

¹³C NMR/DFT/GIAO Studies of Phenylene Bis(1,3-dioxolanium) Dications and 2,4,6-Triphenylene Tris(1,3-dioxolanium) Trication

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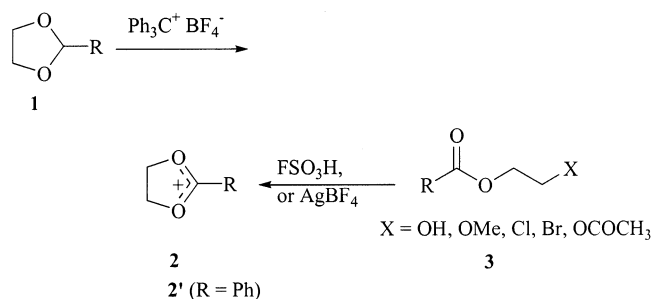
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The *o*-, *m*-, and *p*-phenylene bis(1,3-dioxolanium) dications (**4**–**6**) and 2,4,6-triphenylene tris(1,3-dioxolanium) trication (**7**) have been prepared by the ionization of the corresponding 2-methoxyethyl benzoates in FSO₃H or CF₃SO₃H at 40 and 60 °C, respectively. The charge delocalization in these carbocations was probed by ¹³C NMR chemical shifts and substantiated by GIAO/DFT calculations. Relatively less charge is delocalized into the aromatic ring of the carbocation **7**. The rotational barrier around the C⁺–Ar bond for carbocations **4** and **5** was also estimated to be 8–10 kcal/mol.

Introduction

The dioxolanium carbocations are among the most stable among the heteroatom-stabilized carbocations. These carbocations along with their sulfur analogues have been extensively investigated for synthetic applications as well as for mechanistic studies. They can be readily prepared by hydride abstraction of the corresponding 1,3-dioxolanes using trityl tetrafluoroborates or dehydrative cyclization of 2-hydroxyethyl esters or by Meerwein's method using equimolar amounts of 2-bromoethyl esters and silver tetrafluoroborate.^{1–7} The dioxolanium cations were also used as initiators for the polymerization of 1,3,5-trioxanes,⁸ cyclic siloxanes,⁹ tetrahydrofuran,¹⁰ and cationic graft copolymerization of tetrahydrofuran to polystyrene.¹¹



Analogous carbocations and trications would be ideally suited for the preparation of diblock- and star-

type polymers, respectively. Tomalia and Hart reported the synthesis and ¹H NMR-characterization of the dioxolanium carbocations and trications.¹² The structures of these carbocations were, however, inconclusive as ¹H NMR chemical shifts could not reliably distinguish monomers and dications. Our interests in the cationic polymerization using carbopolycations prompted us to develop convenient synthetic methods for the synthesis of these carbocations and trications. Here, we report the ¹³C NMR characterization of the selected dioxolanium carbocations and a carbocation. We have also calculated the structures and ¹³C NMR chemical shifts of these carbocations using the GIAO (gauge-including atomic orbital)/DFT (density functional theory) method for comparison.

Results and Discussion

The dioxolanium carbocations can be readily obtained by hydride exchange of the corresponding dioxolanes using trityl cation salts. However, this method could not be used for these carbocations, as the initially formed carbocation can initiate the polymerization of the unreacted dioxolane ring. Synthetic methods using silver tetrafluoroborate are also inconvenient for the large-scale preparations. We have found that the *o*-, *m*-, and *p*-phenylene bis(1,3-dioxolanium) dications (**4**–**6**) and 2,4,6-triphenylene tris(1,3-dioxolanium) trication (**7**) can be

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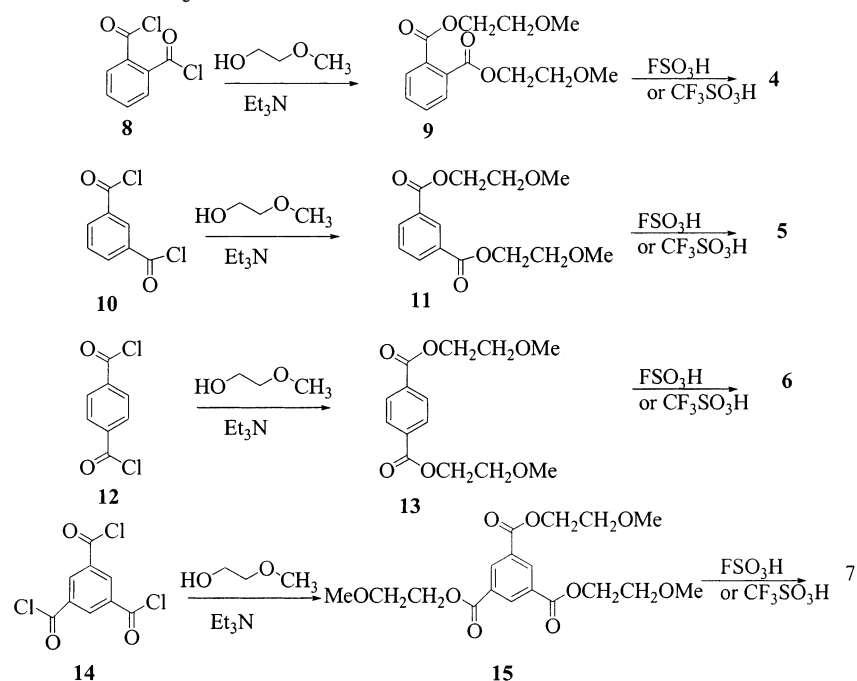
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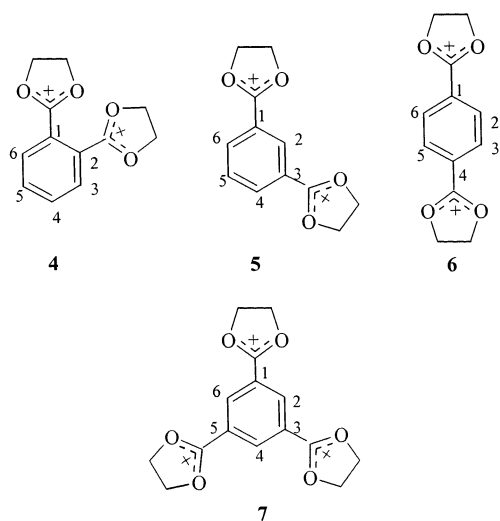
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SCHEME 1. Preparation of Phenylene Bis(1,3-dioxolanium) Dications and Tris(1,3,5-dioxolanium Trication



conveniently prepared by the ionization of the corresponding 2-methoxyethyl benzoates (e.g., **9**).



The reaction of the 1,2-, 1,3-, and 1,4-benzenedicarbonyl chloride or the 1,3,5-benzenetricarbonyl chloride with 2-methoxyethanol in the presence of triethylamine gave the corresponding esters, which could be directly ionized using fluorosulfonic acid or triflic acid to give the carbocations **4–6** and the carbocation **7** at moderate temperatures as illustrated in Scheme 1 for the preparation of carbocation **4**. The ionization in FSO_3H takes place under relatively milder conditions than that for the triflic acid. Typically, the ionizations were carried out at 40 °C in neat FSO_3H and 60 °C in neat triflic acid. The formation of these carbocations is complete in about 30 min under these conditions. The progress of these reactions can be readily followed by ^{13}C NMR spectroscopy using a variable-temperature probe. These carbocations and the carbocation were stable in superacidic media for extended times, even up to 100 °C.

We could not obtain satisfactory ^1H NMR spectra of the cations because of enormous proton signal of the acid media. Furthermore, in neat acid solutions the peaks were relatively broad.

We have calculated the structures and ^{13}C NMR chemical shifts of the ions by the GIAO/DFT method and compared the results with the experimental data. The structures were fully optimized at the B3LYP/6-31G* level using the Gaussian-98 package of programs. The bond lengths of the minimum energy structures are given in Table 2. The ^{13}C NMR chemical shift of the ions were calculated by the GIAO/DFT method using B3LYP/6-31G* geometries.

The experimental ^{13}C NMR chemical shifts for these carbocations can be readily assigned by comparison with those calculated using GIAO/DFT method (Table 1). It is interesting to note that the *o*-, *m*-, and *p*-phenylene dications have very similar ^{13}C chemical shifts for the carbocationic centers ($\delta^{13}\text{C}$ 182.7, 182.3, and 182.2, respectively). The equivalence of the NMR chemical shifts is also in accordance with those calculated by the GIAO/DFT method ($\delta^{13}\text{C}$ 188.5, 187.4, and 188.3, respectively, for **4**, **5**, and **6**). The corresponding $\delta^{13}\text{C}$ for the carbocation, 2-phenyl-1,3-dioxolan-2-ylum cation (182.9 ppm) is also strikingly similar, suggesting the extensive charge delocalization into the neighboring oxygens for the mono-, di-, and tricarbocations.

The ^{13}C NMR chemical shifts for the cationic centers often reflect their stability for closely related carbocations. In other words, the more stable carbocations show relatively shielded chemical shifts. Interestingly, for these carbocations, the calculated (Table 2) relative energies of the meta and para isomers (**5** and **6**), as obtained from the DFT (at B3LYP/6-31G**/B3LYP/6-31G* + ZPE level), are very close to each other; the meta isomer (**5**) is only 0.3 kcal/mol more stable than that of the para isomer (**6**). The energy difference for the carbocations **4** (ortho isomer) and **5** (meta isomer) at

TABLE 1. ¹³C NMR Data (Multiplicity and *J*, Hz, in Parentheses) and GIAO/DFT δ¹³C Values in Brackets) for Carbomonocation **2**, Carbodications **4**, **5**, and **6**, and Carbotrication **7**

ions	C ⁺	C1	C2	C3	C4	C5	C6	CH ₂
2 ^a	182.9 [188.0]	116.7 [117.2]	134.3 [142.0]	131.0 [137.6]	142.2 [154.7]	131.0 [137.6]	134.3 [142.0]	75.6 [76.4] ^b
4	182.2 [188.5]	118.2 (s) [121.6]	118.2 (s) [121.6]	141.3 (dd, 173.7) [150.6]	139.7 (dd, 178.6) [152.4]	139.7 (dd, 178.6) [152.4]	141.3 (dd, 173.7) [150.6]	77.9 (t, 169) [80.8] ^b
5	182.3 (s) [187.4]	119.8 (d, 8) [123.2]	133.6 (d, 174.9) [145.7]	119.8 (d, 8) [123.2]	144.3 (dt, 172.7) [154.6]	138.1 (dt, 174.7) [141.7]	144.3 (dt, 172.7) [154.6]	77.5 (t, 165) [81.1] ^b
6	182.2 (s) [188.3]	125.7 (t, 10) [131.3]	133.9 (d, 175) [142.6]	133.9 (d, 175) [142.6]	125.7 (t, 10) [131.3]	133.9 (d, 175) [142.6]	133.9 (d, 175) [142.6]	77.5 (t, 165) [81.5] ^b
7	188.6 (s) [185.6]	130.4 (s) [128.3]	153.8 (dt, 178.6) [154.4]	130.4 (s) [128.3]	153.8 (dt, 178.6) [154.4]	130.4 (s) [128.3]	153.8 (dt, 178.6) [154.4]	86.9 (t, 167) [85.5] ^b

^a From ref 6. ^b Average.

TABLE 2. Total Energies (–au), ZPE^a (kcal/mol), Relative Energies^b (kcal/mol), and Rotational Barrier^b (kcal/mol)

ion	B3LYP/6-31G*//B3LYP/6-31G*	ZPE	rel energy	rotational barrier
2	498.57947	101.1		14.4
4	764.77582	139.9	15.0	4.7
5	764.79989	140.0	0.0	9.8
6	764.79959	139.9	0.3	8.4
7	1030.92948	178.3		8.3

^a Zero-point vibrational energy (ZPE) at B3LYP/6-31G*//B3LYP/6-31G* scaled by a factor of 0.98; ^b Relative energy and rotational barrier at B3LYP/6-31G*//B3LYP/6-31G* + ZPE level.

this level of calculation is, on the other hand, much higher; i.e., carbodication **4** is 15.0 kcal/mol higher in energy as compared to the carbodication **5** (Table 2). This can be explained in terms of higher steric constraints in the carbodication **4**, as well as charge–charge repulsion due to conjugation.

It is, however, difficult to rationalize the extent of charge–charge delocalization into the aromatic ring in dications **4–6** based on ¹³C NMR chemical shifts of the ring carbons alone. The meta-substituted carbocations **5** should be able to delocalize more positive charge into the aromatic ring compared to ortho- and para-substituted analogues **4** and **6** (vide supra). The minimum energy structures of the dications **4**, **5** and **6** were found to be of C₂, C_{2v}, and D_{2h} symmetry (Table 3) with the C⁺–C1 bond distances of 1.456, 1.453, and 1.460 Å, respectively. For comparison, the structure of the monocation **2** was also computed and listed in Table 3. Optimized structure indicates that the oxolanium ring of dication **4** is rotated out of the benzene ring plane around the C⁺–C1 bond by about 20°.

As can be seen from Table 1, the GIAO/DFT-derived δ¹³C at the B3LYP/6-311G*//B3LYP/6-31G* level of theory match closely with the experimental values. The δ¹³C values for the carbocationic center are deshielded from those of the experimental values by 6.3, 5.1, and 6.1 ppm for the ortho-, meta-, and para-substituted carbodications (**4**, **5**, and **6**), respectively. At higher levels (e.g., ab initio correlated GIAO-MP2 method), the discrepancies may be eliminated. Due to the relatively large number of basis sets involved for these molecules, such calculations could not be carried out. However, the relative trends in these chemical shifts are consistent with the experimental values. Similar deviations are also obtained at this level of calculations for other carbocations.^{13,14} In ions **4** and **5**, there are significant rotational

barriers around the carbocationic center and the aromatic ring (C⁺–Ar bond). At the B3LYP/6-31G*//B3LYP/6-31G* + ZPE level these barriers are estimated as 4.7 and 9.8 kcal/mol for the carbodications **4** and **5**, respectively. Attempts of measuring these barriers experimentally were not successful as, even at –70 °C, the methylene carbons show only broadened signals, but do not merge with the baseline. An upper limit of 8–10 kcal/mol can be estimated for these rotational barriers, based on the significant line broadening at –70 °C.

The carbotrication **7**, obtained from the ionization of the tris(2-methoxyethyl)-1,3,5-benzene tricarboxylate in FSO₃H at 40 °C, showed much higher deshielded δ¹³C for the methylene carbons (δ¹³C 86.7), as compared to the carbodications **4–6**. This points to the enhanced resonance stabilization of the cationic centers by the adjacent oxygen atoms, to minimize the electrostatic repulsion between the carbocationic centers. The relatively less delocalization of the positive charge into the aromatic ring is also evidenced by the fact that the *ipso*-carbons appear at δ¹³C 130.4, which is 10 ppm more deshielded from those of the related carbodications. The enhanced deshielding of the *ipso*-carbons can be explained by the more efficient electron-withdrawing inductive effect of the dioxolanium rings. The minimum energy structure for the trication was found to be of D_{3h} symmetry (Table 3) with the C⁺–C1 bond distance of 1.471 Å.

We have also computed ¹⁷O NMR chemical shifts at the GIAO/DFT B3LYP/6-311G*//B3LYP/6-31G* level. The monocation **2** shows the most shielded shift at δ¹⁷O 223.1 (with respect to δ¹⁷O H₂O). On the other hand, the ortho- and para-substituted dications **4** and **6** indicate comparable deshielded shifts at δ¹⁷O 254.7 and 255.8, respectively. This indicates that there is more positive charge localization in these systems (charge delocalization into the aromatic ring results in vicinal dicationic resonance structure). Interestingly, in the meta isomer, **5**, wherein delocalization can only lead to 1,3-dicationic resonance structure, the charge localization on oxygen is relatively less as reflected by its ¹⁷O NMR chemical shift (δ¹⁷O 248.4). Finally, the trication **7** shows the most localization of the positive charge at δ¹⁷O 265.6.

In summary, we have prepared the dioxolanium carbodications (**4–6**) and dioxolanium trication (**7**) by a novel and convenient method and characterized their struc-

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TABLE 3. Selected Optimized Bond Lengths (Å)

ion	C ⁺ –C1	C ⁺ –O	H ₂ C–O	H ₂ C–CH ₂	C1–C2	C2–C3	C3–C4	C4–C5
2 (C _{2v})	1.429	1.302	1.469	1.540	1.414	1.386	1.401	
4 (C ₂)	1.456	1.292 ^a	1.485 ^a	1.538	1.435	1.402	1.402	1.390
5 (C _{2v})	1.453	1.285 ^a	1.486 ^a	1.541	1.402	1.402	1.413	1.393
6 (D _{2h})	1.460	1.288	1.486	1.541	1.408	1.389	1.408	1.389
7 (D _{3h})	1.471	1.283	1.499	1.543	1.404	1.404	1.404	1.404

^a Average.

tures by comparing the GIAO/DFT-derived $\delta^{13}\text{C}$ with the experimental values. The meta- and para-substituted carbocations (**5** and **6**) are similar in energy, while the ortho-substituted carbocation (**4**) is much higher in energy, reflecting increased steric hindrance in the latter cation, which precludes significant resonance stabilization from the aromatic ring. The carbocation **7**, on the other hand, derives much less stabilization through delocalization into the aromatic ring.

Experimental Section

Triflic acid and FSO₃H were freshly distilled prior to use. Diethyl ether, triethylamine, 2-methoxyethanol, and the aromatic acid chlorides were used as received. ¹H and ¹³C NMR were recorded on a 300 MHz superconducting NMR spectrometer, equipped with a variable-temperature probe, and were referenced with respect to the residual solvent absorptions ($\delta^1\text{H}$ CHCl₃ = 7.27, and $\delta^{13}\text{C}$ CHCl₃ = 77.0). The spectra were referenced with respect to the external capillary tetramethylsilane for carbocations. Interpretation of the ¹³C NMR data was facilitated by the acquisition of both proton-decoupled and the proton-coupled ¹³C NMR spectra, as well as the APT (attached proton test) experiments. Where applicable, the smaller *J* values, indicated next to the directly coupled *J* values, in the ¹³C NMR correspond to the long-range *J* values.

General Procedure for the Preparation of 2-Methoxyethyl Benzoates. The acid chloride was dissolved in diethyl ether, 2 molar equiv of triethylamine was added to the contents, and the mixture was cooled to 0 °C. The 2-methoxyethanol was then added dropwise to the contents using a hypodermic syringe. A white precipitate of triethylamine hydrochloride separated during the addition. Workup involving washing with 5% HCl and saturated sodium bicarbonate solutions provided the esters in nearly quantitative yields, essentially pure by NMR analysis. Further purification was achieved by distillation at reduced pressures. Compound **9**:¹⁵ $\delta^{13}\text{C}$ 131.93 (s, Ar–C1, C2), 131.12 (d, *J* = 158.6 Hz, Ar–C3, C6), 129.02 (d, *J* = 160.4 Hz, Ar–C4, C5), 70.23 (t, CO₂CH₂), 64.67 (t, CH₂O), 58.97 (q, OCH₃), 167.55 (s, >C=O); $\delta^1\text{H}$ 7.76 (dd, 2 H, *J* = 5.8, 3.0 Hz, aromatic C₃-H, C₆-H), 7.53 (dd, 2 H, *J* = 5.8 Hz, 3.0 Hz, aromatic C₄-H, C₅-H), 4.46 (t, 4 H, *J* = 4.6 Hz, CO₂CH₂), 3.69 (t, 4 H, *J* = 4.6 Hz, CH₂OMe), 3.40 (s, 6 H, OCH₃).

Compound **11**:¹⁶ $\delta^{13}\text{C}$ 130.38 (d, *J* = 7.8 Hz, Ar–C1, C3), 128.45 (d, *J* = 163.5 Hz, Ar–C2), 133.89 (dt, *J* = 157.9, 7.3 Hz, Ar–C4, C6), 130.82 (dt, *J* = 167.1, 5.9 Hz, Ar–C5), 70.31 (t, *J* = 141 Hz, CO₂CH₂), 64.26 (t, *J* = 147.4 Hz, CH₂O), 58.94 (q, *J* = 141 Hz, OCH₃), 165.62 (s, >C=O); $\delta^1\text{H}$ 8.74 (d, 1 H, *J* = 1.22 Hz, aromatic C₂-H), 8.26 (dd, 2 H, *J* = 7.8, 1.83 Hz, aromatic C₄–C₆-H), 7.54 (t, 1 H, *J* = 7.6 Hz, aromatic C₅-H), 4.51 (t, 4 H, *J* = 4.7 Hz, CO₂CH₂), 3.75 (t, 4 H, *J* = 4.7 Hz, CH₂OMe), 3.44 (s, 6 H, OCH₃), 3.44 (s, 6 H, OCH₃).

Compound **13**:^{16–18} $\delta^{13}\text{C}$ 133.78 (s, Ar–C1, C4), 129.52 (d, *J* = 166.7 Hz, Ar–C2, C3, C5, C6), 70.29 (t, *J* = 146.5 Hz, CO₂–

CH₂), 64.31 (t, *J* = 148.1 Hz, CH₂O), 58.9 (q, *J* = 141 Hz, OCH₃), 165.65 (s, >C=O); $\delta^1\text{H}$ 7.22 (s, 4 H, aromatic H), 3.6 (t, 4 H, *J* = 4.7 Hz, CO₂CH₂), 2.84 (t, 4 H, *J* = 5.4 Hz, CH₂–OMe), 2.53 (s, 6 H, OCH₃).

Compound **15**:¹⁹ $\delta^{13}\text{C}$ 131.03 (s, Ar–C1, C3, C5), 134.85 (d, *J* = 168.2 Hz, Ar–C2, C4, C6), 70.27 (t, *J* = 144.5 Hz, CO₂CH₂), 64.66 (t, *J* = 148 Hz, CH₂O), 59.02 (q, *J* = 141.52 Hz, OCH₃), 164.94 (s, >C=O); $\delta^1\text{H}$ 8.90 (s, 3 H, aromatic H), 4.53 (t, 6 H, *J* = 4.6 Hz, CH₂OMe), 3.76 (6 H, t, *J* = 4.6 Hz, CH₂OMe), 3.44 (s, 9 H, OCH₃).

Preparation of the Carbocations. Approximately 10 mg of the sample was dissolved in triflic acid or FSO₃H in a 5 mm NMR tube at –78 °C (dry ice/acetone bath) and was followed by warming in the NMR probe to desired temperatures. The formation of the carbocations and the trication is quantitative as shown by the complete disappearance of the starting materials.

Computational Methods. The structures, energies and ¹³C NMR chemical shifts of the carbocations were calculated using Gaussian-98²⁰ series of programs. The structures of the carbocations were fully optimized at the B3LYP/6-31G* level. Vibrational frequencies were calculated at this level to characterize the stationary points as minima (NIMIG = 0), and to obtain the zero point energies, which were scaled by 0.98.²¹ The calculations of ¹³C NMR chemical shifts were performed using GIAO/DFT method²² at the B3LYP/6-311G* level using B3LYP/6-31G* geometries. ¹³C NMR chemical shifts were referenced to tetramethylsilane (TMS) (calculated absolute shift, i.e., $\sigma(\text{C}) = 183.8$). ¹⁷O NMR chemical shifts were referenced to H₂O (calculated absolute shift, i.e., $\sigma(\text{O}) = 332.4$).

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Supporting Information Available: Cartesian coordinates and energies of the optimized structures **2** and **4**–**7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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