

An Observable Model for the S_N2 Transition State [1a]. Hypervalent Trigonal Bipyramidal Carbon (10-C-5) [1b]

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Received 5 November 1992

ABSTRACT

Dicationic 10-C-5 species **14**, formally two-electron oxidation products of 1,8-bis(arythio)-9-(2,6-dimethoxyaryl)-10-phenylanthracenes, are prepared and characterized by NMR spectroscopy. Evidence is presented for a bis-sulfonium structure containing a hypervalent trigonal bipyramidal (TBP) carbon atom. Dicationic species **14**, prepared by the reaction of the appropriate diol with strong acid in liquid sulfur dioxide or sulfurylchlorofluoride, are stable for indefinite periods at room temperature in these solutions. Structural features common to these compounds which stabilize the TBP geometry sufficiently to allow their direct observation are as follows: (a) electronegative apical ligands (sulfonium sulfur atoms), (b) five-membered rings linking each apical position to an equatorial position, (c) geometric constraints built into the tridentate ligand in a pattern designed to stabilize TBP, relative to tetrahedral carbon, (d) three relatively electropositive (σ -donor) equatorial ligands, which decrease the effective electronegativity of the central carbon atom of the three-center bond, (e) a strain-free, bidentate π -acceptor equatorial ligand with its π -axis parallel with the electron-rich three-center four-electron bond axis, and (f) possible residual aromaticity (bis-*ipso*-aromaticity) in the equatorial six-membered ring incorporating the hypervalent carbon atom.

A low-temperature ¹⁹F NMR study of **14b** sets an upper limit for $\Delta G^\ddagger_{-100^\circ\text{C}}$ of ca. 4 kcal/mol for a hypothetical process which would interconvert unsymmetrical species **30** and **30'** if such a tautomeric mixture were to represent the structure of **14**. Evidence

against such a tautomeric equilibrium is adduced from the upfield shift of 0.65 ppm observed for the proton meta to the two methoxyl substituents of dication **14a** relative to the comparable proton in **21a**, the model dication lacking one of the two arylthio substituents of **14a**. This is most easily explained by postulating a nucleophilic interaction of the second thioaryl group in **14** at the hypervalent, 10-C-5 carbon.

INTRODUCTION

The ability of many nonmetallic elements to undergo formal expansion of the electronic valence shell beyond the Lewis-Langmuir octet adds an important dimension to the chemistry of these elements. The hypervalent [2] bond approximation for these species, as formulated by Musher [3], emphasizes the electron-rich three-center four-electron (hypervalent) bond joining the central atom to the two apical ligands [4]. The usual molecular orbital approximation for this bond is pictured in Figure 1. A linear array of three atomic *p*-orbitals, one from each atom, is used to create three molecular orbitals which hold four electrons. For trigonal bipyramidal (TBP) species, other ligands or

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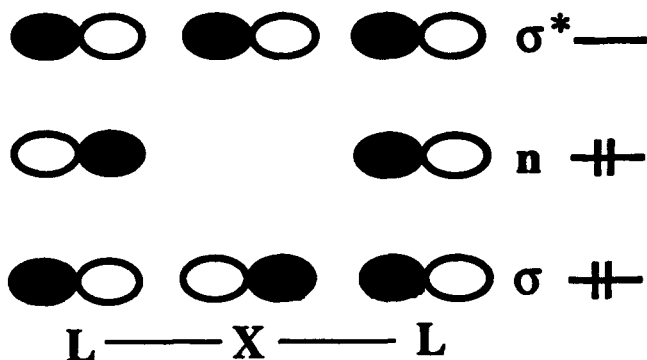


FIGURE 1 An approximate orbital picture for the three-center, four-electron (hypervalent) bond joining two apical ligands, L, to a central atom, X.

electron pairs occupy the three equatorial sites with approximately sp^2 bonds from the central atom.

Four structural factors have been proposed to stabilize TBP hypervalent species: (a) Electronegative apical σ -acceptor ligands [5] are effective in accommodating the charge distribution at the apical positions of TBP species. Two electrons in the hypervalent bond are associated only with the apical ligands in the roughly nonbonding orbital (n). This increases the electron density at these ligands, producing negative charge stabilized by electronegative σ -acceptor ligands at the apical positions. (b) The positive charge developed at this central atom is stabilized by an electropositive atom at this position [6]. (c) Electropositive σ -donor equatorial ligands stabilize this charge distribution by making the central atom effectively more electropositive. (d) Stabilization of hypervalent TBP compounds, relative to their tetrahedral heterolysis products, is also provided via the five-membered ring effect. In TBP species in which axial and equatorial sites of the TBP species are linked in a five-membered ring, an essentially strain-free geometry is provided for the ca. 90° angle between apical and equatorial bonds typical of TBP geometry. The importance of the five-membered ring effect in the chemistry of nonmetals was established, in the seminal researches of Westheimer and his co-workers [7], in kinetic studies of phosphate esters. Other stabilizing effects have also been suggested by calculations [8].

The hypervalent bond approximation is useful in describing the bonding in a wide variety of derivatives of nonmetallic elements above the second row of the periodic table [3,4]. Early explanations for the stability of species of hypervalent nonmetals above the second row of the periodic table generally point to the availability of low-lying d -orbitals of the central atom in such species. Nuclear quadrupole resonance [9,10] spectra of hypervalent (10-I-3) iodine species, however, suggest no significant contribution of d -orbitals in the bond-

ing of the central atom (iodine) to its ligands. A wide variety of quantum mechanical calculations [8] also agree that d -orbitals are unnecessary to provide an adequate picture of the energetics of such species for the simplified picture of the hypervalent bond. We can conclude, therefore, that the contribution of d -orbitals, and other higher atomic orbitals, in the description of the three-center four-electron bond is unnecessary to explain their existence or invoke their stability.

The question therefore arises as to why hypervalent derivatives of second-row elements (boron, carbon, nitrogen, oxygen, and fluorine) have been so elusive to synthesis or observation. One possible explanation for carbon comes from a recent theoretical treatment aimed at modeling the bonding and explaining stability differences in simple trigonal bipyramidal systems of carbon and silicon. A quantitative curve crossing valence bond comparison of TBP CH_5^- and SiH_5^- has suggested [11] that effective delocalization of electron density from the axial bond which bonds the central atom (Si) with the apical ligands and the central atom into the σ^* -orbital of the central atom and equatorial ligands accounts for the existence and stability of the trigonal bipyramidal species SiH_5^- . This species has now been synthesized and characterized in the gas phase [12]. In contrast, this mode of delocalization is destabilizing for trigonal bipyramidal CH_5^- , and the unavailability of this mode of electron delocalization is suggested to account for the lack of stable existence [11] for TBP CH_5^- . Experimental evidence also suggests [13] that the TBP geometry represents not an intermediate but a transition state in displacement reactions at carbon in simple systems such as displacements of halide from methyl halides by halide ion in the gas phase. Theoretical calculations [14] of substitution reactions at carbon in similarly simple systems also agree that the TBP geometry about carbon represents an energy maximum.

The necessity for low-lying unfilled atomic or antibonding electron-acceptor orbitals at the second row central atoms as a condition for the observation of hypervalent species is certainly negated by the stability of the familiar symmetrical, linear bifluoride ion (HF_2^-) and other symmetrically hydrogen bonded species [15]. The valence orbitals of the next principal quantum level are prohibitively high in energy for any significant contribution in the hypervalent bonding picture for hydrogen [16].

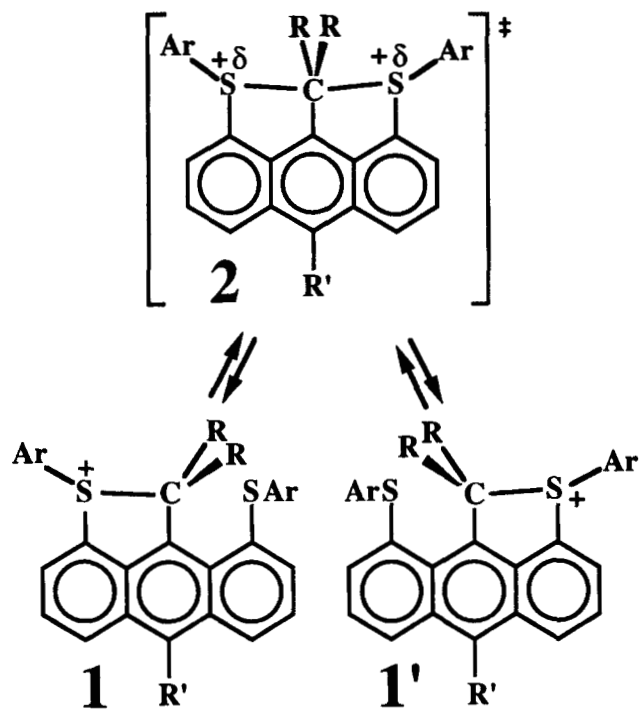
The chemical literature is not devoid of reports of attempts to produce hypervalent derivatives of second row atoms. An early attempt by Wittig [17] to obtain a stable species of hypervalent nitrogen (10-N-5), a species analogous to the phosphoranes (10-P-5), by the addition of a carbon nucleophile to a quaternary ammonium salt gave an ammonium ylide instead. Evidence, interpreted in terms of a

mechanism involving an intermediate, but not observed, derivative of hypervalent nitrogen, NH_5 , was reported [18]. Further work [19] on this same system supported an alternative mechanism not involving the intermediacy of NH_5 .

Despite the lack of evidence for stable derivatives of hypervalent carbon [20–24], there have been recurring suggestions that the TBP geometry about carbon at the midpoint of Walden inversion represents an intermediate rather than the transition state for associative displacement reactions at carbon, e.g., the Doering-Zeiss [25] mechanism of solvolysis, or the Winstein [26a] merged mechanism for substitution-elimination reactions later withdrawn [26b]. Sneen's mechanism [27] for the S_N2 displacement invoked solvated ion-pair intermediates which could be formally viewed as 10-C-5 species, although the apical ligands were postulated to be held to the central TBP carbon primarily by electrostatic forces.

Some accounts of efforts to prepare compounds in which additional structural features stabilize the possible TBP intermediate in a displacement on carbon sufficiently to make the TBP structure an intermediate have been reported. These include studies of substitution reactions at a carbon atom which is incorporated into a three- [28] or four-membered [29] ring. The midpoint of the Walden inversion for such species is expected to be stabilized by the small ring effect [7] resulting from the linkage of an equatorial to an apical position at TBP carbon. If such stabilization were sufficient to make this geometry an energy minimum, it might exist for a time sufficient to allow permutational interconversion of TBP isomers. This could lead to the observation of an associative nucleophilic displacement at carbon with retention, rather than the usual inversion, of configuration. Although two systems have been initially suggested to undergo such reactions, alternative explanations for the observed retention of configuration have prevailed [28,29].

A previous attempt was made by Basalay and Martin [30] to prepare a compound (**2**) in which the TBP geometry about 10-C-5 carbon is more stable than the unsymmetrical 8-C-4 tetrahedral carbon species derived from it by apical bond heterolysis (**1**). Although the ground state for the molecules which were prepared proved to be unsymmetrical sulfonium species of type **1**, the degenerate exchange reaction interconverting **1** and **1'** proved to be very rapid via an associative mechanism with **2** as its transition state. The compounds of type **1** showing the most rapid interconversions in what was called [31] the "bell-clapper rearrangement," were the examples with the more electronegative apical ligands, those with electron-withdrawing substituents on the thioaryl rings. The activation energy for these processes, presumably the difference in energy between **1** and **2**, was as



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low as 10 kcal/mol. Further attempts [32] to prepare more distant analogs of transition state structure **2** with increased electronegativity of the apical ligands resulted in molecules which adopted an alternative ground state structure and also failed to provide observable examples of structures related to **2**.

A related intramolecular displacement at carbon of sulfonium sulfur by sulfide sulfur in which the sulfur atoms were included in six-membered, rather than five-membered, rings was found [33] to proceed by a dissociative mechanism rather than an associative one via TBP carbon.

Despite this overwhelming evidence against simple species of second-row elements with extended coordination spheres involving hypervalent bonding, several reports of observation of hypervalent species of carbon, boron, and fluorine have now appeared. The first report of such species, a TBP hypervalent carbon (10-C-5) species [1a], is the preliminary publication to the expanded work which we now report. By use of related stabilizing molecular features previously developed [1a] with the hypervalent carbon species, hypervalent species of boron, including pentacoordinate neutral species and anion (10-B-5) species, as well as a hexacoordinate anion (12-B-6) species, have been synthesized and characterized [34]. Also, a report [35] of infrared and Raman spectroscopic data of a species observable in an argon matrix presents evidence for the existence of the linear trifluoride anion, F_3^- , a 10-F-2 hypervalent species of fluorine.

We have approached the problem of designing a molecule with a 10-C-5 ground state by considering structure-stability relationships from two domains: (a) those involving observable TBP species of hypervalent nonmetallic elements above the second row of the periodic table and (b) those involving TBP carbon in the transition state of the S_N2 reaction. We now detail the synthesis of molecular species postulated to be the first observable 10-C-5 species and present strong evidence supporting this structural hypothesis.

EXPERIMENTAL

Starting materials were purchased from Aldrich Chemical Company. Sulfur dioxide was dried as a liquid over P_2O_5 before distillation using vacuum-line techniques. Microanalyses performed by Mr. J. Nemeth and associates are within 0.4% of the theoretical value for the elements listed. Melting points were obtained using a micro hot stage. Chemical shifts are reported in parts per million (ppm) downfield of tetramethyl silane (TMS) for 1H and ^{13}C and downfield of $CFCl_3$ for ^{19}F .

General Method for the Preparation of Arylthio-Substituted Anthraquinones **4** and **18**

In 1.7 L of pyridine, 0.35 mol of 1-chloroanthraquinone (**17**) or [1,8-dichloro-anthraquinone (**13**)], 0.36 mol [or 0.72 mol for **3**] of the appropriately substituted thiophenol, and 0.36 mol [or 0.72 mol for **3**] of Cu_2O were boiled for 48 hours under N_2 . The solution was poured into a mixture of ca. 2.5 L of ice and 2 L of concd HCl. A solution of the precipitate in $CHCl_3$ was washed with H_2O and then dried ($MgSO_4$). Solvent was removed in vacuum to give the crude product. The reported amounts of products are conversions, based on the amount of starting anthraquinone.

1,8-Bis(4-methylphenylthio)anthraquinone [**30**] (**4a**)

Treatment of **3** with *para*-thiocresol gave 89% of crude **4a**. Recrystallization from benzene gave orange needles (81%) of **4a**: mp 256–257°C; 1H NMR ($CDCl_3/TMS$) δ 7.97 (d, 2H, 4- and 5-anthryl C-H), 7.53–7.05 (m, 14H, ArH), 2.41 (s, 6H, CH_3); IR ($CDCl_3$) 1670, 1640 cm^{-1} . Anal. ($C_{28}H_{20}S_2O_2$) C, H, S.

1-(4-Methylphenylthio)anthraquinone (**18a**)

Treatment of **17** with *para*-thiocresol gave, after recrystallization from $CHCl_3$ /hexane, 93% of **18a**: mp 226–228°C; 1H NMR ($CDCl_3/TMS$) δ 8.41–8.16 (m, 2H, 5- and 8-anthryl CH), 8.04 (d, 1H, 4-anthryl CH), 7.57–7.03 (m, 8H, ArH), 2.43 (s, 3H, CH_3); IR ($CHCl_3$)

1670 (s), 1660 (s) cm^{-1} ; mass spectrum (10 eV) m/e (relative intensity) 330 (100, M^{+}), 239 (51, $-C_7H_7$).

1-(4-Fluorophenyl)anthraquinone (**18b**)

Treatment of **17** with *para*-fluorothiophenol gave, after recrystallization from $CHCl_3$ /hexane, 72% of **18b**: mp 208–210°C; 1H NMR ($CDCl_3/TMS$) δ 8.30–8.10 (m, 2H, 5- and 8-anthryl CH), 8.06 (d, 1H, 4-anthryl CH), 7.87–6.98 (m, 8H, ArH). Anal. ($C_{20}H_{11}SO_2F$) C, H.

1,8-Bis(4-methylphenylthio)-10-phenyl-10-hydroxy-9-anthrone [**30**] (**5a**)

An ether solution of phenylmagnesium bromide (14 mmol) was added, under N_2 , to 5.50 g (12.2 mmol) of **4a** in 400 mL of benzene. The solution was stirred 1 hour and then treated with saturated aqueous NH_4Cl . The organic layer was washed with H_2O and was then dried ($MgSO_4$). Solvent was removed in vacuum to give crude **5a**. Recrystallization from benzene gave 4.80 g (10.7 mmol, 88%) of yellow platelets of **5a**: mp 249–251°C; 1H NMR ($CDCl_3/TMS$) δ 7.58–7.03 (m, 17H, ArH), 6.74 (d, 2H, 4- and 5-anthryl CH), 2.79 (s, 1H, OH), 2.37 (s, 6H, CH_3). Anal. ($C_{34}H_{26}S_2O_2$) C, H, S.

1-(4-Methylphenylthio)-10-phenyl-10-hydroxy-9-anthrone (**19a**)

An ether solution of phenylmagnesium bromide (15 mmol) was added dropwise to a solution of 5.00 g (15 mmol) of **18a** in a minimum amount of benzene/tetrahydrofuran (THF) under N_2 at 25°C. The product was isolated as described for **5a**. Chromatography (silica gel/ $CHCl_3$) was followed by recrystallization from $CHCl_3$ /hexane. This gave 0.85 g (2.1 mmol, 14%) of yellow needles of **19a**: mp 223–225°C; 1H NMR ($CDCl_3/TMS$) δ 8.26 (d of d, 1H, 8-anthryl CH), 7.60–7.05 (m, 15H, ArH), 6.71 (d, 1H, 4-anthryl CH), 2.67 (s, 1H, OH), 2.40 (s, 3H, CH_3). Anal. ($C_{27}H_{29}SO_2$) C, H.

1-(4-Fluorophenylthio)-10-phenyl-10-hydroxy-9-anthrone (**19b**)

From 4.73 g (14.2 mmol) of **18b**, by the method described for **19a**, was obtained 1.40 g (3.3 mmol, 23%) of **19b**: mp 145–148°C; 1H NMR ($CDCl_3/TMS$) δ 8.26 (d of d, 1H, 8-anthryl CH), 7.66–6.93 (m, 13H, ArH), 6.76 (d, 1H, 4-anthryl CH), 2.97 (s, 1H, OH). Anal. ($C_{26}H_{17}SO_2F$) C, H.

Cis- and Trans-1,8-bis(4-methylphenylthio)-9-methyl-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (**6a**)

Excess methylmagnesium bromide in ether was added to 0.84 g (16.0 mmol) of **5a** in 75 mL of ben-

zene at 25°C under N₂. The solution was stirred for 1 hour and then H₂O was added. The organic layer was washed with H₂O and then dried (MgSO₄). Solvent was removed to give 0.80 g (14.7 mmol, 92%) of **6a**: mp 248–249°C. Anal. (C₃₅H₃₀S₂O₂) C, H, S.

Cis-6a and *trans-6a* were separated by preparative TLC (silica gel/CH₂Cl₂). *Trans-6a*: mp 258–259°C; ¹H NMR (CDCl₃/TMS) δ 7.50–6.70 (m, 18H, ArH), 5.20 (s, 1H, OH), 2.50 (s, 3H, CH₃), 2.36 (s, 7H, SC₆H₄CH₃ and OH). Anal. (C₃₅H₃₀S₂O₂) C, H, S. *Cis-6a*: mp 228–229°C; ¹H NMR (CDCl₃/TMS) δ 7.70–7.03 (m, 18H, ArH), 5.10 (s, 1H, OH), 2.87 (s, 1H, OH), 2.40 (s, 6H, SC₆H₄CH₃), 2.30 (s, 3H, CH₃). Anal. (C₃₅H₃₀S₂O₂) C, H, S.

2-(4-Methylphenyl)-6-phenyl-10-(4-methylphenylthio)-2-thiona-anthracene Chloride [30] (**7a**)

Dry HCl was passed through a solution of 1.48 g (3.0 mmol) of **6a** in 50 mL of methanol. All solids dissolved, and the solution turned yellow. The solvent was evaporated in a stream of N₂ which gave crude **7a**. Recrystallization from acetone gave 1.32 g (2.7 mmol, 90%) of **7a**: mp 205–208°C; ¹H NMR (CDCl₃/TMS, numbered CH values refer to acanthryl protons) δ 8.20 (d, 1H, 5-CH), 8.10 (d, 1H, 3-CH), 8.02 (d, 1H, 7-CH), 7.89 (d, 1H, 9-CH), 7.72–7.41 (m, 7H, 4-CH, 6-CH, C₆H₅), 7.24 (d, 2H, ⁺SC₆H₄CH₃, ortho to S), 7.18 (d, 2H, ⁺SC₆H₄CH₃, meta to S), 6.92 (d, 2H, SC₆H₄CH₃, meta to S), 6.80 (d, 2H, SC₆H₄CH₃, ortho to S), 6.70 (d, 1H, CH₂ hydrogen trans to Ar), 6.12 (d, 1H, CH₂ hydrogen cis to Ar), 2.37 (s, 3H, ⁺SC₆H₄CH₃), 2.18 (s, 3H, SC₆H₄CH₃); mass spectrum (field desorption) *m/e* (relative intensity) 512 (100, M⁺). Anal. (C₃₅H₂₇S₂Cl) C, H, S.

1-(Trifluoroacetyl)-2-(4-methylphenyl)-6-phenyl-10-(4-methylphenylthio)-2-thioniacanthrenide (**8a**)

To 15 g (71 mmol) of trifluoroacetic anhydride (TFAA) in 20 mL of triethylamine-dimethoxyethane (DME) was added 2.00 g (3.7 mmol) of **7a** in 7.5 mL of TFAA and 10 mL of DME at –78°C. After 12 hours at 25°C, this solution was poured into ice water. Ether extraction gave an organic phase which was washed with H₂O and then dried (MgSO₄). Solvent was removed in vacuum to give crude **8a**. Recrystallization from CH₂Cl₂ gave 1.77 g (30 mmol, 80%) of orange needles, **8a**: mp 172–174°C; ¹H NMR (CDCl₃/TMS, numbered CH values refer to acanthryl protons) δ 8.12 (d, 1H, 5-CH), 7.94 (d, 2H, ⁺SC₆H₄CH₃, ortho to S), 7.80 (s, 1H, 3-CH), 7.72 (s, 1H, 7-CH), 7.56–7.50 (m, 4H, 9-CH, meta and para H of Ph), 7.42–7.34 (m, 2H, 4-CH, 8-CH), 7.29–7.20 (d of d, 2H, ortho H of Ph), 6.97 (d, 2H, ⁺SC₆H₄CH₃, meta- to S), 6.91 (d, 2H,

SC₆H₄CH₃, ortho- to S), 6.85 (d, 2H, SC₆H₄CH₃, meta- to S), 2.29 (s, 3H, ⁺SC₆H₄CH₃), 2.14 (s, 3H, SC₆H₄CH₃); ¹⁹F NMR (CDCl₃/CFCl₃) –54.4 (s); mass spectrum (10 eV) *m/e* (relative intensity) 606 (17, M^{o+}), 483 (100, –SC₆H₄CH₃), 392 (19, –SC₆H₄CH₃, –C₇H₇); IR (CHCl₃) 1570 cm^{–1} (C = O). Anal. (C₃₇H₂₅S₂OF₃) C, H, S, F.

Reaction of 8a with Trifluoroacetyl Trifluoromethanesulfonate [36] (TFAT) (Salt **10a**)

To 34 mg (0.05 mmol) of **8a** in 0.4 mL of liquid SO₂ at –80°C, 50 mg (0.2 mmol) of TFAT was added by distillation. Small amounts of tetramethylsilane and CFCl₃ were distilled into the resulting red solution. The NMR tube was sealed, and the spectrum was run at 30°C: ¹H NMR (SO₂/TMS) δ 8.57 (d, 2H), 8.51 (d, 1H), 8.38 (d, 1H), 8.04 (apparent t, 2H), 7.80–7.62 (m, 9H), 7.55 (d, 2H), 7.42 (d, 2H), 2.46 (s, 3H), 2.40 (s, 3H), see the Discussion section for assignments; ¹⁹F NMR (SO₂/CFCl₃) –57.30 (d, 3F, CCF₃), –78.8 (s, 6F, SO₃CF₃).

Protonation of 8a (E- and Z-9a)

To 40 mg (0.066 mmol) of **8a** in 0.4 mL of liquid SO₂ at –80°C was added 0.1 g (0.67 mmol) of trifluoromethanesulfonic (triflic) acid and small quantities of TMS and CFCl₃. The NMR tube was sealed, and the NMR spectrum was run at 30°C: ¹H NMR (SO₂/TMS) δ 8.16–6.83 (m, 19H, ArH), 5.91–5.78 (m, 1H, OH), 2.38 (s, 3.6H, CH₃), 2.32 (s, 1.2H, CH₃), 2.24 (s, 1.2H, CH₃); ¹⁹F NMR (SO₂/CFCl₃) –58.10 (d, 1.6F, ⁴J_{HF} = 6 Hz), –57.02 (d, 1.4F, ⁴J_{HF} = 6 Hz).

1,8-Bis(4-methylphenylthio)-9,10-diphenyl-9,10-dihydroxy-9,10-dihydroanthracene (**11a**)

To 2.28 g (4.3 mmol) of **5a** in 300 mL of benzene/THF (5/1) was added 80 mmol of phenylmagnesium bromide in ether. The solution was stirred 48 hours, and H₂O was added. The organic layer was washed with H₂O and then dried (MgSO₄). Solvent was removed in vacuum, and the crude product was recrystallized from ethanol to give 2.50 g (4.1 mmol, 96%) of colorless needles. **11a**: mp 250–254°C; ¹H NMR (CDCl₃/TMS) δ 7.70–6.73 (m, 24H, ArH), 6.45 (s, 2H, OH), 2.23 (s, 6H, CH₃). Anal. (C₄₀H₃₂S₂O₂) C, H.

Reaction of 11a with TFAT (Salt 12a)

To 40 mg (0.066 mmol) of **11a** in 0.5 mL of CHCl₃ was added 0.45 g (1.8 mmol) of TFAT at 25°C in an NMR tube. The sealed tube was heated at 70°C for 20 minutes. The solution was poured into H₂O and extracted into ether. The ether solution was dried (MgSO₄). Removal of solvent in vacuum gave crude

12a. Recrystallization from CHCl_3 /hexane gave 40 mg (0.055 mmol, 83%) of **12a**: mp 194–196°C; ^1H NMR (CDCl_3/TMS) δ 9.08 (d, 1H), 8.38 (d, 1H), 8.02 (d, 1H), 7.83 (d, 1H), 7.78–6.99 (m, 15H), 6.83 (d, 2H), 6.78 (d, 2H), 2.30 (s, 3H), 2.09 (s, 3H), see the Discussion section for assignments; mass spectrum (field desorption) m/e (relative intensity) 573 (100, M^+), 482 (30, $\text{M}^+ - \text{C}_7\text{H}_7$). Anal. ($\text{C}_{41}\text{H}_{29}\text{S}_3\text{O}_3\text{F}_3$) C, H.

The above procedure was repeated by adding TFAT to **11a** at -80°C . The solution was warmed to -30°C and the ^1H NMR spectrum recorded. In addition to the *para*-tolyl methyl peaks of **11a** (δ 2.23) and **12a** (δ 2.30 and 2.09) a singlet absorption at δ 2.60 was observed. Upon further warming of the sample, the intensity of this absorption at δ 2.60 increased with a corresponding decrease in the absorption of **11a** and increase in the absorption of **12a**. We were not able to obtain a ^1H NMR spectrum of the pure intermediate (δ 2.60), thought to be the analog of **14**, in several experiments carried out at various temperatures.

1,8-Bis(4-methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (13a)

To 5.0 g (23 mmol) of 2,6-dimethoxybromobenzene in 50 mL of THF was added 23 mmol of *n*-butyllithium in hexane at 0°C . After 10 minutes, this solution was added to 1.5 g (3.0 mmol) of **5a** in 125 mL of benzene/THF (1/1) and was stirred for 48 hours at 25°C . Water was added, and the procedure described for **11a** was used to isolate crude **13a**. Recrystallization from THF/hexane gave 1.7 g (2.7 mmol, 90%) of colorless needles of **13a**: mp 287–289°C; ^1H NMR (CDCl_3/TMS , 59°C) δ 8.15 (s, 1H, OH), 7.50 (d, 2H, 2- and 7-anthryl CH), 7.28–6.95 (m, 10H, ArH), 6.90 (d, 4H, $\text{SC}_6\text{H}_4\text{CH}_3$, meta- to S), 6.76 (d, 4H, $\text{SC}_6\text{H}_4\text{CH}_3$, ortho- to S), 6.37 (d, 2H, ArH, ortho- to OCH_3), 3.52 (broad s, 6H, OCH_3), 2.24 (s, 6H, CH_3); mass spectrum (10 eV) m/e (relative intensity) 668 (100, $\text{M}^{+\bullet}$), 651 (12, $\text{M}^{+\bullet} - \text{OH}$), 650 (16, $\text{M}^{+\bullet} - \text{H}_2\text{O}$), 634 (10, $\text{M}^{+\bullet} - \text{O}_2\text{H}_2$), 531 (15, $\text{M}^{+\bullet} - \text{C}_8\text{H}_9\text{O}_2$), 404 (44, $\text{M}^{+\bullet} - \text{SC}_7\text{H}_7$, or $\text{M}^{+\bullet} - \text{C}_8\text{H}_9\text{O}_2$). Anal. ($\text{C}_{42}\text{H}_{36}\text{S}_2\text{O}_4$) C, H.

1,8-Bis(4-fluorophenylthio)-9-(2,6-dimethoxyphenyl)-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (13b)

This compound was prepared from **5b** [30] by the method described for **13a**. Recrystallization from ethanol gave 90% of colorless needles of **13b**: mp 253–257°C; ^1H NMR (CDCl_3/TMS) δ 8.26 (s, 1H, OH), 7.48 (d, 2H, 2- and 7-anthryl CH), 7.33–6.76 (m, 18H, ArH), 6.37 (d, 2H, ArH, ortho- to OCH_3), 3.98 (broad s, 3H, OCH_3), 3.18 (broad s, 3H, OCH_3), 3.14 (s, 1H, OH); ^{19}F NMR ($\text{CDCl}_3/\text{CFCl}_3$) -116.4 (m). Anal. ($\text{C}_{40}\text{H}_{30}\text{S}_2\text{O}_2\text{F}_2$) C, H, S, F.

1,8-Bis(4-methylphenylthio)-9-(4-tert-butyl-2,6-dimethoxyphenyl)-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (13c)

To 2.05 g (3.9 mmol) of **5a** in 100 mL of benzene/THF (5/1) was added 39 mmol of 4-*tert*-butyl-2,6-dimethoxyphenyllithium prepared from the corresponding bromobenzene derivative [37], as described for **13a**. After 3 hours, H_2O was added and **13c** was isolated by the method described for **13a**. Recrystallization from CH_2Cl_2 /hexane gave 0.82 g (1.1 mmol, 28%) of colorless needles of **13c**: mp 287–289°C; ^1H NMR (CDCl_3/TMS , 60°C) δ 8.33 (s, 1H, OH), 7.48 (d, 2H, 2- and 7-anthryl CH), 7.29–6.94 (m, 10H, ArH), 6.85 (d, 4H, $\text{SC}_6\text{H}_4\text{CH}_3$, meta- to S), 6.65 (d, 4H, $\text{SC}_6\text{H}_4\text{CH}_3$, ortho- to S), 6.36 (broad s, 2H, ArH, ortho- to OCH_3), 4.00 (broad s, 3H, OCH_3), 3.22 (s, 1H, OH), 3.18 (broad s, 3H, OCH_3), 2.22 (s, 6H, CH_3), 1.53 (s, 9H). Anal. ($\text{C}_{46}\text{H}_{44}\text{S}_2\text{O}_4$) C, H.

1-(4-Methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (20a)

This compound was prepared from **19a** by the method described for **13a**. Recrystallization from ethanol gave 37% of colorless needles of **20a**: mp 243–246°C; ^1H NMR (CDCl_3/TMS) δ 7.89 (s, 1H, OH), 7.54–6.92 (m, 17H, ArH), 6.61 (broad s, 2H, ArH, ortho- to OCH_3), 4.09 (broad s, 3H, OCH_3), 3.20 (s, 1H, OH), 3.18 (broad s, 3H, OCH_3), 2.28 (s, 3H, CH_3); mass spectrum (10 eV) m/e (relative intensity) 546 (100, $\text{M}^{+\bullet}$), 409 (20, $-\text{C}_8\text{H}_9\text{O}_2$), 317 (38, $-\text{C}_8\text{H}_9\text{O}_2$, $-\text{C}_7\text{H}_8$).

1-(4-Fluorophenylthio)-9-(2,6-dimethoxyphenyl)-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (20b)

This compound was prepared from **19b** by the method described for **13a**. Recrystallization from CHCl_3 /hexane gave 23% of colorless needles of **20b**: mp 197–200°C; ^1H NMR (CDCl_3/TMS) δ 7.86 (s, 1H, OH), 7.54–6.82 (m, 20H, ArH), 6.68 (broad s, 2H, ArH, ortho- to OCH_3), 3.91 (broad s, 6H, OCH_3), 3.14 (s, 1H, OH); mass spectrum (10 eV) m/e (relative intensity) 550 (100, $\text{M}^{+\bullet}$), 413 (15, $\text{M}^{+\bullet} - \text{C}_8\text{H}_9\text{O}_2$), 317 (5, $\text{M}^{+\bullet} - \text{C}_8\text{H}_9\text{O}_2$ or $\text{M}^{+\bullet} - \text{FC}_6\text{H}_5$), 286 (13, $\text{M}^{+\bullet} - \text{C}_8\text{H}_9\text{O}_2$ or $\text{M}^{+\bullet} - \text{FC}_6\text{H}_4\text{S}$).

1,8-Bis(4-methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene Dication Ditriflate (14a)

To 30 mg (0.045 mmol) of **13a** in 0.4 mL of liquid SO_2 in an NMR tube at -80°C was added 0.15 g (1.1 mmol) of triflic acid. When the tube was sealed and warmed to -50°C , a deep green color appeared: ^1H NMR (SO_2 , 28°C , external TMS) δ 8.63 (t, 1H, $J = 8.6$ Hz), 8.59 (d, 2H, $J = 7.1$ Hz), 8.29

(d, 2H, $J = 7.1$ Hz), 8.07 (apparent t, 2H), 7.94–7.78 (m, 5H), 7.53 (d, 4H, $J = 8.3$ Hz), 7.17 (d, 4H, $J = 8.0$ Hz), 6.80 (d, 2H, $J = 8.6$ Hz), 3.52 (s, 6H), 2.59 (s, 6H), see Table 1 for assignments.

An identical spectrum was observed when the dication was generated by treatment of the diol as before but with H₂SO₄ instead of triflic acid. When a solution of **14a** in SO₂ is cooled below –100°C, a solid precipitate appears. Removal of SO₂ in vacuum at temperatures below –78°C gives a solid material which gave a complex spectrum very different from that of **14a** when redissolved in SO₂. At no time was the material warmed above –78°C. The use of SO₂ClF as solvent gives a spectrum identical to that obtained using SO₂ as solvent.

1,8-Bis(4-methylphenylthio)-9-(4-tert-butyl-2,6-dimethoxyphenyl)-10-phenylanthracene Dication Ditriflate (14c)

This compound was prepared from **13c** by the same method used to generate **14a**: ¹H NMR (SO₂/TMS, 28°C) δ 8.57 (d, 2H, $J = 8.9$ Hz), 8.34 (d, 2H, $J = 7.4$ Hz), 8.07 (apparent t, 2H), 8.00–7.80 (m, 5H), 7.60 (d, 4H, $J = 8.4$ Hz), 7.22 (d, 4H, $J = 8.4$ Hz), 6.86 (s, 2H), 3.59 (s, 6H), 2.66 (s, 6H), 1.58 (s, 9H), see Table 1 for assignments.

1,8-Bis(4-fluorophenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene Dication Ditriflate (14b)

This compound was prepared from **13b** by the same method used to generate **14a**: ¹H NMR (SO₂ClF/

TMS, 27°C) δ 8.76 (t, 1H, $J = 8.7$ Hz), 8.62 (d, 2H, $J = 8.7$ Hz), 8.34 (d, 2H, $J = 7.0$ Hz), 8.08 (apparent t, 2H), 7.95–7.78 (m, 5H), 7.48–7.31 (m, 8H), 6.91 (d, 2H, $J = 8.7$ Hz), 3.63 (s, 6H); ¹⁹F NMR (SO₂ClF/CFCl₃, –20°C) –97.0 (complex m, collapses to a singlet upon irradiation of protons). A single sharp ¹⁹F peak was observed at –100°C.

1,8-Bis(4-methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene (15a)

Treatment of 0.4 g (0.6 mmol) of **13a** in 5 mL of liquid SO₂ with 1.5 g (11.0 mmol) of triflic acid generated **14a**. This solution at –78°C was added to concentrated aqueous NaOH solution at –10°C. The yellow precipitate was extracted into CH₂Cl₂. This solution was washed with H₂O and then dried (MgSO₄). Solvent was removed in vacuum. The ¹H NMR spectrum of the crude mixture showed **15a** to be present in >90% yield. Chromatography on silica gel with CHCl₃ followed by recrystallization from CH₂Cl₂/pentane gave 0.18 g (0.28 mmol, 48%) of yellow needles of **15a**: mp 145–147°C; ¹H NMR (CDCl₃/TMS) δ 7.56–7.45 (m, 5H, ArH), 7.33 (d of d, 2H, $J = 7.3$ Hz, 2.5 Hz, 4- and 5-anthryl CH), 7.14 (d, 4H, $J = 8.0$ Hz, SC₆H₄CH₃, meta- to S), 7.05 (d, 4H, $J = 7.9$ Hz, SC₆H₄CH₃, ortho- to S), 6.96–6.90 (m, 4H, ArH), 6.63 (d, 2H, $J = 8.4$ Hz, ArH, ortho- to OCH₃), 3.69 (s, 6H, OCH₃), 2.30 (s, 6H, CH₃); mass spectrum (70 eV) m/e (relative intensity) 634 (100, M⁺), 512 (3, –SC₇H₇), 374 (18, –C₈H₉O₂, –SC₇H₇), 317 (7, M⁺⁺). Anal. (C₄₂H₂₈S₂O₂) C, H, S.

TABLE 1 ¹H and ¹⁹F NMR Chemical Shifts^a for Dications **14** and **21**^b and Anthracene **16**^c

	14a	14b	14c	21a	21b	16a
2-H	8.29(d)	8.34(d)	8.34(d)	8.32(d)	8.34(d)	7.78(d)
3-H	8.07(t)	8.08(t)	8.07(d)	8.05(t)	8.05(t)	
4-H	8.59(d)	8.62(d)	8.57(t)	8.48(d)	8.50(d)	8.44(d)
5-H	8.59(d)	8.62(d)	8.57(d)	8.25(d)	8.27(d)	
6-H	8.07(t)	8.08(d)	8.07(d)	(7.92–7.62)	(7.95–7.53)	
7-H	8.29(d)	8.34(d)	8.34(d)	(7.92–7.62)	(7.95–7.53)	
8-H				7.62(d)	7.24(d)	
3'-H	6.80(d)	6.91(d)	6.86(s)	7.11(d)	7.15(d)	6.70(d) 6.28(d)
4'-H	8.63(t)	8.76(t)		9.26(t)	9.26(t)	7.54(t)
2''-H	7.53(d)	(7.48–7.31)	7.60(d)	(7.92–7.62)	(7.95–7.53)	
3''-H	7.17(d)	(7.48–7.31)	7.22(d)	7.57(d)	(7.95–7.93)	
-OCH ₃	3.52(s)	3.63(s)	3.59(s)	3.92(s)	3.95(s)	3.71(s) 3.07(s)
-CH ₃	2.59(s)		2.66(s)	2.69(s)		2.29(s) 2.24(s)
10-Ph	(7.94–7.78)	(7.95–7.78)	(8.00–7.80)	(7.92–7.62)	(7.95–7.53)	
<i>t</i> -Bu			1.58(s)			
-F ^c		–97.0			–52.8	

^aSee the Experimental section for solvents and temperatures. ^bSame numbering system as **14**; sulfoxide sulfur at position 1 in **16**. ^cChemical shifts are reported in ppm downfield of CFCl₃. Negative values are therefore upfield of CFCl₃ in accord with IUPAC recommendations: *Org. Mag. Res.*, 11, 1978, 267.

1,8-Bis(4-fluorophenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene (15b)

This compound was prepared from **13b** by the method described for **15a**. From 77 mg (0.11 mmol) of **13b**, this method gave 38 mg (0.06 mmol, 52%) of **15b**: mp 240–242°C; ¹H NMR (CDCl₃/TMS) δ 7.52–7.45 (m, 8H, ArH), 7.40–7.35 (m, 4H, ArH), 7.18–6.90 (m, 8H, ArH), 6.59 (d, 2H, *J* = 8.3 Hz, ArH, ortho- to OCH₃), 3.63 (s, 6H, OCH₃); ¹⁹F NMR (CDCl₃/CFCl₃) –114.0 (complex m); mass spectrum (10 eV) *m/e* (relative intensity) 642 (100, M⁺).

1-(4-Methylphenylthio)-8-(4-methylphenylsulfinyl)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene (16a)

Dication **14a** was produced by dissolving 190 mg (0.28 mmol) of **13a** in 5 mL of 98% H₂SO₄. The ¹H NMR spectrum of this solution was identical with that from treatment of **13a** with triflic acid in liquid SO₂ to generate **14a**. This solution was added dropwise to 50 mL of concentrated aqueous NaOH at –10°C. The yellow precipitate was extracted into CH₂Cl₂. This solution was washed (H₂O) and then dried (MgSO₄). Solvent was removed in vacuum. Chromatography on silica gel with CHCl₃ gave 138 mg (0.21 mmol, 75%) of **16a**: mp 148–149°C; ¹H NMR (CDCl₃/TMS) δ 8.45 (d, 1H, *J* = 7.3 Hz, ArH), 7.78 (d, 1H, *J* = 8.5 Hz, ArH), 7.60–7.38 (m, 9H, ArH), 7.09–6.87 (m, 9H, ArH), 6.69 (d, 1H, *J* = 8.4 Hz, ArH), 6.28 (d, 1H, *J* = 8.4 Hz, ArH), 3.71 (s, 3H, OCH₃), 3.06 (s, 3H, OCH₃), 2.28 (s, 3H, CH₃), 2.24 (s, 3H, CH₃), see Table 1 for further assignments; mass spectrum (10 eV) *m/e* (relative intensity) 650 (100, M⁺). Anal. (C₄₂H₂₈S₂O₃) C, H.

Compound **16a** was also obtained by treatment of 52 mg (0.082 mmol) of **15a** in 10 mL of CH₂Cl₂ with 15 mg (0.096 mmol) of ca. 85% *meta*-chloroperbenzoic acid at 25°C. This solution was extracted with 2N NaOH and then dried (MgSO₄). Solvent was removed in vacuum. Chromatography (silica gel/CHCl₃) gave 45 mg (0.069 mmol, 72%) of **16a** identical with that prepared by the other method.

1-(4-Methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene Dication Ditriflate (21a)

This compound was prepared from **20a** by the method described to generate **14a**, using SO₂ClF as solvent. The temperature was kept below –20°C (decomposition was evidenced above –20°C): ¹H NMR (SO₂ClF/TMS, –50°C) δ 9.28 (t, 1H, *J* = 8.6 Hz), 8.48 (d, 1H, *J* = 8.6 Hz), 8.32 (d, 1H, *J* = 7.2 Hz), 8.25 (d, 1H, *J* = 8.9 Hz), 8.05 (apparent t, 1H), 7.92–7.62 (m, 9H), 7.57 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 1H, *J* = 8.1 Hz), 7.11 (d, 2H, *J* = 8.6 Hz), 3.92 (s, 6H), 2.69 (s, 3H), see Table 1 for assignments.

1-(4-Fluorophenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene Dication Ditriflate (21b)

This compound was prepared from **20b** by the method used to generate **14a**: ¹H NMR (SO₂ClF/TMS, –50°C) δ 9.26 (t, 1H, *J* = 8.6 Hz), 8.50 (d, 1H, *J* = 8.6 Hz), 8.34 (d, 1H, *J* = 7.2 Hz), 8.27 (d, 1H, *J* = 8.9 Hz), 8.05 (apparent t, 1H), 7.95–7.53 (m, 11H, ArH), 7.24 (d, 1H, *J* = 8.1 Hz), 7.15 (d, 2H, *J* = 8.6 Hz), 3.95 (s, 6H), see Table 1 for further assignments; ¹⁹F NMR (SO₂ClF/CFCl₃, –40°C) –52.8 (broad s, collapses to a sharp singlet upon irradiation of protons).

1-(4-Methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene (22a)

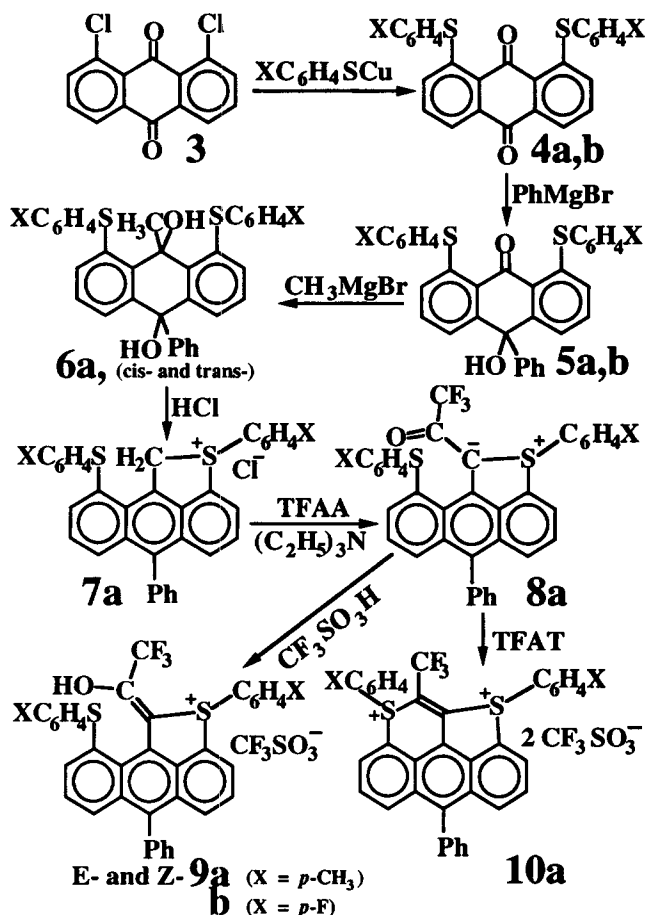
This compound was prepared from **20a** by the method described for **15a**. From 110 mg (0.20 mmol) of **20a**, this gave 63 mg (0.12 mmol, 62%) of **22a**: 188–190°C; ¹H NMR (CDCl₃/TMS) δ 7.59–7.45 (m, 9H, ArH), 7.28–7.23 (m, 3H, ArH), 7.14 (d, 2H, *J* = 8.8 Hz), 7.04 (d, 2H, *J* = 8.8 Hz), 7.00 (d, 2H, *J* = 5.2 Hz), 6.70 (d, 2H, *J* = 8.2 Hz), 3.60 (s, 6H), 2.31 (s, 3H); see Table 1 for assignments; mass spectrum (10 eV) *m/e* (relative intensity) 512 (100, M⁺). Anal. (C₃₅H₂₈SO₂) C, H.

RESULTS

Bis-trifluoroacetylation of Sulfonium Ion 7a

The synthesis of **7a** was accomplished by methods previously described by Martin and Basalay [30] with some modifications. The synthetic route is shown. Sulfonium ylide **8a** was prepared by treatment of **7a** with TFAA in the presence of triethylamine. No further trifluoroacetylation was accomplished even upon boiling **7a** in TFAA. Trifluoroacetyl trifluoromethanesulfonate [36], a more potent trifluoroacetylating reagent, prepared for the first time specifically for this application, reacts immediately with **8a**. Trifluoroacetylation occurs, however, not at carbon but at enolate oxygen to give **10a**. Disulfonium species **10a** in liquid sulfur dioxide appears by ¹⁹F NMR to have two ionic trifluoromethylsulfonates (triflates) on the basis of area measurements for the trifluoromethyl peaks. The downfield shifts in the ¹H NMR of the para-tolyl protons (δ 7.78–7.42) of **10a** relative to the para-tolyl methyl absorptions (δ 2.29 and 2.05) and aromatic para-tolyl proton absorptions (δ 7.5–7.50 and 6.99–6.89) of **8a** are also consistent with this ionic formulation.

Protonation of **8a** with trifluoromethanesulfonic (triflic) acid also occurs on oxygen to give the isomeric enols **9a**. This structural assignment is based upon the overlapping quartets for the hydroxy proton in the ¹H NMR spectrum of **8a** at δ 5.87 and 5.82 (⁴*J* = 6 Hz) and a pair of doublets at



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–57.02 and –58.10 ppm ($J_{\text{HF}} = 6$ Hz) in the ^{19}F NMR spectrum.

Dications of Anthracene Derivatives

The precursors to sulfonium species **12** and dications **14a–c**, the corresponding 9,10-dihydroxy-9,10-dihydroanthracenes **11** and **13a–c**, respectively, were prepared as shown. An interesting feature of **13a–c** is the hindered rotation of the 2,6-dimethoxyphenyl rings as reflected in the presence of two broad absorptions for the methoxy groups in the ^1H NMR spectrum at room temperature, which collapse to a singlet absorption at elevated temperatures.

Treatment of **11** with TFAT at 70°C for 20 minutes or with triflic acid at room temperature in dichloromethane gave the sulfonium triflate **12** which shows ^1H NMR absorptions for the para-tolyl methyl groups at δ 2.46 and 2.05. During the course of the reaction of **11** with TFAT, a superior dehydrating agent, at room temperature in dichloromethane- d_2 , an intermediate is observed, evidenced by the observation of a transient singlet absorption at δ 2.60 in the ^1H NMR spectrum. This

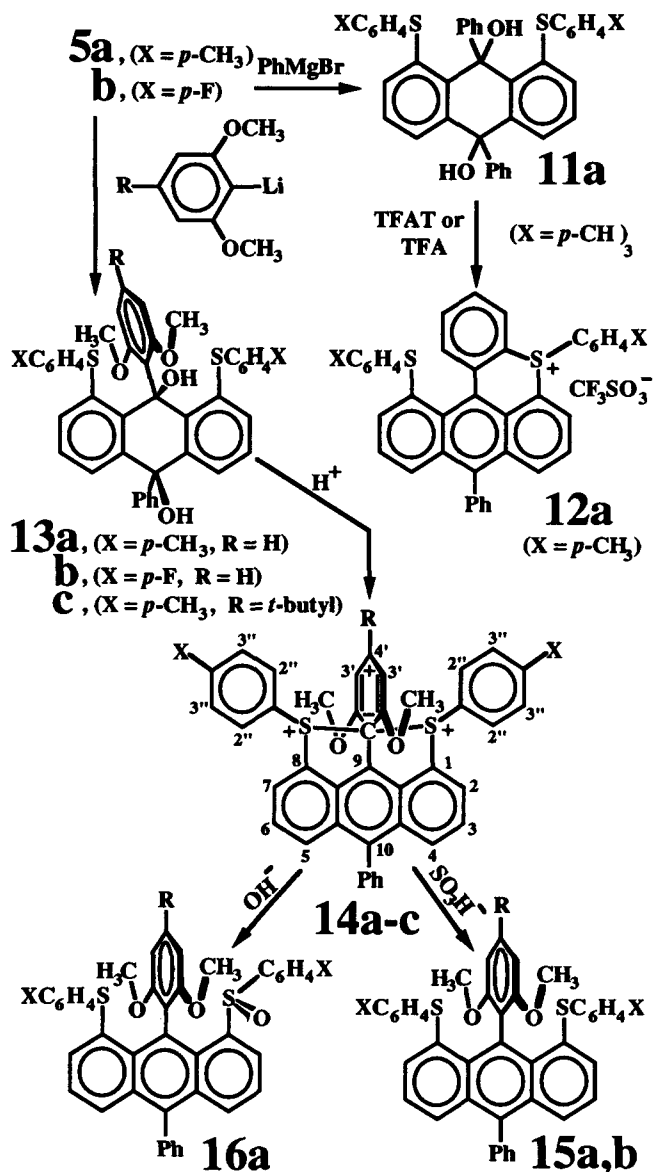
absorption is downfield from the corresponding absorptions of the para-tolyl methyl groups in both starting material **11** (δ 2.27) and product **12** (δ 2.23 and 2.09).

Treatment of a mixture of diastereomeric diols **13** with triflic acid in liquid sulfur dioxide or sulfur chloride fluoride at -80°C results in deep green solutions which are stable for weeks at room temperature in sealed tubes. A sulfur dioxide solution of **14a**, formed from the reaction of diol **13a** with triflic acid, reacted with aqueous sodium hydroxide to produce the neutral anthracene **15a**, a two-electron reduction product. The reducing agent is presumed to be the sulfite formed from sulfur dioxide and hydroxide ion. In keeping with this, if **14a** is generated by treatment of **13a** with concentrated sulfuric acid and this solution is added to aqueous sodium hydroxide, mono-sulfoxide **16a** is produced. The ^1H and ^{19}F NMR assignments for dications **14** and compound **16** are reported in Table 1.

Diols **20** were prepared by the indicated route. They also show hindered rotation of the 9-(2,6-dimethoxyphenyl) group, as was observed for compounds **13**. The reaction of **18** in the sequence with phenylmagnesium bromide is not regioselective, as it is for the more hindered **5**, so both regioisomers are formed. Chromatography was required for their separation. The regioisomer from the addition of phenylmagnesium bromide to the least hindered carbonyl of **18**, compound **19**, shows a characteristic absorption for the proton peri to the carbonyl (δ 8.26, doublet of doublets).

Treatment of **20a** or **20b** with triflic acid in sulfur chloride fluoride at -80°C gave compounds which are assigned structures **21a** and **21b**. Dications **21** are assigned this sulfonium structure based upon the ^1H and ^{19}F data shown in Table 1. The para-thio aromatic protons of **21a** (δ 7.92–7.57) compared to those of the corresponding anthracene **22a** (δ 7.14–7.04) suggest the presence of the positively charged sulfur in structure **21a**. The fluorine absorption of **21b** (-52.8 ppm) relative to **15b** (-114.0 ppm) is also indicative of sulfonium sulfur in **21**. The observed chemical shift of carbon 4' (Table 1) for **21a** at δ 9.28 relative to the same proton of **22a** (δ 7.50) suggests considerable positive charge delocalization at this position in the 2,6-dimethoxyphenyl ring. These observations are consistent with **21** as the structure of these dications. Treatment of a sulfur dioxide solution of **21a** with aqueous sodium hydroxide produced anthracene **22a**, a two-electron reduction product, parallel to that observed in the conversion of **14a** to **15a**.

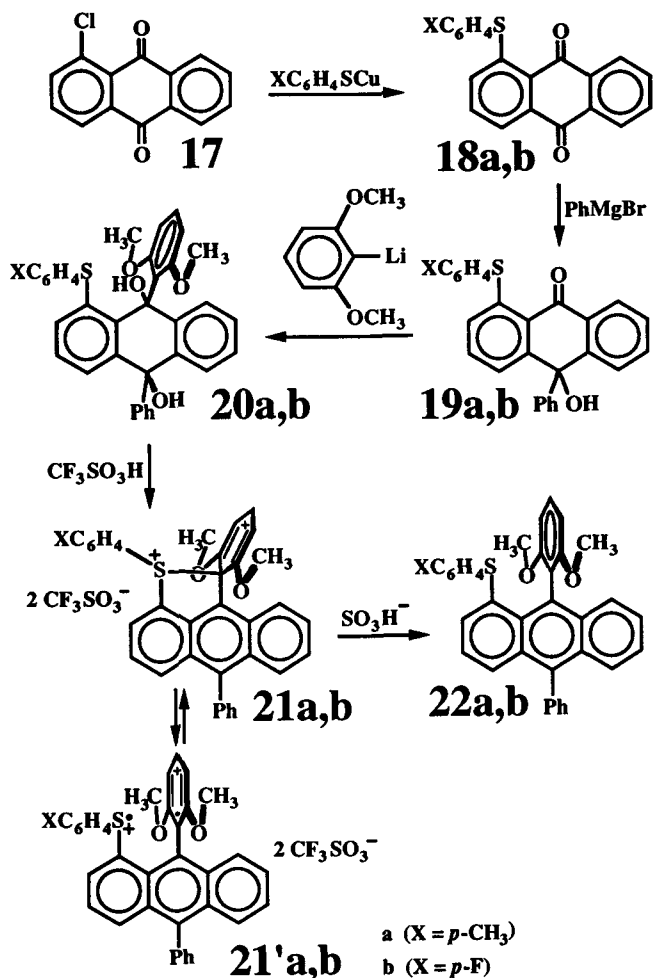
An unexpected feature in the ^1H NMR spectra of dications **21** is the observation of only a single absorption for the methoxy groups. The pyramidal sulfonium sulfur would be expected to produce nonequivalence in these groups from shielding of one of them by the aryl group attached to sulfur,



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as observed in sulfoxide **16a**. A rapid rearrangement which is the operational equivalent of a pyramidal inversion about sulfonium sulfur is necessary to explain the observation of a single NMR peak for these groups in a sample of **21**. Pyramidal inversion about sulfonium sulfur is ordinarily a process with a substantial energy barrier [31,38]. It is probable that this rapid inversion results from the close juxtaposition of two relatively localized positive charges in **21**. The unfavorable electrostatic interaction can be relieved by homolysis of the C-S bond to give a singlet diradical transition state or intermediate **21'** for the inversion of sulfur. This suggests that the C-S bond in **21** is a very weak one.

Evidence that the absorptions corresponding



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to protons 3' and 4' in **14** and **21** are correctly assigned is revealed in the ¹H NMR spectrum of **14c**. The proton of **14a** is replaced by a *tert*-butyl group in **14c**. The ¹H NMR spectrum of **14c** does not show the triplet absorption at δ 8.63 which is observed in **14a**. The peak assigned to proton 3' is a singlet in **14c** (δ 6.86) and a doublet in **14a** (δ 6.80). These observations make unambiguous the assignments of protons 3' and 4' in **14**, as the lowest (4') and highest (3') field absorptions in the aromatic regions of these spectra.

DISCUSSION

Attempts to Introduce π-Acceptor Trifluoroacetyl Ligands into Sulfonium Ion **7a**

The earlier [31] finding that a degenerate rearrangement interconverts **1** and **1'** (R = CH₃ or H) via an intramolecular S_N2-type associative displacement with Δ*H*[‡] as low as 10 kcal/mol (curve e, Figure 2) suggested that it would be interesting to replace the equatorial ligands, R, on the carbon

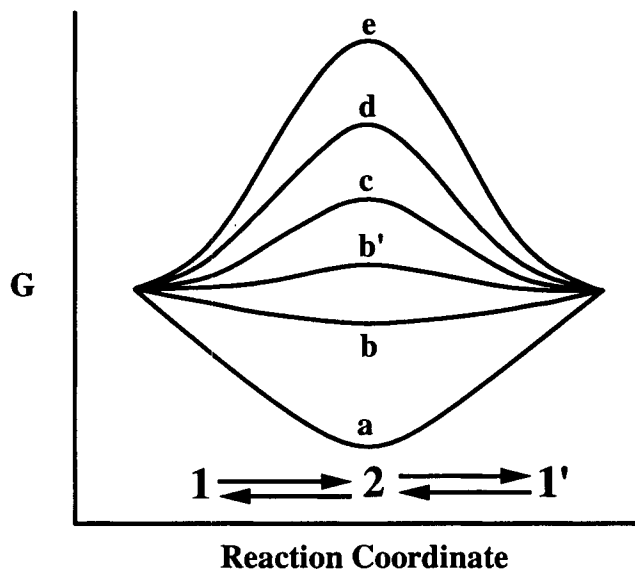


FIGURE 2 Energy diagram for relative stabilities of unsymmetrical (1 and 1') vs. symmetrical (2) structures.

undergoing displacement with groups which had been shown to lower the activation energy for S_N2 displacements in other systems. This would be expected to stabilize the symmetrical structure 2 relative to the unsymmetrical structures 1 and 1'. A sufficiently large stabilization (>10 kcal/mol) of the symmetrical structure relative to the unsymmetrical isomers would give an observable compound containing a 10-C-5 species with a TBP hypervalent carbon atom (curve a or b in Figure 2). Salts 1 already have structural and electronic features which have been found to stabilize compounds of TBP hypervalent atoms above the second row of the periodic table, namely the following: (a) the five-membered rings using bidentate ligands to link apical and equatorial positions on TBP carbon; (b) benzoannulation which holds the sulfurs closely juxtaposed to the central carbon atom, facilitating interaction between these atoms; and (c) the enhanced electronegativity of the apical sulfur ligands resulting from their positive charge.

Carbonyl groups alpha to the reaction center have long been known to facilitate nucleophilic displacements at carbon. There is a stabilizing interaction between the π -acceptor carbonyl π^* -orbital and electron-rich orbitals of entering and leaving groups apical to TBP in the transition state (Figure 3). Bartlett and Trachtenberg [39] demonstrated the geometrical constraint necessary for the orbital overlap demanded for lowering of the energy barrier for displacement.

Tricoordinate (10-S-3) sulfuranes [40] 23 have been shown to have remarkable stability when a π -acceptor equatorial ligand is aligned with the hypervalent bond of sulfur. Sulfuranes have not

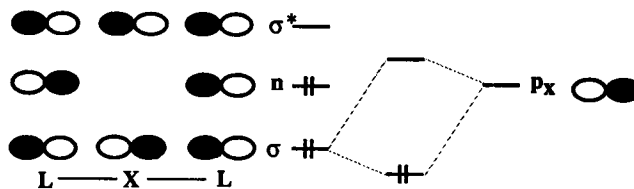
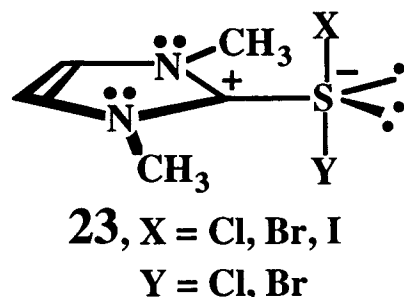


FIGURE 3 Stabilizing interaction of a π -acceptor orbital with the σ -bonding orbital of a hypervalent bond.

been observed with two apical bromines or an iodine ligand in the absence of this stabilizing feature.



The first attempt to introduce π -acceptor equatorial ligands into analogues of 1 involved the trifluoroacetylation of 8a. However, the only trifluoroacetylating reagent found to react with 8a, TFAT, reacted at the carbonyl oxygen instead of at carbon. Upon nucleophilic displacement of trifluoroacetate by neighboring sulfonyl sulfur in the postulated intermediate O-acyl derivative, 10a was obtained. Reaction of 8a with strong acid failed to yield the mono-trifluoroacetyl derivative of 1 or 2 ($R_1 = CF_3C(O)$, $R_2 = H$) but rather gave O-protonation to produce enols *E*- and *Z*-9a.

Anthracene Dication Derivatives

The hypervalent bond to carbon in the approach to this problem discussed above was regarded as resulting from the interaction of filled orbitals of two nucleophiles (sulfenyl sulfurs) with an electron-deficient (empty) $2p$ -orbital of carbon to form the three-center bond. An alternative conceptual approach, which has been found to be useful in the further development of these ideas, views the hypervalent bond to carbon to result from the interaction of two electrophilic radicals (such as sulfide cation radicals) with an electron-rich (filled) $2p$ -orbital of carbon (Figure 4). This alternative conceptualization is suggested from the work of Chau and Martin [41]. The thermal decomposition of perester 24a and 24b was found to proceed by simultaneous scission of two O-O bonds to give sulfurane 26a or iodine 26b.

In the transition state for this conversion, a filled p -orbital of sulfur or iodine interacts with the de-

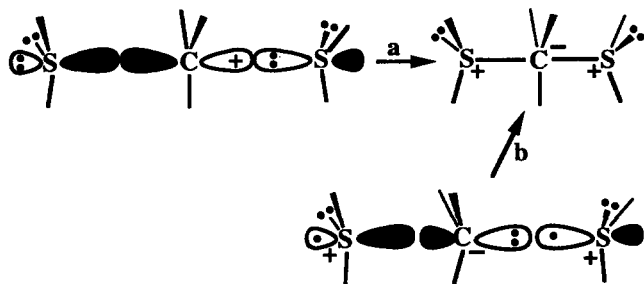
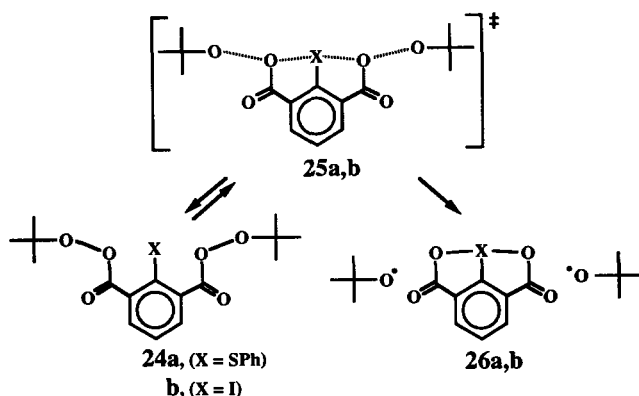


FIGURE 4 Interaction of (a) two nucleophiles with a vacant orbital of carbon and (b) two electrophiles with a filled orbital of carbon to generate a 10-C-5 TBP carbon species.

veloping acyloxy radical center as O–O bond scission progresses. This results in a three-center four-electron interaction which culminates in the formation of the hypervalent bond of **26**.



This conceptual approach led to the probing of the interaction of the sulfide cation radicals with a filled *p*-orbital of a carbon incorporated in a benzene ring (Figure 5). Polarization of the π -electrons of the phenyl ring, as depicted in Figure 5, places a filled *p*-orbital of carbon between two sulfide carbon radicals in the proper geometry for the desired four-electron interaction to give a three-center four-electron (hypervalent) bond linking two apical sulfonium sulfurs to TBP carbon. Coincident with the development of this interaction is the formation of a bidentate π -acceptor pentadienyl ligand which has its π -orbitals aligned with the σ -

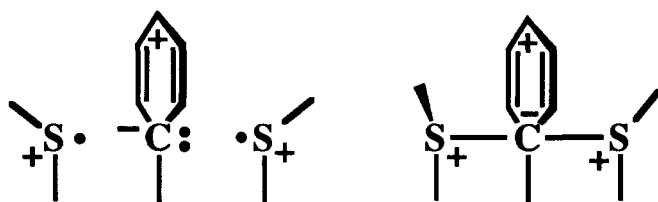


FIGURE 5 Interaction of two sulfide cation radicals with a carbon of a polarized phenyl group to generate a three-center bond.

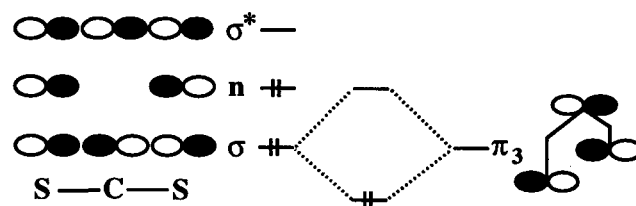


FIGURE 6 Two-electron two-orbital stabilizing interaction of the unfilled pentadienyl cation LUMO with the *s*-bonding orbital of the hypervalent bond.

orbitals of the hypervalent bond. The symmetry of the pentadienyl LUMO allows interaction with the lowest energy σ -orbital (bonding) of the hypervalent bond. The mixing of these orbitals is expected to lower the energy of the hypervalent bond, as depicted in Figure 6. This bidentate ligand forms a six-membered ring of sp^2 carbons linking two equatorial positions, the appropriate ring size for a strain-free geometry in the equatorial plane of TBP carbon.

A feasible structure for the long-lived intermediate observed at low temperature in the ^1H NMR during the conversion of **11a** to **12a** is species **27a**. An intermediate with this structure accounts for the singlet methyl ^1H NMR peak observed downfield relative to starting material **11a** and product **12a** during the conversion. Rearrangement of a sulfur apical ligand in **27a** to an adjacent position on the ring to give **28a** is followed by a 1,2-elimination to give the observed product (**12a**).

The introduction of methoxy groups at the ortho positions of the 9-phenyl ring, by blocking the 1,2-elimination step, removes the possibility of the reaction course proposed to convert **11** to **12**. It also has a stabilizing influence on the positive charge generated in this ring. A caveat must be issued. Although these methoxy substituents are expected to stabilize the structure overall by preventing further reaction, their π -donating ability would be expected to reduce the π -acceptor ability of the pentadienyl cation ligand and therefore to directionally destabilize this symmetrical structure relative to the unsymmetrical structure analogous to **21**.

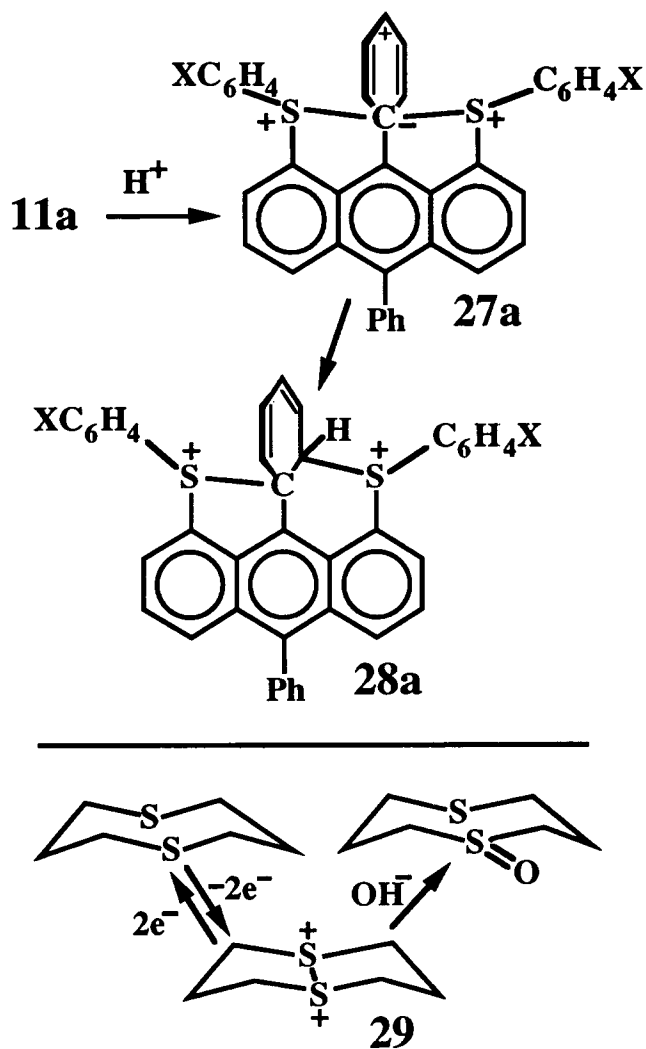
Evidence which supports the structural assignment (**14**) for these dication is based upon ^1H and ^{19}F NMR chemical shift data and the chemical reactions of these species. The proton labeled 4' (Table 1) of the 2,6-dimethoxyphenyl ring is observed at lowest field, indicating positive charge delocalization to this position consistent with that expected for **14**. The upfield shift of the methoxy absorption upon going from neutral **15** (δ 3.69) to dication **14** (δ 3.52) is contrary to that expected based upon introduction of positive charge in conjugation with the carbons bearing the methoxy groups. This is logically explained by invoking shielding by the magnetically anisotropic para-to-

lyl groups attached to the pyramidal sulfonium sulfurs. This shielding is clearly evident in sulfoxide **16a**. The methoxy groups of **16a**, a good model for probing the shielding effect of a para-tolyl group, attached to a pyramidal sulfur, are observed at δ 3.71 and δ 3.07, a large difference which is most easily accounted for by this shielding mechanism. The generation of **14a** from **13a** with sulfuric acid gives a species with the same ^1H NMR spectrum as that from generation with triflic acid in sulfur dioxide or sulfuryl chloride fluoride. This excludes structures in which one of the anions of **14** is covalently bonded to generate a monocation. The reaction of a solution of **14a** in sulfuric acid with aqueous hydroxide gives sulfoxide **16a**. This is consistent with attack of hydroxide ion at the sulfonium sulfur in structure **14a**. This result is analogous to that reported [42] for the reaction of hydroxide ion with *bis*-sulfonium salt **29**. This reaction is therefore not unexpected for a sulfonium structure such as **14**. Salts **29** further undergo two-electron reduction with reducing agents as does **14**.

Despite evidence consistent with these dications having structure **14**, a number of alternatives must be specifically excluded. The most plausible alternative structural hypothesis involves fluctuational isomers, the degenerate pair of unsymmetrical sulfonium structures **30** and **30'**. If rapidly equilibrating, these could give NMR spectra difficult to distinguish from that expected for symmetrical structure **14**. The temperature-dependent ^1H NMR spectrum of **14a** in the temperature range of $+30^\circ\text{C}$ to -50°C showed no detectable broadening in the para-tolyl methyl absorption at a frequency of 220 MHz. Using compounds **15a** and **21a** as appropriate models for the frequency difference expected for the para-tolyl methyl absorptions of unsymmetrical structure **30** (or **30'**), a difference of about 64 Hz at 220 MHz is anticipated. This sets an upper limit of 6 kcal/mol (curve **d** in Figure 2) for $\Delta G^\ddagger_{-50^\circ\text{C}}$ for the process interconverting **30** and **30'**.

More convincingly, the four-fluoro singlet in the proton-decoupled ^{19}F spectrum of **14b** (52.6 MHz) shows only minimal broadening (ca. 3 Hz, the approximate magnitude expected for viscosity broadening) upon lowering the temperature from 30°C to -100°C . This sets an upper limit of ca. 4 kcal/mol for $\Delta G^\ddagger_{-100^\circ\text{C}}$ (curve **c**, Figure 2) for the process interconverting **30** and **30'**. This estimate is based on the use of **21b** (-52.8 ppm, SO_2) and **15b** (-114.0 ppm, CDCl_3) as models for the fluorine chemical shifts of the unsymmetrical structure with an estimated chemical shift difference of 3500 Hz at 56.2 MHz.

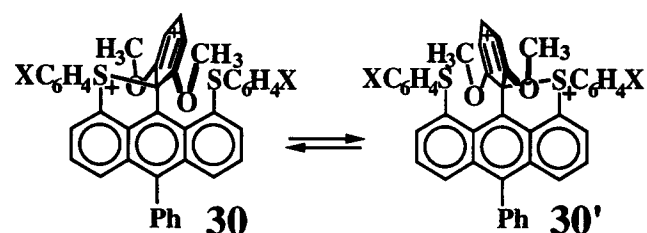
The proton labeled 4' in **14a**, in a rapidly equilibrating mixture of the unsymmetrical structures **30** and **30'**, would be expected to have a chemical shift comparable with that of the analogous proton of **21a** (δ 9.28, SO_2/ClF). The appearance of this pro-



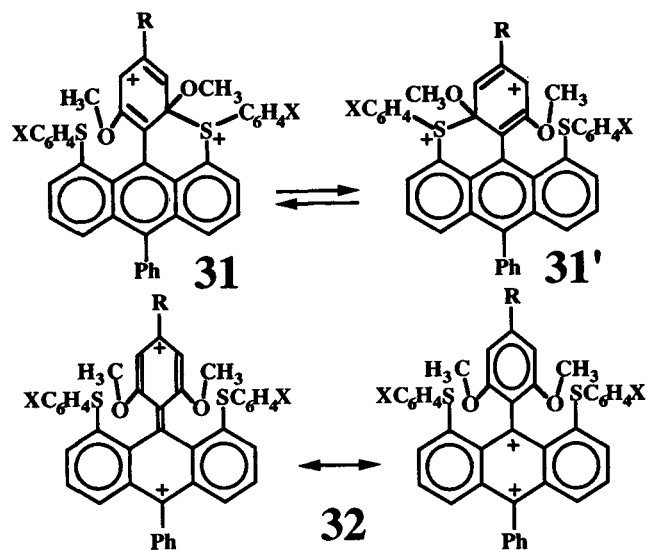
SCHEME

ton at 0.65 ppm higher field (δ 8.63 in **14a**, SO_2) is best explained by postulating nucleophilic involvement of the second sulfur atom, as depicted for structure **14**.

Another possible structural alternative to **14** which provides nucleophilic involvement of the sulfur atoms is based on a postulated fluctuational equilibrium between structures **31** and **31'**. This is



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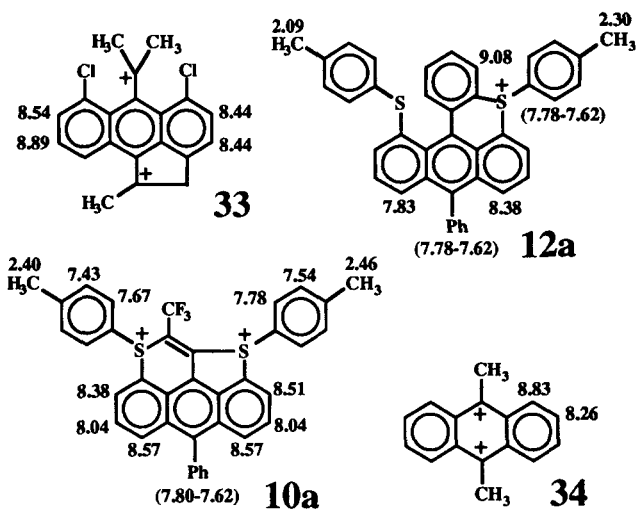
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ruled out by the finding that the absorption of proton 4' (δ 8.63 in **14a**) occurs at much lower field than protons 3' (δ 6.80 in **14a**), a finding consistent with structure **14a** but not **31** and **31'**. Resonance structures drawn for **31** or **31'** place positive charge on positions 3' but not 4'.

Another structural hypothesis for **14** is the π -delocalized structure **32**. This is suggested to be an unlikely structural alternative by comparison of the ^1H NMR chemical shifts for the anthracene protons of **14** (**14a**, δ 8.59–8.07) with appropriate model compounds. The anthracene proton chemical shifts of dication **33** (δ 9.32–8.44, SO_2ClF , $\text{HSO}_3\text{F}/\text{SbF}_5$) [32] which has its charges delocalized throughout the anthracene π -system are observed at much lower field than those of **14**. This same observation is evident from the 9,10-dimethylantracene dication [43] (**34**), in which the anthracene protons are observed in the chemical shift range of δ 8.83–8.26 (SO_2ClF , SbF_5). The ^{13}C NMR chemical shifts for cationic species provide a better probe for charge distribution in π -cations [44] and dications [45]. Structural alternative **32** is ruled out based on considerations of the ^{13}C NMR chemical shifts without ambiguity. This is discussed subsequently.

The chemical shifts of the anthracene protons of **14** are quite similar in magnitude to the chemical shifts of comparable protons in *bis*-sulfonium species **10a**. This is also consistent with the proposed *bis*-sulfonium structure **14** which, like **10a**, places little positive charge in the anthracene π -system.

The observation that only one methoxy methyl singlet is seen in the ^1H NMR spectra of dications **14** must be considered. The pyramidal geometries of the sulfonium sulfurs make possible a pair of



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isomers (*cis* and *trans* configurations for the substituted phenyl groups of the sulfonium sulfurs) for **14**. The observation of a single ^1H NMR peak for the methoxy groups of **14** is consistent with the presence of only the *trans* isomer in concentration sufficient to be detected by ^1H NMR. If this is the reason only one methoxy peak is observed, an explanation is suggested from the results [31] of the degenerate rearrangement of **1** and **1'** ($\text{R} = \text{CH}_3$). Rearrangements interconverting both the R groups and the arylthio groups of **1** and **1'** through a transition state with *trans*-arythio groups but not R groups. The symmetrical structure (**2**) with *trans* arylthio groups (*trans*-**2**) is therefore preferred over that with *cis*-arythio groups (*cis*-**2**) by a factor of 3.3. This can be explained by the presence of greater steric repulsion in the buttressed *cis* transition state (than in the *trans*) between the arylthio groups and the methyl (R) groups. Similar steric effects might be expected in **14**. From an inspection of models, the steric interaction in *cis*-**14** may be quite severe. If the energy of *cis*-**14** is higher than *trans*-**14**, it may not be present in sufficient quantity to be detected by ^1H NMR.

Another explanation for failure to observe more than one methoxy absorption is more plausible however. It is reasonable to expect that the hypervalent bond of **14** is deformed (curve **b**, Figure 2). Deformation away from TBP geometry which would effectively break one of the C–S bonds might be expected to require little input of energy. Such geometries represent the extreme geometries of molecular vibrational modes which are populated at relatively low temperature. These vibrational modes could, of course, be coupled with partial rotations about the C–S bond joining the arylthio group to the anthracene nucleus rapidly interconverting the *cis* and *trans* isomers of **14** even at low temperature.

The stabilization of the symmetrical structure **14**, which results from the introduction of the pentadienyl cation bidentate diequatorial π -acceptor ligand, is accompanied by a destabilization of the unsymmetrical geometries of **30** and **30'**. This is an expected result of the close juxtaposition of two relatively localized positive charges in **30** and **30'** and parallels the destabilization manifested in the apparent weakness of the S–C bond in **21** which was discussed earlier (see the Results section).

The possibility exists that the TBP geometry represents a very low energy maximum (curve **b'**, Figure 2) separating two energy minima where there is appreciable bonding to both sulfurs in the geometry of each minimum. This would still represent the first example of a pentacoordinate carbon (10-C-5) species, but one with geometry at the pentacoordinate carbon somewhat distorted from the regular TBP geometry which has formed the basis of the earlier discussion.

SUMMARY

The evidence presented above is best interpreted in terms of the direct observation of a 10-C-5 species with approximate, if not exactly, symmetrical TBP geometry about carbon (**14**). Geometric and electronic features of **14** favoring the TBP structure include the following: the large electronegativity of the apical ligands (sulfonium sulfurs); the linking of apical positions with an equatorial position into five-membered rings; benzoannulation of these five-membered rings; and linking of the remaining equatorial sites into a strain-free six-membered ring of sp² carbons of which the LUMO is of the proper symmetry to interact with the hypervalent σ -bonding orbital, thus stabilizing the hypervalent bond and the TBP geometry about carbon.

A further possibility is that the six-membered ring of sp² carbons may retain some of its aromatic character by using a pair of electrons in the hypervalent bond to complete its (4n + 2) shell. The possibility of such, which might appropriately be termed *bis-ipso* aromaticity, deserves further study.

ACKNOWLEDGMENT

This article was supported by a grant from NIH (GM 33064) for JCM when he was at the University of Illinois. Other help was provided by the University of Illinois, Vanderbilt University, and Mobil Oil Corp.

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