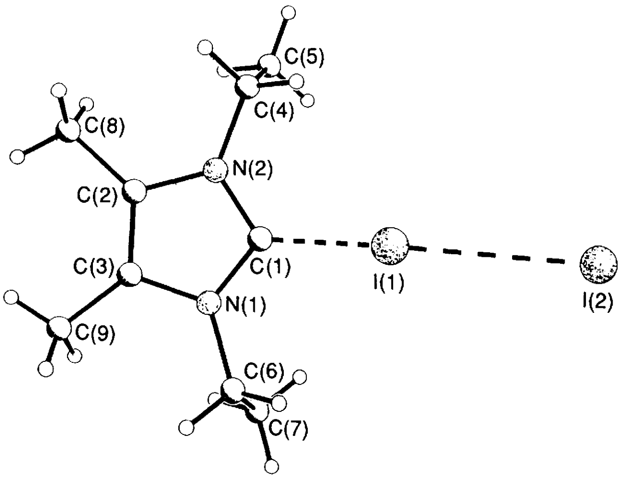

Fig. 1 The structure of $C_9H_{16}N_2I_2$ **2**. Selected bond lengths (Å) and angles (°): C(1)–I(1) 2.104(3), I(1)–I(2) 3.348(1), C(1)–N(1) 1.332(3), N(1)–C(3) 1.391(4), C(3)–C(2) 1.357(5), C(2)–N(2) 1.391(3), N(2)–C(1) 1.331(5); C(1)–I(1)–I(2) 176.0(1), I(1)–C(1)–N(1) 125.5(3), C(1)–N(1)–C(3) 109.3(3), N(1)–C(3)–C(2), 106.3(2), C(3)–C(2)–N(2) 107.2(3), C(2)–N(2)–C(1) 108.7(3), N(2)–C(1)–N(1) 108.4(3), N(2)–C(1)–I(1) 126.0(2).

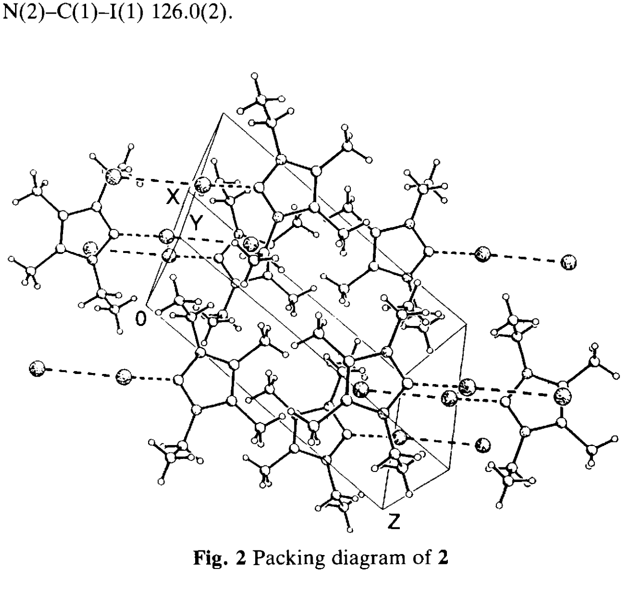

Fig. 2 Packing diagram of **2**

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† 1,3-Diethyl-4,5-dimethylimidazol-2-ylidene **1** (0.752 g 4.94 mmol) and iodine (1.254 g, 4.94 mmol) were mixed in tetrahydrofuran (30 ml), and the mixture was stirred for 2 h. The solvent was removed *in vacuo*. Crystallisation from CH_2Cl_2 at −78 °C gave 62% of **2** as colourless crystals; mp 217 °C (decomp); satisfactory C, H and N analyses were obtained, Λ_0(MeOH) = 71.0(7) S cm^2 mol^{-1}; ^{1}H NMR (400 MHz; CH_2Cl_2): δ 1.34 [t, 6H, N(1,2)–CH_2CH_3, ^3J 7.3 Hz], 2.28 [s, 6H, C(2,3)–CH_3], δ 4.16 [q, 4H, N(1,2)–CH_2CH_3].

‡ *Crystal data* for **2**: $C_9H_{16}N_2I_2$, M = 406.04, triclinic, space group $P1$, a = 7.672(1), b = 8.018(1), c = 12.327(2) Å, α = 93.36(1), β = 105.94(1), γ = 116.97(1)°, V = 634.83 Å^3, Z = 2, μ(Mo-Kα) = 4.92 mm^{-1}, D_x = 2.124 g cm^{-3}, $2\theta_{max}$ = 54°, ω-scan, crystal dimensions *ca.* 0.49 × 0.35 × 0.31 mm, direct methods, full-matrix least-squares refinements, non-hydrogen atoms anisotropic, H atoms at idealized positions, one common isotropic temperature factor for H within each residue, one extinction parameter, one scaling factor, $R(R_w)$ = 0.025(0.039) for 2671 reflections with $I > 2\sigma(I)$, 122 variables. Siemens P4RA four circle diffractometer, rotating anode generator, Mo-Kα radiation (λ 0.71073 Å), graphite monochromator, scintillation counter, T = 150 K, empirical absorption corrections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 ^{13}C NMR data of 2[a]

	CPMAS[b]	CD_2Cl_2[c]	CD_3OD[c]
C(2,3)	129.49	128.07	130.85
C(1)	109.62	109.39	99.74
C(4,6)	46.49	44.76	46.13
C(5,7)	15.88	15.00	15.01
C(8,9)	11.96	9.61	9.42

[a] Numbering scheme according to Fig. 1. [b] δ, adamantane ext. ref. [c] $SiMe_4$ (ext. ref.).

the central iodine atoms [I(1)···I(1)′ 4.069(1) Å] is close to the sum of the Van der Waals radii.

On comparison with the adducts **3**[5] and **4**[6], we see the structure of **2** to be analogous to the isolable phosphane adduct [I(1)–I(2) 3.326(1) Å, P–I(1)–I(2) 177.6(1)°], while in **3** the interactions between the imidazol-2-ylidene base and the iodine centre are much weaker [C(2)–I 2.754(3) Å]. If we consider the geometry at the central iodine atom to be indicative for the base strength of the attached nucleophiles[7] it may be concluded that the properties of tertiary phosphanes and imidazol-2-ylidenes are quite similar as regards their basicity towards soft acids. In contrast to **4**[6], no rapid exchange for **2** could be detected on addition of excess neutral base.

In dipolar solvents, the structure of **2** seems to be retained as indicated by NMR data (Table 1) and vapour pressure osmometry. Protic solvents, however, cause ionic dissociation to the 2-iodoimidazolium ion **5**, which is isoelectronic with the tellurourea **6** reported recently.[8]

The properties of **2** demonstrate the highly basic character of the carbene **1** towards soft acids similar to that of tertiary phosphines.

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