there should be less of an activation barrier to the approach of these two Lewis acids precisely because of all of those factors which make borane a dimer instead of a monomer (VI). The two mechanisms (hydrogenolysis vs. the BH_3 reaction) diverge subsequent to achieving transition states V and VI, again due to the higher valence of the BH_2 fragment than the H. Thus, while the emerging RH in hydrogenolysis has no unsatisfied valence orbitals (and is therefore a superb leaving group), the emerging BRH_2 has obvious reasons to remain. In the latter case, the inferiority of akyl relative to hydrogen as a bridging group necessitates only an intramolecular rearrangment of VI to form the product $Cp_2Zr[(\mu\text{-}H)_2BHR]Y$. The BH_3 reaction observed here gives a primary product which evokes the label "insertion reaction".[23] While such a generic name has limitations, it does point out the unimolecular nature of the product, a feature lacking in the labels "alkyl transfer" and "transmetalation".

Conclusion

The idea that the empty d orbital of unsaturated Cp_2ZrMe_2 is the initial site of attack by $BH_3{\cdot}THF$[24] may also explain the initially anomalous observation that $Cp_2Zr[C(O)Me]Me$, which lacks this empty orbital, is unreactive toward borane. Because of the operation of equilibrium 1, borane is rapidly consumed by Cp_2ZrMe_2 and any reactivity of $Cp_2Zr[C(O)Me]Me$ is so slow as to be kinetically imperceptible. The absence of such an empty metal orbital in $CpFeCO(PR_3)[C(O)Me]$ does not diminish its reactivity toward $BH_3{\cdot}THF$, a result which speaks for a mechanism involving initial coordination of the "acidic hydride" borane to the η^1-C(O)Me oxygen lone pair.[2] On the other hand, CpFeCO(PR_3)Et, once formed, is observed to be stable to ethyl transfer to BH_3; this follows from our mechanistic proposal since BH_3 finds no empty iron orbital to initiate ethyl transfer (i.e., BH_3 insertion).[25]

We have argued that π donation by chlorine in Cp_2ZrCl_2 diminishes the Lewis acidity of this complex relative to Cp_2ZrMe_2.[26] It is therefore significant that we find $BH_3{\cdot}THF$ to leave Cp_2ZrCl_2 unchanged under our reaction conditions. It has also been noted[27] that transmetalation from Cp_2ZrClR to stoichiometric (1:1) $AlCl_3$ yields *free* $(RAlCl_2)_n$ and Cp_2ZrCl_2 and that the latter compound is only weakly coordinated to added $AlCl_3$. π-donor ligands can thus effectively diminish the unsaturation of Zr(IV).

We find that $Cp_2Zr(C_6H_5)_2$ does not react with $BH_3{\cdot}THF$ under the reaction conditions employed here. This is consistent with a mechanism passing from Zr–R through the intermediate $Zr(\mu\text{-}H)(\mu\text{-}R)BH_2$, *if* we postulate that phenyl is inferior to methyl in bridging to zirconium. This suggests that selective conversion of $Cp_2Zr(Me)Ph$ to $Cp_2Zr(BH_4)Ph$ might be achieved.

Finally, we suggest that insertion of Lewis acidic main group hydrides into M–X bonds (M = an unsaturated transition metal) may be a generally mechanistic feature of alkyl transfer (transmetalation). The Schwartz group has established this point for several reactions of diisobutylaluminum hydride.[21] Nöth and co-workers have reported several preparations of BH_4^- complexes that also fit this pattern (eq 10[28] and 11[29]), with the added feature

$$Cr(O\text{-}t\text{-}Bu)_4 + BH_3{\cdot}THF \rightarrow Cr(BH_4)_2{\cdot}2THF + ... \quad (10)$$

$$Ti(OR)_4 + 5BH_3(THF) \rightarrow Ti(BH_4)_3 + 2HB(OR)_2 + 0.5H_2 \quad (11)$$

of reduction of the metal.

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Registry No. Cp_2ZrMe_2, 12636-72-5; $BH_3{\cdot}THF$, 14044-65-6; $Cp_2Zr(BH_4)Me$, 81064-02-0; $Cp_2Zr(BH_4)_2$, 12083-77-1; $Cp_2Zr[C(O)Me]Me$, 60970-97-0; $Cp_2ZrMeCl$, 1291-45-8.

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Structure of Oxonium Ions: An X-ray Crystallographic Study of Triethyloxonium Hexafluorophosphate and Triphenyloxonium Tetraphenylborate[1]

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Abstract: Single-crystal X-ray diffraction data were collected on two tricoordinate oxonium salts, triethyloxonium hexafluorophosphate and triphenyloxonium tetraphenylborate. While the triethyloxonium ion is established as being pyramidal, the triphenyloxonium ion is nearly flat but deviates significantly from planarity. The average O–C distances are 1.499 (10) Å for Et_3O^+ and 1.472 (9) Å for Ph_3O^+. For the triphenyloxonium ion, the phenyl rings are tilted by an average of 59.7° from the equatorial plane. This value indicates nearly no p–π interaction between oxygen and its aromatic ligands. The unusually large ipso angle, 125.8°, of the triphenyloxonium ion suggests that the oxonium substituent (i.e., $^+OPh_2$) on the aromatic ring is a powerful σ-electron-withdrawing group. $Ph_3O^+BPh_4^-$ crystallizes in the monoclinic space group $P2_1/n$, with a = 21.101 (5) Å, b = 11.107 (3) Å, c = 13.603 (7) Å, β = 90.75 (3)°, V = 3188 (4) Å^3, and Z = 4. The final R factor is 0.048 for 1379 reflections with $I > 3\sigma(I)$. $Et_3O^+PF_6^-$ crystallizes in the orthorhombic space group $Pnma$, with a = 16.475 (3) Å, b = 9.965 (2) Å, c = 6.557 (1) Å, V = 1076.5 (3) Å^3, and Z = 4. The final R factor is 0.058 for 618 reflections with $I > 3\sigma(I)$.

The synthesis and structural characterization of compounds containing a tricoordinate, positively charged oxygen (R_3O^+, oxonium ions) has remained a long-term challenge for chemists ever since Meerwin's pioneering work in 1937.[2a] The only

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quantitative structural information on this class of compounds relates to the parent oxonium ion,[2b,c] H_3O^+, which has undergone intense scrutiny. Neutron diffraction studies have been performed in recent years by J. O. Lundgren and J. M. Williams on oxonium *p*-toluenesulfonate[3] and by J. O. Lundgren et al. on oxonium trifluoromethanesulfonate.[4] These investigations have shown the oxonium ion to be pyramidal, possessing average H–O–H angles of 110.4° and 112.9°, respectively. In both of the above cases, the oxonium ion was strongly hydrogen bonded to the oxygens of the sulfonate group of the counterion. Various studies in solution[5-8] have indicated that the H_3O^+ ion is also nonplanar (and participates in strong H-bonding interactions) in the liquid phase. In the absence of hydrogen bonding, however, molecular orbital calculations[9] at various levels of sophistication predict the oxonium ion to be either planar or pyramidal (H–O–H angle 111.6°), with a small barrier to inversion (2.05 kcal/mol[9d]).

The present study is an effort to extend the structural information of H_3O^+ to oxonium ions substituted by organic ligands,[10] R_3O^+, in which the hydrogen-bonding effects would be absent. In our study, $Et_3O^+PF_6^-$ and $Ph_3O^+BPh_4^-$ will be used as the specific examples. Again the central question is whether the overall structure of the cation is planar or pyramidal. To our knowledge, no previous crystallographic analysis of trialkyl- or triaryloxonium ions has been reported. However, some examples of the isoelectronic nitrogen (R_3N) and carbon (R_3C^-) analogues have been structurally characterized. Electron diffraction studies have shown that Me_3N has a pyramidal geometry (C–M–C = 111.8°),[11] while Ph_3N appears to be nearly planar (C–M–C = 116°).[12] Crystallographic studies on Ph_3C^- indicate a planar structure (C–M–C = 120.0°);[13] Me_3C^- has not been crystallographically analyzed, but theoretical calculations suggest that the anion is pyramidal, with a barrier to inversion of 8.0 kcal/mol.[14] In our work we show that Et_3O^+ is pyramidal while Ph_3O^+ is essentially planar.

Experimental Section

Materials. Triphenyloxonium tetraphenylborate was prepared in a manner analogous to that for diphenylhalonium tetraphenylborates,[15a] an improved procedure to that reported previously.[15b] Single crystals were formed by vapor diffusion with 1,2-dichloroethane and diethyl ether as the soluble and insoluble components, respectively. Since this compound is unreactive toward moisture and is stable at room temperature, crystals were mounted on glass fibers for the X-ray diffraction experiment.

Triethyloxonium hexafluorophosphate was prepared as described in the literature.[15c] The crystals were washed with sulfuryl chloride fluoride (SO_2ClF) before being transferred to a drybox with a recirculating nitrogen atmosphere which is continuously dried and deoxygenated to less than 5 ppm. Since this compound reacts slowly with moisture in the air and also decomposes slowly at room temperature in the absence of water, crystals were mounted in 0.3-mm capillaries (in the drybox), which were subsequently sealed and then stored below 0 °C prior to use.

X-ray Data Collection and Analysis. Triphenyloxonium Tetraphenylborate. A rodlike crystal of of dimensions 0.30 × 0.31 × 0.20 mm was used for the diffraction experiment. Data collection was performed at room temperature by use of a Syntex P2$_1$ diffractometer. The centering of 15 reflections obtained from a rotation photograph indicated a monoclinic space group whose crystal dimensions are presented in Table I. A total of four molecules per unit cell was assumed, since this gave a reasonable calculated density of 1.180 g/cm^3. The θ–2θ scan technique was employed with graphite-monochromatized Mo K_α radiation (λ = 0.71069 Å) up to a $(\sin\theta)/\lambda$ limit of 0.5385 Å^{-1} for two duplicate quadrants of data $(+h,+k,\pm l)$ and $(+h,-k,\pm l)$. During data collection, the intensity of three reflections (8,0,0; 0,2,0; 0,0,2) was measured for every 50 data points collected. No significant variation in the intensities of these three "check" reflections was observed. The data were processed in the following manner: (1) reflections whose observed intensities were less than zero were immediately discarded, (2) corrections to the raw intensities were made for Lorentz and polarization effects[16] and for absorption by the empirical ψ-scan method,[17] (3) the data from the two duplicate quadrants were merged into one set $(+h,+k,\pm l)$, and (4) reflections whose intensities were less than 3 times their estimated standard deviation[18] were rejected as unobserved. Examination of the $0k0$ and $h0l$ reflections indicated space group $P2_1/n$, a nonstandard setting of $P2_1/c$, whose general equivalent positions are (x, y, z), $(-x, -y, -z)$, $(^1/_2 + x,$

Table I. Crystal Data for $Ph_3O^+BPh_4^-$ and $Et_3O^+PF_6^-$

mol formula	$C_{42}H_{35}BO$	$C_6H_{15}F_6OP$
color	colorless	colorless
cryst dimensions, mm	0.30 × 0.31 × 0.20	0.30 × 0.35 × 0.40
space group	$P2_1/n$	*Pnma*
cell dimensions		
a, Å	21.101 (5)	16.475 (3)
b, Å	11.107 (3)	9.965 (2)
c, Å	13.603 (7)	6.557 (1)
β, deg	90.75 (3)	90.00
molecules/cell	4	4
cell volume, Å^3	3188 (1)	1076.5 (3)
calcd density, g cm^{-3}	1.180	1.531
wavelength, Å	0.71069 (Mo Kα)	1.5418 (Cu Kα)
mol wt	566.56	248.15
$(\sin\theta)/\lambda$ limit, Å^{-1}	0.5385	0.5617
total no. of reflctns collected	7322	1587
total no. of unique reflctns collected	4061	846
no. of reflctns used in structural analysis $[I > 3\sigma(I)]$	1379	618
no. of parameters refined	397	85
final agreement factors	$R_F = 0.048$; $R_{wF} = 0.041$	$R_F = 0.058$; $R_{wF} = 0.066$

(1) This publication is no. 23 in the Onium Ions series.

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Table II. Fractional Coordinates ($\times 10^5$) and Thermal Parameters ($\times 10^4$) for the Triphenyloxonium Cation[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	49035 (21)	22029 (46)	79039 (35)	416 (33)	574 (38)	1067 (40)	72 (30)	205 (31)	225 (32)
C1	52309 (40)	32736 (73)	75521 (54)	481 (54)	632 (64)	741 (58)	112 (54)	232 (49)	238 (50)
C2	58492 (38)	34598 (73)	78014 (52)	501 (56)	771 (70)	754 (55)	153 (50)	108 (47)	256 (50)
C3	61213 (39)	45055 (90)	74555 (73)	704 (63)	703 (71)	1340 (82)	−62 (61)	414 (60)	217 (61)
C4	57858 (54)	52992 (86)	69131 (83)	1116 (95)	695 (78)	1708 (102)	322 (74)	715 (89)	699 (71)
C5	51615 (55)	50526 (110)	66596 (82)	902 (86)	1376 (113)	1818 (105)	553 (82)	313 (85)	1040 (88)
C6	48738 (37)	40052 (98)	69844 (69)	590 (61)	1198 (93)	1220 (78)	284 (65)	232 (56)	597 (70)
C7	42851 (34)	23189 (72)	84047 (53)	421 (51)	647 (60)	557 (50)	133 (47)	235 (43)	58 (44)
C8	37968 (39)	16510 (66)	80392 (46)	568 (53)	632 (60)	618 (52)	1 (49)	−187 (47)	−168 (43)
C9	32312 (33)	17669 (73)	85497 (62)	274 (47)	712 (65)	1006 (69)	−36 (44)	−2 (45)	109 (55)
C10	31837 (37)	25237 (74)	93367 (62)	626 (61)	631 (66)	773 (61)	200 (51)	215 (51)	39 (49)
C11	36929 (45)	31840 (69)	96695 (52)	762 (60)	557 (59)	710 (54)	120 (51)	52 (51)	−152 (45)
C12	42678 (33)	30761 (67)	91913 (61)	417 (51)	538 (58)	942 (61)	−19 (43)	67 (46)	−64 (51)
C13	52402 (29)	10620 (64)	80690 (56)	369 (45)	413 (52)	577 (52)	97 (41)	−16 (40)	35 (47)
C14	53080 (33)	3516 (83)	72566 (50)	521 (52)	802 (68)	513 (53)	56 (50)	−51 (41)	−88 (50)
C15	55957 (36)	−7365 (80)	74181 (61)	584 (57)	745 (72)	687 (63)	90 (50)	159 (49)	−132 (52)
C16	57877 (32)	−10823 (67)	83295 (73)	426 (49)	489 (57)	959 (62)	53 (43)	41 (50)	107 (58)
C17	57230 (32)	−3270 (81)	91213 (52)	537 (53)	629 (60)	550 (53)	56 (48)	50 (41)	156 (48)
C18	54423 (32)	7713 (72)	90057 (50)	401 (45)	641 (63)	512 (54)	−29 (43)	81 (38)	−16 (45)

[a] Thermal parameters are of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

$^1/_2 - y, {}^1/_2 + z$), ($^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$). Direct methods (using the program MULTAN[19]) were employed to locate all nonhydrogen atoms.[20] During least-squares refinement,[21] all nonhydrogen atoms were assigned anisotropic thermal parameters. The position of each hydrogen atom was calculated to be 1.084 Å from its attached carbon and in the plane of the aromatic ring. Isotropic temperature factors were assigned to these H atoms equal to the value of their attached carbons. The positions and thermal parameters of all nonhydrogen atoms were refined in one matrix and gave a final agreement factor of 4.8%. The results are summarized in Table I.

Triethyloxonium Hexafluorophosphate. A brick-shaped crystal of dimensions 0.30 × 0.35 × 0.40 mm was initially centered at room temperature by using 15 reflections obtained from a rotation photograph. In order to prevent the crystal from decomposing, we carried out subsequent operations with the LT-1 low-temperature unit on the Syntex $P2_1$ diffractometer. When the temperature had been lowered (by using maximum cooling, 10 ft^3 min^{-1} of nitrogen gas through a liquid nitrogen heat exchanger), each peak was observed to be split into two poorly resolved peaks. This phenomenon was temperature dependent and reversible and presumably represents a reordering of the molecules in the crystal. After plotting peaks at various settings of the nitrogen stream heater, we settled upon −50 °C as the optimum temperature: this was safely above the transition temperture and yet low enough to prevent decomposition of the crystal during data collection. Recentering of the original 15 orienting reflections indicated an orthorhombic crystal system whose unit cell parameters are presented in Table I. An assumed total of four molecules per unit cell yielded a calculated density of 1.5312 g/cm^3. Data were collected by use of the θ–2θ scan technique and Cu K_α radiation (λ = 1.5418 Å). Two duplicate data sets, ($+h,+k,+l$) and ($-h,+k,+l$), were collected, up to a $(\sin\theta)/\lambda$ limit of 0.5617 $Å^{-1}$ (2θ = 120°). During data collection, the intensities of three reflections, (600), (040), and (002), were monitored for every 50 data points collected, and they did not vary significantly during the course of the data collection. The data were processed in the same manner as described above,[22] with the ($-h,+k,+l$) and the ($+h,+k,+l$) reflections being averaged. Systematic absences indicated either space group $Pna2_1$ or $Pnma$. Application of direct methods (MULTAN)[23] in the centric space group $Pnma$ resulted in the location of the positions of all nonhydrogen atoms in the molecule. These

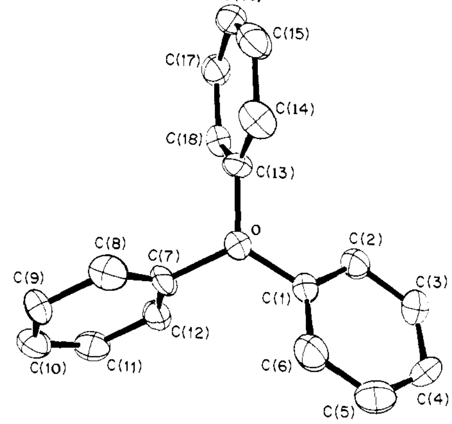

Figure 1. Top view of the triphenyloxonium ion.

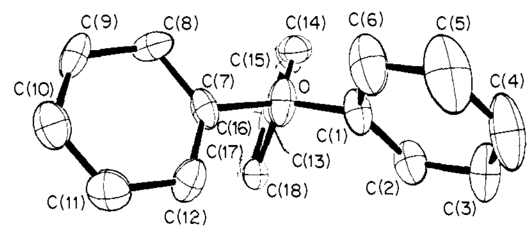

Figure 2. Side view of the triphenyloxonium ion.

coordinates provided the starting point for refinement.[24] Both PF_6^- fragment and the Et_3O^+ fragment lie on mirror planes. During the anisotropic least-squares refinement, the shapes of the methylene carbons of the Et_3O^+ cation indicated that they were disordered. The final refinement, based on disordered methylene carbons in space group $Pnma$, resulted in an agreement factor of 5.8%. The results of the refinement are summarized in Table I.

As a final check that the correct space group had been chosen, further refinement in the alternative space group $Pna2_1$ (on the basis of an ordered model) was carried out. The observed reflections were reindexed ($+h,+k,+l$ transformed to $+h,+l,+k$), and the coordinates (for the PF_6^- anion and one rotamer of the Et_3O^+ cation) were transformed accordingly. The transformation from $Pnma$ to $Pna2_1$ results in the removal of the mirror planes that bisect the Et_3O^+ and PF_6^- ions. After refinement[24] with all atoms possessing anisotropic temperature factors, the final agreement factor was 7.6%, with 45 sets of parameters having large correlation coefficients (i.e., greater than 0.50). Since this result was

(19) MULTAN is a system of computer programs for the direct solution of crystal structures from X-ray diffraction data. See: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(20) For the MULTAN solution, 330 reflections having the largest E values were used, and the phases of six reflections were varied to generate 64 starting sets. The correct solution was the one having the highest combined figure-of-merit (2.91), and this yielded an E map from which all the nonhydrogen positions were located.

(21) Least-squares refinement of this compound was accomplished by using CRYM, a set of programs developed by Dr. Richard Marsh's group at the California Institute of Technology.

(22) The ψ scan was performed by using the (−1,0,1) reflection (2θ = 14.53°, χ = 290.35°); the minimum/maximum intensity ratio was 0.93.

(23) For the MULTAN solution, 220 reflections having the largest E values were used, and the phases of four reflections were varied to generate 16 starting sets. The correct solution was the one having the highest combined figure-of-merit (2.00), and all nonhydrogen atoms were located from the subsequent E map.

(24) For $Et_3O^+PF_6^-$, least-squares refinement was carried out by using UCIGLS, a modified version of W. R. Busing and H. A. Levy's ORELS. See: Doedens, R. J. In "Crystallographic Computing"; Ahmed. F. R., Ed.; Munksgaard: Cophenhagen, 1970; p 198–200.

Table III. Fractional Coordinates (×10[5]) and Thermal Parameters (×10[4]) for the Tetraphenylborate Anion[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
B	75984 (36)	21622 (73)	101142 (56)	426 (56)	479 (60)	477 (57)	−79 (51)	11 (46)	48 (48)
C19	68772 (29)	23812 (62)	105194 (47)	388 (45)	380 (50)	459 (44)	−61 (42)	−18 (39)	−53 (38)
C20	65284 (34)	33620 (68)	101719 (45)	391 (47)	563 (58)	627 (51)	−82 (44)	−8 (43)	−51 (45)
C21	59081 (37)	36089 (69)	104872 (58)	537 (58)	523 (60)	949 (65)	46 (46)	−43 (49)	−87 (50)
C22	56304 (32)	28273 (88)	111422 (60)	386 (51)	802 (68)	704 (59)	−106 (52)	149 (46)	−329 (52)
C23	59542 (40)	18458 (81)	114705 (50)	548 (57)	821 (73)	590 (56)	−134 (52)	83 (48)	−57 (51)
C24	65708 (34)	16328 (62)	111744 (48)	417 (49)	618 (57)	510 (44)	−73 (43)	51 (38)	53 (43)
C25	75118 (28)	20483 (59)	89118 (45)	309 (40)	382 (49)	409 (46)	22 (36)	59 (38)	67 (39)
C26	71483 (30)	11029 (62)	85063 (48)	497 (48)	478 (52)	407 (47)	−57 (42)	70 (39)	−7 (41)
C27	70371 (31)	10065 (64)	75003 (54)	466 (49)	607 (59)	544 (53)	0 (43)	−63 (43)	−98 (48)
C28	72834 (34)	18317 (75)	68565 (50)	549 (54)	675 (64)	496 (51)	−51 (49)	81 (42)	−9 (50)
C29	76423 (37)	27516 (74)	72147 (56)	689 (57)	749 (66)	582 (58)	−280 (50)	−26 (46)	232 (46)
C30	77571 (31)	28583 (64)	82273 (54)	520 (50)	672 (57)	514 (49)	−244 (44)	−136 (43)	118 (45)
C31	80736 (32)	33029 (68)	103676 (43)	412 (49)	551 (58)	330 (44)	−67 (43)	19 (37)	19 (39)
C32	78952 (32)	43756 (70)	108130 (51)	444 (51)	568 (56)	638 (55)	−62 (49)	−12 (42)	−36 (43)
C33	83163 (43)	53189 (66)	109709 (60)	727 (64)	413 (61)	1032 (68)	−134 (54)	−230 (58)	−7 (49)
C34	89371 (45)	52189 (80)	106942 (59)	803 (71)	641 (67)	718 (61)	−287 (59)	−198 (54)	112 (52)
C35	91403 (33)	41512 (88)	102886 (52)	417 (51)	959 (77)	632 (54)	−277 (53)	80 (43)	1 (55)
C36	87161 (35)	32047 (68)	101410 (45)	512 (49)	699 (63)	458 (48)	−111 (48)	77 (41)	−141 (41)
C37	79157 (30)	9611 (67)	105888 (51)	412 (48)	530 (57)	444 (50)	−66 (42)	84 (40)	34 (44)
C38	81236 (33)	−253 (76)	100505 (50)	521 (50)	566 (60)	560 (51)	118 (47)	−23 (41)	129 (50)
C39	84109 (36)	−10187 (78)	104861 (65)	651 (62)	741 (70)	777 (65)	10 (54)	−23 (51)	2 (57)
C40	85034 (37)	−10521 (84)	114912 (85)	474 (58)	686 (76)	1273 (91)	−50 (56)	−181 (61)	404 (72)
C41	83051 (37)	−1151 (101)	120397 (57)	515 (61)	974 (89)	678 (64)	−234 (59)	−108 (49)	292 (63)
C42	80215 (32)	8819 (71)	116084 (56)	471 (50)	575 (63)	609 (59)	−65 (44)	−33 (43)	31 (48)

[a] See footnote a in Table II for the definition of the thermal parameters.

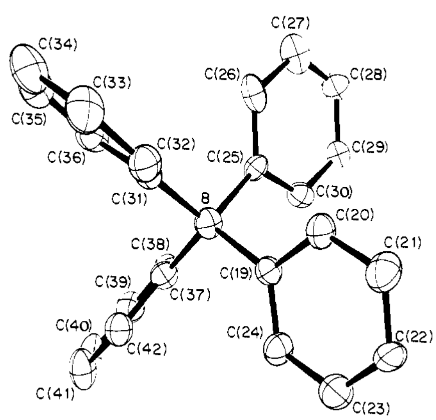

Figure 3. The tetraphenylborate ion.

substantially inferior to that of the disordered refinement in space group *Pnma* (R = 5.8%), the latter was considered to be the final result of the structure analysis.

Results

Description of Triphenyloxonium Tetraphenylborate. ORTEP[25] plots of the triphenyloxonium ion and the tetraphenylborate anion are shown in Figures 1–3. Figure 1 illustrates the near 3-fold symmetry, or what is commonly referred to as the symmetrical-propeller nature, of the cation. Figure 2 shows the slight nonplanarity of the oxygen center (out-of-plane displacement of the O atom = 0.142 Å) and the rather large degree of rotation of the phenyl groups. A stereoview of the contents of the unit cell is presented in Figure 4. The refined coordinates, temperature factors, and intramolecular distances and angles are presented in Table II–VI. In Table VII are reported the values of the parameters that describe the conformation of this oxonium ion. What is immediately striking about the rotation angles is that there is almost no indication of conjugation between the lone pair of electrons on oxygen and the π systems of the aromatic rings. For maximum overlap to occur, the oxygen would have to lie in the plane of the three ipso carbons (C1, C7, and C13) and the angles between the normals of the least-squares planes of the phenyl rings and the plane of the three ipso carbons (i.e., the phenyl rotation angles) would have to be zero. In contrast, the isoelectronic triphenylmethyl carbanion[13a] (as the TMEDA-complexed sodium salt) is planar within experimental error (the central carbon is 0.004 Å from the plane of the ipso carbons). In addition, the phenyl rotation angles are small in the carbanion (28.3°, 34.7°, and 27.6°), reflecting a high degree of π-electron conjugation between the aromatic groups and the charged center. In Ph_3C^-,

(25) Johnson, C. K. "ORTEP-II", Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Table IV. Calculated Fractional Coordinates (×10[4]) and Isotropic Thermal Parameters for the H Atoms in Triphenyloxonium Tetraphenylborate

	x	y	z	B
H2	6111	2827	8261	5.09
H3	6616	4675	7602	6.40
H4	6001	6141	6701	7.55
H5	4894	5674	6202	7.88
H6	4388	3774	6787	5.36
H8	3844	1082	7406	4.75
H9	2821	1272	8313	5.35
H10	2737	2606	9706	5.71
H11	3653	3758	10304	5.83
H12	4680	3573	9425	4.74
H14	5145	624	6536	4.65
H15	5672	−1347	6810	4.73
H16	6000	−1962	8437	5.53
H17	5886	−618	9836	4.63
H18	5394	1392	9618	4.72
H20	6747	3968	9650	5.02
H21	5651	4377	10219	5.27
H22	5158	2992	11400	4.60
H23	5732	1226	11971	5.49
H24	6820	854	11468	4.44
H26	6949	447	8996	3.99
H27	6755	273	7215	4.56
H28	7187	1756	6071	5.03
H29	7837	3406	6719	4.20
H30	8050	3593	8489	4.01
H32	7413	4469	11048	4.51
H33	8158	6143	11306	5.08
H34	9261	5962	10788	5.31
H35	9632	4047	10098	4.72
H36	8888	2359	9831	4.20
H38	8061	−11	9261	4.72
H39	8556	−1765	10019	5.64
H40	8736	−1824	11815	4.83
H41	8370	−153	12820	4.79
H42	7877	1623	12067	4.10

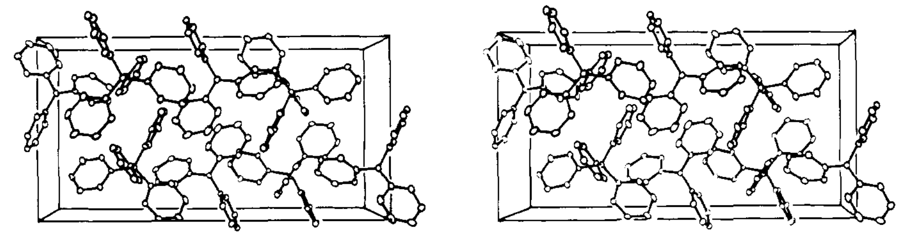

Figure 4. A stereoscopic view of the contents of the unit cell of $Ph_3O^+BPh_4^-$.

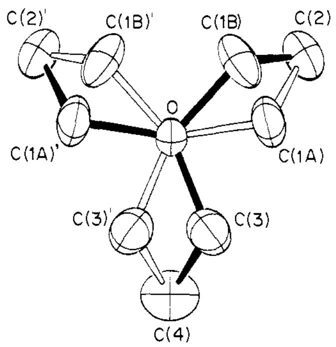

Figure 5. Top view of the disordered triethyloxonium ion.

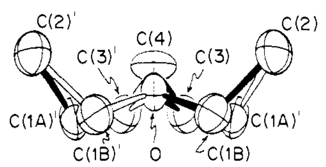

Figure 6. Side view of the disordered triethyloxonium Ion.

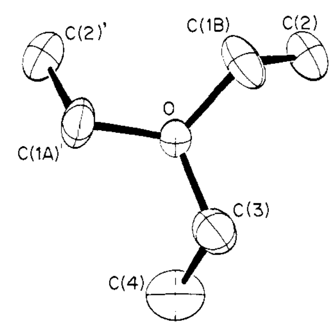

Figure 7. Top view of one rotamer [C(1A)′, C(1B), C(3)] of the Et_3O^+ ion.

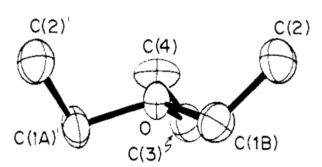

Figure 8. Side view of the [C(1A)′, C(1B), C(3)] rotamer.

there is also a considerable shortening of the bond between the central carbon and the ipso carbon (1.461 Å) relative to that in triphenylmethane[26] (1.524 Å). On the other hand, the average oxygen–carbon bond length in Ph_3O^+ (1.471 Å, Table V) is significantly longer than the corresponding bond lengths in anisole[27] (1.361 (15) Å) and 1,2-diphenoxyethane[28a] (1.37 (1) Å). Thus,

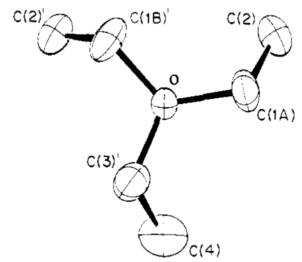

Figure 9. Top view of the other rotamer [C(1A), C(1B)′, C(3)′] of the Et_3O^+ ion.

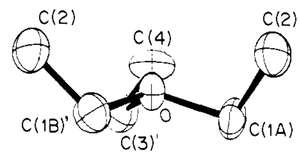

Figure 10. Side view of the [C(1A), C(1B)′, C(3)′] rotamer.

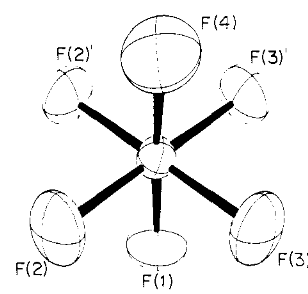

Figure 11. The hexafluorophosphate anion.

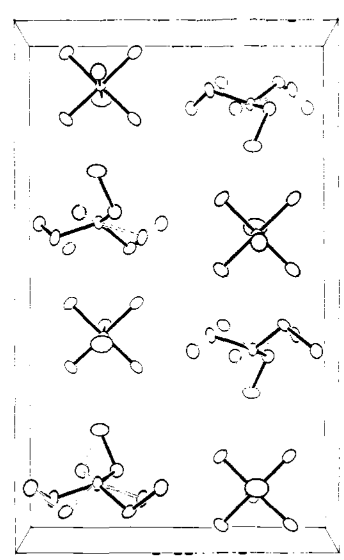

Figure 12. The contents of the unit cell of $Et_3O^+PF_6^-$.

there is some evidence for antibonding character[28b] developing between the oxygen and the aromatic groups in Ph_3O^+. Some intermolecular contacts for triphenyloxonium tetraphenylborate are reported in Table VIII. There are no intermolecular C···C

(26) Riche, P. C.; Pascard-Billy, C. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1874–1876.
(27) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1973**, *27*, 4024–4027.
(28) (a) Yasuoka, N.; Ando, T.; Kurizabashi, S. *Bull. Chem. Soc. Jpn* **1967**, *40*, 270–273. (b) One of the referees offered an alternative explanation—"There is an alternative to the anti-bonding argument presented here. If we take a covalent radius for a trigonal carbon (73 pm) and add a covalent radius for oxygen (73 pm) we get an expected C–O bond of 146 pm; found, 147 pm. Then the shortening of the anisole and diphenoxyethane bonds is due to π bonding, as expected".

Table V. Distances and Angles for the Triphenyloxonium Cation

atoms	distances, Å	atoms	angles, deg
O-C(1)	1.459 (9)	C(1)-O-C(7)	120.1 (6)
O-C(7)	1.486 (8)	C(1)-O-C(13)	121.6 (5)
O-C(13)	1.469 (9)	C(7)-O-C(13)	115.5 (5)
C(1)-C(2)	1.359 (12)	O-C(1)-C(2)	119.9 (7)
C(1)-C(6)	1.345 (12)	O-C(1)-C(6)	114.6 (7)
C(2)-C(3)	1.381 (13)	C(2)-C(1)-C(6)	125.4 (8)
C(3)-C(4)	1.345 (14)	C(1)-C(2)-C(3)	116.4 (7)
C(4)-C(5)	1.385 (16)	C(2)-C(3)-C(4)	121.3 (8)
C(5)-C(6)	1.387 (16)	C(3)-C(4)-C(5)	119.9 (10)
C(7)-C(8)	1.359 (11)	C(4)-C(5)-C(6)	120.4 (10)
C(7)-C(12)	1.362 (11)	C(5)-C(6)-C(1)	116.4 (8)
C(8)-C(9)	1.395 (11)	O-C(7)-C(8)	116.8 (6)
C(9)-C(10)	1.366 (12)	O-C(7)-C(12)	116.5 (6)
C(10)-C(11)	1.373 (12)	C(8)-C(7)-C(12)	126.6 (7)
C(11)-C(12)	1.389 (12)	C(7)-C(8)-C(9)	114.5 (7)
C(13)-C(14)	1.367 (11)	C(8)-C(9)-C(10)	121.3 (7)
C(13)-C(18)	1.377 (10)	C(9)-C(10)-C(11)	121.5 (7)
C(14)-C(15)	1.369 (12)	C(10)-C(11)-C(12)	118.9 (7)
C(15)-C(16)	1.355 (13)	C(11)-C(12)-C(7)	117.0 (7)
C(16)-C(17)	1.373 (12)	O-C(13)-C(14)	119.2 (6)
C(17)-C(18)	1.364 (12)	O-C(13)-C(18)	115.5 (6)
		C(14)-C(13)-C(18)	125.3 (7)
		C(13)-C(14)-C(15)	115.5 (7)
		C(14)-C(15)-C(16)	121.6 (8)
		C(15)-C(16)-C(17)	120.9 (7)
		C(16)-C(17)-C(18)	120.2 (7)
		C(17)-C(18)-C(13)	116.4 (7)
Average Distances and Angles[a]			
O-C(ipso)	1.472 (9)	C(ipso)-O-C(ipso)′	119.1 (5)
C(ipso)-C(ortho)	1.362 (11)	O-C(ipso)-C(ortho)	117.1 (6)
C(ortho)-C(meta)	1.381 (13)	C(ortho)-C(ipso)-C(ortho)′	125.8 (7)
C(meta)-C(para)	1.366 (13)	C(ipso)-C(ortho)-C(meta)	116.0 (7)
		C(ortho)-C(meta)-C(para)	120.6 (8)
		C(meta)-C(para)-C(meta)′	120.8 (8)

[a] The numbers in parentheses are the averages of the standard deviations.

Table VI. Distances and Angles for the Tetraphenylborate Anion

atoms	distances, Å	atoms	angles, deg
B-C(19)	1.643 (10)	C(19)-B-C(25)	104.7 (5)
B-C(25)	1.648 (10)	C(19)-B-C(31)	112.3 (6)
B-C(31)	1.649 (11)	C(19)-B-C(37)	111.5 (6)
B-C(37)	1.623 (11)	C(25)-B-C(31)	109.0 (5)
C(19)-C(20)	1.394 (10)	C(25)-B-C(37)	111.8 (6)
C(19)-C(24)	1.384 (9)	C(31)-B-C(37)	107.6 (5)
C(20)-C(21)	1.410 (11)	B-C(19)-C(20)	119.3 (6)
C(21)-C(22)	1.380 (12)	B-C(19)-C(24)	124.7 (6)
C(22)-C(23)	1.359 (12)	C(20)-C(19)-C(24)	116.0 (6)
C(23)-C(24)	1.387 (11)	C(19)-C(20)-C(21)	122.5 (6)
C(25)-C(26)	1.409 (9)	C(20)-C(21)-C(22)	118.5 (7)
C(25)-C(30)	1.400 (10)	C(21)-C(22)-C(23)	120.1 (7)
C(26)-C(27)	1.390 (10)	C(22)-C(23)-C(24)	120.7 (7)
C(27)-C(28)	1.374 (10)	C(23)-C(24)-C(19)	122.1 (7)
C(28)-C(29)	1.358 (11)	B-C(25)-C(26)	119.9 (6)
C(29)-C(30)	1.400 (11)	B-C(25)-C(30)	125.0 (6)
C(31)-C(32)	1.391 (10)	C(26)-C(25)-C(30)	115.0 (6)
C(31)-C(36)	1.399 (10)	C(25)-C(26)-C(27)	121.8 (6)
C(32)-C(33)	1.389 (11)	C(26)-C(27)-C(28)	121.0 (6)
C(33)-C(34)	1.372 (13)	C(27)-C(28)-C(29)	119.1 (7)
C(34)-C(35)	1.379 (13)	C(28)-C(29)-C(30)	120.3 (7)
C(35)-C(36)	1.393 (11)	C(29)-C(30)-C(25)	122.6 (7)
C(37)-C(38)	1.392 (11)	B-C(31)-C(32)	125.6 (6)
C(37)-C(42)	1.405 (10)	B-C(31)-C(36)	118.9 (6)
C(38)-C(39)	1.388 (12)	C(32)-C(31)-C(36)	115.6 (6)
C(39)-C(40)	1.379 (15)	C(31)-C(32)-C(33)	122.5 (7)
C(40)-C(41)	1.350 (14)	C(32)-C(33)-C(34)	120.5 (7)
C(41)-C(42)	1.386 (13)	C(33)-C(34)-C(35)	118.8 (8)
		C(34)-C(35)-C(36)	120.3 (7)
		B-C(37)-C(38)	124.7 (6)
		B-C(37)-C(42)	120.2 (6)
		C(38)-C(37)-C(42)	115.0 (7)
		C(37)-C(38)-C(39)	122.7 (7)
		C(38)-C(39)-C(40)	120.0 (8)
		C(39)-C(40)-C(41)	119.1 (9)
		C(40)-C(41)-C(42)	121.2 (8)
		C(41)-C(42)-C(37)	122.0 (7)

Table VII. Topology of the Oxonium Ions

Ph_3O^+		Et_3O^+	
Distance of O to the Plane of Its Attached Carbons, Å			
0.143		0.413	
(0.491)[a]		(0.500)[a]	
Rotation Angles, deg			
ring [C(1)-C(6)[b]]	42.2	C(1A), C(2)[c]	34.8
ring [C(7)-C(12)]	63.6	C(1B)′, C(2)′	34.1
ring [C(13)-C(18)]	73.2	C(3)′, C(4)	35.6
		C(1A)′, C(2)′	−34.8
		C(1B), C(2)	−34.1
		C(3), C(4)	−35.6

[a] The number in parentheses is what the distance would be if the oxygen atom were perfectly tetrahedral (i.e., 109.5°). [b] The angle between the normal of the least-squares plane of the phenyl rings and the plane of the three ipso carbons C(1), C(7), and C(13). [c] Torsional angles of the ethyl group [i.e., (lone pair)-O-C(methylene)-C(methyl)] according to the convention of: Klyne, W.; Prelog, V. *Experientia* 1961, *16*, 521-523.

Table VIII. Short Intermolecular Contacts (in angstroms)

$Ph_3O^+BPh_4^-$		$Et_3O^+PF_6^-$	
C(15)···H(27)	2.709	C(3)···F(3)	3.334
C(17)···H(26)	2.733	C(3)···F(2)	3.412
C(20)···H(2)	2.798	C(4)···F(4)	3.225
C(22)···H(18)	2.658	C(1A)···F(3)	3.159
C(23)···H(18)	2.815	C(1A)···F(2)	3.419
C(33)···H(8)	2.723	C(1A)···F(1)	3.457
C(34)···H(8)	2.749	C(1B)···F(3)	3.354
C(35)···H(14)	2.709	C(1B)···F(1)	3.412
C(9)···H(42)	2.790		
C(41)···H(9)	2.739		
C(41)···H(6)	2.753		
H(10)···H(28)	2.314		
H(14)···H(35)	2.254		

contacts (and only a few C···H and H···H contacts) that are less than the normal van der Waals values.[29] Thus, crystal packing forces are not expected to play an important role in determining the intramolecular distances and angles in this structure.

Description of Triethyloxonium Hexafluorophosphate. ORTEP[25] drawings of the triethyloxonium ion are shown in Figures 5–10 and that of the hexafluorophosphate anion in Figure 11. As discussed in the Experimental section, the methylene carbons are disordered (see Figure 5). The oxygen atom and the methyl carbon C(4) lie on the mirror plane that is perpendicular to the plane of the paper. Thus the hollow bonds, associated with C(1A), C(1B)′, and C(3)′, describe one rotamer while the solid ones, associated with C(1A)′, C(1B), and C(3), describe the other. Figure 6 shows that the disordered methylene groups all lie in one plane below the oxygen atom while the terminal methyl groups lie above this plane. Figures 7 and 9 show that each cation is a symmetric pyramidal propellar and that each rotamer has a sense of rotation that is opposite to the other. Figure 11 is a plot of the ordered, octahedral hexafluorophosphate anion. Figure 12 shows the general arrangement of the anions and cations in the unit cell. The refined coordinates, temperature factors, and intramolecular distances and angles are presented in Tables IX and X. In Table VII are reported the distances of the oxygen atom to the plane of the methylene carbon atoms (0.413 Å) and the torsional angles of the ethyl groups. The opposite signs of the torsional angles for the two rotamers reflect their different senses of rotation. These angles are calculated relative to the lone pair

(29) Normal van der Waals contact distances for C···C, C···H, and H···H interactions are 3.4, 2.9, and 2.4 Å, respectively (see: Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441–451.)

Table IX. Fractional Coordinates ($\times 10^5$) and Thermal Parameters ($\times 10^4$) for Triethyloxonium Hexafluorophosphate[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	87320 (21)	25000 (0)	14785 (57)	457 (21)	721 (20)	2771 (25)	0 (0)	201 (16)	0 (0)
C1A	90354 (68)	11035 (97)	15039 (180)	670 (66)	787 (47)	3601 (64)	175 (42)	−74 (55)	−168 (46)
C1B	92391 (54)	15152 (114)	2854 (196)	433 (51)	1296 (66)	5164 (93)	217 (48)	39 (53)	−963 (67)
C2	87384 (28)	5039 (49)	−6354 (76)	641 (30)	1269 (30)	4281 (38)	85 (24)	−2 (24)	−684 (26)
C3	85728 (53)	19448 (90)	35826 (149)	543 (50)	1313 (50)	3633 (66)	−20 (37)	150 (40)	−406 (44)
C4	78009 (38)	25000 (0)	43095 (117)	444 (36)	2621 (71)	4173 (56)	0 (0)	−191 (35)	0 (0)
P	9994 (6)	25000 (0)	56679 (19)	263 (8)	874 (9)	2196 (9)	0 (0)	−37 (5)	0 (0)
F1	8167 (25)	25000 (0)	33074 (58)	766 (28)	1739 (28)	2615 (22)	0 (0)	−118 (18)	0 (0)
F2	16618 (15)	36148 (27)	53621 (55)	498 (15)	1346 (17)	6721 (32)	−329 (13)	161 (16)	−452 (17)
F3	3272 (16)	36190 (28)	59673 (51)	506 (17)	1515 (18)	6144 (30)	316 (13)	205 (15)	−598 (16)
F4	11454 (34)	25000 (0)	80670 (76)	895 (37)	4246 (62)	2930 (29)	0 (0)	−520 (24)	0 (0)

[a] See footnote *a* in Table II for the definition of the thermal parameters.

Table X. Distances and Angles for Triethyloxonium Hexafluorophosphate

atoms	distances, Å	atoms	angles, deg
O–C(1A)	1.479 (10)	C(1A)–O–C(1B′)	115.5 (6)
O–C(1B)	1.508 (11)	C(1A)–O–C(3′)	113.2 (6)
O–C(3)	1.509 (10)	C(1B)–O–C(3)	109.4 (6)
C(1A)–C(2)	1.601 (12)	O–C(1A)–C(2)	103.8 (7)
C(1B)–C(2)	1.436 (12)	O–C(1B)–C(2)	110.9 (6)
C(3)–C(4)	1.467 (11)	O–C(3)–C(4)	108.0 (6)
P–F(1)	1.577 (4)	F(1)–P–F(2)	90.4 (2)
P–F(2)	1.570 (3)	F(1)–P–F(3)	89.3 (2)
P–F(3)	1.584 (3)	F(1)–P–F(4)	177.7 (3)
P–F(4)	1.591 (5)	F(2)–P–F(2′)	90.1 (1)
		F(2)–P–F(3)	90.2 (1)
		F(2)–P–F(3′)	179.6 (2)
		F(2′)–P–F(3)	179.6 (2)
		F(2)–P–F(4)	91.2 (2)
		F(3)–P–F(3′)	89.5 (1)
		F(3)–P–F(4)	89.0 (2)
	Average Distances and Angles[a]		
O–CH_2	1.499 (10)	CH_2–O–CH_2	112.7 (6)
CH_2–CH_3	1.501 (12)	O–CH_2–CH_3	107.6 (6)

[a] The numbers in parentheses are the averages of the standard deviations.

on oxygen, which is assumed to form equal obtuse angles with the three methylene carbons. The values of the (lone pair)-O–C–C torsion angles are halfway between what would be expected for the staggered (60°) or eclipsed (0°) conformations. Again, as in Ph_3O^+, the oxygen–carbon bond lengths in Et_3O^+ show appreciable weakening relative to that of the neutral analogue. In diethyl ether[30] this bond distance is 1.433 Å vs. an average distance of 1.499 Å in the triethyloxonium ion. As in the triphenyloxonium structure, intermolecular van der Waals interactions do not appear to be playing a significant role in determining the overall geometry of this ion. Some intermolecular distances are presented in Table VIII.

Discussion

In Table XI are presented some structural features of tricoordinate hydrido, alkyl, and phenyl derivatives of the main group elements. Three factors should be kept in mind when the data presented are reviewed: (1) *steric effects*—in going from hydrogen to methyl to phenyl, the steric requirements of the ligand increases and thus in the absence of other effects the C–M–C angle is expected to increase to a maximum of 120° (furthermore, in the case of the phenyl compounds steric requirements would favor a ring rotation angle near 90°); (2) *electron-delocalization effects*—the π systems of the aromatic rings (through p–π overlap) and the C–H bonds of the alkyl derivatives (through hyperconjugation) offer an electronic means of overall stabilization of the molecule requiring, for optimum effect, a C–M–C angle of 120° and phenyl rotation angle of 0° in the case of the phenyl derivatives and a C–M–C angle of 120° and a (lone pair) M–C–C torsional angle of 0°, 60°, 120°, or 180° in the case of the alkyl derivatives; (3) *lone-pair effects*—the absence or presence of a nonbonding pair of electrons on the central atom can affect the molecule sterically (requiring, if present, a C–M–C angle near 109.5°). Notice among the above-mentioned factors that in some cases it would be difficult to tell whether a compound having a C–M–C angle of 120° is flat because of steric or electronic reasons. It is only in the case of the phenyl derivatives, which possess a ring rotation angle, that this difference can be discerned. Accordingly, this group of compounds in Table XI will be inspected first.

Triphenyl Derivatives. These can be broadly separated into two classes: (a) electron-deficient species, such as Ph_3B, Ph_3Ga, Ph_3In, and Ph_3C^+, in which the central atom formally has only six electrons, and (b) electron-precise species, such as Ph_3C^-, Ph_3N, Ph_3P, (p-tolyl)$_3$As, Ph_3Bi, and Ph_3O^+, in which the central atom has a full octet of electrons.

Triphenyl compounds of the electron-deficient type (Ph_3B, Ph_3Ga, Ph_3In, and Ph_3C^+) are all flat, with low rotation angles that decrease with increasing M–C distance. The fact that these rotation angles are not exactly 0° is of course of due to C–H(ortho)/C–H(ortho) nonbonded interactions between adjacent phenyl rings. It seems apparent that such molecules are stabilized by p–π interactions between the phenyl rings and the empty p orbital on the central atom. For group 3A elements this means decreased π-electron density (and presumably development of some positive charge) in the aromatic rings and a simultaneous buildup of negative charge on the central atom. For the isoelectronic Ph_3C^+ cation, p–π overlap entails partial fulfillment of the octet of electrons on the central atom, with concomitant dispersal of its positive charge.

Most of the triaryl compounds of the electron-precise type [Ph_3P, (p-tolyl)$_3$As, and Ph_3Bi] are pyramidal, with C–M–C angles decreasing with increasing M–C distances. Exceptions are found, however, for the first-row elements ([$Ph_3C]^-$, Ph_3N, and [$Ph_3O]^+$), which have essentially planar structures (C–M–C angles of 120.0°, 116°, and 119.1°, respectively). In the case of [$Ph_3C]^-$, the small average rotation angle (30.2°) indicates a substantial amount of p–π overlap, which in this case provides an avenue for dispersing the negative charge from the central atom. On the other hand, the phenyl rotation angles in Ph_3N and Ph_3O^+ are considerably larger (47° and 59.7°, respectively), indicating minimal overlap with the phenyl rings. One rationalization for this observation is to state that, for both Ph_3N and Ph_3O^+, charge dispersal is either not necessary or not possible (at least through the π system alone). Ph_3N has a nonbonded electron pair, fulfilling its requirement for an octet of electrons with no overall charge. Ph_3O^+ also possesses a full octet of electrons and because of this cannot accept electrons from the aromatic rings to offset its positive charge. Thus, one could argue that the planarity of Ph_3N and Ph_3O^+ (as opposed to the nonplanarity of Ph_3P, (p-tolyl)$_3$As, and Ph_3Bi) is probably due to steric effects: M–C distances for these compounds (1.4–1.5 Å) are substantially shorter than those involving the heavier elements (1.8–2.3 Å; cf. table XI).

Trialkyl Derivatives. For trialkyl derivatives, the structural trends are more straightforward: the monomeric group 3A derivatives are all essentially planar while those of groups 5A and

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Table XI. Structural Data for Tricoordinate Derivatives[a] of the Main Group Elements (R_3M)

	R = H		R = CH_3		R = C_6H_5			
element	M-H	H-M-H	M-C	C-M-C	M-C	C-M-C	C_o-C_i-C_o'	rot angle, deg
B			1.578 (1)[c]	119.4 (3)	1.577 (4)[m]	120.0 (4)	116.8 (4)	30.3
Al			1.957 (3)[e]	120.0				
Ga			1.967 (2)[h]	118.6	1.961 (6)[r]	120.0 (3)	117.1 (5)	25.5
In			2.093 (6)[j]	119.7	2.14 (1)[r]	120.0 (4)	116 (2)	13
C^+					1.45 (2)[u]	120	115 (2)	31.8
C^-					1.461 (3)[n]	120.0 (2)	114.9 (3)	30.2
N	1.019 (2)[v]	109.1 (10)	1.455 (2)[d]	111.8 (6)	1.42 (4)[o]	116 (2)		47 (5)
P	1.424[b]	93.5	1.846 (3)[f]	98.6 (3)	1.828 (5)[p]	103.0 (2)	119.8 (5)	
As	1.523[b]	91.6	1.98 (2)[i]	96 (5)	1.96 (5)[s]	102 (2)	119 (2)	
Sb	1.711[b]	91.5						
Bi			2.264 (4)[l]	96.7 (10)	2.24 (2)[t]	94 (1)	120 (2)	
O^+			1.499 (10)	112.7 (6)	1.471 (9)	119.1 (5)	125.8 (7)	59.7
S^+			1.75 (3)[g]	107 (1)	1.82 (2)[q]	103 (1)	123 (2)	
Te^+			2.146 (9)[k]	91.3 (5)				

[a] Only those compounds which are monomeric or are unassociated with the counterion are listed here. In the following references, structural data derived from electron diffraction experiments are indicated by (ED) and those derived from X-ray diffraction experiments are indicated by (XR). [b] Infrared Data: Nielsen, H. H. *J. Chem. Phys.* 1952, *20*, 759. [c] ED: Bartell, L. S.; Carroll, B. L. *J. Chem. Phys.* 1965, *42*, 3076–3078. [d] ED: Beagley, B.; Hewitt, T. G. *Trans. Faraday Soc.* 1968, *64*, 2561–2570. [e] ED: Almenningen, A.; Halvorsen, S.; Haaland, A. *Acta Chem. Scand.* 1971, *25*, 1937–1945. [f] ED: Bartell, L. S.; Brockway, L. O. *J. Chem. Phys.* 1960, *32*, 512–515. [g] XR: Biscarini, P.; Fusina, L.; Nivellini, G.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* 1977, 664–668. [h] ED: Beagley, B.; Schmidling, D. G. *J. Mol. Struct.* 1974, *21*, 437–444. [i] ED: Springall, H. D.; Brockway, L. O. *J. Am. Chem. Soc.* 1938, *60*, 996–1000. [j] ED: Barbe, G.; Hencher, J. L.; Shen, Q.; Tuck, D. G. *Can. J. Chem.* 1974, *52*, 3936–3940. [k] XR: Ziolo, R. F.; Troup, J. M. *Inorg. Chem.* 1979, *18*, 2271–2274. [l] ED: Beagley, B.; McAloon, K. T. *J. Mol. Struct.* 1973, *17*, 429–430. [m] XR: Zettler, F.; Hausen, H. D.; Hess, H. *J. Organomet. Chem.* 1974, *72*, 157–162. [n] XR: Koster, H.; Weiss, E. *J. Organomet. Chem.* 1979, *168*, 273–279. [o] ED: Sasaki, Y.; Kimura, K.; Kubo, M. *J. Chem. Phys.* 1959, *31*, 477–481. [p] XR: Daly, J. J. *J. Chem. Soc.* 1964, 3799–3810. [q] XR (dimethylphenylsulfonium): Lopez-Castro, A.; Truter, M. *Acta Crystallogr.* 1964, *17*, 465–471. [r] XR: Malone, T. F.; McDonald, W. S. *J. Chem. Soc. Sect. A* 1970, 3362–3367. [s] XR (tri-*p*-tolylarsine): Trotter, J. *Can. J. Chem.* 1963, *41*, 14–17. [t] XR: Hawley, D. M.; Ferguson, G. *J. Chem. Soc. A* 1968, 2059–2063. [u] XR: Gomes de Mesquita, A. H.; MacGillavry, C. H.; Eriks, K. *Acta Crystallogr.* 1965, *18*, 437–443. [v] ED: Bastiansen, O.; Beagley, B. *Acta Chem. Scand.* 1964, *18*, 2077–2080.

6A are pyramidal (a different situation, of course, exists for the more stable *dimeric* group 3A trialkyl derivatives). No structural information is available for group 4A trialkyl ions free of any association with adjacent counterions. The methyl ligands in all of the group 3A compounds experience intramolecular nonbonded interactions with adjacent methyls. For the group 3A and group 4A trialkyls, the relationship between structure and cause is somewhat ambiguous: their planar configurations can be explained equally well by invoking either steric or electron-delocalization effects (i.e., hyperconjugation[31]). For trialkyl compounds of groups 5A and 6A, their pyramidal geometry is almost certainly the result of steric interactions between the lone pair on the central atom and the alkyl ligands.

Trihydride Derivatives. As can be seen in Table XI, scant data are available for the hydride derivatives with the exception of the group 5A elements. These compounds all possess a pyramidal geometry as do their methyl and phenyl counterparts. Thus, it is likely that the "free" oxonium ion is pyramidal, with a similar H–M–H angle as NH_3.

C–C–C Ipso Angles. In Table XI, one notices the unusually large C–C–C ipso angle of triphenyloxonium as compared to that of other derivatives. Coulson, Domenicano, and Vaciago[32] have correlated this angle with Taft's inductive parameter (σ_I) and Huheey's group electronegativity parameter (χ_H). Unfortunately, neither of these values is reported in the literature for the "$^+OPh_2$" group. However, if one uses the average ipso angle reported in Table XI and extrapolates the least-squares lines of the above authors' plots, one obtains values of 1.0 and 5.8 for σ_I and χ_H, respectively [as compared to σ_I (NO_2) = 0.65[33] and χ_H (NO_2) = 4.83[34]]. Thus, while the oxonium center shows no inclination to interact with its groups through p–π resonance, it appears to be an extremely powerful σ-electron-withdrawing group. Further work, exploring the electronic properties of organooxonium ions by use of ^{17}O NMR spectroscopy, is reported in the subsequent paper.

Conclusion

In the present investigation, the X-ray crystal structures of triethyloxonium hexafluorophosphate and triphenyloxonium tetraphenylborate are reported. The oxonium centers are concluded to be highly electronegative, showing little or no resonance interactions with their ligands (either through through p–π overlap with the aromatic rings or through hyperconjugation with the methylene hydrogens of the ethyl groups). Finally, the parent oxonium ion, if free of any hydrogen bonding, is suggested to be pyramidal owing to the known pyramidality of NH_3 and the strong similarity in the structures of alkyl and phenyl derivatives of tricoordinate nitrogen and oxygen.

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Registry No. $[Et_3O]^+[PF_6^-]^-$, 17950-40-2; $[Ph_3O]^+[BPh_4]^-$, 60874-79-5.

Supplementary Material Available: Listings of the structure factor amplitudes for the X-ray diffraction analysis are available as supplementary material (42 pages). Ordering information is given on any current masthead page.

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