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Synthesis and X-Ray Structure Determination of 1,4-Bis[trimethylsilylethynyl(trifluoromethanesulfonyloxy)iodo]benzene, $Me_3SiC{\equiv}CI^+C_6H_4I^+C{\equiv}CSiMe_3\ 2CF_3SO_3^-$, a Novel Alkynyliodonium Salt

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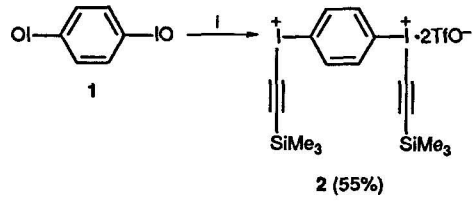
The novel bis(alkynyliodonium) salt, **2**, has been prepared by the reaction of *p*-bis(iodosyl)benzene with trimethylsilyl trifluoromethanesulfonate and bis(trimethylsilyl)acetylene; X-ray structure analysis reveals an unusual basket-like structure for this compound.

Alkynyliodonium salts are valuable reagents for the preparation of alkynyl esters and other substituted acetylenes.[1,2] In this communication we report the preparation of an alkynyliodonium salt of a new structural type, namely, *p*-phenylene bis(alkynyliodonium) triflate **2**.† Compound **2** can be prepared in moderate yield in a single step by the reaction of *p*-bis(iodosyl)benzene with trimethylsilyltriflate and bis(trimethylsilyl)acetylene in CH_2Cl_2 at room temperature (Scheme 1). Product **2** is isolated from the reaction mixture as a relatively stable white microcrystalline solid and identified by its spectral data.‡ The ^{1}H NMR spectrum of this compound displays only two singlets for the trimethylsilyl and *p*-phenylene protons at δ 0.22 and 8.31, respectively. Most characteristic is the ^{13}C NMR spectrum, particularly the signals of the acetylenic carbons that appear in the typical regions for alkynyliodonium salts.[1] To clarify the structural features for this novel iodonium salt **2** an X-ray investigation was carried out of a single crystal grown from acetonitrile.§ The ORTEP and the key structural para-

† Triflate (TfO) = trifluoromethanesulfonate.

‡ *Characterisation data* for **2**: m.p. 183–185 °C (decomp.); ^{1}H NMR (300 MHz, CD_3CN) δ 0.22 (s, 18H, 6Me), 8.31 (s, 4H, C_6H_4); ^{13}C NMR (75 MHz, CD_3CN, ^{1}H decoupled) δ_C 44.81 (C≡CI), 120.5 (q, $CF_3SO_3^-$, J_{C-F} = 318 Hz), 121.05 (*C*≡CI), 121.78 (C_6H_4, $2C_{ipso}$), 138.63 (C_6H_4, 4CH); ^{19}F NMR (282 MHz, CD_3CN) δ_F −78.9 (s, $CF_3SO_3^-$); IR ν/cm^{-1} (CCl_4) 3093 (Ar), 2969 (Me), 1275, 1218 ($CF_3SO_3^-$); FAB MS *m/z* 673 (70%), 427 (100%), 300 (50%); HRMS *m/z* 672.888119 $[M-CF_3SO_3^-]^+$, calcd. for $C_{17}H_{22}F_3I_2O_3SSi_2$ 672.886738.

§ *Crystal data* for **2**: $C_{18}H_{22}F_6I_2O_6S_2Si_2$, M − 822.471, triclinic, space group $P\bar{1}$, a = 10.919(3), b = 11.041(6), c = 13.863(5) Å, α = 98.06(2), β = 107.64(2), γ = 89.29(2)°, V = 1576.05 Å^3, Z = 2, D_c = 1.733 g cm^{-1}. Data collection description: radiation Mo 0.70930 Å, No. of reflections measured 5842, No. of unique reflections 5525, 2θ range 4.00 to 50.00 deg., scan technique θ–2θ scan, scan width 0.8000 + 0.3400(tan θ)°, data collection position bisecting, with ω = 0. Decay correction anisotropic. Absorption correction: empirical. Minimum % transmission: 47.2996. Maximum % transmission: 99.4591. Average % transmission: 67.2797. Final difference Fourier: highest peak in final difference Fourier 0.904 E Å^{-3}. Summary of final least squares refinement: weighting scheme: non-poisson contribution; ignorance factor, P = 0.05; data rejected if I < 3.00 σ(I); No. of observations 2513; No. of variables 326; data to parameter ratio 7.709; shift to error ratio 0.009; error in an observ. of unit weight 1.1335; R factor 0.0665; R_w factor 0.0741. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.



Scheme 1 *Reagents and conditions*: i, Me_3SiOTf (3 mol equiv.), $Me_3SiC{\equiv}CSiMe_3$ (3 mol. equiv.), CH_2Cl_2, −40 to 25°C, 5 h

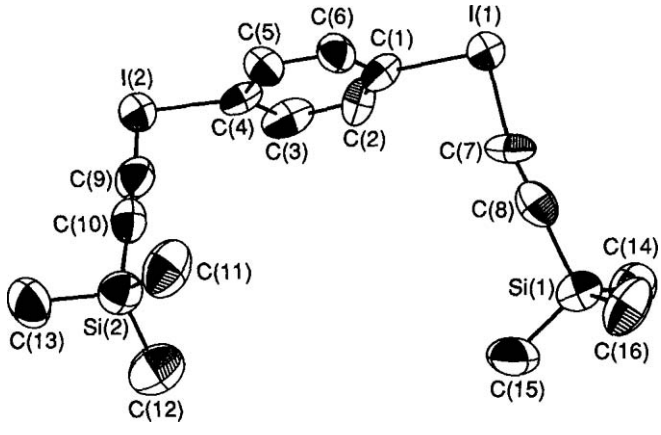


Fig. 1 ORTEP of the dication **2**. Bond lengths (Å): C(1)—I(1) 2.06(2), I(1)—C(7) 1.96(2), C(7)—C(8) 1.20(3), C(8)—Si(1) 1.88(3), C(4)—I(2) 2.06(2), I(2)—C(9) 1.93(2), C(9)—C(10) 1.21(3), C(10)—Si(2) 1.90(3). Bond angles (°): C(1)—I(1)—C(7) 92.6, I(1)—C(7)—C(8) 168.0(2), C(4)—I(2)—C(9) 91.4(8), I(2)—C(9)—C(10) 175.0(2), C(9)—C(10)—Si(2) 176.0(2), C(7)—C(8)—Si(1) 176.0(2)

meters for compound **2** are shown in Fig. 1. The structural data reveal, as expected for an iodonium salt, a pseudo-trigonal-bipyramidal or T-shaped geometry consistent with the 10-I-3 nature in the Martin–Arduengo formalism.[3] However, some structural parameters deviate from those of typical alkynyliodonium salts.[1] First of all, the C—C triple bonds have bond lengths of 1.21 and 1.20 Å, which are slightly longer than usual in alkynyliodonium salts (1.14–1.16 Å).[4] Secondly, the C_{sp}—I distances of 1.96 and 1.93 Å are shorter than the typical 2.1–2.2 Å.[4] The C—I—C angles in **2** are slightly different from the expected 90°. The most interesting structural feature of this compound is the *gauche* conformation of the acetylenic groups, considering the rotation along the *p*-phenylene line (Fig. 1). The dihedral angle between the two triple bonds is close to 60°. This arrangement provides a unique basket-like structure for this bisiodonium salt. Moreover, the spatial proximity of the triple bonds makes **2** interesting as a model compound for possible cyclizations and formation of charged molecular boxes.

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