to dryness, and the residue was taken up in a small volume of methanol and treated with diazomethane in ether. Following evaporation of the solvent, the residue was subjected to GC–MS analysis.

The natural occurrence of **7** was demonstrated by incubating the washed mycelia from two 100-mL cultures of *Claviceps* sp., SD 58 in 2 × 100 mL 1/15 M phosphate buffer, pH 7.3, with shaking for 3 h, removing the mycelia by filtration, and extracting the filtrate with 1-butanol. The residue from the butanol extract was then treated with excess diazomethane in ether and analyzed by GC–MS. Selective ion monitoring at m/z 116 revealed the presence of a peak at t_R 21.8 min corresponding to **7**: mass spectrum, m/z (rel. intensity, %) 312 (24), 253 (8), 196 (71), 181 (42), 168 (46), 116 (100).

Acknowledgment. We are indebted to the National Institutes of Health for financial support of this work through research grant GM 41363.

Synthesis, Reactions, and Crystal Structure of a Stable 10-I-4 Periodonium Ion[1a]

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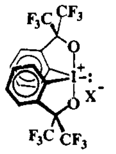
Received July 31, 1992. Revised Manuscript Received November 12, 1992

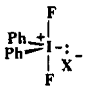
Abstract: The structure of the 10-I-4 periodonium ion of bis[α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,O^α]iodine(1+) triflate, salt **1a**, was confirmed by an X-ray crystallographic structure determination. The periodonium ion of **1a** was the first example of a stable cationic 10-I-4 species lacking fluorine ligands. In contrast to other periodonium ions, that of **1a** is not hydrolyzed by atmospheric moisture nor by water in neutral or acidic media. It does not react with weak nucleophiles such as pyridine or methanol. The unreactivity of **1a** is attributed to the stabilizing effects of its spirobicyclic ligand system with electronegative apical oxygen ligands and electropositive equatorial carbon ligands designed to stabilize a pseudo-trigonal-bipyramidal hypervalent species. The periodonium ion of **1a** reacts with stronger nucleophiles by attack at iodine. Treatment of the 10-I-3 tetra-*n*-butylammonium 2-[3,3-bis(trifluoromethyl)-1,2-benziodoxol-1(3H)-yl]-α,α-bis(trifluoromethyl)-benzenemethanolate (**6**) with bromine gave the 12-I-5 bis[α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,O^α]bromoiodine (**8b**), the first example of a stable 12-I-5 bromoperiodinane. Treatment of alkoxydiaryliodinane **6** with chlorine gave 12-I-5 chloroperiodinane **8a**. Treatment of **8b** with trifluoromethanesulfonic (triflic) anhydride gave the very stable 10-I-4 periodonium salt **1a**. Treatment of **8b** with trifluoroacetic acid gave nearly equal amounts of iodinane **9** and 10-I-4 periodonium trifluoroacetate **1b**, with oxidation of the bromide to bromine. Reaction with excess hydroxide ion is postulated to produce the 12-I-5 periodinanide oxide anion **10a**. Reaction with excess *tert*-butylamine provides the analogous 12-I-5 adduct **11a**. Reaction with phenyllithium gives the 10-I-4 adduct **12**, isolable as a crystalline solid. Addition of triflic acid to a solution of **10a**, **11a**, or **12** regenerates the periodonium ion of **1a**.

Introduction

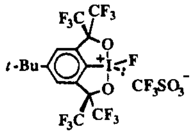
Prior to the synthesis and isolation of **1a**,[2] the periodonium ion of **2a,b**[3] was the only reported isolable pseudo-trigonal-bipyramidal (Ψ-TBP) 10-I-4 organoiodine species. The highly reactive inorganic salt $IF_4^+SbF_6^-$ was isolated in 1950,[4] and its structure was determined by X-ray crystallography.[5] Since the first report of **1a**,[2] periodonium salt **3** and related species stabilized by this tridentate ligand have been isolated.[6] Other less stable periodonium ions such as $C_6F_5IF_3^+$ have been observed in solution.



1 a, X = $CF_3SO_3^-$
b, X = $CF_3CO_2^-$



2 a, $X^- = F^-$
b, $X^- = CF_3CO_2^-$



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The study of periodonium ions (10-I-4 species) may be approached from either of two important avenues. Periodonium ions may be viewed in the context of the study of high-coordinate iodine species[8] or in the more general setting of the study of hypervalent 10-X-4 species in which X is a nonmetal.[9] The study of this type of organo-nonmetallic[9b] compound has attracted much attention in recent years. This paper uses both approaches.

Experimental Section

General Procedures. Chemical shifts are reported in parts per million downfield from tetramethylsilane as an internal standard for ^1H and ^{13}C NMR spectra and $CFCl_3$ as an internal standard for ^{19}F NMR spectra. Elemental analysis values were within 0.4% of calculated values for the indicated elements, unless otherwise noted. The X-ray crystallographic structure determination was done by Dr. Scott Wilson of the X-ray Crystallography Laboratory of the University of Illinois at Urbana–Champaign.

Tetrabutylammonium 2-[3,3-Bis(trifluoromethyl)-3*H*-1,2-benziodoxol-1-yl]-α,α-bis(trifluoromethyl)benzenemethanolate (6). A solution of chloroiodinane **5**[9a] (40.5 g, 0.102 mol) in THF (80 mL) was slowly added to a solution of dilithio species **4**[9a] (0.1 mol) in hexane (95 mL), THF (16 mL), and tetramethylethylenediamine (TMEDA, 3 mL) at 0 °C over a 45-min period. The solvent was removed under vacuum to give a viscous brown oil. Addition of 20 mL of 12 N HCl to the oil gave vigorous bubbling. The mixture was diluted with CH_2Cl_2 and extracted

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with water and then with aqueous tetrabutylammonium bromide (64.0 g, 0.2 mol) and KOH (20.0 g, 0.3 mol). The methylene chloride layer was extracted with 3 × 200 mL of water. Removal of CH_2Cl_2 under vacuum gave a dark oil, which was triturated with hexane to give a solid. Recrystallization from CH_2Cl_2–hexane gave large colorless prisms of **6** (34.0 g, 0.04 mol, 40%): mp 200–202 °C; ^1H NMR (CD_3CN) δ 0.96 (t, 12, $J_{HH} = 7.3$ Hz, $C\mathit{H}_3CCCN^+$), 1.34 (m, 8, $CC\mathit{H}_2CCN^+$), 1.63 (m, 8, $CCC\mathit{H}_2CN^+$), 3.11 (t, 8, $J_{HH} = 3.1$ Hz, $CCCCH_2N^+$), 7.27 (t, 1, $J_{HH} = 8$ Hz) and 7.45 (t, 1, $J_{HH} = 7.3$ Hz) (ArH at C-4 and C-5), 7.62 (d, 1, $J_{HH} = 8$ Hz) and 7.70 (d, 1, $J_{HH} = 7$ Hz) (ArH at C-3 and C-6); ^{19}F NMR (THF-d_8, 25 °C) δ −76.23 (s); ^{19}F NMR (−80 °C) δ −72.93 (br s); ^{19}F NMR (−100 °C) −71.33 (br s, 6), −72.93 (br s, 6); ^{13}C NMR (CD_2Cl_2, 25 °C) δ 13.55 ($\mathit{C}CCCN^+$), 19.95 ($C\mathit{C}CCN^+$), 24.02 ($CC\mathit{C}CN^+$), 58.55 ($CCC\mathit{C}N^+$), 85.45 ($\mathit{C}(CF_3)_2$), 122.4, 125.90 (q, $J_{FC} = 292.5$ Hz, $\mathit{C}F_3$), 128.87, 129.40 (C-2), 133.20, 142.26 (C-1); mass spectrum (field desorption) *m/z* 853 (M^+). Anal. ($C_{32}H_{44}F_{12}IO_2N$) C, H, F, I, N.

Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,O^α]chloroiodine (Chlorine Adduct 8a). Chlorine (0.64 g, 9.1 mmol) condensed into a solution of iodinane **6** (2.0 g, 2.3 mmol) in CH_2Cl_2 (12 mL) at −78 °C gave a yellow precipitate. Washing with CH_2Cl_2 gave an insoluble white solid, **8a** (1.02 g, 1.60 mmol, 67%): mp 209–211 °C; mass spectrum (10 eV) *m/z* (relative intensity) 611 (100, $M^+ - Cl$), 577 (14, $M^+ - CF_3$). Anal. ($C_{18}H_8ClF_{12}IO_2$) C, H, F.

Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,O^α]bromoiodine (Bromine Adduct 8b). Bromine (1.87 g, 11.7 mmol) was slowly added to a solution of iodinane **6** (5.8 g, 6.8 mmol) in CH_2Cl_2 (20 mL). The resulting precipitate was washed with CH_2Cl_2 to give a light yellow-orange, very insoluble solid (4.33 g, 6.3 mmol, 92%): mp 193–196 °C; mass spectrum (10 eV) *m/z* (relative intensity) 690, 692 (7, M^+), 621, 623 (30, $M^+ - CF_3$), 611 (49, $M^+ - Br$). Anal. ($C_{18}H_8BrF_{12}IO_2$) C, H, F.

2-[3,3-Bis(trifluoromethyl)-3*H*-1,2-benziodoxol-1-yl]-α,α-bis(trifluoromethyl)benzenemethanol (9). Bromine adduct **8b** (0.32 g, 0.46 mmol) was boiled in CH_3CN (7 mL) for 20 min, the solvent was removed under vacuum, and the remaining solid (0.23 g, 0.38 mmol, 81%) was washed with hexane. Recrystallization from CH_2Cl_2–pentane gave small white crystals of **9**: mp 225–227 °C; ^1H NMR (CD_3CN) δ 7.38 (d, 1, $J_{HH} = 7.0$ Hz), 7.60 (m, 2), 7.78 (d, 1, $J_{HH} = 7.6$ Hz); ^{19}F NMR ($CDCl_3$) δ −75.66 (s); mass spectrum (field desorption) *m/z* 543 ($M^+ - CF_3$). Anal. ($C_{18}H_9F_{12}IO_2$) C, H, F.

Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,O^α]iodine(1+) Trifluoromethanesulfonate (Periodonium Triflate 1a). A suspension of **8b** (1.39 g, 2.0 mmol) in trifluoromethanesulfonic (triflic) anhydride (5.1 g, 18 mmol) was boiled for 4 h, converting the light yellow solid bromoperiodinane to a white solid. Filtration under N_2 and washing with acetonitrile gave periodonium triflate **1a** (1.44 g, 1.9 mmol, 95%): mp 288–291 °C; ^1H NMR (CD_3CN) δ 8.03–8.25 (m); ^{19}F NMR (CD_3CN) δ −72.10 (q, 6, $J_{FF} = 9$ Hz), −75.05 (q, 6, $J_{FF} = 9$ Hz), −78.40 (s, 3, $C\mathit{F}_3SO_3^-$); mass spectrum (field desorption) *m/z* 760 (M^+), 611 ($M^+ - CF_3SO_3$). Anal. ($C_{19}H_8F_{15}IO_5S$) C, H, F, I, S; osmometric M_r (CH_3CN) 420 (calcd M_r, 380). Recrystallization from acetonitrile gave small colorless prisms: mp 294–295 °C dec.

Crystal Data of 1a: $C_{19}H_8F_{15}O_5SI$, mol wt = 760.16, triclinic, $a = 12.041(2)$ Å, $b = 12.472(2)$ Å, $c = 11.056(2)$ Å, $V = 1294.1(4)$ Å^3, $\rho_{calcd} = 1.951$ g/mL. A Syntex P2 diffractometer equipped with a graphite monochromator, λ(Mo Kα) = 0.71069 Å, was used in obtaining the data set and cell parameters.

Crystals of **1a** were obtained by slowly cooling a saturated solution of **1a** in acetonitrile. The size of the selected crystal was ca. 0.25 × 0.50 × 0.60 mm. The variable-scan option was used between 2.0°/min and 58.6°/min. Data in the $\pm h,\pm k,\pm l$ quadrant were collected out to $2\theta = 50°$. Three reflections were monitored every 97 reflections; an examination of these at the end of the data collection showed no signs of crystal decomposition. The data were corrected for Lorentz, absorption, and polarization effects. Out of 5960 unique reflections collected, 5411 were considered to be observed at the $3.0\sigma(I)$ level.

Solution and Refinement of Structure 1a. The iodine position was deduced from a Patterson map, and a subsequent difference Fourier synthesis revealed positions for all remaining atoms. In the final cycle of least squares refinement all non-hydrogen atoms were varied with anisotropic thermal parameters, all hydrogen atoms were fixed in calculated positions, and a group isotropic thermal coefficient was refined.[10] The largest change/error in the final cycle was 0.26, indicating convergence with conventional agreement factors R and R_w of 0.0348 and 0.0467, respectively. The final value of $[\sum W(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of observations (5411) and n is the number of variables (371), was 2.49. The range in the final difference Fourier synthesis was broad but balanced with very slight amounts of residual electron density in the vicinity of iodine. No peak was greater than 0.54 e Å^{-3}. The data were not corrected for extinction. The data are all included in the supplementary material. Selected bond lengths and angles are included in Table I.

Periodonium Trifluoroacetate 1b. Bromoperiodinane **8b** (0.77 g, 1.11 mmol) was dissolved in CF_3COOH (10 mL). Water was added until a precipitate formed. The mixture was heated until the solid dissolved. Slow cooling gave small colorless crystals of **1b** (0.274 g, 0.397 mmol, 35%): mp 200–202 °C; ^{19}F NMR (DMF) δ −71.97 (q, 6, $J_{FF} = 8.4$ Hz), −74.87 (s, 3, $C\mathit{F}_3COO^-$), −75.27 (q, 6, $J_{FF} = 8.4$ Hz); IR (Nujol) 1655 cm^{-1}. Anal. ($C_{20}H_8F_{15}IO_6$) C, H, I, F.

The mother liquor was carefully neutralized with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The solution was dried ($MgSO_4$) and the solvent removed. The resulting solid was recrystallized from CH_2Cl_2–pentane to give iodinane **9** (0.27 g, 0.44 mmol, 40%).

Reactions of Periodonium Triflate 1a. (a) Reaction with Tetrabutylammonium Forming 12-I-5 with an O^- (10a). Tetrabutylammonium hydroxide (1.53 mmol, 1 mL of a 1.53 M solution in water) was added to a slurry of **1a** (0.48 g, 0.6 mmol) in ether (40 mL). The resulting solution was extracted with 2 × 20 mL of water. The ether layer was dried ($MgSO_4$), and the ether was removed under vacuum. Attempts to recrystallize the remaining oil from a large number of solvent systems failed to give crystalline material. Hexane–CH_2Cl_2 gave **10a** as a hard glassy solid of 12-I-5: ^1H NMR ($CDCl_3$) δ 0.95 (t, 12, $J_{HH} = 7$ Hz, $C\mathit{H}_3CCCN^+$), 1.37 (m, 8, $C{-}C\mathit{H}_2CCN^+$), 1.62 (m, 8, $CCCH_2CN^+$), 3.22 (t, 8, $J_{HH} = 7$ Hz, $CCCC\mathit{H}_2N^+$), 6.84 (d, 1, $J_{HH} = 7.9$ Hz, H_a), 7.21 (t, 1, $J_{HH} = 7.4$ Hz), 7.42 (t, 1, $J_{HH} = 7.3$ Hz), 7.53–7.85 (m, 4), 8.75 (d, 1, $J_{HH} = 7$ Hz, H_b); ^{19}F NMR (CD_3CN) δ −74.12 (m, 6), −74.88 (q, 3, $J_{FF} = 8.4$ Hz), −76.93 (q, 3, $J_{FF} = 8.4$ Hz).

(b) Reaction with *tert*-Butylamine (11). *tert*-Butylamine (1.54 mg, 0.0021 mmol) was added to a solution of **1a** (8.0 mg, 0.0011 mmol) in CD_3CN (0.06 mL) to attack to form the nitrogen to the I^+ with the loss of the H of N forms **11a**: ^1H NMR δ 1.27 (s, 13.7 H, $(C\mathit{H}_3)_3CNHI$), 1.34 (s, 5.1, $(C\mathit{H}_3)_3CNH_2^+$), 5.25 (s, 4.6, $N\mathit{H}$), 6.89 (d, $J_{HH} = 8.0$ Hz, H_a), 7.52 (t, 0.43, $J_{HH} = 8.0$ Hz), 7.77 (t, 0.43, $J_{HH} = 8.0$ Hz), 7.85 to 8.20 (m, 5.3), 8.72 (d, 0.41, $J_{HH} = 7.8$ Hz, H_b); ^{19}F NMR (CD_3CN) δ −72.97 (q, 1, $J_{FF} = 9.8$ Hz), −73.48 (q, 1, $J_{FF} = 9.8$ Hz), −74.35 (q, 1, $J_{FF} = 9.8$ Hz), −75.42 (q, 1, $J_{FF} = 9.8$ Hz), −78.10 (s, 3, $C\mathit{F}_3SO_3^-$).

(c) Reaction with Phenyllithium (12). Phenyllithium (1.46 mmol, 0.73 mL of a 2 M solution in ether–benzene) was added to a solution of **1a** (1.04 g, 1.37 mmol) in THF (70 mL). The solution was stirred for several minutes, and the solvent was removed under vacuum. The remaining solid was dissolved in 5 mL of ether. The solution was extracted with 2 × 1.5 mL of water, and the ether was removed in vacuum. Recrystallization of the remaining solid from hexane–CH_2Cl_2 gave small white rosettes of **12** (0.31 g, 0.45 mmol, 33%): mp 191–193 °C, dec; ^1H NMR (THF-d_8, −40 °C) δ 6.93 (d, 0.8, $J_{HH} = 8.3$ Hz, H_a), 7.08 (t, 0.7, $J_{HH} = 8.64$ Hz), 7.50 (t, 1.1, $J_{HH} = 8$ Hz), 7.57 (m, 0.8), 7.72 (t, 1.1, $J_{HH} = 7.4$ Hz), 7.80–8.15 (m, 7.8), 8.45 (d, 1, $J_{HH} = 7.8$ Hz); ^{19}F NMR (THF-d_8, −40 °C) δ −73.80 (q, 3, $J_{FF} = 8.2$ Hz), −74.47 (q, 3, $J_{FF} = 8.2$ Hz), −75.65 (q, 3, $J_{FF} = 8.2$ Hz), −76.30 (q, 3, $J_{FF} = 8.2$ Hz); mass spectrum (field desorption) *m/z* 688 (M^+). Anal. ($C_{24}H_{13}F_{12}IO_2$) C, H, I.

(d) Reaction with Potassium Fluoride (15). Potassium fluoride (1.7 mg, 0.0029 mmol) was added to a solution of **1a** in acetonitrile (22 mg, 0.0029 mmol) in CD_3CN (0.6 mL), resulting in a solution of **15**: ^1H NMR δ 7.75–8.15 (m); ^{19}F NMR (25 °C) δ −51.48 (br s, 1 $I\mathit{F}$), −74.21 (br s, 6), −75.28 (br s, 6); ^{19}F NMR (−45 °C) −52.43 (s, 1, $I\mathit{F}$), −73.59 (br s, 3), −74.66 (br s, 6), −75.55 (br s, 3). Addition of a slight excess of triflic acid to the solution of **15** reconverts it to **1a**, identified by ^{19}F NMR.

Determination of the pK_a of Hydroxyiodinane Oxide 24. A solution of **24**[11] in 1:1 acetone–water was titrated with KOH. Comparisons with benzoic acid and 4-nitrobenzoic acid in the same media showed the pK_a of **24** (corrected for pure aqueous solvent) to be 3.8.

Results

Synthesis of Periodonium Salts. Addition of dilithio species **4**[9a] to a solution of chloroiodinane **5**[9a] gives alkoxydiaryliodinane **6** in moderate yield (39%) (Scheme I). Iodinane **6** is readily isolated as a pure crystalline solid which has an indefinite shelf life. The ^{19}F NMR spectrum of **6** shows a sharp singlet at 25

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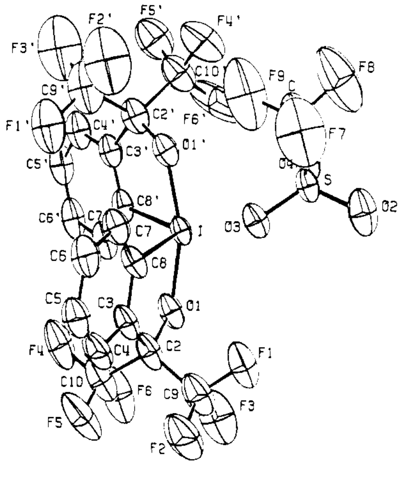
Table I. X-ray Structure of **1a**



Bond Lengths (Å) for **1a**[a]

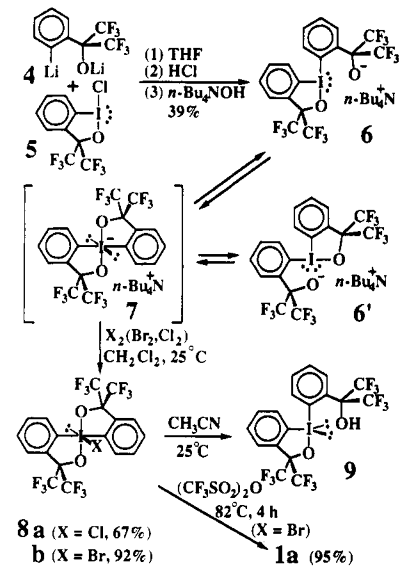
$I-O_1$	2.014(3)	$S-O_2$	1.426(3)	$S-O_3$	1.438(3)
$S-O_4$	1.436(3)	$I-O_1'$	2.004(3)	$S-C$	1.812(7)
F_7-C	1.326(9)	F_8-C	1.295(8)	F_9-C	1.306(6)
O_1-C_2	1.400(5)	C_2-C_3	1.530(6)	C_3-C_4	1.406(7)
C_4-C_5	1.378(7)	C_5-C_6	1.355(7)	C_6-C_7	1.388(6)
$I-C_8$	2.095(3)	C_3-C_8	1.385(5)	C_7-C_8	1.362(5)
F_1-C_9	1.352(6)	F_2-C_9	1.323(6)	F_3-C_9	1.290(8)
C_2-C_9	1.547(6)	F_4-C_{10}	1.322(5)	F_5-C_{10}	1.346(6)
F_6-C_{10}	1.336(8)	C_2-C_{10}	1.537(7)	$O_1'-C_2'$	1.405(6)
$C_2'-C_3'$	1.498(6)	$C_3'-C_4'$	1.398(6)	$C_4'-C_5'$	1.367(7)
$C_5'-C_6'$	1.392(7)	$C_6'-C_7'$	1.391(6)	$I-C_8'$	2.107(3)
$C_3'-C_8'$	1.370(5)	$C_7'-C_8'$	1.364(6)	$F_1'-C_9'$	1.301(9)
$F_2'-C_9'$	1.334(10)	$F4'-C_9'$	1.341(9)	$C_2'-C_9'$	1.562(6)
$F_4'-C_{10}'$	1.327(8)	$F_5'-C_{10}'$	1.340(7)	$F_6'-C_{10}'$	1.317(7)
$C_2'-C_{10}'$	1.565(6)				

Bond Angles (deg) for **1a**[a]

O_1-I-O_1'	162.8(1)	$C_3'-C_2'-C_{10}'$	111.4(4)
$O_1'-I-C_8$	88.8(1)	$C_2'-C_3'-C_8'$	118.2(3)
O_2-S-O_3	114.3(2)	$C_4'-C_5'-C_6'$	122.1(4)
O_3-S-O_4	112.0(2)	$I-C_8'-C_3'$	111.6(2)
$I-O1-C_2$	117.8(3)	$F_1'-C_9'-F_2'$	108.1(5)
$S-C-F_8$	111.2(5)	$F_2'-C_9'-F_3'$	108.2(6)
F_7-C-F_9	108.5(6)	$F_4'-C_{10}'-F_5'$	107.9(4)
$O_1-C_2-C_9$	106.4(4)	$F_5'-C_{10}'-F_6'$	107.9(5)
$C_3-C_2-C_{10}$	110.4(4)	O_1-I-C_8'	89.4(1)
$C_2-C_3-C_8$	117.0(4)	C_8-I-C_8'	105.9(1)
$C_4-C_5-C_6$	120.4(4)	O_2-S-C	105.1(2)
$I-C_8-C_3$	112.5(3)	O_4-S-C	104.8(2)
$F_1-C_9-F_2$	105.5(5)	$S-C-F_7$	110.2(5)
$F_2-C_9-F_3$	108.6(4)	F_7-C-F_8	107.0(5)
$F_4-C_{10}-F_5$	108.2(5)	$O_1-C_2-C_3$	111.0(3)
$F_5-C_{10}-F_6$	108.7(4)	$C_3-C_2-C_9$	110.8(4)
$O_1'-C_2'-C_3'$	111.2(3)	$C_2-C_3-C_4$	126.4(4)
$C_3'-C_2'-C_9'$	110.3(4)	$C_3-C_4-C_5$	120.0(4)
$C_2'-C_3'-C_4'$	124.2(4)	$C_6-C_7-C_8$	116.6(4)
$C_3'-C_4'-C_5'$	118.9(4)	$C_3-C_8-C_7$	124.4(3)
$C_6'-C_7'-C_8'$	117.0(4)	$F_1-C_9-C_2$	108.2(4)
$C_3'-C_8'-C_7'$	124.9(3)	$F_3-C_9-C_2$	112.6(5)
$F_1'-C_9'-C_2'$	110.0(6)	$F_4-C_{10}-C_2$	109.5(4)
$F_3'-C_9'-C_2'$	111.0(5)	$F_6-C_{10}-C_2$	111.7(5)
$F_4'-C_{10}'-C_2'$	111.0(5)	$O_1'-C_2'-C_{10}'$	104.9(4)
$F_6'-C_{10}'-C_2'$	109.0(4)	$C_9'-C_2'-C_{10}'$	113.4(4)
O_1-I-C_8	80.7(1)	$C_4'-C_3'-C_8'$	117.7(3)
$O_1'-I-C_8'$	80.4(1)	$C_5'-C_6'-C_7'$	119.4(4)
O_2-S-O_4	115.6(2)	$O_1-C_2-C_{10}$	106.9(4)
O_3-S-C	103.5(2)	$C_9-C_2-C_{10}$	111.2(3)
$I-O_1'-C_2'$	117.2(2)	$C_4-C_3-C_8$	116.6(4)
$S-C-F_9$	112.0(4)	$C_5-C_6-C_7$	122.0(4)
F_8-C-F_9	107.8(6)	$I-C_8-C_7$	122.8(2)
$F_1-C_9-F_3$	108.7(5)	$I-C_8'-C_7'$	123.2(3)
$F_2-C_9-C_2$	113.(5)	$F_1'-C_9'-F_3'$	108.6(6)
$F_4-C_{10}-F_6$	107.0(4)	$F_2'-C_9'-C_2'$	110.8(6)
$F_5-C_{10}-C_2$	111.7(4)	$F_4'-C_{10}'-F_6'$	109.9(5)
$O_1'-C_2'-C_9'$	105.4(4)	$F_5'-C_{10}'-C_2'$	111.1(5)

[a] Estimated standard deviations in parentheses.

Scheme I



°C, but shows two singlets at −100 °C. The coalescence temperature is −80 °C. The perfluoroalkoxy groups in **6** undergo intramolecular ligand exchange with a free energy of activation, at −80 °C, of 8 kcal/mol. The exchange is thought to occur via the 12-I-4 transition state (or intermediate) **7**.

Treatment of **6** in methylene chloride with chlorine or bromine gives adducts **8a,b** in good yield. The structures of **8a** and **8b** were not determined due to their insolubility. This is different from the behavior observed for the ionic salt **1a** and could suggest either a polymeric structure or possibly the bromo- and the chloroperiodinane depicted in Scheme I. It is possible to formulate a hypohalite structure for these compounds if the incoming halogen were delivered to the alkoxide center of **6**. Either a hypohalite structure or a periodinane structure might explain the reactivity toward acetonitrile and THF. If the periodinane structure is the correct one, reactivity toward bromoperiodinane **8b** is the first example of a pseudooctahedral (Ψ-Oc) 12-I-5 species with an I–Br bond. A stable 12-I-5 chloroperiodinane has been reported.[7]

The unprecedented ease with which iodinane **6** is oxidized by Br_2 or Cl_2 is attributed to the ligand system. The *gem*-dialkyl groups[9a] force the alkoxide anion into close proximity to the iodine atom, raising the energy of an electron pair on iodine. It is possible that anionic 12-I-4 species **7** is a metastable intermediate, analogous to IF_4^-, rather than a transition state in the exchange process between **6** and **6′** and that chlorine or bromine reacts directly with this 12-I-4 intermediate as suggested in Scheme I to form **8**. Direct reaction with **6** to form a hypohalite species could occur, with addition of the O–X bond to the iodine to form **8**. Periodinanes **8a** and **8b** precipitate from solution and are isolated in analytical purity simply by filtering and washing with methylene chloride. Neither compound reacts with atmospheric moisture, and both are stable for several months at room temperature. Adducts **8a** and **8b** dissolve slowly in acetonitrile or tetrahydrofuran to give the reduced product, iodinane **9**. Therefore it was not possible to obtain ^1H or ^{19}F NMR spectra for these compounds, making the assignment of stereochemistry of **8a,b** arbitrary. The pictured structure is only one of several possible stereoisomers. Adducts of **8a** and **8b** give correct elemental analyses, and the mass spectrum of adduct **8b** shows a molecular ion. The insolubility of adducts **8a,b** suggests that they are polymeric solids, which we suggest to have bridging bromine or chlorine atoms linking iodine atoms intermolecularly. Trifluoroperiodinanes[11,12] formed with only one of the bidentate ligands of **8a,b** are very soluble in methylene chloride or acetonitrile.

Reaction of the adduct **8a** or **8b** with triflic anhydride or even

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(12) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5294.

triflic acid leads to the formation of periodonium salt **1a**. Triflic anhydride is the more effective reagent for converting **8a,b** to a periodonium salt and gives almost quantitative yields of triflate **1a**. It is obtained analytically pure by filtering the reaction mixture and washing the solid with acetonitrile. The 10-I-3 cation with anionic triflate, **1a**, is stable at 25 °C and does not react with atmospheric moisture. It is moderately soluble in acetonitrile, tetrahydrofuran, acetone, or dimethyl formamide. Osmometric measurements show that it is almost completely dissociated in acetonitrile. The ^{19}F NMR spectrum of periodonium triflate **1a** shows two quartets and a singlet for the three types of trifluoromethyl groups.

Periodonium trifluoroacetate **1b** is obtained by dissolving **8b** in boiling trifluoroacetic acid. Addition of water to the solution causes trifluoroacetate **1b** to precipitate. The reduction of the

$$2\,(\mathbf{8b}) \xrightarrow{CF_3COOH} \mathbf{1b} + \mathbf{9} + Br_2$$

iodine(V) species by bromide or chloride ions in the presence of acid is a standard reaction.[13] Iodinane **9** is isolated by neutralization of the mother liquor with sodium bicarbonate and extraction with methylene chloride. Periodonium trifluoroacetate **1b**, only sparingly soluble in acetonitrile or tetrahydrofuran, is moderately soluble in dimethyl formamide. The ^{19}F NMR spectrum of **1b** shows two quartets and a singlet (relative areas 2:2:1) for the three types of trifluoromethyl groups. The infrared spectrum has a strong band at 1655 cm^{-1}, showing that there is little interaction, if any, between the trifluoroacetate ion and the periodonium ion.

X-ray Structure of Periodonium Triflate 1a. Figure 1 shows the KANVAS[14a] plot and the ORTEP[14b] crystal packing diagram of **1a**. Selected bond lengths and angles are listed in Table I.

The distance between iodine and the nearest oxygen on the triflate anion, 2.7723(0.0031) Å, is less than the sum of the van der Waals radii (3.3 Å)[15a] for these atoms, but it is greater than the sum of the covalent radii (2.0 Å).[15b] This is not surprising since the van der Waals radius for iodine was calculated from various iodine(I) species. The van der Waals radius for an iodine(V) species is expected to be less than for an iodine(I) species since the effective nuclear charge on an iodine(V) species is greater than on an iodine(I) species. The interaction between triflate and periodonium iodine is therefore not appreciably covalent. Other than this, there are essentially no unusual intermolecular or intramolecular contacts between atoms.

Reactions of Periodonium Triflate 1a with Nucleophiles. The reaction between the periodonium ion of **1a** and 2 equiv of hydroxide ion gives a compound whose ^{1}H and ^{19}F NMR spectra are consistent with structure **10a**. The ^{19}F NMR spectra of **10a** show four quartets for the four types of trifluoromethyl groups; the ^{1}H NMR spectra shows a doublet upfield of the other aromatic signals (6.84 ppm) and a doublet (8.75 ppm) downfield of the other aromatic signals. The high-field doublet is assigned to H_a, which is held in the shielding region of the other aryl group.[16] the low-field doublet is assigned to H_b, which is held near the exocyclic I–O$^-$ bond. The downfield shift of the ortho hydrogen, H_b, arises from the proximity of the C–H_b bond to the I–O$^-$ charge dipole and from their relative orientations.[17] The electrons in the C-H_b bond are polarized in such a way as to markedly increase the NMR deshielding of H_b, as discussed later.

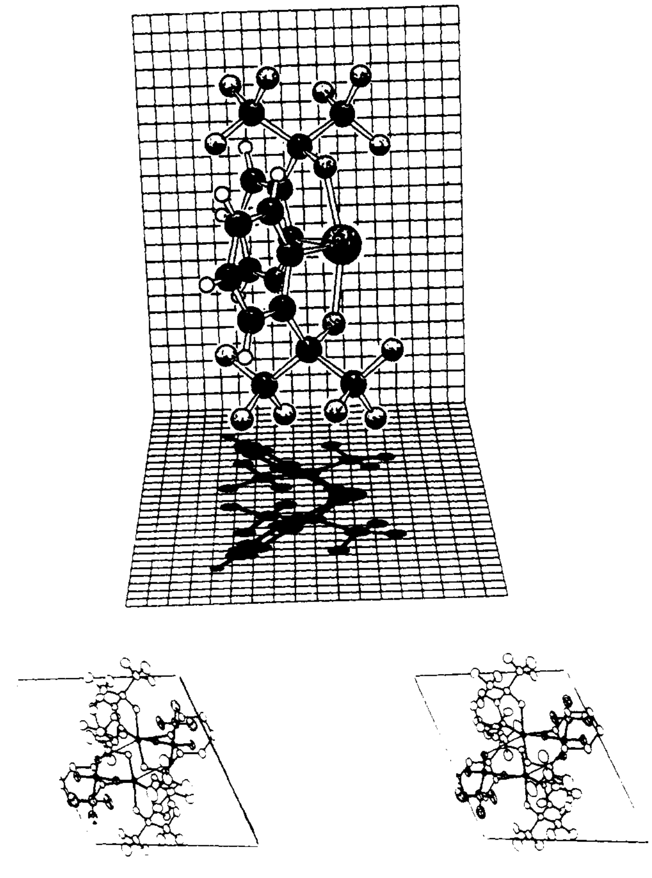
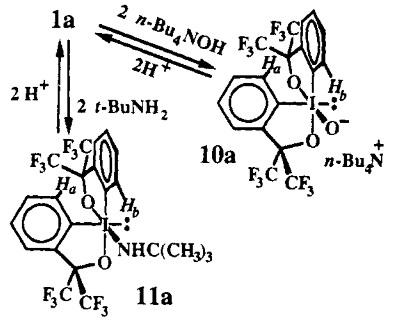
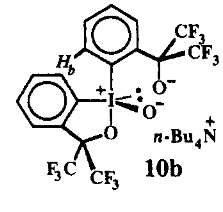


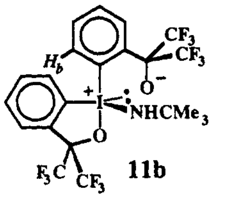
Figure 1. KANVAS plot and ORTEP crystal packing diagram of **1a**.



The reaction between the periodonium ion of **1a** and 2 equiv of *tert*-butylamine produces a mixture of compounds. The ^{19}F NMR and ^{1}H NMR spectra of the mixture are consistent with the presence of approximately 40–45% of **11a**, a structure closely analogous to **10a**. The ^{19}F NMR spectrum shows four quartets; the ^{1}H NMR spectrum shows an upfield doublet (6.89 ppm) and a downfield doublet (8.75 ppm) which are assigned to H_a and H_b, respectively. Other possible structures for the hydroxide and amine adducts, such as **10b** and **11b**, are not compatible with those parts of the observed spectra, since H_b is not held in close proximity to the I–N or I–O$^-$ charge dipole as in **10a** or **11a**.



10b



11b

The main product (55–60%) from the reaction with *tert*-butylamine is evidenced as a broad underlying peak at 73.0–74.5 ppm in the ^{19}F NMR spectrum and a broad peak at 7.85–8.20

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[13] (a) Beringer, F. M.; Bodlaender, P. *J. Org. Chem.* **1968**, *33*, 2981. (b) Willgerodt, C. *Chem. Ber.* **1892**, *25*, 2494.

[14] (a) Using the coordinates from the X-ray crystallographic analysis, the KANVAS program plots a shaded ball and stick model, perpendicular back and shadow planes, and a shadow projection. The spacing between the grid lines represents 0.5 Å. In the plots in Figure 1, the light source is normal to the plane of the phenyl ring. This program is based on the program SCHAKAL of E. Keller (Kristallographischer Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (at the University of Illinois, Urbana, IL; A.J.A. is now at Du Pont, Wilmington, DE), to produce the back and shadowed planes. (b) Johnson, C. K. *ORTEP II: A thermal ellipsoid plot program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

[15] (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 224; (b) p 260.

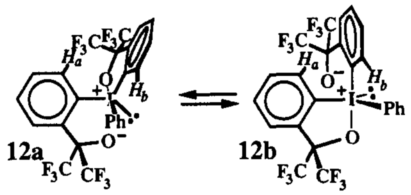
[16] Del Mazza, D.; Reinecke, M. G.; Smith, W. B. *Org. Magn. Reson.* **1980**, *14* (6), 540.

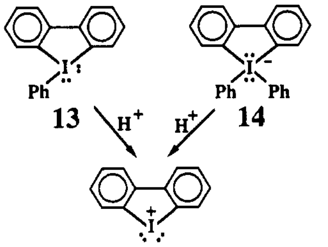
[17] Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2711.

ppm in the ^{1}H NMR spectrum. The identity of this product was not established.

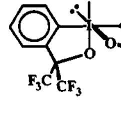
If only 1 equiv of hydroxide anion is added to a solution of **1a**, 50% of **10a** is formed. The remainder is unreacted starting material. Addition of excess triflic acid to a solution of **10a** or **11a** regenerates periodonium ion salt **1a**. Attempts to isolate hydroxide adduct **10a** as a crystalline solid failed. Both the tetraethylammonium and tetrabutylammonium salts of **10a** come out of solution as glasses or oils.

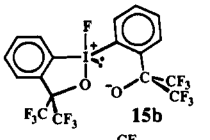
Periodonium salt **1a** reacts with phenyllithium to give a compound whose ^{19}F NMR spectrum in tetrahydrofuran-d_8 shows four broad peaks at 22 °C which sharpen to four well-defined quartets at −10 °C. The ^{19}F NMR spectrum of this compound in dimethyl sulfoxide-d_6 shows four quartets at 22 °C. Its ^{1}H NMR spectrum in tetrahydrofuran-d_8 at 22 °C shows broad peaks, but at −40 °C shows a sharp doublet at 6.93 ppm. The broad peaks observed in the spectra at 22 °C may be attributed to intramolecular ligand exchange of the perfluoroalkoxy groups. The effects of solvent polarity are consistent with an exchange process which involves zwitterionic pseudo-trigonal-bipyramidal (Ψ-TBP) 10-I-4 ground states such as **12a,b** and a neutral 12-I-5 pseudooctahedral (Ψ-Oc) transition state. The upfield doublet in **12** is assigned to H_a as in **10a** and **11a**. Adduct **12** was isolated as a pure crystalline solid. It is stable enough to survive an aqueous workup and can be recrystallized from methanol or hexane–methanol mixtures. Addition of excess triflic acid to a solution of **12** gives electrophilic cleavage of the I–Ph bond to regenerate periodonium triflate **1a**. Phenyllithium adduct **12** is the first example of an isolable triaryl 10-I-4 cation. A relatively large number of stable triaryl 10-I-3 species have been reported.[18] Most of them are analogues of 5-phenyl-5H-dibenziodole, **13**. Evidence for the formation of tetraaryl 12-I-4 species **14** from the reaction between diphenyliodonium chloride and 2,2′-dilithiobiphenyl was reported by Beringer,[19] but this compound was not isolated. Compounds **13** and **14** react with acid in a manner similar to that of adduct **12**, by cleavage of an I–C bond.[18,19]

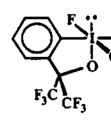


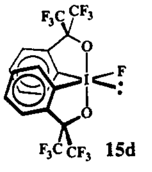


Addition of potassium fluoride to a solution of **1a** in acetonitrile gives a compound whose ^{19}F NMR spectrum shows three broad peaks (relative areas 1:6:6) at 25 °C. At −45 °C four peaks are observed (relative areas 1:3:6:3), and slower. This makes one single exchange at −45 °C, but a much lower position, which is hard to form, might show all four groups of **15a–d**. The ^{1}H NMR spectrum at −45 °C does not show an upfield doublet for the ortho proton (H_a of **12**), ruling out structures analogous to **10a**, **11a**, or **12** for the fluoride adduct. Of these structures **15b** is compatible with the low-temperature ^{19}F NMR data, although the remaining structures cannot be ruled out if there is an accidental near equivalence of two of the resonances. The observation that the periodonium ion of **1a** reacts rapidly with fluoride ion makes it difficult to explain the reported[3] failure of the difluoroperiodonium ion of **2** to react with fluoride ion. Compound **15** is much more soluble than the chloro (**8a**) or bromo (**8b**) adducts, clearly compatible with the different structures proposed for **15**.


15a

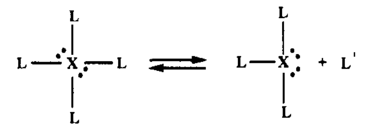

15b


15c


15d

Discussion

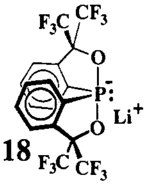
Stability of 10-I-3 Species versus 12-I-4 Species. The 10-I-3 iodinane **6** is more stable than the square planar 12-I-4 species **7**, which may simply be a transition state. It is interesting to compare Ψ-TBP **6** to stable 12-X-4 species such as Ψ-Oc (or square planar) **16a–d**.[20] The ionization of **16** to 10-X-3 species **17** should be favored by electron-releasing substituents, such as the aryl groups of **6**, and disfavored by the electron-withdrawing fluorine ligands of **16a** or **16b**.

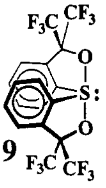


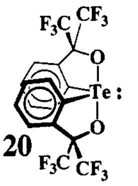
16a, X = Xe, L = F
b, X = I^-, L = F
c, X = I^-, L = Cl
d, X = I^-, L = CF_3COO

17a, X = Xe^+, L = F, L′ = F^-
b, X = I, L = F, L′ = F^-
c, X = I, L = Cl, L′ = Cl^-
d, X = I, L = CF_3CO_2, L′ = $CF_3CO_2^-$

Stability of the Spirobicyclic 10-I-4 Periodonium Ion and Related Spirobicyclic 10-X-4 Species. The periodonium ion of **1a,b** is isostructural and isoelectronic with the 10-P-4 phosphoranide anion of **18**, with neutral 10-S-4 sulfuranes **19**,[9a,21] and with 10-Te-4 tellurane **20**.[22] The sulfuranes were the first members of this series to be synthesized.[20] The remarkable stability of the spirobicyclic sulfuranes, compared to their acyclic analogues,[23,24] demonstrated the effectiveness of the bidentate ligand, common to all five compounds, in stabilizing Ψ-TBP 10-X-4 hypervalent main group element species. The stabilizing effects of the bidentate ligand have been discussed in detail.[9a] The electronegativity of the CF_3-substituted apical alkoxides stabilizes the negative charges at the apical positions of the three-centered four-electron bonds, while the relatively positive charge on the central atom is stabilized by the two electropositive carbon ligand centers. The bidentate


18


19


20

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[18] (a) Wittig, G.; Clauss, K. *Justus Liebigs Ann. Chem.* **1952**, *578*, 136. (b) Clauss, K. *Chem. Ber.* **1955**, *88*, 268. (c) Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1971**, *36*, 4055. (d) Reich, H. J.; Cooperman, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 5077.

[19] Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1972**, *37*, 1516.

[20] (a) Classen, H. H.; Selig, H.; Malm, J. G. *J. Am. Chem. Soc.* **1962**, *84*, 3593. (b) Hargreaves, G. B.; Peacock, R. D. *J. Chem. Soc.* **1960**, 2373. (c) Buckles, R. E.; Mills, J. F. *J. Am. Chem. Soc.* **1954**, *76*, 3716. (d) Naumann, D.; Schmeisser, M.; Scheele, R. *J. Fluorine Chem.* **1972**, *1*, 321. (e) X-ray crystal structures of compounds describable as dimers of 10-I-3 iodinane species show somewhat distorted 12-I-4 square planar structures: Stang, P. J.; Wingert, H.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 7235. Nguyen, T. T.; Wilson, S. R.; Martin, J. C. *Ibid.* **1986**, *108*, 3803.

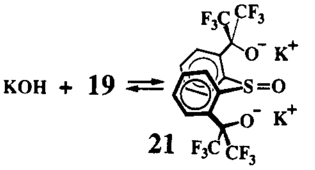
[21] Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155.

[22] Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529.

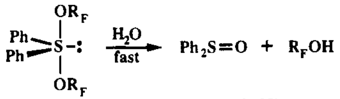
[23] Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2339, 2341.

[24] Michalak, R. S.; Martin, J. C. Unpublished results.

ligands are therefore properly designed to stabilize TBP structures. Sulfurane **19** was found to be inert toward most nucleophiles.[21,24] To hydrolyze **19** it is necessary to treat it with refluxing ethanolic potassium hydroxide for several days.[24] Addition of acid to sulfoxide dialkoxide **21** instantly regenerates sulfurane **19**.[24]



Sulfurane **19**[21,24] is unaffected by boiling in aqueous strong acid for long periods of time. In sharp contrast, the closely analogous acyclic sulfurane **22** is rapidly hydrolyzed, even at very low temperature, upon exposure to moisture.[23] This reflects the stabilizing effect of the five-membered ring linking apical to equatorial sites.[25]



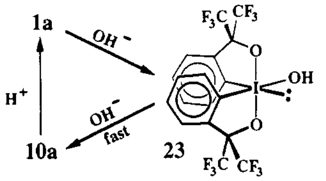
$$\mathrm{Ph_2S(OR_F)_2} \xrightarrow[\text{fast}]{\mathrm{H_2O}} \mathrm{Ph_2S{=}O} + \mathrm{R_FOH}$$

22

$R_F = PhC(CF_3)_2$

It is not surprising to find that the periodonium ion of **1a** reacts with nucleophiles somewhat more readily than sulfurane **19**, due to the positive charge at the iodine atom. This periodonium ion is, however, much less reactive than the periodonium ions of $IF_4^+SbF_6^-$,[4] **2a,b**,[3] and **3**[6] because of the stabilizing effects of the bidentate ligand system with two equatorial carbon ligand centers. All of the acyclic and monoaryl periodonium ions mentioned earlier are rapidly hydrolyzed upon exposure to atmospheric moisture.

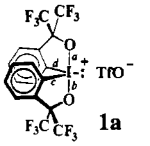
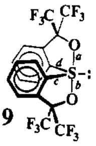
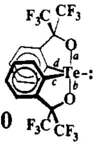
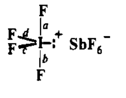
The periodonium ion of **1a** is surprisingly unreactive even toward strong nucleophiles such as hydroxide ion. If only 1 equiv of hydroxide ion is added to a solution of **1a**, only 0.5 equiv of anion **10a** is formed. This demonstrates that the initially formed hydroxyperiodinane **23** (or an isomer) is more reactive toward hydroxide ion than is the periodonium ion of **1a**.



The ease with which the periodonium ion of **1a** is regenerated from its adducts by treatment with acid demonstrates the greater effectiveness of the spirobicyclic ligand system in stabilizing Ψ-TBP 10-I-4 species compared to 12-I-5 Ψ-Oc species. The spirobicyclic ligand system accommodates the charge distribution in the hypervalent bond of the periodonium ion of **1a** by placing electronegative oxygen atoms in the apical ligand sites and electropositive carbon atoms in the equatorial ligand sites.[9a] Because Ψ-Oc 12-I-5 species have four equivalent ligand sites, they cannot take full advantage of the difference in electronegativity between oxygen and carbon to accommodate the charge distribution in both hypervalent bonds.

X-ray Structures of Spirobicyclic 10-X-4 Species. The X-ray structures of sulfurane **19**,[26] tellurane **20**,[22] and IF_4SbF_6[5] have been reported. Selected bond lengths and angles for these species are listed in Tables I and II. The O–S–O bond in sulfurane **19** deviates from linearity by only 2.9°, while the corresponding O–Te–O and O–I–O bonds in **20** and **1a** deviate by 19.5° and 17.2°, respectively. These rather large deviations are a consequence of the greater lengths of bonds a, b, c, and d in tellurane **20** and the periodonium ion of **1a**, compared to those of sulfurane **19a**. The values of ∠da and ∠cb for the 10-Te-4 and 10-I-4 species are much smaller than the ideal 90° for Ψ-TBP species. Similar distortions of five-membered-ring geometries have been observed in the X-ray structures of several 10-I-3 iodinanes.[27]

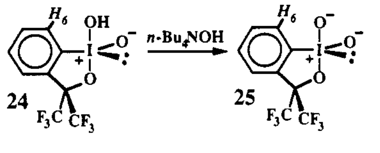
Table II. Structural Data for **1a**, **19**, **20**, and IF_4SbF_6

	bond	distance (Å)	angle (deg)	ref
 **1a**	a	2.004(4)	ab 162.8(1)	this work
	b	2.014(4)	cd 105.9(2)	
	c	2.095(4)	da′ 80.4(1)	
	d	2.107(4)	cb 80.7(1)	
 **19**	a	1.831(5)	ab 178.2(2)	26
	b	1.816(5)	cd 107.6(3)	
	c	1.798(8)	da 86.5(3)	
	d	1.803(7)	cb 86.7(3)	
 **20**	a	2.077(2)	ab 160.5(7)	22
	b	2.082(2)	cd 104.6(1)	
	c	2.106(2)	da 79.1(8)	
	d	2.103(2)	cb 79.1(8)	
	a	1.811(0.017)	ab 153.27	5
	b	1.811(0.017)		
	c	1.792(0.25)	cd 107.07	
	d	1.792(0.25)		

The X-ray structure of the periodonium ion of $IF_4^+SbF_6^-$ shows that the apical F–I–F bond deviates from linearity by 27°.[5] The severe distortion from Ψ-TBP geometry observed here is not a result of the structural constraints referenced for **20** and **1a**, but reflects the geometrical deviation toward the square pyramidal geometry made more favored by the presence of four identical fluorine ligands. Note that the ∠cd values for this compound increase to 107.07°, compatible with this explanation of the decrease in ∠ab.

The structures of the periodonium ion of **1a** and the isoelectronic tellurane **20** are very similar. The Te–C and I–C bond distances are similar. The Te–O bonds (2.08 Å) are slightly longer than the I–O bonds (2.01 Å) of the cationic periodonium ion. The equatorial ∠cd is slightly smaller in the periodonium ion of **1a** (105.9°) and tellurane **20** (104.6°) than in sulfurane **19a** (108.1°). As the equatorial bonds in the 10-X-4 species are lengthened, the centers of electron density in these bonds move away from the central atom. This decreases the repulsive interaction between these electron centers and explains the observed decrease in the equatorial bond angle upon exchanging tellurium for sulfur.

Structures of Analogues of Anion 10a, with Anionic Oxide Ligands to Iodine. Anionic **10a** has the unusual structural feature of a negatively charged, hence significantly electropositive, oxide ligand in the terminal site of a three-center bond of the Ψ-Oc 12-I-5 species. The trans site is occupied by an electronegative fluoroalkoxy ligand. The related 10-I-4 anion **25** was shown[11]



by X-ray crystallography to be a Ψ-TBP species, also with an apical anionic oxide ligand. The two apical I–O bonds of **25** are markedly different in length, with the apical endocyclic I–O bond (2.30 Å) being much longer than that to the more electropositive oxide ligand (1.78 Å). Such distortions were found in 10-S-4 and 12-S-6 sulfur species,[28] with elongation of the bond to the more electronegative apical ligand and contraction of the bond to the

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(25) Ross, M. R. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1981.

(26) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735.

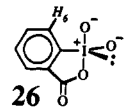
(27) For a compilation of X-ray structures of hypervalent iodine compounds, see ref 8b.

(28) (a) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 120. (b) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001.

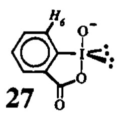
more electropositive apical ligand trans to the electronegative one. The distortion of the Ψ-TBP geometry of **25** is therefore as expected. It is a bit surprising that the apical I–O$^-$ bond in **25** is a bit shorter[11] (1.78 Å) than the equatorial I–O$^-$ bond (1.79 Å). The interaction of the fluoroalkoxide oxygen with the apical I–O$^-$ bond, together with the interaction of the two equatorial I–O$^-$ bonds in the dimeric structure, does constrain one of the O$^-$ ligands to the apical site as pictured for **25**.

The downfield chemical shift (8.62 ppm) for the ortho proton (H_6) of **25** indicates[29a] a geometry in which H_6 is constrained to a position near the strongly dipolar exocyclic apical I–O bond, as pictured. Despite the weakness of the long endocyclic I–O bond, it does constrain one of the two iodoxy oxygens to the apical site and the other to an equatorial position. It also increases the negative charge at this apical oxygen and the relative positive charge at the iodine, as expected for such hypervalent species,[29b] to increase the downfield shift of ortho proton H_6.[29] This is closely analogous to the effect of the 12-I-5 Ψ-Oc structure of **10a**. The position of the unsymmetrical O–I–O bond of **10a** provides the downfield shift of proton H_6 to 8.75 ppm, similar to that of H_6 of **25**.

Analogous species with structures proposed[30,31] as **26** and **27** are similar to **25**, with a carbonyl group replacing the bis(trifluoromethyl)methylene group of **25**. These compounds are of



26



27

particular interest in that they have been found by Moss, Alwis, and Shin[30a] to provide catalysis for the hydrolyses of phosphate and carboxylate esters. It is likely that nucleophilic attack of the apical O$^-$ of **26** or **27** at the phosphorus[30b] or at the carbonyl carbon of these esters provides the initial step of the catalytic procedure. The chemical shifts of the protons ortho to the iodine[30a] of **26** or **27** (H_6) do, however, fail to provide evidence for these structures, in contrast to **10a** or **25**.

The lowest field H_6 chemical shift for **26** is at 8.16 ppm,[11] while the H_6 is near 7.9 ppm. This suggests that the endocyclic I–O bond is considerably weaker for **26** and **27** than for **10a** or **25**, both of which have much lower field chemical shifts for the ortho protons (8.62 and 8.72 ppm). The strength of the O–I–O bond of anion **25** can be estimated by measurement of the acidity of **24** (pK_a = 3.8). As shown in Figure 2, the stabilization provided by the cyclization of the anion to form **25** can be estimated as it was for analogous sulfur species.[32]

Spectroscopic (NMR) evidence for the unsymmetrical structure of **24** shows no detectable amounts (<2%) of **28** in equilibrium with **24**, so $\Delta G_1 > 2.3$ kcal/mol. The measured pK_a of **24** (3.8) provides the value $\Delta G_3 = 5.2$ kcal/mol. In basic media the NMR spectra show no detectable amount of anion **29** in equilibrium with **25**. The pK_a values for a variety of meta- and para-substituted hexafluorocumyl alcohols have been measured,[25] allowing us to use the Hammett equation to estimate the pK_a value for 2-iodoxyhexafluorocumyl alcohol (**28**), assuming no through-space interaction between the iodoxy group and the carbinol oxygen of **28** or **29**. The calculated pK_a value for 4-iodoxyhexafluorocumyl alcohol (pK_a = 8.9) would be approximately the same for **28**. There were no through-space interactions, making ΔG_2 estimated as 12.1 kcal/mol. The value of ΔG_4 is therefore at least 9.3 kcal/mol, a significant stabilization being provided by formation of the three-center O–I–O bond upon conversion of **24** to **25**. (The OH proton of **24** may, indeed, be on the equatorial oxygen rather than on the apical oxygen, as pictured.)

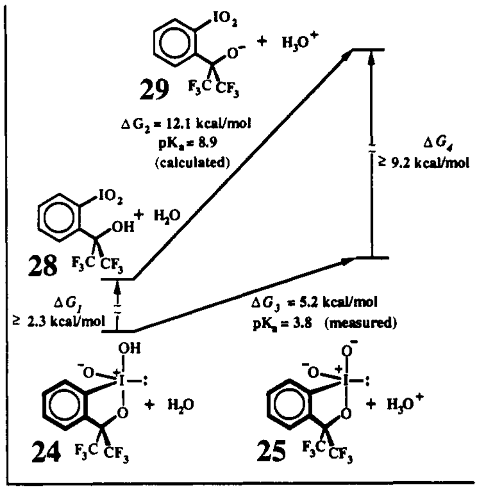
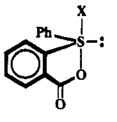
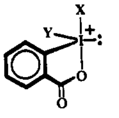
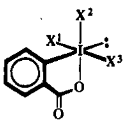
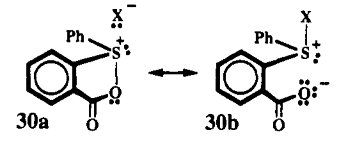


Figure 2. Free energy differences, calculated by the Hammett equation for **28** vs **29** and measured by pK_a determination for **24** vs **25**.

Table III. Carbonyl Stretching Frequencies in Sulfuranes, Iodinanes, and Periodinanes

		$\nu_{C=O}$, cm^{-1}	ref
	**31a**, X = OSO_2CF_3	1832	34
	31b, X = Cl	1740	34
	31c, X = O-*t*-Bu	1640	34
	31d, X = EP	1609	34
	**32a**, X = Cl, Y = EP	1698	34, 35
	32b, X = OAc, Y = EP	1692	34, 35
	32b, X = OCH_3, Y = EP	1667	34, 35
	26, X = O$^-$, Y = O$^-$	1617	11
	27, X = O, Y = EP	1595	36
	**33a**, $X_1 = X_2 = X_3$ = OAc	1708, 1727	11
	33b, $X_1 = X_2 = X_3$ = F	1753	11
	33c, $X_1 = X_2$ = $O(C(CH_3)_2)_2CO$, X_3 = OAc	1690	11

We suggest that the endocyclic I–O bonds of **26** and **27** are weaker than that of **25** because of the higher field chemical shift of the ortho protons (H_o). Another source of evidence supporting this conclusion is the carbonyl stretching frequencies ($\nu_{C=O}$) in the infrared spectra[11] of **26** and **27**. Earlier studies of 10-S-4 sulfuranes[32] and 12-S-6 persulfuranes[33] showed the unsymmetrical three-center four-electron bonds to be strongly polarized when the two apical ligands differed in electronegativity. The effect of such polarization was earlier correlated to the $\nu_{C=O}$ value observed for an apical carboxylate ligand as the apical ligand X, trans to the carboxylate apical ligand, was varied from an electronegative substituent, which made the carboxylate O–S bond stronger, to an electropositive substituent, which made the O–S bond weaker.[34] The weaker the O–S bond the lower the $\nu_{C=O}$ frequency, approaching that of the carboxylate anion with no trans apical substituent X, reflecting the increased contribution of resonance structure **30b** relative to **30a** (Table III).



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(29) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2711. (b) Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *Ibid.* **1985**, *107*, 6359.

(30) (a) Moss, R. A.; Alwis, K. W.; Shin, J. *J. Am. Chem. Soc.* **1984**, *106*, 2651. A recent paper describes several related species: Katritzky, A. R.; Duell, B. L.; Durst, H. D.; Knier, B. L. *J. Org. Chem.* **1988**, *53*, 3972. (b) Moss, R. A.; Alwis, K. W.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1983**, *105*, 681.

(31) Comparable structures for the neutral acids were suggested: Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow, A. J. *J. Chem. Soc.* **1965**, 3721. The X-ray crystal structure of the electrically neutral *o*-iodoxybenzoic acid showed it to be cyclic, as is **24**: Gougontas, J. *Z. Cryst. Struct. Commun.* **1981**, *10*, 489.

(32) Perkins, C. W.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3209.

(33) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127.

(34) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761.

J. Am. Chem. Soc. 1993, 115, 2495–2503

The dependence of $\nu_{C=O}$ on the electronegativity of X is seen in the data of Table III for 10-S-4 sulfuranes,[34] 10-I-3 iodinanes,[11,34,35] 10-I-4 iodinane oxide,[36] and 12-I-5 periodinanes.[11] The 10-S-4 sulfuranes clearly have a more polarizable three-center hypervalent bond than the 10-I-3 analogues. The low frequencies of $\nu_{C=O}$ for **26** (1617 cm^{-1}) and **27** (1595 cm^{-1}) suggest that since both have frequencies near that of a carboxylate anion, the endocyclic I–O bond is indeed a very weak one, as already suggested by the NMR chemical shifts of their ortho protons.

The reported[30] catalytic action of **26** or **27** in hydrolyses of phosphate or carboxylate esters is indeed likely to proceed by an initial nucleophilic attack of the apical oxygen of the iodine of **26** or **27** at the electrophilic center of the ester. The evidence which we have interpreted in terms of weak bonding between iodine and the ortho carboxylate substituent might initially lead one to suspect that the apical oxygen should not be strongly nucleophilic. As the transition state forms a bond to the electrophilic ester, however, the increased strength of bonding to the ortho carboxylate oxygen in the more symmetrical three-center O–I–O bond of the transition state lowers the energy of activation for the catalysis by **26** or **27**. This would not occur for an iodosoarene or iodoxyarene lacking the ortho carboxylate substituent.

Conclusion

The lack of reactivity of the periodonium ion of **1a** is better rationalized by comparison with other spirobicyclic 10-X-4 systems than with other known 12-I-5 or 10-I-4 species. Striking parallels between the structures and properties of 10-X-4 species with identical bidentate ligands, including periodonium cation **1a** (10-I-4), phosphoranide anion **18** (10-P-4), and neutral sulfurane **19a** (10-S-4), support the idea[9a] that properties of isovalent and isostructural hypervalent 10-X-4 species are predictable on the basis of ligand properties. Indeed the most striking aspect of the reactivity of the periodonium ion of **1a** is how little it resembles the reactivity of other known iodine species in the same oxidation state. This is a direct result of the specific geometry and electron distribution imposed on the central atom of a 10-X-4 species by the spirobicyclic ligand system, which was designed for specific stabilizing features for Ψ-TBP and TBP 10-X-L systems.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, CHE 81-13142, at the University of Illinois. The Alexander von Humboldt Stiftung, with R. Schmutzler as host of J.C.M. at the Technische Universität, Braunschweig, Germany, provided support during manuscript preparation.

Supplementary Material Available: X-ray structure and listings of coordinates, thermal parameters, bond lengths, and bond angles for periodonium salt **1a** (8 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(35) Etter, M. L. *J. Solid State Chem.* **1976**, *16*, 399.
(36) Bell, R.; Morgan, K. J. *J. Chem. Soc.* **1960**, 1209.

Scanning Tunneling and Atomic Force Microscopy Study of Layered Transition Metal Halides Nb_3X_8 (X = Cl, Br, I)

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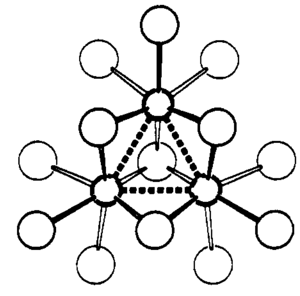
Received September 28, 1992

Abstract: Niobium halides Nb_3X_8 (X = Cl, Br, I) are made up of layers of composition Nb_3X_8, and the two surfaces (A and B) of their individual Nb_3X_8 layers are not equivalent in atomic corrugations. The surfaces of these halides were examined by atomic force microscopy (AFM) and scanning tunneling microscopy (STM) to obtain atomic resolution images. For a given surface, AFM images differ significantly from STM images, and the resolution of the STM images depends on the tunneling conditions. The observed AFM and STM images were analyzed by calculating the total electron density distribution, $\rho(r_0)$, and the partial electron density distribution, $\rho(r_0, e_f)$, for the two surfaces of single Nb_3X_8 (X = Cl, Br, I) layers. Our work shows that the AFM and STM images are well described by the $\rho(r_0)$ and $\rho(r_0, e_f)$ plots, respectively. A combined use of AFM and STM is useful in characterizing the surfaces of layered materials, and calculations of $\rho(r_0)$ and $\rho(r_0, e_f)$ plots are indispensable in interpreting their AFM and STM images.

Introduction

Layered transition metal chalcogenides and halides exhibit interesting physical properties associated with their low-dimensional structures. Individual layers of these compounds have a structure in which a sheet of transition metal atoms is sandwiched between sheets of chalcogen or halogen atoms. Such layers stack to form a three-dimensional structure, with van der Waals (VDW) interactions between adjacent layers. Thus, these compounds are easily cleaved along the layer plane to give clean and flat surfaces and hence are attractive for surface studies with scanning probe techniques. Since the advent of scanning tunneling microscopy (STM)[1,2] and atomic force microscopy (AFM),[3,4] many layered materials have been investigated.



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