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Structures of Some Dialkoxyphenylmethylium Ions; Steric Inhibition of Resonance[1]

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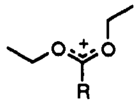
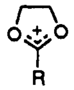
Abstract: In order to investigate the observation of decreased stability of phenyl vs methyl dialkoxy carbenium salts, the single crystal X-ray structures and properties of three aryl-substituted dialkoxy carbenium salts have been examined. Diethoxyphenylmethylium hexachloroantimonate, **3**, crystallizes in the orthorhombic space group $Pbn2_1$, with a = 7.651(2) Å, b = 13.543(3) Å, and c = 17.792(3) Å, V = 1843.5(7) Å^3, and z = 4. Dimethoxy(*p*-methoxyphenyl)-methylium hexachloroantimonate, **4**, crystallizes in a monoclinic crystal system, space group $P2_1/n$, with a = 10.816(3) Å, b = 14.119(4) Å, c = 11.917(3) Å, β = 98.420(20)°, V = 1800.2(8) Å^3, and z = 4. Diethoxy(2,4,6-trimethylphenyl)-methylium hexachloroantimonate, **5**, crystallizes in the monoclinic space group $P2_1/n$, with a =10.872(2) Å, b = 14.804(3) Å, c = 14.050(2) Å, β = 102.366 (15)°, V = 2208.7(7) Å^3, and z = 4. The X-ray studies revealed that in each case the aryl substituent is substantially twisted out of conjugation with the dialkoxy carbenium center (**3**, 38.9°; **4**, 30.5°; **5**, 64.6°). This is consistent with the decrease in the stability of these compounds compared to their methyl analogues. The ^{13}C NMR shift of the *para* carbon of the aryl substituent was found not to be a good indication of the fraction of positive charge transferred to the aromatic ring.

Introduction

The stabilization of a carbenium ion by a neighboring phenyl group is one of the basic tenets of organic chemistry. However, quantitative examinations of this effect have shown that the degree of stabilization resulting from conjugation of a phenyl group can vary considerably in different systems.[2,3] A good example of this is found with the dialkoxy carbenium ions **1** and **2–4**.[3,4] As might be expected, replacement of the methyl in **2A** by phenyl, **2B**, decreases its rate of reaction with water[5] and increases its relative thermodynamic stability.[6] However, a similar replacement of methyl by phenyl in **1A** has little effect on the relative rate of collapse of the cation with water[5] and, in fact, decreases its stability.[7] While various explanations of this effect have been considered, the generally accepted view is that structural differences, particularly variation of the angle between the planes of the aryl groups and the cationic centers, are the key determining factor.[5,6,8]



1A: R = Me
1B: R = C_6H_5



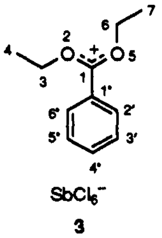
2A: R = Me
2B: R = C_6H_5
2C: R = *p*-$CH_3OC_6H_4$

The suggestion that the difference in reactivity/stability of ions **1A** and **2A** is due to conformational restriction of resonance stabilization by the phenyl group is open to direct test by determination of the structures of these ions. Crystal structures have been reported for **2A** and a variety of other alkyl- and aryl-substituted dioxolanylium cations.[9–11] In each of the aryl-substituted cations the aromatic ring has been shown to be almost coplanar with the heterocyclic ring, (twist angles <3.5°). No structure has yet been reported for **1B** or, indeed, of any acyclic dialkoxy carbenium ions.[12] This is surprising given the importance of this type of ion in the reactions of derivatives of carboxylic acids.[12]

We report here the structure of three aryl-subsituted cation salts related to cations of type **1** above. In contrast to the near planar arrangment of the corresponding dioxolanylium ions, we have found that in each of these acyclic cations the aryl substituent is substantially twisted out of conjugation with the dialkoxy carbenium ion center. The twisting of the aryl groups from the plane of the carbenium ion center affects the structures and spectroscopic properties of these cations.

Results

The cations **3–5** were prepared as their $SbCl_6^-$ salts by reaction of the corresponding triethyl orthobenzoate with $SbCl_5$ in dichloromethane.[13] The salts were characterized by solution phase ^{1}H and ^{13}C NMR spectroscopy, Tables 1 and 2, respectively. The NMR spectra of **3** and **5** were very similar to those previously



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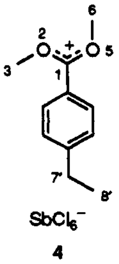

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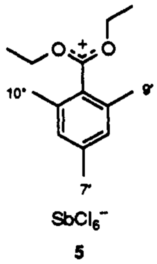

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Table 1. ^1H NMR Data[a] for Cations **3–5**

	chemical shifts (ppm)							
ion	3,6	4,7	2′,6′	3′,5′	4′	7′	8′	9′,10′
3	5.19	1.68	8.03	7.77	7.97			
4	4.72		8.14	7.24			3.97	
5	5.10	1.64		7.09		2.40		2.36

[a] Recorded at −20 °C in SO_2; TMS in SO_2 as external reference.

Table 2. ^{13}C NMR Data for Methylium Ions and Neutral Benzoates

	chemical shifts (ppm)									
	4,7	3,6	1	1′	2′,6′	3′,5′	4′	8′	7′,9′	10′
2B		75.6	182.9	116.7	134.3	131.0	142.2			
3[a]	13.8	78.6	183.0	122.0	131.7	130.3	138.6			
3[b]	15.6	82.5 75.5	182.4	121.9	132.7	132.7	139.0			
4[a]		65.3	182.3	112.4	135.6	115.7	167.3	56.0		
5[a]	13.5	78.6	187.7	120.7	136.4	129.8	145.6		18.6	20.8
6[c]	14.3	60.9	166.4	130.6	129.5	128.3	132.7			
7[d]		51.8	166.8	122.7	131.6	113.6	163.4	55.4		
8[e]	14.5	61.1	170.2	131.8	135.3	128.7	139.5		19.8	21.2

[a] ^{13}C NMR spectrum, SO_2 at −20 °C. [b] Solid state ^{13}C NMR CPMAS spectrum. [c] Pelletire, S. W.; Djarmat, Z.; Pape, C. *Tetrahedron* **1976**, *32*, 995. [d] Budesinsky, M.; Exner, O. *Magn. Reson. Chem.* **1989**, *27*, 586. [e] ^{13}C NMR spectrum, CH_2Cl_2.

reported for these ions.[14] In the case of **4**, which has not previously been reported, the spectra were fully in accord with the assigned structure. The UV spectra of **3–5** are given in Table 3.

The ^{13}C and ^1H spectra of **3–5** at −20 °C in SO_2 showed in each case only a single set of resonances for the ethyl or methyl groups. It is known from the earlier, variable temperature NMR work of Ramsey and Taft[15] and other more recent workers[16] that dialkoxy carbenium ions adopt an *E,Z* conformation in preference to either an *E,E* or *Z,Z* form. Lowering the temperature of the solutions of **3** and **5** slowed the interconversion of the two alkoxy groups and allowed distinct ^1H NMR resonances to be observed for the two ethyl substituents. The barriers to the interconversion of the alkoxy groups of **3** and **5** were determined by comparison of the observed spectra with those simulated with DNMR-3.[17]

In the case of **4** it was not possible to slow sufficiently the isomerization about the C(1)–O(2) and C(1)–O(5) bonds in order to stop averaging of the methyl proton resonances in the ^1H NMR spectra. At −115 °C, the lowest temperature reached before the sample crystallized from the solvent, a small degree of line broadening of the methoxy signal was observed. Assuming the same chemical shift difference betweeen the two different methoxy groups in the frozen spectrum as was observed with the methylene resonances in **3**, the barrier to interconversion of the two conformers was estimated to be 7.4 ± 0.2 kcal/mol.

The solid state ^{13}C CPMAS NMR spectrum of **3** was obtained. The spectrum was found to be very similar to that observed for SO_2 solutions of this salt at −20 °C, Table 2. The one notable difference was that the solid state spectrum shows separate resonances for the methylene carbons, C(3) and C(6), where as in solution only a single resonance is observed. The average of the chemical shifts of the two methylene carbon resonances seen in the solid state spectrum (79.0 ppm) was almost identical to the averaged shift observed in solution (78.6 ppm).

The structures of **3–5** were determined using single crystal X-ray crystallography with diffraction data being collected at low temperatures. Selected bond lengths and angles are given in Table 6, and the structures of the cations are shown in Figures 1–3.[18,19] In the case of **5** large temperature factors were found to be associated with the alkyl carbons C(3), C(4), C(6), and C(7) and large aniostropies with C(4′) and C(7′). There are large errors associated with the bond distances and bond angles for **5**.

Discussion

General Structural Features. The structures determined for **3–5** are all consistent with those expected for the $SbCl_6^-$ salts of dialkoxy carbenium ions. Each cation consists of a phenyl (**3**) or substituted phenyl (**4** and **5**) ring bonded to a dialkoxy methylium fragment. In each of the cations C(1) and the atoms directly bonded to this atom, O(2), O(5), and C(1′), lie in a plane (plane A) indicating C(1) is sp^2 hybridized, Table 7. Examination of Figures 1–3 clearly shows that each of the three cations has adopted a sickle conformation in the crystal lattice. Such a conformation is consistent with the variable temperature NMR results obtained here for these ions in solution.

The aryl carbon–carbon bond distances and angles for **3–5** and the carbon–oxygen bond distances and angles for the *p*-methoxy fragment in **4** are similar to the corresponding ones found for (*p*-methoxyphenyl)diphenylcarbenium tetrafluoroborate.[20] As has been found for other alkoxy-substituted carbenium ions,[11] the C(1)–O(2)/C(1)–O(5) bond distances in each of the ions are intermediary in length between those typically found for C—O single and double bonds.[21] Compared with previously reported structures for alkoxy-substituted carbenium ions[9,10,12,22] the O(2)–C(3) and O(5)–C(6) internuclear distances in **3** (1.488(7) and 1.482(6) Å, respectively) and in **4** (1.479(10) and 1.481(11) Å, respectively) are significantly lengthened from those of typical ethyl (1.452(2) Å) and methyl (1.448(10) Å) esters[21] (differences 4.9 and 4.7σ, where $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$. We have shown previously that this lengthening of the *O*-alkyl bonds is accompanied by a transfer of positive charge to the alkyl groups.[22,23] In the anions, the bond distances and angles are similar to those found in other antimonate salts.[10,22]

For **3–5** the crystal lattices consist of alternating planes of cations and anions. The closest cation–anion contact in **3** is between H(3A) and Cl(2) (2.624 Å) in one layer with other close contacts in the next layer between H(6A)–Cl(4) (2.722 Å), H(2′)–Cl(5) (2.874 Å), and H(4B)–Cl(4) (2.786 Å). For compound **4**, the closest anion–cation interaction is 2.780 Å between H(3C) and Cl(1) and the closest cation–cation interaction is 2.522 Å (H(3A)–O(7′)). Other important interactions are H(6′)–Cl(4) (2.824 Å) and H(8′A)–Cl(3) (2.846 Å). In **5**, the closest nonbonding interaction between the cation layer and the anion layer is between H(4C) and Cl(4) (2.729 Å). Packing diagrams have been deposited as supplementary material.

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Table 3. Spectroscopic Data

	2B	**2C**	**3**	**4**	**5**
barrier (kcal/mol)	–	–	8.2 ± 0.3	7.4 ± 0.2	11.2 ± 2
UV (nm)	300	320	264	316	272
Δδ (ppm)[1]	9.5	7.1	5.9	3.9	6.1
twist angle (deg)	2.4	3.4	38.9	30.5	64.6
C(1)–C(1′) (Å)	1.442(3)	1.414(9)	1.480(8)	1.454(11)	1.467(10)

[a] Δδ is defined as δ^{13}C (*para* carbon, methylium ion) – δ^{13}C (*para* carbon, neutral benzoate).

Table 4. Crystal Data for Cations **3**–**5**

	3	**4**	**5**
formula	$C_{11}H_{15}O_2SbCl_6$	$C_{10}H_{13}O_3SbCl_6$	$C_{14}H_{21}O_2SbCl_6$
fw, g mol^{-1}	513.70	515.65	555.8
system	orthorhombic	monoclinic	monoclinic
space group	$Pbn2_1$	$P2_1/n$	$P2_1/n$
a, Å	7.651(2)	10.816(3)	10.872(2)
b, Å	13.543(3)	14.119(4)	14.804(3)
c, Å	17.792(3)	11.917(3)	14.050(2)
β, deg		98.420(20)	102.366(15)
V, Å^3	1843.5(7)	1800.2(8)	2208.7(7)
Z	4	4	4
D_{calcd}, g cm^{-1}	1.85	1.90	1.67
$F(000)$	1000	1000	1096
μ (Mo Kα), cm^{-1}	23.17	22.52	19.79
final R_1,R_2[b]	0.0264,0.0260	0.0571,0.0553	0.0452,0.0683
weighting scheme	$\omega = (\sigma^2F + 0.000230F^2)^{-1}$	$\omega = (\sigma^2F + 0.000500F^2)^{-1}$	$\omega = (\sigma^2F + 0.0010F^2)^{-1}$
error in observation of unit weight[c]	1.0774	1.6736	1.7741
highest peak, e Å^{-3}	1.25	1.19	0.69
lowest peak, e Å^{-3}	–0.68	–1.83	–1.62

[a] Nonstandard setting of $Pna2_1$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_2 = (\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega F_o^2)^{1/2}$. [c] $S = (\Sigma(F_o - F_c)^2/(m - n))^{1/2}$ (m = no. of reflections, n = no. of variables).

Conformation of the Aryl Groups. As a result of the adoption of an *E*,*Z*-conformation about the two C(1)–O partial double bonds of cations **3**–**5**, steric crowding occurs between O(2) and C(6′) or, in the case of **5**, O(2) and C(10′). The impact of this steric interaction can be seen in three different structural effects in these cations. First, as can be seen from the data given in Table 6, there is a systematic distortion of the bond angles about C(1′), C(1), and O(2) so as to minimize this interaction. Thus, the C(1)–C(1′)–C(6′), C(1′)–C(1)–O(2) and C(1)–O(2)–C(3) angles of **3**, **4**, and **5** are in each case significantly larger than the corresponding C(1)–C(1′)–C(2′), C(1′)–C(1)–O(5), and C(1)–O(5)–C(6) bond angles. It is interesting to note that while the nature of the steric interactions in these three cations varies, within the error limits of the structure determinations, there is no significant difference between the corresponding bond angles in each of the three cations.[24]

The second structural effect is the disposition of the dialkoxy portions of the molecules. Carbon atoms C(3) and C(6) in each ion are found to lie in positions close to the carbonyl planes, plane A. In the case of **3** the methyl carbon C(4) is found to be displaced from plane A (–0.561 Å), while C(7) is found to be close to this plane with the maximum displacement being 0.041 Å. For **4**, the methyl carbons (4) and C(7) both lie in the carbonyl plane. The conformation of the ethyl groups in **5** is different from that found in **3** in that neither of the methyl carbons C(4) and C(7) lie in the carbonyl plane with displacements of 1.064 and –1.109 Å, respectively.

The third and most important structural effect of the steric interactions is that the phenyl ring in these cations is substantially twisted from the plane of the carbenium ion center. For example, this twisting in **3** is clearly evident on examination of view **B**, Figure 1. It is important to note that the magnitude of this twist angle would appear to depend on the nature of the steric interaction. In **4** the plane defining the phenyl group (plane **B**, consisting of atoms C(1′)–C(6′)) is set at an angle of 30.5° from that of the carbenium ion center, plane A. The corresponding twist angle in **3** is 38.9(2)°. This larger twist angle in **3** as compared to **4** presumably results from the presence of the sterically larger ethyl groups in the former cation as compared to methyl groups in **4**. In **5**, as might be expected from the presence of the two ortho methyl substituents on the aryl ring, the twist angle is much larger (64.4°), Table 3. A similar effect has been noted for related neutral benzoate species as determined by X-ray studies[25] and MM2 calculations.[26]

The twist angles observed for cations **3**–**5** are sufficiently large to result in an attenuation of the degree of conjugation between the aryl groups and the carbenium ion centers.[4,7,8] Moreover, as the twist angles observed with these cations **2**–**5** range from 2.4° to 64.4° there should be a systematic reduction in conjugation which should be reflected in the structures and other properties of these ions.

Reduced conjugation resulting from twisting of the aryl ring from the plane of the carbenium ion center of these ions should result in a lengthening of the C(1)–C(1′) bond distance. Indeed, this effect can be seen in comparing the C(1)–C(1′) bond distance of **3** (1.480(8) Å) with that of the corresponding bond in **2B**, (1.442(3) Å), (difference 4.4σ) Table 3. With a smaller twist angle associated with **4** it would be expected that the difference in the C(1)–C(1′) bond distances between this cation and **2C** would be smaller than that found for the two unsubstituted ions. In fact there is no significant difference in the C(1)–C(1′) bonds of **4** and **2C** (difference 2.8σ). However, it should be noted that the errors reported for the bond distances of **2C** are larger than those associated with **2B**.

Other structural differences would be expected as a result of twisting between the carbenium ion center and the aryl ring of these cations. These include differences in the C–O bond distances as less charge is distributed to the aryl ring as the twist angle is increased and a reduction in the typical "quinonoid" type distortion

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(24) Means of the C(1)–C(1′)–C(6′) bond angles 122.6(8)°, the C(1′)–C(1)–O(2) bond angles 127.0(10)°, C(1)–O(2)–C(3) 123.4(10)°, C(1)–C(1′)–C(2′) 117.1(7)°, C(1′)–C(1)–O(5) 115.6(3)°, and C(1)–O(5)–C(6) 119.7(11)°.

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Table 5. Positional Parameters (10^4) for Cations **3**–**5**

atom	*x*	*y*	*z*
Phenyldiethoxymethylium Hexachloroantimonate (**3**)			
Sb	−572.7(4)	8232.0(2)	5000
Cl(1)	422(2)	6578(1)	5012(2)
Cl(2)	1599(2)	9874(1)	4995(1)
Cl(3)	−66(3)	8310(1)	3679(1)
Cl(4)	−1076(3)	8169(1)	6314(1)
Cl(5)	2301(2)	8780(1)	5213(1)
Cl(6)	−3446(2)	7673(1)	4785(1)
O(2)	3257(5)	3173(3)	7799(2)
O(5)	1180(5)	2678(3)	7039(2)
C(1)	1803(6)	3348(4)	7467(3)
C(3)	4231(8)	3935(5)	8233(4)
C(4)	6075(8)	3588(5)	8331(4)
C(6)	2173(6)	1757(4)	6894(3)
C(7)	1004(9)	1112(5)	6426(4)
C(1′)	743(6)	4260(5)	7519(3)
C(2′)	−79(9)	4570(5)	6858(3)
C(3′)	−1133(8)	5419(5)	6883(4)
C(4′)	−1377(8)	5914(5)	7551(3)
C(5′)	−572(8)	5598(5)	8211(4)
C(6′)	507(6)	4768(5)	8194(4)
(*p*-Methoxyphenyl)dimethoxymethylium Hexachloroantimonate (**4**)			
Sb	102.7(5)	2887.9(4)	1283.1(4)
Cl(1)	−1464(2)	2742(2)	2465(2)
Cl(2)	1703(2)	3037(2)	133(2)
Cl(3)	1551(2)	2069(1)	2624(2)
Cl(4)	705(2)	4342(1)	2208(2)
Cl(5)	−549(2)	1412(2)	407(2)
Cl(6)	−1268(2)	3698(2)	−112(2)
O(2)	−2243(5)	4952(4)	3080(5)
O(5)	−1515(5)	5015(4)	4880(5)
O(7′)	465(5)	9041(4)	3657(5)
C(1)	−1610(7)	5451(6)	3873(7)
C(3)	−2643(8)	5288(7)	1908(7)
C(6)	−2224(9)	4234(7)	5057(8)
C(1′)	−999(7)	6357(6)	3769(7)
C(2′)	−912(8)	6967(6)	4699(7)
C(3′)	−422(8)	7865(6)	4651(7)
C(4′)	35(7)	8157(6)	3645(6)
C(5′)	11(7)	7521(6)	2718(7)
C(6′)	−527(7)	6643(6)	2785(6)
C(8′)	897(9)	9395(6)	2659(8)
(Trimethylphenyl)diethoxymethylium Hexachloroantimonate (**5**)			
Sb	2069(1)	7255(1)	1173(1)
Cl(1)	2132(2)	5762(1)	1771(1)
Cl(2)	3421(2)	7751(1)	2616(1)
Cl(3)	3854(2)	6952(2)	504(2)
Cl(4)	308(2)	7544(1)	1865(2)
Cl(5)	1967(2)	8731(1)	516(1)
Cl(6)	715(2)	6755(2)	−290(1)
O(2)	7174(6)	6435(3)	2025(4)
O(5)	7743(6)	5192(4)	1405(4)
C(1)	7466(7)	5611(5)	2127(5)
C(3)	7010(12)	7017(6)	2854(7)
C(4)	7588(13)	7812(6)	2861(7)
C(6)	7892(8)	5722(6)	481(5)
C(7)	6636(9)	5781(7)	−158(7)
C(1′)	7546(7)	5075(4)	3016(5)
C(2′)	8762(6)	4718(5)	3483(5)
C(3′)	8832(8)	4191(5)	4296(6)
C(4′)	7780(8)	3976(5)	4655(5)
C(5′)	6634(7)	4331(4)	4197(5)
C(6′)	6493(6)	4882(4)	3388(5)
C(7′)	7908(10)	3385(6)	5511(6)
C(9′)	9911(7)	4903(6)	3062(7)
C(10′)	5202(7)	5210(6)	2884(6)

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for Cations **3**–**5**

	3	**4**	**5**
O(2)–C(1)	1.282(7)	1.291(10)	1.261(9)
O(5)–C(1)	1.278(6)	1.286(9)	1.279(9)
O(2)–C(3)	1.488(7)	1.479(10)	1.489(11)
O(5)–C(6)	1.482(6)	1.481(11)	1.554(10)
C(3)–C(4)	1.498(9)		1.334(14)
C(6)–C(7)	1.502(8)		1.467(12)
C(1)–C(1′)	1.480(8)	1.454(11)	1.467(10)
C(1′)–C(2′)	1.399(9)	1.396(11)	1.387(10)
C(2′)–C(3′)	1.405(9)	1.379(11)	1.387(9)
C(3′)–C(4′)	1.375(9)	1.423(11)	1.378(10)
C(4′)–C(5′)	1.394(9)	1.421(11)	1.383(12)
C(5′)–C(6′)	1.395(9)	1.376(11)	1.371(11)
C(6′)–C(1′)	1.395(9)	1.405(11)	1.444(9)
C(4′)–O(7′)		1.331(10)	
O(7′)–C(8′)		1.431(11)	
C(2′)–C(9′)			1.517(12)
C(4′)–C(7′)			1.419(11)
C(6′)–C(10′)			1.509(11)
Bond Angles (deg)			
C(1′)–C(1)–O(2)	126.9(5)	128.0(8)	126.0(7)
C(′1)–C(1)–O(5)	115.2(5)	116.0(8)	115.6(6)
O(2)–C(1)–O(5)	117.9(5)	116.0(7)	118.4(6)
C(1)–O(2)–C(3)	123.0(4)	124.5(6)	122.7(6)
O(2)–C(3)–C(4)	108.3(5)		112.4(10)
C(1)–O(5)–C(6)	120.7(4)	118.4(7)	120.1(6)
O(5)–C(6)–C(7)	106.3(5)		106.9(7)
C(1)–C(1′)–C(2′)	116.4(6)	117.0(7)	117.8(7)
C(1)–C(1′)–C(6′)	122.4(5)	123.4(7)	121.9(6)
C(2′)–C(1′)–C(6′)	121.2(6)	119.6(7)	120.2(6)
C(1′)–C(2′)–C(3′)	118.4(6)	121.1(8)	117.9(7)
C(2′)–C(3′)–C(4′)	120.4(6)	119.0(8)	122.2(7)
C(3′)–C(4′)–C(5′)	121.1(6)	120.2(8)	118.5(7)
C(4′)–C(5′)–C(6′)	119.4(6)	119.0(8)	122.7(7)
C(5′)–C(6′)–C(1′)	119.5(6)	121.0(7)	118.4(6)
C(5′)–C(4′)–O(7′)		124.6(7)	
C(3′)–C(4′)–O(7′)		115.3(7)	
C(1′)–C(2′)–C(9′)			120.5(7)
C(3′)–C(2′)–C(9′)			121.6(7)
C(1′)–C(6′)–C(10′)			121.1(6)
C(5′)–C(6′)–C(10′)			120.3(7)
C(3′)–C(4′)–C(7′)			119.7(7)
C(5′)–C(4′)–C(7′)			121.8(8)

seen in the aryl ring of **4** as compared to **2C**. However, the uncertainties in the bond distances determined for cations **3**–**5** and **2C** are such that no significant differences are observed.

The structures determined here are of the cations in their solid state. Most reported studies on the stability and reactivity of these ions have been carried out in solution. The question arises as to whether these structures are a good representation of those in solution and in particular whether the twist angles observed here are also maintained in solution? We have previously found for a variety of carbenium ions whose structures we have determined that there is generally a close correspondence between the solid state CPMAS and solution phase ^{13}C NMR spectra.[27] This indicates that in most instances the determination of the solid state crystal structure of a carbenium ion will give a good indication of the structure and charge distribution of the cation present in solution. As can be seen on comparison of the NMR data in Table 2, cation **3** is no exception to this general trend. The close similarity of the ^{13}C NMR spectra of **3** in the solid state and solution noted above means that there is no major difference in conformation or charge distribution of this cation in the two phases. Thus the solid state structure found here is a good model for that found in solution.

Relationship between the Structures and Properties of These Ions. The presence of the large twist angles in **3**–**5** as compared to **2B** and **2C** is reflected in the UV spectra of these ions. Examination of the data given in Table 3 shows that the absorption maxima of ions **3** and **4** are blue shifted from those of **2B** and **2C**. The blue shift observed is the largest with **3**/**2B** reflecting the larger twist angle observed in **3** as compared to **4**. The changes

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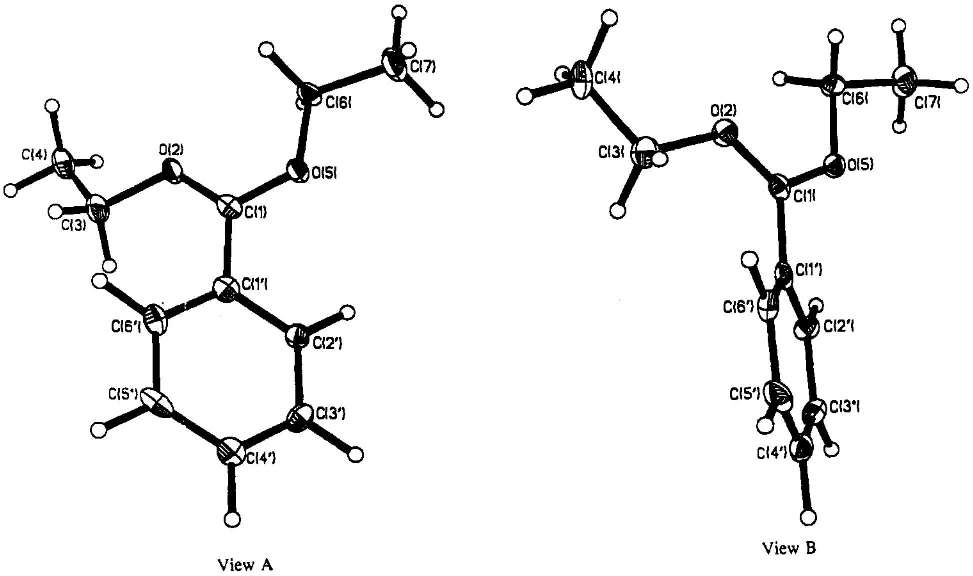
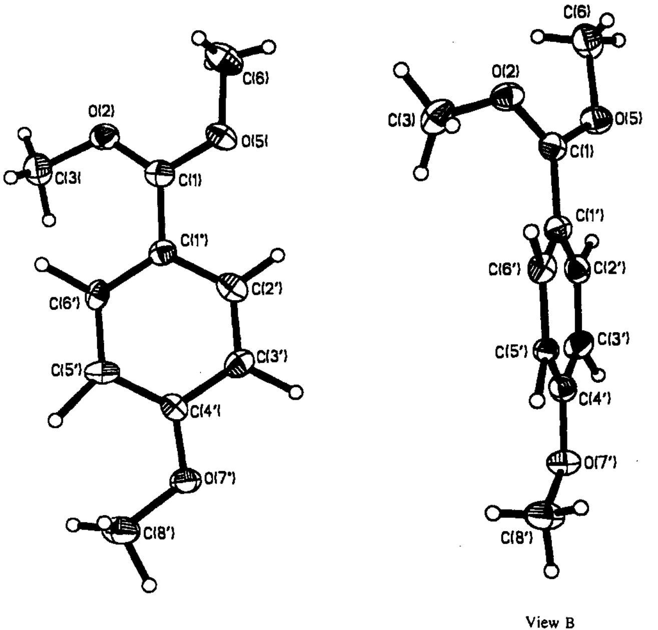
[27] Childs, R. F.; Mahendran, M.; Zweep, S. D.; Shaw, G. S.; Chadda, S. K.; Burke, N. A. D.; George, B. E.; Faggiani, R.; Lock, C. J. L. *Pure Appl. Chem.* **1986**, *58*, 111.



View A

View B

Figure 1. Structure of the cation of **3**; 35% thermal ellipsoids are shown.



View A

View B

Figure 2. Structure of the cation of **4**; 35% thermal ellipsoids are shown.

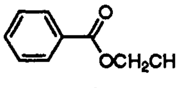
in absorption maxima are fully consistent with a reduction of conjugation accompanying twisting.[28]

The barriers to conformational isomerization about the C—O bonds observed in **3**–**5**, Table 3, would also seem to be determined in part by the differing twist angles. The averaging of the NMR signals of the *O*-alkyl groups in ions of this type involves rapid interconversion between the two conformations shown in Scheme 1. Previous work has shown that such *E*/*Z* isomerizations about the C—O bonds of such cations involves a rotation process.[29] Positive charge buildup occurs on the carbonyl carbon in the transition state for this rotation and as such charge stabilizing groups joined to the carbonyl carbon of one of these cations facilitate the C—O isomerization reactions by stabilizing the transition state for the isomerization to a greater extent than the ground states.[29]

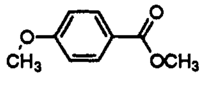
Examination of the barriers to the interconversion of the *O*-alkyl substituents in cations **3**–**5** (Table 3) show that the lowest barrier (7.4 kcal/mol) occurs with **4** and the highest (11.2 kcal/mol) with **5**. This ordering of barriers cannot simply be due to the formal conventional charge stabilizing abilities of the three different aryl groups as this would lead to an order where **5** would be expected to have a lower barrier than **3**. Equally, the replacement of OMe in **4** by OEt in **3** is not expected to be an important factor in that the barriers to comparable conformational exchange in $HC(OMe)_2^+$ (14.7 ± 0.2 kcal/mol) and $HC(OEt)_2^+$ (15.0 ± 0.3 kcal/mol) are the same within experimental error.[30] Rather we would suggest that the differences in the barriers to conformational exchange result from the relative donor properties of the aryl substituents as modified by the twisting noted above. In making this suggestion we note that the degree of twisting observed here for the ground states of these molecules must be largely maintained in the transition states for the conformational isomerizations.

The twisting observed in these aryl-substituted carbenium ions should also lead to an attenuation of the fraction of positive charge transferred onto the aryl rings. Indeed one would expect that the greater the degree of twisting, the smaller the fraction of charge transferred to the aromatic ring. Shifts in the positions of the ^{13}C NMR resonances on formation of a carbocation are indicative of the amount of charge induced on particular carbon atom.[2,3] While the interpretation of these shifts in a quantitative manner has been controversial, it is recognized that they can be informative if used with care in closely related systems, and particularly, if the changes in the chemical shift of a remote atom in a series of cations is used as the marker.[2,3] In the case of aryl-substituted carbenium ions the position of the ^{13}C resonance of the *para* carbon has been widely used as an indicator of the fraction of the charge being delocalized into the aryl ring.[31]

The corresponding benzoates **6**–**8** were selected as neutral precursor "models" for both **2A** and **2C**, **3**, **4**, and **5**. In each case



6



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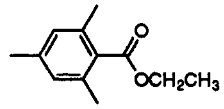

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the difference ($\Delta\delta$) in the position of the chemical shift of the *para* ring carbon of the neutral ester and the corresponding cations

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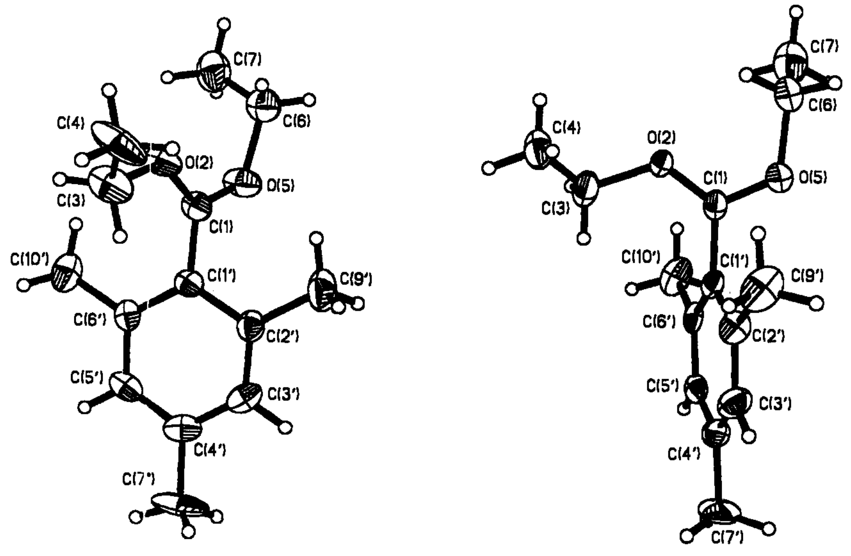
[28] (a) Braude, E. A.; Sondheimer, F. *J. Chem. Soc.* **1955**, 3754. (b) Gompper, R.; Wagner, H.-U. *Tetrahedron Lett.* **1968**, *2*, 165.

[29] (a) Cremer, D.; Gauss, J.; Childs, R. F.; Blackburn, C. *J. Am. Chem. Soc.* **1985**, *107*, 2435. (b) Blackburn, C.; Childs, R. F.; Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1985**, 107, 2442.

[30] The values were determined using data from ref 15.

[31] (a) Budesinsky, M.; Exner, O. *Magn. Reson. Chem.* **1989**, *27*, 586. (b) Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3419.



View A

View B

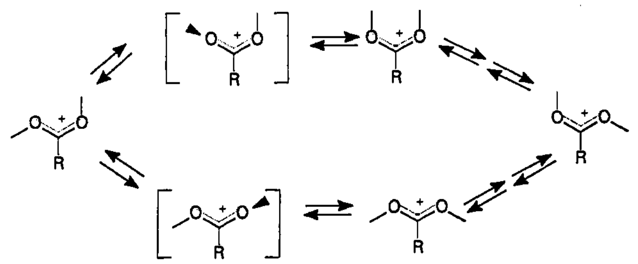
Figure 3. Structure of the cation of 5; 35% thermal ellipsoids are shown.

Table 7. Least-Squares Planes for Cations 3–5

		plane A[a]	plane B[a]	angle between plane A and B, deg
3	C(1′)	–0.001*	0.002*	38.9
	C(2′)	–0.776	–0.008*	
	C(3′)	–0.771	0.008*	
	C(4′)	–0.0204	–0.001*	
	C(5′)	0.754	–0.006*	
	C(6′)	0.754	0.005*	
	C(1)	0.002*	–0.05*	
	O(2)	0.000*	0.57	
	C(3)	–0.174	1.59	
	C(4)	–0.561	2.40	
	O(5)	0.000*	–0.79	
	C(6)	–0.0972	–0.85	
	C(7)	0.041	-1.89	
4	C(1′)	0.001*	–0.013*	30.5
	C(2′)	–0.629	–0.005*	
	C(3′)	–0.758	0.023*	
	C(4′)	–0.201	–0.018*	
	C(5′)	0.502	–0.002*	
	C(6′)	0.567	0.019*	
	C(1)	0.003*	–0.08*	
	O(2)	0.000*	–0.64	
	C(3)	–0.224	1.52	
	O(5)	0.000*	0.47	
	C(6)	–0.137	0.32	
	O(7′)	–0.396	–0.07	
	C(8′)	0.092	–0.14	
5	C(1′)	0.002*	–0.006*	64.6
	C(2′)	1.145	–0.005*	
	C(3′)	1.136	0.013*	
	C(4′)	0.060	–0.009*	
	C(5′)	-1.015	–0.002*	
	C(6′)	-1.065	0.009*	
	C(1)	0.009*	–0.074*	
	O(2)	0.002*	0.818	
	C(3)	0.185	2.16	
	O(5)	0.002*	-1.13	
	C(6)	0.214	-1.23	
	C(4)	1.064	3.14	
	C(7)	-1.109	-1.72	

[a] Atoms defining the plane are indicated with an asterisk.

Scheme 1



was taken as a measure of the amount of charge induced on the ring. It is clear from the data summarized in Table 3 that no simple relationship exists between the degree of twisting and $\Delta\delta$, the chemical shift difference. In comparing the $\Delta\delta$s of **2B** with **3**, and **2C** with **4**, it can be seen in each case that the downfield shift observed in the two twisted cations (**3** and **4**) is significantly reduced from that found with the nearly planar dioxolanylium ions. However, the magnitude of the attenuation in **4** as compared to **2C** is greater than that observed for **3**/**2B** despite the difference in twist angles in the former cation pair being less than that in the **3**/**2B**. It should also be noted that there is a substantial downfield shift ($\Delta\delta$) observed with **5** as compared to **8**. In the case of **5** with the very large twist angle of 64°, there should be little conjugative transmission of positive charge onto the *para* position of the aryl ring. The *para* carbon should not experience any substantial deshielding as a result of the operation of an inductive (σ) effect due to its remoteness from the positively charged site. However, the downfield shift observed is as large as that observed with **3**. The conclusion that has to be reached is that the use of the ^{13}C NMR shifts of the *para* carbons in aryl-substituted cations is a poor indicator of the fraction of positive charge transferred to the aromatic ring. It may be possible to obtain more information regarding the amount of positive charge transferred to the aromatic ring by examining the ^{13}C chemical shift tensors of single crystals[32] or liquid crystals.[33]

In conclusion, it is clear that the properties of the dialkoxyphenyl carbenium ions can be understood in terms of their structures. Conjugative stabilization of the carbenium ion center by its adjacent aryl group is attenuated by a twisting of the aryl portion of the cation. These findings fully support the suggestions by Kresge and other workers[6–8] that the anomalous charge stability of phenyl groups in **3** as compared to **2B** is due to the conformational restriction of resonance stabilization in the former cation.

Experimental Section

Solution ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM 500, Bruker WM 250, or Varian EM 390. Solid state ^{13}C NMR spectra were obtained with a Bruker MSL 100. UV spectra were recorded on

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[32] (a) Veeman, W. S. *Prog. NMR Spectrosc.* **1984**, *16*, 193. (b) Carter, C. M.; Facelli, J. C.; Alderman, D. W.; Grant, D. M.; Dalley, N. K.; Wilson, B. E. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3673.

[33] Fung, B. M.; Kong, C. F. *J. Am. Chem. Soc.* **1984**, *106*, 6193.

an HP 8451 diode array spectrophotometer. Triethyl orthobenzoate was obtained from Aldrich Chemical Co. Chemical shift values are given in δ with the trace of protonated solvent as the internal reference. Reactions were performed under a nitrogen atmosphere.

Preparation of Orthoesters. Trimethylortho-*p*-methoxybenzoate was prepared using the procedure described in ref 34.[34]

Triethyl ortho-2,4,6-trimethylbenzoate was prepared using the procedure described in ref 35.[35] bp 102–106 °C/0.5mm. ^{1}H NMR ($CDCl_3$): 6.83 (2H, s), 3.40 (6H, q, J = 8 Hz), 2.53 (6H, s), 2.28 (3H, s), 1.23 (9H, t, J = 8 Hz).

Preparation of Cations. Compounds **3**–**5** were prepared following a procedure slightly modified from that given in ref 13. A representative method is described below.

Diethoxyphenylmethylium Hexachloroantimonate, 3. To a 2 mL CH_2Cl_2 solution of triethylorthobenzoate (0.45 g, 2 mmol) at -20 °C was added $SbCl_5$ (1.20 g, 4 mmol) slowly with stirring. A white precipitate formed during the addition of $SbCl_5$. After the reaction mixture was stirred for 30 min at -20 °C and then for 15 min at 0 °C, the precipitate was removed by filtration and washed with CCl_4 at -20 °C to give a white powder. The solid was washed three times with CCl_4 and dried *in vacuo*. Yield 0.62 g. ^{1}H NMR (SO_2, -20 °C): 8.03 (2H, d, J = 7.5 Hz), 7.79 (1H, t, J = 7.5 Hz), 7.77 (2H, t, J = 7.5 Hz), 5.19 (4H, q, J = 7.0 Hz), 1.68 (6H, t, J = 7.0 Hz). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of CCl_4 into a CH_2Cl_2 solution of **3** at -20 °C.

Dimethoxy(*p*-methoxyphenyl)methylium Hexachloroantimonate, 4. Yield 0.49 g of yellow crystals. ^{1}H NMR (SO_2, -20 °C): 8.14 (2H, d, J = 9.5 Hz), 7.24 (2H, d, J = 9.5 Hz), 4.72 (6H, s), 3.97 (3H, s).

Diethoxy(2,4,6-trimethylphenyl)methylium Hexachloroantimonate, 5. Yield 0.87 g of yellow crystals. ^{1}H NMR (SO_2, -20 °C): 7.09 (2H, s), 5.10 (4H, q, J = 7.0 Hz), 2.40 (3H, s), 2.36 (6H, s), 1.64 (6H, t, J = 7.0 Hz).

X-ray Data Collection and Reduction. Crystals of **3**–**5** were obtained by vapor diffusion of CCl_4 into CH_2Cl_2 solutions of the respective compounds at –20 °C. Suitable crystals were selected and sealed in Lindemann capillaries under a nitrogen atmosphere. Diffraction experiments were performed at low temperature on a Nicolet P3 diffractometer for **3** (173 K) and **4** (153 K) and a Siemens R3m/V for **5** (193 K), using Mo Kα (λ = 0.71069 Å). The initial orientation matrices were obtained from 15 machine centered reflections for **3** (22.1° < 2θ < 28.4°) and **4** (18.37° < 2θ < 25.18°), and 29 machine centered reflections for **5** (20.11° < 2θ < 27.74°). The observed extinctions were consistent with the orthorhombic space group $Pbn2_1$ for **3** and the monoclinic space group $P2_1/n$ for **4** and **5**. For **3** and **4** $h,k,\pm l$ data ($2\theta \leq 45°$) were collected, while $\pm h,k,l$ data ($2\theta \leq 45°$) were collected for **5**. In each case, standard reflections were monitored and showed no statistically significant change during data collection. Data were collected with a scan range of 1.0° below Kα_1 and 1.0° above Kα_2, using a background to scan time ratio of 0.5. Corrections were made for Lorentz-polarization factors for all data. Semiempirical absorption corrections were applied to the data for **4** and **5**.

Structure Solution and Refinement. The coordinates of the antimony atoms were found from three-dimensional Patterson syntheses for **3** and **4**, while direct methods was used for **5**. Full-matrix least-squares refinements of these coordinates, followed by a three dimensional electron density synthesis, in each case, revealed the positional parameters of all the non-hydrogen atoms and confirmed those of the heavy atoms. The refinements were carried out using full-matrix least-squares techniques on F, minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$, where the weight, ω, is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. The temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic, and further cycles of refinement revealed the positional parameters of the hydrogen atoms. The hydrogen atoms were included in the final cycles with fixed U values of 0.05 Å^2 for **3** and 0.06 Å^2 for **5**. The isotropic thermal parameters for all of the hydrogens in **4** were refined to a value of 0.0446 Å^2. Correction for secondary extinctions was not necessary for any of the structures. Throughout the refinement, scattering curves and anomalous dispersion corrections were applied to the curves for antimony and chlorine. All calculations were performed on a VAX 6420 computer. Programs used for **3** and **4** include XTAL[36] for data reduction and least-squares plane calculations, SHELXS-86 for structure solution, and SHELX-76[37] for structure refinement. For **5**, the system used was SHELXTL PLUS[38] for data reduction and structure solution and refinement. All thermal ellipsoid plots were created using SHELXTL PLUS (PC Version).[39] Crystal data are given in Table 4. Positional parameters are given in Table 5. Selected bond lengths and angles are given in Table 6, and least-squares planes calculations are given in Table 7.

Acknowledgment. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada. Dr. C. Campana of Siemens Analytical X-ray Instruments, Madison, WI, is thanked for assistance with the X-ray crystal structure of diethoxy(2,4,6-trimethylphenyl)methylium hexachloroantimonate.

Supplementary Material Available: Anisotropic displacement coefficients (Table S1), anion bond lengths and angles (Table S2), hydrogen atom parameters (Table S3), and packing diagrams (Figure S1, **3**; Figure S2, **4**; Figure S3, **5**) (12 pages); observed and calculated structure factors (41 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[35] McClelland, R. A.; Mahmood, A. *J. Am. Chem. Soc.* **1977**, *99*, 5356.

[36] Stewart, J. M.; Hall, S. R. The XTAL System of Crystallographic Programs Tech. Rept. TR-1364, University of Maryland, College Park, MD, 1983.

[37] Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.

[38] SHELXTL-PLUS 4.2, Siemens Crystallographic Research Systems, Siemens Analytical X-ray Instruments, Inc., May 1990.

[39] SHELXTL-PC 4.1, Siemens Crystallographic Research System Analytical X-ray Instruments, Inc., May 1990.