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An NMR Study of a ^{13}C-Labeled Hypervalent (10-C-5) [1] Pentacoordinate Carbon Species

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ABSTRACT

*Removal of two electrons from 1,8-bis(4-methylphenylthio)-9-(2,6-dimethoxyphenyl-1-^{13}C)-10-phenylanthracene (**2**) provides stable dication **1**. Isotopic enrichment (85%) of ^{13}C at the labeled site of the aromatic carbon, between the two sulfurs, makes possible the observation of spin-spin coupling constants between this ^{13}C-carbon and the directly bonded equatorial ligand carbons. The magnitudes of these coupling constants (two $^1J_{C1'C2'}$ = 61.9 Hz and one $^1J_{C1'C9}$ = 56.3 Hz) suggest that this carbon is sp^2 hybridized, with the postulated trigonal bipyramidal (TBP) geometry about this carbon center. The ^{13}C NMR chemical shifts for the 10-C-5 carbon (δ 109.3) and for other carbons provide strong evidence against alternative structures for this dication. The data are consistent with the 10-C-5 species, with apical sulfonium ligands and equatorial carbons of the hypervalent TBP carbon species **1**.*

INTRODUCTION

Efforts of both NMR spectroscopists and theoreticians in the measurement and interpretation of the spin-spin coupling constants between directly bonded magnetic nuclei have resulted in the formulation of relationships between these coupling constants and bond hybridization parameters [2]. For directly bonded carbons, the main determinant of the coupling constants ($^1J_{CC}$) is the Fermi contact term [2]. Other factors which have been examined in relationship to their contribution to the magnitude of $^1J_{CC}$ are π-bond order [3], substitution patterns [3,4], ring size [4], and substituent orientation [4]. The principle determinant of $^1J_{CC}$ is the shared valence-shell σ-electron density between the directly bonded coupling carbons. The value of $^1J_{CC}$ has become a generally acceptable probe of hybridization. The measurement of $^1J_{CC}$ in classes of compounds having coupled carbons in a variety of hybridization combinations has yielded ranges of values for $^1J_{CC}$ that correlate well with other estimates of the hybridizations of coupled carbons [3].

The interest in obtaining further evidence for a structure (**1**) containing hypervalent TBP carbon (a 10-C-5 species) led us to the preparation of dication **1**, with the central 10-C-5 carbon atom enriched (85%) with carbon-13 in order to determine the spin-spin coupling constants for the coupling of the TBP carbon with adjacent bonded carbons and to make important peak assignments free of ambiguity.

EXPERIMENTAL

The ^{13}C-enriched compounds were identified by comparison of the ^{1}H and ^{13}C NMR spectra, with spectra obtained from authentic unenriched samples. The ^{13}C NMR chemical shift assignments for the carbons of dication **1** and anthracene **2** are presented in Table 2. The assignments for the carbons of compounds **4–12** are recorded. The values ob-

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TABLE 1 Coupling Constants, $^nJ_{CH}$, and $^nJ_{CC}$, in Units of Hertz

Compound	$^1J_{CH}$	$^3J_{CH}$	$^4J_{CH}$	$^1J_{CC}$	$^2J_{CC}$	$^3J_{CC}$
4	129			35.2		
5	126			36.8	3.1	
6	127			40.3	14.6	
7	161			63.2	6.8	
8		2.0		33.2	15.1	
9		8.1	1.6	73.8	4.4	5.0
10		8.1	1.6	79.4	4.3	5.3
11	158	[a]	[a]	70.5	[b]	3.6[c]
12		8.3	1.6	79.3	3.4	3.8
1		6.0	[d]	61.9,[e] 56.3[f]	4.2[g]	[h]
2		5.6	[b]	74.3,[e] 40.3[f]	[d]	[b]

[a] Overlap of absorptions; coupling constants not determined. [b] Not observed. [c] $^3J_{CC}$ = 2.9 Hz (methoxy carbons). [d] Broadened in spectrum of ^{13}C labeled species; sharp in unlabeled species. [e] $^1J_{CC}$ (carbons-2′). [f] $^1J_{CC}$ (carbon-9). [g] $^1J_{CC}$ = 1.2 Hz (carbons-1″). [h] $^3J_{CC}$ = 1.3 Hz (methoxy carbons-5′).

tained for carbon-hydrogen and carbon-carbon coupling constants are reported in Table 1.

Methanol-^{13}C

In a modification of the method of Nystrom [5], a sample of 16.5 g (0.43 mol) of $LiAlH_4$ in 600 mL of 2(3)-(tetrahydrofurfuryloxy)tetrahydropyran (Aldrich Chemical Company, twice distilled in vacuum from $LiAlH_4$) was stirred for 24 hours. Into this vigorously stirred solution was slowly bubbled 16.9 g (0.38 mol) of ca. 90%-^{13}C enriched carbon dioxide (Mounds Laboratory). Further stirring (48 hours) was followed by dropwise addition at 0°C of 260 mL of tetrahydrofurfuryl alcohol. A simple distillation with a pot temperature of ca. 315°C provided distillate with vapor temperature 25–115°C which was shown by ^1H NMR to be pure methanol, 10.25 g (0.32 mol, 84%). The amount of ^{13}C-enrichment was determined from the ^1H NMR spectrum to be ca. 85%.

Iodomethane-^{13}C

A mixture of 10.25 g (0.32 mol) of methanol-^{13}C in 350 mL of 47% HI was boiled for 1 hour. Distillation gave wet iodomethane, bp 25–43°C. Redistillation from P_2O_5 gave 3.91 g (0.27 mol, 85%) of pure iodomethane, bp 43°C.

2-(Methyl-^{13}C)-2-carbomethoxycyclopentanone (**4**)

In a modification of the method of Pond and Cargill [6], to 48.75 g (0.27 mol) of freshly prepared potassium 2-carbomethoxycyclopentanone [7] (**3**) in 300 mL of freshly distilled (from CaH_2) dimethyl sulfoxide was added dropwise 39.0 g (0.27 mol) of iodomethane-^{13}C at 0°C. The solution was diluted with H_2O and extracted with pentane for 24 hours. Removal of solvent in vacuum gave 36.0 g (0.21 mol, 78%) of an oil of **4**: ^{13}C NMR ($CDCl_3$/TMS) δ 57.84 (s, -OCH_3), 56.00 (d, J = 35.2 Hz, 2-*C*), 51.54 (s, 5-*C*), 37.64 (s, 4-*C*), 36.18 (s, 3-*C*), 19.52 (s, -CH_3).

2-(Methyl-^{13}C)cyclopentanone (**5**)

A solution of 38.5 g (0.25 mol) of **4** in 2.5 L of 3 N HCl was boiled for 24 hours. The solution was cooled and continuously extracted with pentane for 24 hours. The solution was dried ($MgSO_4$). Solvent was removed in vacuum. Distillation gave 16.9 g (0.17 mol, 69%) of **5**: bp 139.5–140.5°C; ^{13}C NMR ($CDCl_3$/TMS) δ 200.54 (s, *C*-1), 44.01 (d, J = 36.8 Hz, *C*-2), 37.64 (s, *C*-5), 31.91 (s, *C*-4), 20.67 (d, J = 3.1 Hz, *C*-3), 14.21 (s, -CH_3).

Methyl 5-Oxohexanoate-6-^{13}C (**6**)

In a modification of the method of Schaeffer and Snoddy [8], a solution of 31.0 g (0.31 mol) of CrO_3 and 45 g of 98% H_2SO_4 in 125 mL of water was added dropwise to a vigorously stirred suspension of 14.7 g (0.15 mol) of **5** in 25 mL of water at 0°C. The solution was stirred for 24 hours at 25°C. The solution was diluted with saturated $(NH_4)_2SO_4$ and was extracted with ether for 48 hours. The ether solution was dried ($MgSO_4$). Solvent was removed in vacuum. To the yellow oil was added 75 mL of methanol, 75 mL of 2,2-dimethoxypropane, and ca. 1 g of *p*-toluenesulfonic acid in a modification of the method of Lorette and Brown [9]. The solution was stirred for 20 hours at 25°C. All volatile materials were removed in vacuum at 40°C, and a solution of 1.0 g of $NaHCO_3$ in 250 mL of H_2O was added to the remaining liquid. The solution was continuously extracted for 12 hours with ether. The ether solution was dried ($MgSO_4$), and the solvent was removed in vacuum. Distillation gave 19.9 g of a mixture of 85% of cyclohexen-1-ol-3-one (**7**) and 15% dimethyl succinate as was determined by ^1H NMR spectroscopy. Ester **6** was used in the next step without purification: ^{13}C NMR ($CDCl_3$/TMS) δ 207.80 (d, J = 40.3 Hz, *C*-5), 173.56 (s, *C*-1), 51.51 (s, -OCH_3), 42.46 (d, J = 14.6 Hz, *C*-4), 30.62 (s, *C*-2), 29.89 (s, *C*-6), 17.03 (s, *C*-3).

1,3-Cyclohexanedione-2-^{13}C (**7**)

In a modification of the method of Kishi et al. [10], a solution prepared by the reaction of 10 g (0.39 g-atom) of potassium with 250 mL of *tert*-butyl alcohol (three times distilled from CaH_2) was diluted with 250 mL of dry ether, and 19.9 g of a mixture of 85% **7** (0.12 mol) and 15% dimethyl succinate in 100 mL of dry ether was added dropwise with stirring at 0°C. After 8 hours at 25°C, the solution was extracted with 50 mL of 10 N NaOH followed by

5 100 mL portions of 1 N NaOH. This solution was acidified at 0°C with 10% HCl and then continuously extracted with CH_2Cl_2 for 24 hours. The extract was dried ($MgSO_4$), and solvent was removed. Titration of the oil with ether induced crystallization of **8**, 10.1 g (0.09 mol, 75%): ^{13}C NMR ($CDCl_3$/TMS; enol form) δ 169.05 (d, J = 63.2 Hz, *C*-1 and -3), 98.69 (s, *C*-2), 41.32 (d, J = 6.8 Hz, *C*-4 and -6), 32.40 (s, *C*-5); (keto form) δ 62.09 (s, *C*-2), 47.43 (d, J = 2.8 Hz, *C*-4 and -6), 15.61 (s, *C*-5).

2,2-Dichloro-1,3-cyclohexadione-2-C^{13} (**8**)

In a modification of the method of Schamp [11], a solution of 9.5 g (84 mmol) of **7** in 150 mL of chloroform was cooled to −10°C and saturated with HCl gas. Chlorine gas was then bubbled through this solution until a precipitate had formed and then subsequently redissolved. The solvent was removed in vacuum at 25°C to give the unstable compound **8**: ^{13}C NMR ($CDCl_3$/TMS) δ 192.27 (d, J = 33.2 Hz, C-1 and -3), 85.96 (s, C-2), 35.42 (d, J = 15.1 Hz, C-2 and -6), 17.13 (s, C-5).

2-Chlororesorcinol-2-^{13}C (**9**)

By the method of Schamp [11], freshly prepared **8** was dissolved in 50 mL of dimethylformamide (DMF) saturated with HCl and 50 mL of DMF. Upon heating this solution at 160°C for 15 minutes, vigorous gas evolution was observed. Most of the DMF was removed at 65°C (6 Torr), 20 mL of 2 N NaOH was added, and the mixture was diluted to 500 mL with H_2O. This solution was continuously extracted with ether for 12 hours to remove the DMF. The solution was acidified at 0°C with concentrated HCl and then, again, continuously extracted for 24 hours with ether. The ether was removed in vacuum. The red oil was chromatographed (silica gel/chloroform) to give solid **9**. Recrystallization from $CHCl_3$/hexane gave 10.6 g (73 mmol, 87% based on starting **7**) of **9** as white needles: ^{13}C NMR ($CDCl_3$/TMS) δ 152.09 (d, J = 73.8 Hz, *C*-1 and -3), 128.08 (d, J = 5.0 Hz, *C*-5), 108.25 (d, J = 4.4 Hz, *C*-4 and -6), 107.38 (s, *C*-2).

2-Chloro-1,3-dimethoxybenzene-2-^{13}C (**10**)

To a solution of 2.08 g (87 mmol) of NaH (washed with tetrahydrofuran) in 250 mL of tetrahydrofuran (THF) was added dropwise 6.29 g (43 mmol) of **9** in 20 mL of THF with stirring at 0°C. After the evolution of H_2 had ceased, 11.0 g (87 mmol) of dimethyl sulfate in 20 mL of THF was added dropwise at 0°C. The solution was stirred for 3 hours at 25°C and then boiled for 22 hours. This solution was poured into ice water. The organic layer was washed twice with 50 mL portions of 2 N NaOH and once with saturated NaCl solution and then was dried ($MgSO_4$). Solvent was removed in vacuum to give crude **10**. Recrystallization from pentane gave 7.28 g (42 mmol, 98%) of **10** as white needles: ^{13}C NMR ($CDCl_3$/TMS) δ 156.30 (d, J = 79.4 Hz, *C*-1 and -3), 127.17 (d, J = 5.3 Hz, *C*-5), 110.70 (s, *C*-2), 104.72 (d, J = 4.3 Hz, *C*-4 and -6), 56.29 (s, -OCH_3).

1,3-Dimethoxybenzene-2-^{13}C (**11**)

A solution of 6.90 g (40 mmol) of **10** in 350 mL of 0.2 N NaOH in ethanol was shaken with 30 g of freshly prepared W-6 Raney nickel under 40 psi of H_2 at 25°C for 12 hours. The solvent was removed in vacuum, and the remaining material was dissolved in ether. The ether solution was washed twice with H_2O and dried ($MgSO_4$). Solvent was removed in vacuum to give 4.58 g (33 mmol, 83%) of **11**. This material was determined to be of high purity by ^{1}H NMR spectroscopy and was used without further purification: ^{13}C NMR ($CDCl_3$/TMS) δ 160.90 (d, J = 70.5 Hz, *C*-1 and -3), 129.90 (d, J = 3.6 Hz, *C*-5), 106.16 (s, *C*-4 and -6), 100.46 (s, *C*-2), 55.22 (d, J = 2.9 Hz, -OCH_3).

2-Bromo-1,3-dimethoxybenzene-2-^{13}C (**12**)

In a modification of the method of Wittig and Pockels [12], 4.58 g (33 mmol) of **11** in 100 mL of ether was added dropwise to *n*-butyllithium (41 mmol, 2.3 N in hexane) at 0°C. This solution was stirred for 10 hours at 25°C and then 8.42 g (45 mmol) of 1,2-dibromoethane was added dropwise. The solution was boiled for 36 hours and then mixed with H_2O. The organic layer was washed with H_2O and then dried ($MgSO_4$). Solvent was removed in vacuum to give crude **12**. Recrystallization from hexane gave 41.0 g (19 mmol, 57%) of **12** as colorless needles: ^{13}C NMR ($CDCl_3$/TMS) δ 157.24 (d, J = 79.3 Hz, C-1 and -3), 128.24 (d, J = 3.8 Hz, C-5), 104.74 (d, J = 3.4 Hz, C-4 and -6), 101.01 (s, C-2), 56.41 (s, -OCH_3).

1,8-Bis(4-methylphenylthio)-9-(2,6-dimethoxyphenyl-1-^{13}C)-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (**13**)

To 1.570 g (2.97 mmol) of 1,8-*bis*(4-methylphenylthio)-10-phenyl-10-hydroxy-9-anthrone (14) [13] in 60 mL of benzene-THF (2:1) was added 3 mmol of *n*-butyllithium in hexane at 0°C. A solution of 1,3-dimethoxyphenyllithium-1-^{13}C was made by the reaction of 0.88 g (4 mmol) of **12** in 10 mL of THF with 4 mmol of *n*-butyllithium at 0°C. After 20 minutes, this solution was added to the solution of **14** and stirred for 12 hours at 25°C. Saturated NH_4Cl was added to the solution. This mixture was extracted into CH_2Cl_2, washed with H_2O, then dried ($MgSO_4$). Removal of solvent in vacuum gave crude **13**. Two recrystallizations from CH_2Cl_2-hexane gave

1.18 g (1.76 mmol, 60%) of **13** as a colorless solid mixture of syn and anti isomers, which was used without further purification.

1,8-Bis(4-tolylthio)-9-(2,6-dimethoxyphenyl-1-^{13}C)-10-phenyl-anthracene Dication Ditriflate (**1**)

As described previously in paper 1 [13], **13** (from the preceding step) in liquid SO_2 was treated with trifluoromethanesulfonic (triflic) acid: ^{13}C NMR (SO_2/CF_3SO_3H/TMS) δ 176.55 (d, J = 61.9 Hz), 158.96 (s), 149.23 (s), 147.68 (s), 137.71 (d, J = 4.2 Hz), 135.44 (s), 132.97 (s), 132.74 (s), 131.87 (s), 131.11 (s), 130.56 (s), 130.14 (s), 128.50 (s), 126.40 (s), 122.65 (d, J = 1.2 Hz), 117.78 (d, J = 55.7 Hz), 109.25 (s), 61.17 (d, J = 1.9 Hz), 21.72 (s).

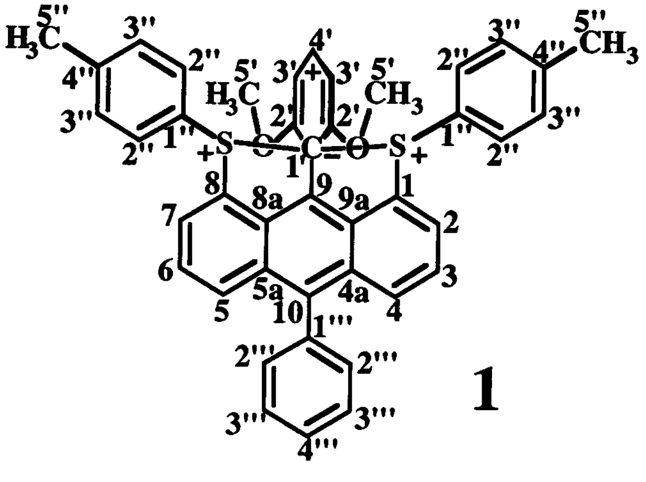
1,8-Bis(4-tolylthio)-9-(2,6-dimethoxyphenyl-1-^{13}C)-10-phenyl-anthracene (**2**)

Anthracene **2** was prepared by adding a liquid SO_2 solution to aqueous NaOH at −10°C, as previously described in Ref. [13]: ^{13}C NMR ($CDCl_3$/TMS) δ 161.85 (d, J = 74.3 Hz), 140.71 (s), 138.18 (s), 137.36 (s), 136.09 (s), 134.48 (s), 133.95 (s), 132.21 (s), 132.10 (s), 131.51 (s), 130.51 (d, J = 40.3 Hz), 130.01 (s), 129.92 (s), 128.51 (s), 127.21 (s), 124.04 (s), 118.01 (s), 104.63 (s), 56.18 (s), 21.14 (s).

RESULTS

The synthetic route leading to **1** and **2** is shown. The overall yield in the multistep transformation of ^{13}C-enriched iodomethane to compound **12** was approximately 16%. All carbon-hydrogen ($^nJ_{CH}$) and carbon-carbon ($^nJ_{CC}$) coupling constants to the ^{13}C-enriched position for these compounds are recorded in Table 1. Assignments for the ^{13}C NMR spectra of these singly labeled compounds (**4–12**) are reported in the Experimental section. Assignments for the ^{13}C NMR spectra of **1** and **2** are reported in Table 2, with the peak multiplicities from carbon-hydrogen coupling which was determined from off-resonance proton decoupled spectra of the unenriched species. Coupling constants (Table 1) for carbon-hydrogen coupling ($^nJ_{CH}$) were determined from the spin-spin splitting observed in the ^{1}H NMR spectra of these compounds.

The ^{13}C NMR assignments for **1** and **2** are based upon the data in Tables 1 and 2, with comparisons of appropriate models and interpretations of substituent chemical shift [14], where appropriate models were absent.



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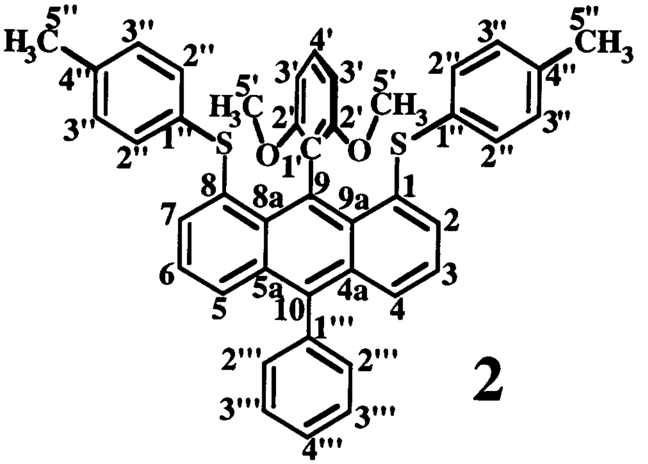

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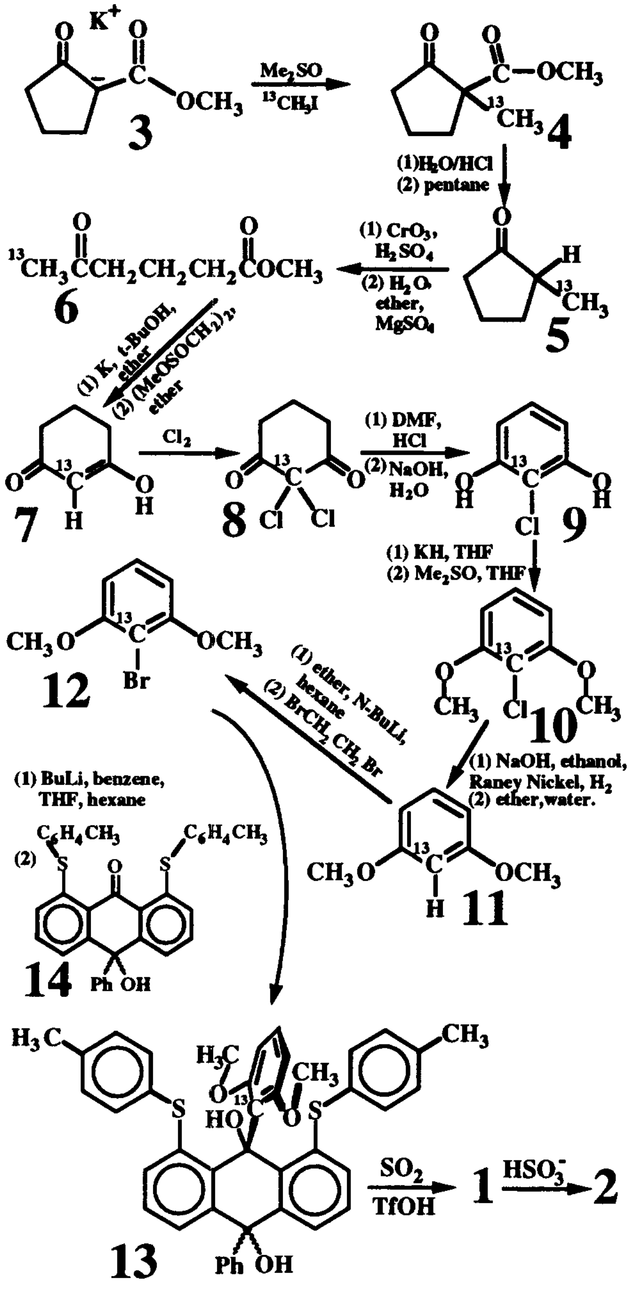
DISCUSSION

The postulated structure of **1**, centered about a hypervalent 10-C-5 carbon (C-1′), requires approximate sp^2 hybridization about this carbon in its bonding to the equatorial sp^2-carbon ligands (C-2′ and C-9). If this proposed structure is correct, then the value of the coupling constants between carbon 1′ and carbons 2′ and 9 should be observed in the general range of other sp^2-sp^2 directly bonded carbon-carbon coupling constants. If this dication has the alternate unsymmetrical ground state structure **15a** and **15b** in which symmetrical structure **1** is the transition state for the interconversion of the pair (**15a** and **15b**), then carbon 1′ should have approximately sp^3 hybridization. Its coupling to the directly bonded sp^2-carbon atoms should then be expected in the general range of other sp^2-sp^3 directly bonded carbon-carbon coupling constants.



SCHEME 1

The observed coupling constants between carbons 1′ and 2′ in **1** is $^1J_{CC}$ = 61.9 Hz. The magnitude of the coupling constant is reduced relative to that observed for the neutral species **2** ($^1J_{CC}$ = 74.3 Hz). The ($^1J_{CC}$ = 61.9 Hz) for carbons 1′ and 2′ of dication **1** is of larger magnitude than any sp^2-sp^3 coupling previously reported (see Table 3) which provides evidence against the rapidly equilibrating unsymmetrical structure **15a** and **15b** as the structure of **1**. The reduced magnitude of this coupling in dication **1** relative to neutral **2** is expected to be due to the reduction in π-bond order between carbons 1′ and 2′ in **1** accompanying hy-

TABLE 2 ^{13}C NMR Chemical Shift Assignments and Multiplicities of Carbon-Hydrogen Splittings for Compounds **1** and **2**

	Compound	
Carbon	*1*	*2*
1	126.4(s)	138.2(s)
2	133.0(d)	128.5(d)
3	130.1(d)	124.0(d)
4	134.5(d)	125.7(d)
4a		132.2(s)
8a		130.0(s)
9	117.8(s)	130.5(s)
10	147.7(s)	136.1(s)
1′	109.3(s)	118.0(s)
2′	176.6(s)	161.9(s)
3′	137.7(d)	104.6(d)
4′	159.0(d)	132.1(d)
5′	61.2(q)	56.2(q)
1″	122.7(s)	134.5(s)
2″	132.7(d)	134.0(d)
3″	130.6(d)	129.9(d)
4″	149.2(s)	137.4(s)
5″	21.7(q)	21.1(q)
1‴	138.1(s)	140.7(s)
2‴	128.5(d)	128.3(d)
3‴	131.9(d)	131.5(d)
4‴		127.2(d)

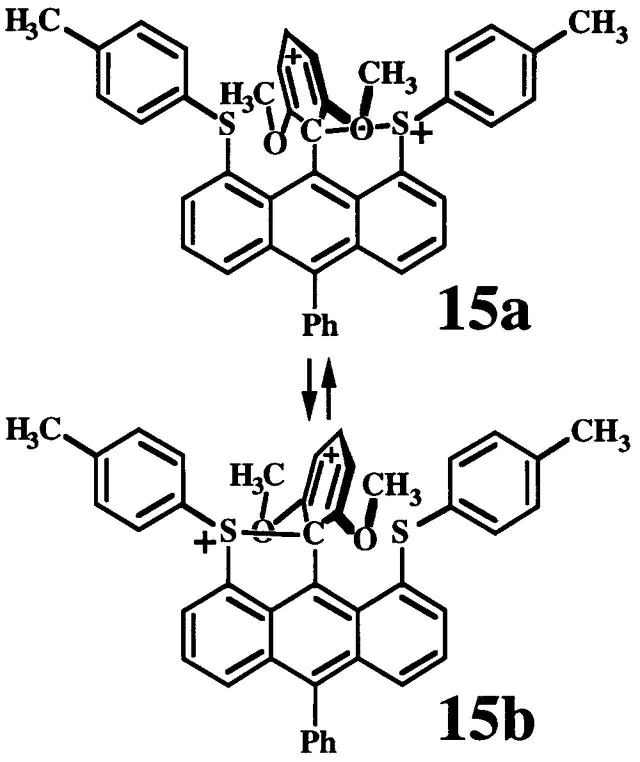
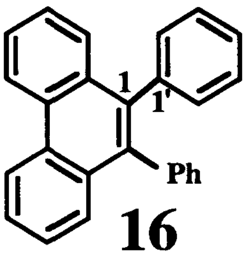


TABLE 3 Ranges of $^1J_{CC}$ for Coupling of C_1 and C_2 (sp^2-sp^2 and sp^2-sp^3 Carbons) Observed in the Exhaustive Compilation of Ref. [3]

	C₂	
C₁	*sp³ Carbon*[a]	*sp² Carbon*
sp^2 Carbonyl carbons: carboxylic acids, esters, amides, acid halides, etc.	59.2–46.2 Hz	80.5–53.3 Hz
sp^2 Carbonyl carbons: ketones and aldehydes	51.8–29.5 Hz	61.0–50.5 Hz
sp^2 Aromatic carbons	49.3–42.1 Hz	75.8–51.2 Hz
sp^2 Olefinic carbons	52.0–34.0 Hz	104.5–44.0 Hz[b]

[a] Excluding carbons of three-membered rings which are more sp^2 in character.

[b] Excluding allenes.



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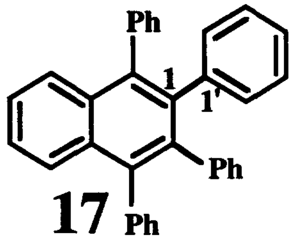

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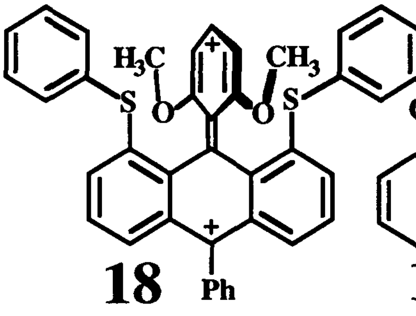

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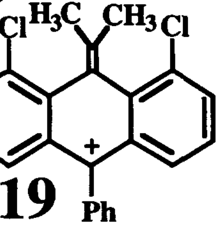

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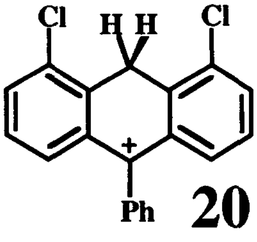

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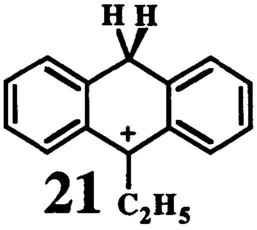

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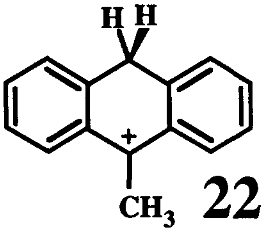

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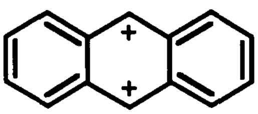

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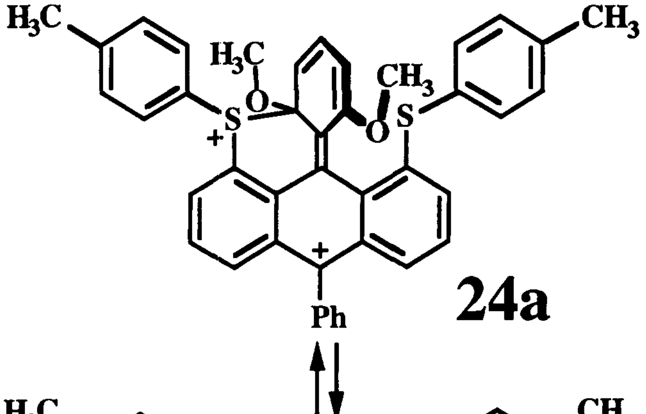
pervalent bond formation. The localization of electron density in the hypervalent bond, to the extent it occurs, must reduce the π-bond order in the bond joining carbons 1′ and 2′. For most known one-bond carbon-carbon couplings, a reduction in π-bond order results in reduced values for $^1J_{CC}$ [3,15].

The observed coupling between carbon 1′ and 9 in **1** was observed to be 55.7 Hz. This is also in the range for directly bonded sp^2 carbons. The magnitude of this coupling is increased relative to that observed for carbon 9 in **2** ($^1J_{CC}$ = 40.3 Hz). This coupling in **1** is of the same magnitude as the value of the coupling constant ($^1J_{CC}$) observed for carbons 1 and 1′ in **16** ($^1J_{CC}$ = 56.2 Hz) [15] and **17** ($^1J_{CC}$ = 56.3 Hz) [15]. Models for **1**, in which the reported coupling is between two sp^2 carbons in different rings, are expected to be strongly twisted from coplanarity by severe steric interactions.

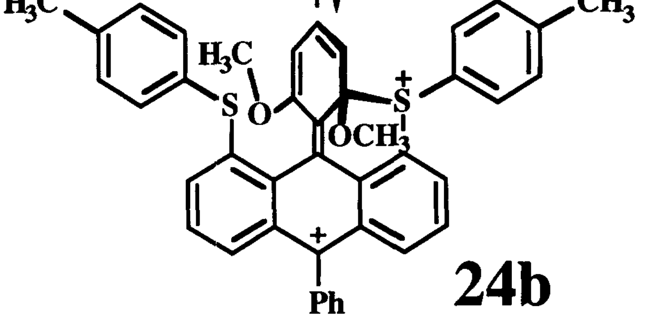
These observed values of $^1J_{CC}$ for **1** can also be interpreted in terms of structure **18**—a π-dication. The ^{13}C chemical shift assignments for **1** suggest, however, that **18** is not a likely structure for this dication. This is based upon comparisons of the data for **1** with data for anthracene cations in which a positive charge is postulated to be localized in the π-system (**19**,**20**,**21**, and **22**). These π-cation derivatives of anthracene are reported to have large positive charge density at the anthracene 10-position carbon similar to that expected for the related hypothetical dication **18**. The chemical shifts for these carbons are observed at very low field relative to the other sp^2 carbons of the anthracene **19** (δ 187.6) [16], **20** (δ 196.8) [16], **21** (δ 200.5), [17] **22** (δ 205.1) [17]. Similarly, the 9- and 10-position carbons of the anthracene dication (**23**) [18] bear the major amount of positive charge and are observed at lowest field (δ 187.1) relative to the other carbons. In the ^{13}C NMR spectrum of **1** no singlet absorption is observed in the proton noise decoupled spectrum at lower field than δ 149.2. If this absorption at δ 149.2 represented the chemical shift of carbon 10 in the hypothetical structure **18**, this would represent a 38.4 ppm shift upfield from the anthracene carbon-10 in the related monocation **19**. This argues strongly against structure **18** as an alternative for **1**. The hypothetical degenerate unsymmetrical structure **24a** and **24b** is also incompatible with the ^{13}C NMR spectrum of **1** based on the same chemical shift arguments that discount **18**. This wrong dication (**24a** and **24b**) would also be expected to have a low-field chemical shift for anthracene carbon 10. Arguments against both of these structures (**18** and **24**) on the basis of ^1H NMR chemical shift data are found in paper 1 [13].

The observed upfield chemical shift of anthracene carbon 9 in dication **1** (δ 117.8) relative to anthracene **2** (δ 130.5) is also inconsistent with the expected change in the resonance of this carbon if the structure for **1** is instead represented by π-dication **18**. In structure **18**, the charge in the 2,6-dimethoxyphenyl ring would be delocalized into the anthracene ring. This would be expected to cause a downfield shift of the resonance for carbon 9 in **18** relative to **2**. The effect [3] of conjugation of sp^2 carbons with positive charge is generally known to be accompanied by a downfield shift of the resonances of carbons in conjugation with the charge. The observation of the opposite shift (upfield) for carbon 9 in **1** and relative to **2** is further evidence against **18** as the structure of dication **1**. The actual reason for the upfield shift of the resonance of carbon 9 is not clear. Chemical shifts for ipso carbons have been found to vary with substituent changes in a manner which is not well understood [19].

The chemical shifts of the carbons (other than carbon 1′) of the 2,6-dimethoxyphenyl ring of dication **1** relative to those of the comparable carbons of anthracene **2** (Table 2: carbons 2′, 3′, and 4′) show the expected shift to lower field that is generally known to be accompanied by a downfield shift of the resonances of carbons in conjugation with the charge. The observation of the opposite shift (upfield) for carbon 9 in **1** and relative to **2** is further evidence against **18** as the structure of dication **1**. The actual reason for the upfield shift of the resonance of carbon 9 is not clear. As stated previously, chemical shifts for ipso carbons have been found to vary with substituent changes in a manner which is not well understood [19].

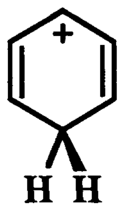


24a



24b

The chemical shifts of the carbons (other than carbon 1′) of the 2,6-dimethoxyphenyl ring of dication **1** relative to those of the comparable carbons of anthracene **2** (Table 2: carbons 2′, 3′, and 4′) show the expected shift to lower field accompanying introduction of positive charge into this π-system. The shift to lower field that accompanies the introduction of positive charge into the π-system of alternate aromatics is well known [3] and has been used extensively for chemical shift assignments. Carbons 3′ of **1** are observed at δ 137.7. This chemical shift is comparable to carbons 3 of the recently reported static cyclohexadienyl cation [17] (**25**, δ 136.9). Similar chemical shifts of these carbons in **1** and in **25** are expected, since the methoxy groups which are conjugated with carbons 2′ and 4′ are expected to have little if any resonance π-interaction with carbons 3′ in **1** upon introduction of positive charge in the 2,6-dimethoxyphenyl ring. In anthracene **2**, carbons 3 do have direct resonance interaction with the π-donating methoxy oxygen which is responsible for their occurrence at higher field (δ 104.6) relative to benzene (δ 128.5)



25

Carbons 2′ (δ 176.6) and 4′ (δ 159.0) of dication **1** are also shifted to lower field relative to the related carbons of **2** [2′ (δ 161.8), 4′ (δ 132.1)]. This is consistent with the expected downfield shift of the carbons bearing most of the positive charge in structure **1**. The magnitude of the downfield shifts of these carbons is less relative to the related carbons 2 (δ 186.6) and 4 (δ 178.1) of **25**. This is the expected result due to the π-donating ability of the methoxy oxygens which are conjugated with these carbons of **1** and are expected to reduce the amount of charge localized at these positions and thus the magnitude of the downfield shifts.

By a process of elimination, the conclusion is that the remaining positive charge of **1** resides on the sulfur atoms, since evidence is strong that it is not directly delocalized throughout the π-system of the anthracene. Evidence that the sulfur atoms bear the remaining charge is the upfield shift of carbons 1′ and the downfield shift of carbons 4′ in **1** relative to **2**. These shielding effects have been demonstrated by the conversion of this sulfur(II) in thioanisole [8] to sulfonium sulfur(II) in the phenyldimethylsulfonium ion [8]. An upfield shift of ca. 13 ppm for the ipso carbon and a downfield shift of ca. 11 ppm for the carbon para to sulfur occur. If one assumes that a similar effect would be seen in the chemical shifts of the para-tolyl carbons of **2** (C-1″, δ 134.5; C-4″, δ 137.4), one predicts for **1** a chemical shift for carbon 1″ of ca. δ 121.5 (observed, δ 122.6) and carbon 4″ of ca. δ 148.4 (observed, δ 149.2). The small splitting (1.2 Hz) of the peak at δ 122.6 could represent ${}^2J_{CC}$ coupling of carbon 1′ and carbon 1″ through sulfur. Other small two-bond couplings through heteroatoms (O, N, S, Se) have been reported [20]. A similar effect on the chemical shifts of the anthracene carbons 1 and 4 of **1**, relative to **2** by this change from thio (**2**) to sulfonium sulfur (**1**), would be expected. Carbons 1 (δ 138.2) and 4 (δ 125.7) in **2** are predicted to have a chemical shift for carbon 1 of **1** of ca. δ 125.2 (observed, δ 126.4) and 4 of ca. δ 136.7 (observed, δ 135.4).

The chemical shift of carbon 1′ of dication **1** is observed at δ 109.3. This represents an upfield shift ($\Delta\delta$ 8.7) relative to the two-electron reduction product, anthracene **2** (δ 118.0). The upfield shift of this carbon resonance in **1** relative to **2** has precedence in analogous species. Upfield shifts are observed for 10-P-5 pentacoordinate phosphorus(V) compounds in ^{31}P NMR. Similarly, upfield shifts in silicon resonances are observed for 10-Si-5 anionic pentacoordinate silicon(V) species relative to 8-Si-4 tetracoordinate silicon(IV) compounds in ^{29}Si NMR spectra. The magnitude of these upfield shifts for phosphorus and silicon compounds is as much as 100 ppm in the extreme cases. The change at carbon 1′ upon going from **2** to **1** is not as large as the change from tetracoordinate to pentacoordinate phosphorus or silicon, but the upfield shift is not surprising in view of the large upfield shifts seen in pentacoordinate phosphorus or silicon.

SUMMARY

The evidence presented here suggests that carbon 1′ is an sp^2 hybridized carbon atom in dication **1** from the value of ${}^1J_{CC}$ measured for its coupling to its directly bonded carbon ligands [19]. Evidence is strong against a π-dication (structures **18, 24a**, and **24b**) as the structure of dication **1** based upon ^{13}C NMR chemical shifts, observed for **1** to discount such structures. The chemical shifts of the arylthio ring carbons suggest that positive charge is localized at sulfur. The chemical shifts of the 2,6-dimethoxyphenyl ring carbons suggest that positive charge is localized in this π-system. All of this evidence suggests that this dication has the postulated structure **1** with a hypervalent 10-C-5 carbon atom—the first example of an observable 10-C-5 species.

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REFERENCES

[1] C. W. Perkins, J. C. Martin, A. J. Arduengo, III, W. Lau, A. Alegria, J. K. Kochi, *J. Am. Chem. Soc.*, *102*, 1980, 7753. These workers proposed the *N-X-L* classification scheme for species in which *N* valence shell electrons are formally involved in bonding *L* ligands to a central atom *X*.

[2] For reviews of both theoretical and experimental work, see: (a) G. E. Maciel: in T. Axenrod, G. A. Webb, (eds): *NMR Spectroscopy of Nuclei other than Protons*, Wiley Interscience, New York, 1974; (b) J. R. Llinas, E. J. Vincent, G. Peiffer, *Bull. Soc. Chim. Fr.*, *11*, 1973, 3209; (c) J. B. Strothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972; (d) R. E. Wasylishen: in *Annual Reports in NMR Spectroscopy*, G. A. Webb (ed), Academic Press, New York, vol. 7 (1978). (e) J. L. Marshall, D. E. Muller, S. A. Conn, R. Seiwell, A. M. Ihrig, *Acc. Chem. Res.*, *7*, 1974, 333.

[3] P. E. Hansen, *Org. Mag. Res.*, *12*, 1979, 109 and references therein.

[4] V. Wray: in *Progress in NMR Spectroscopy*, Pergamon Press Ltd., Great Britain, vol. 13 and references therein (1979).

[5] R. F. Nystrom, W. H. Yanko, W. G. Brown, *J. Am. Chem. Soc.*, *70*, 1948, 441.

[6] D. M. Pond, R. L. Cargill, *J. Org. Chem.*, *32*, 1967, 4064–4065.

[7] R. Mayer, G. Wenschuh, W. Töpfelmann, *Chem. Ber.*, *91*, 1958, 1616–1620.

[8] J. R. Schaeffer, A. O. Snoddy, *Org. Syn. Coll.*, vol. IV, p. 19.

[9] N. B. Lorette, J. H. Brown, Jr., *J. Org. Chem.*, *24*, 1959, 261–262.

[10] T. Fukuyama, L. V. Dunkerton, M. Aratani, Y. Kishi, *J. Org. Chem.*, *40*, 1975, 2011–2012.

[11] N. Schamp, *Bull. Soc. Chim. Belg.*, *73*, 1964, 35.

[12] G. Wittig, U. Pockels, *Ber.*, *72B*, 1939, 89–92.

[13] T. R. Forbus, Jr., J. C. Martin, *Heteroatom Chem.*, 1993, 113–128.

[14] D. F. Ewing, *Org. Mag. Res.*, *12*, 1979, 499 and references therein.

[15] P. E. Hansen, O. K. Poulsen, A. Berg, *Org. Mag. Res.*, *12*, 1972, 43 and references therein.

[16] W. J. Work: Ph.D. Thesis, University of Illinois, Urbana–Champaign, IL., 1976, with J. C. Martin, to be published.

[17] G. A. Olah, J. S. Staral, G. Asencio, G. Liang, D. A. Forsyth, G. D. Mateescu, *J. Am. Chem. Soc.*, *100*, 1978, 6299–6308.

[18] (a) G. A. Olah, D. A. Forsyth, *J. Am. Chem. Soc.*, *98*, 1976, 4086–4090; (b) K. Mullen, *Helv. Chim. Acta*, *59*, 1976, 1357.

[19] G. A. Olah, P. W. Westerman, D. A. Forsyth, *J. Am. Chem. Soc.*, *97*, 1975, 3419–3427.

[20] P. E. Hansen, *Org. Mag. Res.*, *11*, 1978, 215 and references therein.