

significantly through space. Examination of molecular models renders this latter contingency unlikely. On the premise that through-bond spin-spin coupling is the predominant mechanism and from comparison of coupling constants in structural analogs, the isopropyl fluorine is assumed to couple to the two CF_3 groups on carbon more strongly than does the S-F; however,

this assignment is not unequivocal. Decoupling experiments were inconclusive.

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Synthesis of Two Crystalline Species of the Friedel-Crafts Intermediate Antimony Pentachloride-*p*-Toluoyl Chloride. Crystal Structures of the Donor-Acceptor Complex and of the Ionic Salt

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Abstract: We report for the same Friedel-Crafts intermediate the crystal structures of two well-defined adducts, the donor-acceptor complex $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$ and the ionic salt $[\text{SbCl}_6]^- [\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$. The first adduct (A) isolated from CCl_4 solutions crystallizes in the space group *Pbcm* with unit cell constants $a = 9.250 \pm 0.010$, $b = 22.408 \pm 0.025$, $c = 7.107 \pm 0.008$ Å; $Z = 4$. The second compound (B) isolated from CHCl_3 solutions crystallizes in the space group *P2₁/c* with unit cell constants $a = 11.840 \pm 0.009$, $b = 10.325 \pm 0.008$, $c = 12.498 \pm 0.010$ Å; $\beta = 93.90 \pm 0.20^\circ$; $Z = 4$. Intensities of 1063 (A) and 2586 (B) independent, statistically significant reflections were collected with a linear Pailred diffractometer. The structures, including positions of hydrogen atoms, were solved using Patterson and Fourier methods and refined by full-matrix least-squares calculations to conventional unweighted R_1 factors of 0.039 (A), 0.042 (B) and weighted R_2 factors of 0.047 (A), 0.056 (B). The donor-acceptor complex (A) is composed of an SbCl_5 group coordinated with the oxygen atom of the *p*-toluoyl chloride group. The Sb-O bond length is 2.253 (6) Å. The observed distortions of the octahedron SbCl_5O have been interpreted as arising from intramolecular steric effects. The ionic salt (B) consists of discrete hexachloroantimonate anions and methyl-4-phenyloxocarbenium cations. The closest interionic distances are found between the chlorine atoms of the $[\text{SbCl}_6]^-$ anions and the carbonyl carbon of the $[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$ cations. The C-O bond length of 1.097 (9) Å is equivalent to that determined in alkyloxocarbenium ions, but the adjacent C-C bond length of 1.396 (10) Å is appreciably shorter than that generally found in alkyloxocarbenium ions. On the other hand, the positive charge of the $[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$ cation is largely delocalized into the phenyl ring, whereas this charge is mainly localized on the carbonyl carbon atom in aliphatic oxocarbenium ions.

The presence of two functional groups in acyl halides, the carbonyl donor group and the ionizable halogen atom, suggests that two types of intermediates may intervene in the interaction of acyl halides with Lewis acid type Friedel-Crafts catalysts, *viz.* the oxocarbenium salt and the covalent donor-acceptor complex.

The evidence of stable species of both types has been demonstrated by infrared²⁻⁶ and nmr^{7,8} studies and X-ray crystallography.⁹⁻¹² Solution studies by nmr

and infrared techniques suggest also some evidence that both species of a same compound may coexist.^{7,13} Until now, however, no Friedel-Crafts intermediate has been isolated in both structural states. We report here a study of this type. It also represents the first direct structural determination of an aromatic oxocarbenium ion.

Experimental Section

The compounds are extremely sensitive to moisture and all manipulations were carried out in a drybox (VAC Model) under strictly anhydrous conditions.

The crystalline addition complexes were prepared from antimony pentachloride and *p*-toluoyl chloride using carbon tetrachloride or chloroform as solvents. Two nonidentical compounds have been isolated. The first variety (A) obtained in CCl_4 corresponds to a donor-acceptor compound; the second variety (B) isolated from CHCl_3 solutions is an ionic salt.

For X-ray diffraction studies, single crystals of the two hygroscopic addition compounds A and B were sealed in Lindeman glass capillary tubes. Precession photographs indicated that the crystal system of A was orthorhombic and the crystal system of B monoclinic. Space groups and crystal data are listed in Table I.

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Table I. Crystal Data

	Crystal A	Crystal B
Space group	<i>Pbcm</i>	<i>P2₁/c</i>
<i>a</i> , Å	9.250 ± 0.010	11.840 ± 0.009
<i>b</i> , Å	22.408 ± 0.025	10.325 ± 0.008
<i>c</i> , Å	7.107 ± 0.008	12.498 ± 0.010
β, deg		93.90 ± 0.20
<i>Z</i>	4	4
Volume, Å ³	1473	1524
Density (X-ray), g cm ⁻³	1.96	1.98

Intensity data were collected on a linear Pailred diffractometer equipped with a scintillation counter. Mo K α radiation monochromatized with a silicon plate was used ($\lambda = 0.71069$ Å). The counter aperture was 2°. Intensities were measured with a scan rate of 2.5°/min; stationary background counts of 20-sec duration were taken at both ends of the scan. All independent reflections for which intensities satisfied the criterion $\sigma(I)/I < 0.40^{14}$ were thus retained and used for the determination and the refinement of the structures (crystal A, 1063; and crystal B, 2586 reflections). The recorded intensities were corrected for Lorentz and polarization effects. No correction was made for absorption but the linear-absorption coefficient for Mo K α radiation ($\mu = 29$ cm⁻¹) and the approximate crystal dimensions (A, 0.18 × 0.16 × 0.95 mm; B, 0.16 × 0.16 × 1.20 mm) suggest variations of the absorption correction factor in the range 1.4–1.6.

Crystal structures were solved by the heavy atom method. The positions of the Sb atoms were readily obtained from three-dimensional Patterson functions. A structure factor calculation phased by these antimony atoms followed by a three-dimensional Fourier synthesis revealed all remaining nonhydrogen atoms. In all structure factor calculations the atomic scattering factors used were those tabulated by Cromer and Waber.¹⁵ The effects of anomalous dispersion were included; the values of $\Delta f'$ and $\Delta f''$ are those given in the "International Tables for X-Ray Crystallography."¹⁶ Atomic coordinates and individual atom anisotropic thermal parameters were refined by a full-matrix least-squares procedure using the SFLS 5 program.¹⁷ In this and subsequent calculations the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The weight w was taken as defined by Corfield, Doedens, and Ibers¹⁸ with a p value of 0.06. The refinement converges to give a discrepancy factor $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ equal to 0.05 for both crystals.

A difference Fourier map computed at this point showed all aromatic and methyl hydrogen atom positions. A new series of least-squares refinements was then performed. The hydrogen atoms were included with coordinates calculated from the difference synthesis and isotropic temperature factors of the form $B_H = 1.6 B_C - 2.0$,¹⁹ but only their positional parameters were varied. The atomic parameters for all nonhydrogen atoms were also refined.

After these refinements, the values of the conventional R_1 factor were 0.039 for crystal A and 0.042 for crystal B. The weighted factors $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|)^{1/2}$ were 0.047 and 0.056, respectively.

Table II shows the final atomic coordinates and Table III the thermal parameters. The estimated standard deviations of the least significant figures are given in parentheses.²⁰

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(20) Listings of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5718. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Table II. Fractional Atomic Coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Crystal A			
Sb	0.2142 (0)	0.1006 (0)	0.2500 (0)
Cl(1)	0.1381 (2)	0.1680 (1)	0.4778 (5)
Cl(2)	0.3310 (2)	0.0464 (1)	0.4815 (3)
Cl(3)	0.0065 (2)	0.0439 (1)	0.2500 (0)
Cl(4)	0.6419 (2)	0.1045 (1)	0.2500 (0)
O	0.4049 (6)	0.1632 (2)	0.2500 (0)
C(1)	0.5362 (10)	0.1680 (3)	0.2500 (0)
C(2)	0.6071 (9)	0.2249 (3)	0.2500 (0)
C(3)	0.7567 (8)	0.2309 (4)	0.2500 (0)
C(4)	0.8168 (10)	0.2873 (4)	0.2500 (0)
C(5)	0.7344 (11)	0.3382 (4)	0.2500 (0)
C(6)	0.5833 (12)	0.3322 (4)	0.2500 (0)
C(7)	0.5205 (10)	0.2753 (3)	0.2500 (0)
C(8)	0.8027 (16)	0.3992 (4)	0.2500 (0)
H(3)	0.832 (12)	0.193 (4)	0.250 (0)
H(4)	0.906 (13)	0.292 (5)	0.250 (0)
H(6)	0.517 (13)	0.365 (5)	0.250 (0)
H(7)	0.418 (13)	0.270 (4)	0.250 (0)
H(8a)	0.729 (17)	0.428 (6)	0.250 (0)
H(8b)	0.882 (11)	0.399 (3)	0.132 (19)
Crystal B			
Sb	0.7558 (0)	-0.0181 (0)	0.1616 (0)
Cl(1)	0.9326 (1)	-0.1292 (1)	0.1696 (1)
Cl(2)	0.7027 (1)	-0.1368 (1)	0.3129 (1)
Cl(3)	0.6787 (1)	-0.1800 (2)	0.0472 (1)
Cl(4)	0.5815 (1)	0.0916 (2)	0.1572 (1)
Cl(5)	0.8395 (1)	0.1451 (1)	0.2748 (1)
Cl(6)	0.8124 (1)	0.1001 (1)	0.0121 (1)
O	0.0767 (4)	0.1597 (5)	0.1139 (4)
C(1)	0.1278 (5)	0.1094 (7)	0.1776 (6)
C(2)	0.1929 (5)	0.0442 (7)	0.2579 (5)
C(3)	0.1445 (6)	0.0189 (8)	0.3554 (6)
C(4)	0.2100 (6)	-0.0391 (8)	0.4357 (6)
C(5)	0.3228 (5)	-0.0721 (7)	0.4201 (5)
C(6)	0.3679 (6)	-0.0469 (8)	0.3231 (5)
C(7)	0.3040 (6)	0.0093 (7)	0.2410 (6)
C(8)	0.3936 (7)	-0.1350 (8)	0.5107 (7)
H(3)	0.065 (8)	0.057 (11)	0.366 (8)
H(4)	0.175 (8)	-0.052 (11)	0.506 (8)
H(6)	0.444 (8)	-0.065 (11)	0.305 (8)
H(7)	0.340 (8)	0.051 (11)	0.184 (8)
H(8a)	0.428 (9)	-0.040 (12)	0.545 (8)
H(8b)	0.449 (9)	-0.169 (12)	0.488 (8)
H(8c)	0.365 (8)	-0.163 (10)	0.582 (9)

Results and Discussion

Crystal A corresponds to the molecular addition compound $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$ and crystal B to the ionic salt $[\text{SbCl}_6]^- [\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$. The two crystal structures are examined below.

(A) **Molecular Addition Compound $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$.** Figure 1 shows the molecular structure and includes the atomic numbering scheme used. Bond distances and angles are recorded in Table IV. The space group *Pbcm* requires symmetry *m* for the molecule. The *p*-toluoyl chloride part of the molecule and the Sb and Cl(3) atoms are situated in the symmetry plane; the Cl(1) and Cl(2) chlorine atoms and the H(8b) methyl hydrogen atom are located above and below the plane. The molecular planes consist of the space group planes $z = 1/4$ and $z = 3/4$.

Antimony is coordinated to five chlorine atoms and to the keto oxygen of the *p*-toluoyl group. The six atoms coordinated to antimony form a distorted octahedron SbCl_5O . The observed deviations from ideal octahedral coordination of the acceptor atom can be interpreted as arising from steric factors. The values of the

Table III. Thermal Parameters^a

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}
Crystal A							
Sb	84 (0)	16 (0)	247 (3)	2 (0)	0	0	3.7
Cl(1)	224 (3)	40 (0)	788 (13)	-18 (1)	208 (6)	-101 (2)	10.6
Cl(2)	210 (3)	35 (0)	325 (6)	-23 (1)	-92 (3)	42 (1)	6.9
Cl(3)	109 (3)	26 (0)	468 (10)	-12 (1)	0	0	6.1
Cl(4)	115 (3)	18 (0)	430 (9)	8 (1)	0	0	5.4
O	96 (8)	18 (1)	326 (18)	-1 (2)	0	0	4.5
C(1)	116 (12)	18 (1)	143 (18)	1 (3)	0	0	3.5
C(2)	101 (10)	17 (1)	157 (18)	-1 (3)	0	0	3.3
C(3)	74 (10)	22 (2)	222 (22)	1 (3)	0	0	3.8
C(4)	100 (12)	27 (2)	257 (25)	-11 (4)	0	0	4.6
C(5)	138 (14)	18 (1)	219 (21)	-7 (4)	0	0	4.2
C(6)	159 (16)	17 (2)	212 (22)	8 (4)	0	0	4.3
C(7)	107 (11)	15 (1)	232 (23)	5 (3)	0	0	3.8
C(8)	215 (23)	19 (2)	420 (38)	-30 (6)	0	0	6.6
Crystal B							
Sb	41 (0)	90 (0)	38 (0)	-0 (0)	1 (0)	3 (0)	2.8
Cl(1)	49 (1)	119 (2)	76 (1)	14 (1)	5 (1)	7 (1)	4.2
Cl(2)	83 (1)	112 (2)	56 (1)	9 (1)	21 (1)	19 (1)	4.2
Cl(3)	96 (1)	151 (2)	69 (1)	-40 (1)	-13 (1)	-18 (1)	5.4
Cl(4)	54 (1)	151 (2)	108 (1)	25 (1)	20 (1)	44 (1)	5.3
Cl(5)	90 (1)	114 (2)	56 (1)	-16 (1)	4 (1)	-18 (1)	4.4
Cl(6)	74 (1)	123 (2)	48 (1)	-0 (1)	11 (1)	16 (1)	4.1
O	71 (4)	155 (6)	58 (3)	4 (4)	-10 (3)	4 (4)	4.7
C(1)	59 (5)	117 (8)	61 (5)	-19 (5)	7 (4)	-24 (5)	4.0
C(2)	53 (4)	110 (7)	54 (4)	-8 (4)	-5 (3)	2 (4)	3.7
C(3)	54 (4)	145 (9)	65 (5)	1 (5)	5 (4)	-2 (5)	4.4
C(4)	69 (5)	131 (9)	54 (4)	6 (5)	8 (4)	-1 (5)	4.2
C(5)	69 (5)	106 (7)	45 (4)	-9 (5)	-4 (3)	-14 (4)	3.7
C(6)	55 (5)	130 (9)	61 (5)	1 (5)	4 (4)	-4 (5)	4.1
C(7)	59 (5)	128 (8)	57 (4)	-17 (5)	0 (3)	-5 (5)	4.1
C(8)	87 (7)	111 (8)	64 (5)	12 (6)	-16 (5)	-5 (5)	4.6

^a The anisotropic thermal parameters are multiplied by 10^4 and the exponent has the form $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. B_{eq} values correspond to the equivalent isotropic thermal factors of the atoms and are given in square ångströms.

Table IV. Bond Lengths and Angles in the Adduct $SbCl_5 \cdot CH_3-4-C_6H_5COCl$

Bond Lengths, Å			
Sb-Cl(1)	2.323 (3)	C(1)-O	1.220 (11)
Sb-Cl(2)	2.314 (2)	C(1)-Cl(4)	1.726 (9)
Sb-Cl(3)	2.305 (2)	C(1)-C(2)	1.434 (12)
Sb-O	2.253 (6)	C(2)-C(3)	1.391 (11)
		C(3)-C(4)	1.380 (14)
C(3)-H(3)	1.10 (11)	C(4)-C(5)	1.371 (14)
C(4)-H(4)	0.84 (12)	C(5)-C(6)	1.405 (15)
C(6)-H(6)	0.97 (12)	C(6)-C(7)	1.401 (13)
C(7)-H(7)	0.95 (12)	C(7)-C(2)	1.385 (12)
C(8)-H(8a)	0.95 (15)	C(8)-C(5)	1.505 (14)
C(8)-H(8b)	1.11 (12)		
Bond Angles, deg			
Cl(1)-Sb-Cl(1')	88.37 (0.09)	C(6)-C(7)-C(2)	120.14 (0.38)
Cl(1)-Sb-Cl(2)	89.27 (0.09)	C(7)-C(2)-C(3)	119.75 (0.37)
Cl(2)-Sb-Cl(2')	90.67 (0.09)	C(7)-C(2)-C(1)	117.44 (0.36)
Cl(3)-Sb-Cl(1)	96.11 (0.09)	C(8)-C(5)-C(4)	121.45 (0.46)
Cl(3)-Sb-Cl(2)	95.71 (0.07)	C(8)-C(5)-C(6)	120.33 (0.46)
O-Sb-Cl(1)	80.38 (0.12)	C(2)-C(3)-H(3)	124.1 (3.1)
O-Sb-Cl(2)	87.75 (0.11)	C(3)-C(4)-H(4)	121.5 (3.5)
Sb-O-C(1)	146.62 (0.21)	C(4)-C(3)-H(3)	116.5 (3.1)
O-C(1)-Cl(4)	119.44 (0.21)	C(5)-C(4)-H(4)	115.9 (3.5)
O-C(1)-C(2)	122.28 (0.34)	C(5)-C(4)-H(6)	123.3 (3.4)
Cl(4)-C(1)-C(2)	118.28 (0.22)	C(6)-C(7)-H(7)	120.9 (3.2)
C(1)-C(2)-C(3)	122.81 (0.36)	C(7)-C(6)-H(6)	116.6 (3.4)
C(2)-C(3)-C(4)	119.33 (0.38)	C(2)-C(7)-H(7)	118.9 (3.2)
C(3)-C(4)-C(5)	122.54 (0.39)	C(5)-C(8)-H(8a)	109.4 (3.9)
C(4)-C(5)-C(6)	118.22 (0.41)	C(5)-C(8)-H(8b)	106.3 (4.2)
C(5)-C(6)-C(7)	120.03 (0.39)		

Cl-Sb-O bond angles (80.3 and 87.7°) and of the Cl(3)-Sb-Cl bond angles (95.7 and 96.1°) clearly indicate

that the chlorine atoms are drawn in toward the oxygen atom. This first distortion is attributed to the smaller size of the oxygen atom in comparison to the chlorine atoms, as has been previously reported for other $SbCl_5$ adducts.²¹ A second distortion arises from a steric interaction between the Cl(4) chlorine atom of the *p*-toluoyl group and the Cl(2), Cl(2') atoms coordinated to antimony. The short Cl(4)-Cl(2) distance of 3.56 Å largely reduces the steric hindrance between the oxygen atom and the Cl(2), Cl(2') chlorine atoms, as indicated by the typical bond angles Cl(2)-Sb-O of 87.75 (0.11)° and Cl(1)-Sb-O of 80.38 (0.12)°.

The Sb-O bond length is 2.253 (6) Å, which is slightly shorter than that determined in the adducts $SbCl_5 \cdot C_6H_5COCl$, 2.317 (5) Å, and $SbCl_5 \cdot CH_3-3-C_6H_4COCl$, 2.295 (3) Å.¹² However, this bond length is significantly greater than that observed in $SbCl_5 \cdot (CH_3)_3PO$, for which the Sb-O distance was found to be 1.94 Å.²² The value of 146.62° determined for the Sb-O-C(1) bond angle is equivalent to that observed in the compounds $SbCl_5 \cdot C_6H_5COCl$ and $SbCl_5 \cdot CH_3-3-C_6H_4COCl$. The considerable deviation from the usual angle of 120° for sp^2 hybridized oxygen atom might be attributed to a steric intramolecular effect. The mean distance of the six carbon-carbon distances in the phenyl ring is 1.389 Å, which is in good agreement with the accepted carbon-carbon distance of 1.395 Å in aromatic compounds.¹⁶

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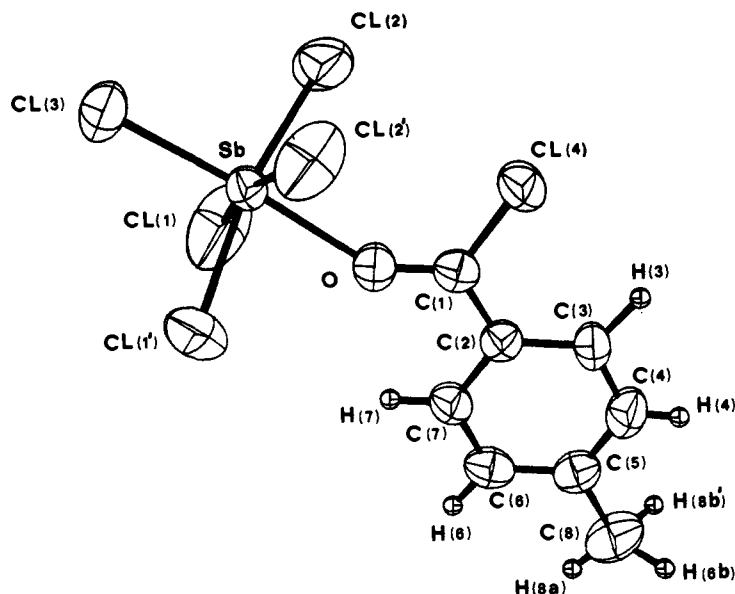


Figure 1. Perspective view of the $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$ molecule.

Figure 2 was drawn with the aid of the Johnson thermal ellipsoid program²³ and shows a stereoscopic view of the unit cell content. The molecules are located in layers which are separated by 3.55 Å ($c/2$). The packing of the molecules is largely governed by chlorine-chlorine contacts and also by chlorine-methyl contacts (see Table V).

(B) **Ionic Addition Compound** $|\text{SbCl}_6|^- \cdot |\text{CH}_3\text{-4-C}_6\text{H}_4\text{-CO}|^+$. The structure of methyl-4-phenyloxycarbonium

Table V. Interatomic Contacts in $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$

Selected Intramolecular Contacts, Å			
Cl(1)···Cl(1')	3.23	O···Cl(1)	2.95
Cl(1)···Cl(2)	3.25	O···Cl(2)	3.16
Cl(2)···Cl(2')	3.29		
Cl(3)···Cl(1)	3.44	Cl(4)···Cl(2)	3.56
Cl(3)···Cl(2)	3.42		

Intermolecular Contacts Less Than 3.80 Å ^a					
Cl(1)···Cl(1)	5/001	3.68	C(3)···C(3)	5/000	3.65
Cl(1)···C(4)	5/101	3.68	C(3)···C(3)	5/001	3.65
Cl(2)···Cl(2)	2/101	3.76	C(4)···C(3)	5/000	3.62
Cl(3)···Cl(4)	1/100	3.63	C(4)···C(3)	5/001	3.62
Cl(3)···C(8)	6/110	3.69	C(4)···Cl(1)	5/101	3.68
Cl(4)···Cl(3)	1/100	3.63	C(4)···Cl(1)	7/101	3.68
C(1)···C(6)	5/000	3.58	C(6)···C(1)	5/000	3.58
C(1)···C(6)	5/001	3.58	C(6)···C(1)	5/001	3.58
C(1)···C(7)	5/000	3.77	C(6)···C(2)	5/000	3.78
C(1)···C(7)	5/001	3.77	C(6)···C(2)	5/001	3.78
C(2)···C(7)	5/000	3.64	C(7)···C(2)	5/000	3.64
C(2)···C(7)	5/001	3.64	C(7)···C(2)	5/001	3.64
C(2)···C(2)	5/000	3.72	C(7)···C(7)	5/000	3.73
C(2)···C(2)	5/001	3.72	C(7)···C(7)	5/001	3.73
C(2)···C(6)	5/000	3.78	C(7)···C(1)	5/000	3.77
C(2)···C(6)	5/001	3.78	C(7)···C(1)	5/001	3.77
C(3)···C(4)	5/000	3.62	C(8)···Cl(3)	6/100	3.69
C(3)···C(4)	5/001	3.62			

^a Second atoms not in the crystal chemical unit (*i.e.*, not listed in Table II) are specified by the subscript I/uvw which denotes the manner in which the atomic parameters can be derived from the corresponding atom in the crystal chemical unit. I refers to one of the following symmetry operations: 1, $x y z$; 2, $\bar{x} \bar{y} \bar{z}$; 3, $x y \bar{z} + 1/2$; 4, $\bar{x} \bar{y} z + 1/2$; 5, $x \bar{y} + 1/2 z$; 6, $\bar{x} y + 1/2 \bar{z}$; 7, $x \bar{y} + 1/2 z + 1/2$; 8, $\bar{x} y + 1/2 \bar{z} + 1/2$. The u, v, w digits code a lattice translation as $ua + vb + wc$.

(23) C. K. Johnson, Program ORTEP, ORNL 3794, 1965.

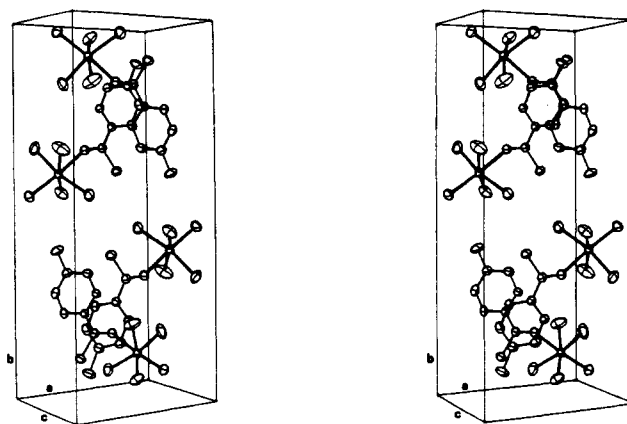


Figure 2. Molecular content of the unit cell of $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$ (stereoscopic view).

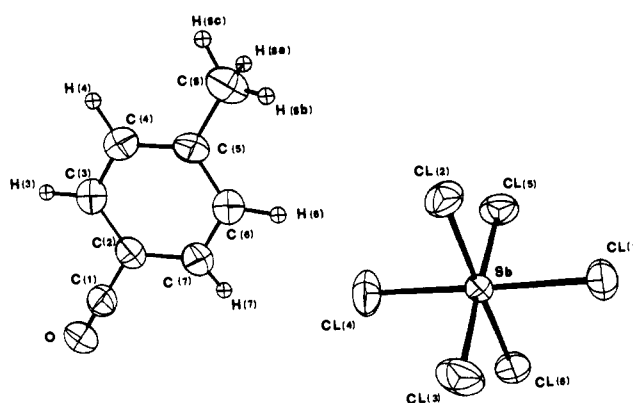


Figure 3. The methyl-4-phenyloxycarbonium hexachloroantimonate: ion geometry and atomic nomenclature.

hexachloroantimonate consists of discrete $|\text{SbCl}_6|^-$ anions and $|\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}|^+$ cations. Figure 3 shows the molecular geometry of these ions and the labeling scheme used.

Interionic distances are listed in Table VI. A stereoscopic view of the packing arrangement in a unit cell is

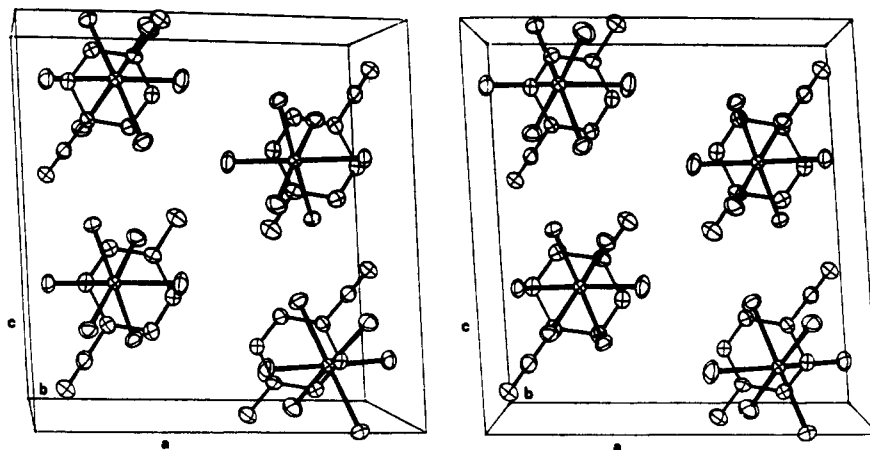


Figure 4. A stereoscopic view of the ionic packing of $[\text{SbCl}_6]^-[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$.

Table VI. Interatomic Distances Less Than 3.60 Å in $[\text{SbCl}_6]^-[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$ ^a

Distances between $[\text{SbCl}_6]^-$ Anions					
Cl(1)···Cl(5)	4/210	3.59	Cl(3)···Cl(2)	3/011	3.51
Cl(2)···Cl(3)	3/010	3.51	Cl(5)···Cl(1)	4/200	3.59
Distances between $[\text{SbCl}_6]^-$ Anions and $[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$ Cations					
Cl(1)···C(1)	1/100	3.37	Cl(4)···O	1/100	3.56
Cl(1)···C(1)	4/110	3.40	Cl(5)···O	1/100	3.56
Cl(1)···O	4/110	3.48	Cl(6)···C(1)	2/100	3.32
Cl(1)···O	1/100	3.53	Cl(6)···O	1/100	3.35
Cl(1)···O	2/100	3.55	Cl(6)···O	2/100	3.41
Cl(2)···C(1)	4/110	3.29	Cl(6)···C(7)	2/100	3.55
Cl(2)···O	4/110	3.42			

^a See footnote a of Table V; here *l* corresponds to 1, *x y z*; 2, $\bar{x} \bar{y} \bar{z}$; 3, $x \bar{y} + \frac{1}{2} z + \frac{1}{2}$; 4, $\bar{x} y + \frac{1}{2} \bar{z} + \frac{1}{2}$.

shown in Figure 4. The various $[\text{SbCl}_6]^-$ anions are separated by typical van der Waals chlorine–chlorine contacts in the range 3.50–3.60 Å. The closest anion–cation contacts occur between the C(1) carbonyl carbon and two chlorine atoms Cl(2) and Cl(6) at distances of 3.29 and 3.32 Å, respectively. Such as previously observed in other oxocarbenium salts,^{9,11,12} chlorine atoms show no tendency to associate with the oxygen of the methyl-4-phenyloxocarbenium ion. The eight chlorine–oxygen contacts are greater than 3.35 Å, well above the sum of the van der Waals radii (see Table VI).

Bond distances and angles determined in the $[\text{SbCl}_6]^-$ ion are summarized in Table VII. The octahedral $[\text{SbCl}_6]^-$ ion presents only slight angular deviations from ideal symmetry but large variations in the bond length, 2.34–2.38 Å, apparently as a result of differences in the environments of chlorine atoms.

Bond lengths and angles found in the methyl-4-phenyloxocarbenium ion are given in Table VIII. The O–C(1)–C(2) bond angle of 179.39 (0.55)° shows no appreciable deviation from the expected linearity. The $[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$ cation is not planar within experimental error. The best least-squares planes (i) through the benzene ring C(2)···C(7) and (ii) through the entire ion were calculated according to the method of Schomaker, Waser, Marsh, and Bergman.²⁴ The equations of the planes referred to the axial system \bar{a} , \bar{b} , \bar{c}^* are: (i) $0.2820X + 0.8986Y + 0.3363Z = 2.0663$; (ii) $0.2929X + 0.8896Y + 0.3505Z = 2.1748$. The de-

(24) V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).

Table VII. Bond Distances and Angles in the $[\text{SbCl}_6]^-$ Anion

Bond distances, Å		Bond angles, deg	
Sb–Cl(1)	2.383 (1)	Cl(1)–Sb–Cl(2)	89.83 (0.06)
Sb–Cl(2)	2.373 (1)	Cl(1)–Sb–Cl(3)	89.23 (0.07)
Sb–Cl(3)	2.344 (2)	Cl(1)–Sb–Cl(5)	89.26 (0.06)
Sb–Cl(4)	2.351 (2)	Cl(1)–Sb–Cl(6)	89.21 (0.06)
Sb–Cl(5)	2.373 (1)	Cl(2)–Sb–Cl(3)	90.25 (0.07)
Sb–Cl(6)	2.368 (1)	Cl(2)–Sb–Cl(4)	89.34 (0.07)
		Cl(2)–Sb–Cl(5)	90.82 (0.07)
Cl(1)···Cl(2)	3.358 (2)	Cl(3)–Sb–Cl(4)	91.41 (0.08)
Cl(1)···Cl(3)	3.320 (2)	Cl(3)–Sb–Cl(6)	90.35 (0.07)
Cl(1)···Cl(5)	3.341 (2)	Cl(4)–Sb–Cl(5)	90.11 (0.07)
Cl(1)···Cl(6)	3.336 (2)	Cl(4)–Sb–Cl(6)	91.61 (0.07)
Cl(2)···Cl(3)	3.343 (2)	Cl(5)–Sb–Cl(6)	88.55 (0.06)
Cl(2)···Cl(4)	3.321 (2)		
Cl(2)···Cl(5)	3.380 (2)	Cl(1)–Sb–Cl(4)	178.95 (0.07)
Cl(3)···Cl(4)	3.360 (3)	Cl(2)–Sb–Cl(6)	178.86 (0.06)
Cl(3)···Cl(6)	3.342 (3)	Cl(3)–Sb–Cl(5)	178.15 (0.07)
Cl(4)···Cl(5)	3.344 (2)		
Cl(4)···Cl(6)	3.383 (2)		
Cl(5)···Cl(6)	3.309 (2)		

Table VIII. Bond Lengths and Angles in the $[\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}]^+$ Cation

Bond Lengths, Å			
C(1)–O	1.097 (9)	C(3)–H(3)	1.03 (10)
C(1)–C(2)	1.396 (10)	C(4)–H(4)	1.01 (10)
C(2)–C(3)	1.406 (10)	C(6)–H(6)	0.97 (10)
C(3)–C(4)	1.365 (10)	C(7)–H(7)	0.95 (11)
C(4)–C(5)	1.405 (10)	C(8)–H(8a)	1.13 (12)
C(5)–C(6)	1.383 (10)	C(8)–H(8b)	0.81 (12)
C(6)–C(7)	1.363 (10)	C(8)–H(8c)	1.01 (11)
C(7)–C(2)	1.393 (10)		
C(8)–C(5)	1.509 (11)		
Bond Angles, Deg			
O–C(1)–C(2)	179.39 (0.55)	C(2)–C(3)–H(3)	118.2 (4.5)
C(1)–C(2)–C(3)	118.35 (0.47)	C(3)–C(4)–H(4)	117.4 (4.6)
C(2)–C(3)–C(4)	118.37 (0.47)	C(4)–C(3)–H(3)	122.7 (4.6)
C(3)–C(4)–C(5)	120.12 (0.47)	C(5)–C(6)–H(6)	126.1 (4.4)
C(4)–C(5)–C(6)	120.26 (0.48)	C(6)–C(7)–H(7)	119.7 (4.6)
C(5)–C(6)–C(7)	120.85 (0.46)	C(7)–C(6)–H(6)	113.0 (4.5)
C(6)–C(7)–C(2)	118.53 (0.46)	C(2)–C(7)–H(7)	118.0 (4.5)
C(7)–C(2)–C(3)	121.83 (0.48)	C(5)–C(8)–H(8a)	95.0 (4.4)
C(7)–C(2)–C(1)	119.79 (0.46)	C(5)–C(8)–H(8b)	110.6 (4.4)
C(8)–C(5)–C(4)	119.03 (0.49)	C(5)–C(8)–H(8c)	125.8 (4.1)
C(8)–C(5)–C(6)	120.71 (0.49)		

viations of the C(1) and O carbonyl atoms from the benzene ring plane are 0.078 (7) and 0.123 (5) Å, respectively (Table IX). These displacements from the re-

Table IX. Distances (Å) of Atoms of Methyl-4-phenyloxocarbenium Ion from Mean Planes

Atoms	i	ii
O	0.123 (5)	0.028 (5)
C(1)	0.078 (7)	0.006 (7)
C(2)	0.008 (7)	-0.035 (7)
C(3)	-0.002 (8)	-0.034 (8)
C(4)	-0.005 (8)	-0.010 (8)
C(5)	0.003 (7)	0.013 (7)
C(6)	0.004 (8)	0.002 (8)
C(7)	-0.011 (7)	-0.040 (7)
C(8)	0.014 (8)	0.055 (8)

quired planarity most probably result from steric interactions in the ionic packing. The C(1)–O bond distance of 1.097 (9) Å, which is equivalent to the distance of 1.128 Å found in carbon monoxide,²⁵ is then consistent with triple bond character. Similar values were observed in the methyl-, ethyl-, isopropyl-, and methyl-2-phenyloxocarbenium ions (Table X). The C(1)–

Table X. Comparison of C–O and Adjacent C–C Bond Length in Oxocarbenium Ions

Compounds	C–O	C–C
$\text{SbF}_6^- \text{CH}_3\text{CO} ^+{}^a$	1.108 (15)	1.385 (16)
$\text{SbCl}_6^- \text{CH}_3\text{CO} ^+{}^b$	1.109 (24)	1.452 (30)
$\text{GaCl}_4^- \text{CH}_3\text{CH}_2\text{CO} ^+{}^b$	1.099 (20)	1.435 (24)
$\text{SbCl}_6^- (\text{CH}_3)_2\text{CHCO} ^+{}^b$	1.116 (10)	1.439 (12)
$\text{SbCl}_6^- \text{CH}_3\text{-2-C}_6\text{H}_4\text{CO} ^+{}^c$	1.111 (13)	1.387 (14)
$\text{SbCl}_6^- \text{CH}_3\text{-4-C}_6\text{H}_4\text{CO} ^+{}^c$	1.097 (9)	1.396 (10)

^a Reference 9. ^b Reference 11. ^c Reference 12.

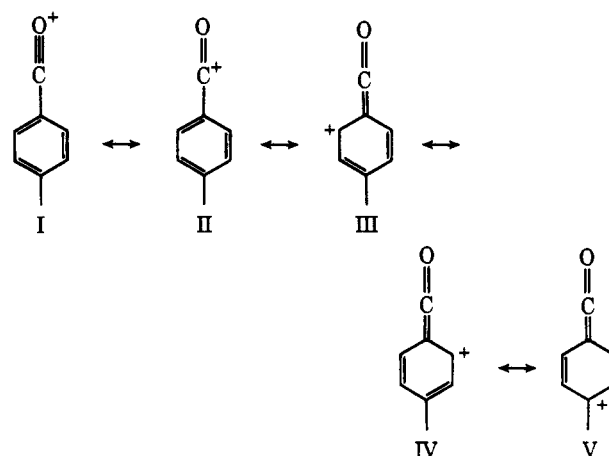
C(2) bond distance of 1.396 (10) Å is similar to the recorded value of 1.387 Å in the methyl-2-phenyloxocarbenium ion¹² but slightly shorter than that found in benzonitrile (1.419 Å), where carbon is also sp hybridized.²⁶ This carbon–carbon distance is particularly short as compared to the corresponding distances observed in alkyloxocarbenium ions except that found by Boer⁹ in the methyloxocarbenium ion. The standard deviations given in Table X are still large to suggest a correct value for this carbon–carbon bond in alkyloxocarbenium ions. However, a theoretic study of the $|\text{CH}_3\text{CO}|^+$ and $|(\text{CH}_3)_2\text{CHCO}|^+$ species through LCAO–MO–SCF *ab initio* calculations²⁷ yields a carbon–carbon distance of 1.45 Å.

(25) G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, Princeton, N. J., 1959, p 522.

(26) D. R. Lide, *J. Chem. Phys.*, **22**, 1577 (1954).

(27) B. Rees, A. Veillard, and R. Weiss, *Theor. Chim. Acta*, **23**, 266 (1971).

The methyl-4-phenyloxocarbenium ion can be described by the following mesomeric structures.



The bond lengths in the phenyl ring, especially the shortest distances C(3)–C(4), 1.365 Å, and C(6)–C(7), 1.363 Å, imply that mesomeric structure V, in which the positive charge is stabilized by the methyl group, contributes significantly to the structure of this cation. A similar result is also reported for the ionic structure of the $|\text{CH}_3\text{-2-C}_6\text{H}_4\text{CO}|^+$ species.¹² Thus, in aryloxocarbenium ions the positive charge is partly delocalized into the phenyl ring, whereas in alkyloxocarbenium ions^{9–11} this charge is mainly localized on the carbonyl carbon atom.

Cook¹³ has previously stated that the adduct $\text{AlCl}_3 \cdot \text{CH}_3\text{COCl}$ is present as a donor–acceptor complex in solvents of low dielectric constant and as an ionic salt in solvents of high dielectric constant. This study clearly proves the existence of two different structural forms in the solid state for the same addition compound and confirms the important role of the solvents used. Since the donor–acceptor complex $\text{SbCl}_5 \cdot \text{CH}_3\text{-4-C}_6\text{H}_4\text{COCl}$ can be isolated from CCl_4 solutions and the ionic salt $|\text{SbCl}_6^-||\text{CH}_3\text{-4-C}_6\text{H}_4\text{CO}|^+$ from CHCl_3 solutions, the influence of the solvents may be explained on the basis of their polarity and their dielectric constant (CCl_4 , $\epsilon = 2.2$ and nonpolar; CHCl_3 , $\epsilon = 5.05$ and polar). When dissolved in CHCl_3 , the donor–acceptor complex recrystallizes as the ionic salt; inversely, the ionic salt is converted to the donor–acceptor complex when dissolved in CCl_4 . This result shows that equilibrium actually exists between the two structural forms in solution

