brated with 0.01 N H_2SO_4. The increased swelling in the more concentrated acid caused the spontaneous flow rate to slow markedly, but the faster, more convenient rate was restored by the dilute acid wash.

Results are summarized in Table VII.

Acknowledgments. The author thanks Eleanor G. Applegate for expert technical assistance and Joan D. Hogan, Lucretia C. Hovsepian, and Harry C. Hauger for the metal ion analyses. Helpful discussions with Dr. M. Panar are also gratefully acknowledged.

References and Notes

(1) (a) M. J. Slater, *Chem. Ind.* (*London*), 478 (1971); (b) A. W. Fletcher, *Ibid.*, 776 (1971).

(2) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960).

(3) This compound would not crystallize and was used as a crude sirup.

(4) The difference is apparently a solubility effect; **5** is so insoluble in isopropyl alcohol that it crystallizes immediately on being formed.

(5) Reduction of the nonphenolic imines to **1**, **6**, and **7** required a large excess of sodium borohydride and reaction times of 24–48 hr, whereas the phenolic imines **8** and **11** required only slightly more than the theoretical amount of reducing agent and were reduced in less than an hour. This rate enhancement may reflect the formation of phenoxyboron hydrides in which the reducing residue is restrained near the reducing site and protected from solvolytic decomposition.

(6) The ligands were almost instantaneously sequestered into the aqueous phase.

(7) The magnetic moment was determined by NMR for which I am grateful to Drs. W. D. Phillips and C. C. McDonald and Mr. F. V. Ferrari of this laboratory.

(8) U.S. standard 200–400 mesh, 1% cross-linked with divinylbenzene.

(9) Good yields of triethylammonium chloride were recovered as by-products, thus the reaction was not a simple quaternization.

(10) L. R. Melby and D. R. Strobach, *J. Org. Chem.*, **34**, 421 (1969).

(11) The polymers were used in conventional chromatography columns equipped with an outlet for eluate collection and backwashing. The neutral polymers are hydrophobic and thus ineffective when packed in pure water. They were activated by treatment with 15% sulfuric acid followed by washing and equilibration with 0.01 N acid. The metal salt solutions were 0.05 M in metal ion in 0.01 N sulfuric acid; see Experimental Section.

(12) Since all the polymers virtually totally excluded Fe(II) and Fe(III), the competitive experiments with iron and Cu(II) give values essentially equivalent to absolute capacities for Cu(II).

(13) Aldrich Chemical Co., Milwaukee, Wis.

(14) The reduction proceeded fairly well in ethanol solvent, but ethyl acetate gave better yields of purer product. Contrary to our observations, J. L. Everett and W. J. C. Roos, *J. Chem. Soc.*, 1972 (1949), report that reduction in ethanol produces benzocinnoline.

(15) R. B. Carlin and G. E. Foltz, *J. Am. Chem. Soc.*, **78**, 1997 (1956).

(16) D. Heinert and A. E. Martell, *Tetrahedron*, **3**, 49 (1958), describe an aqueous, acidic manganese dioxide oxidation which was unsatisfactory in our hands. This modification of the anhydrous procedure of E. P. Papadapoulos, A. Jassar, and C. H. Issidorides, *J. Org. Chem.*, **31**, 615 (1966), proved superior.

(17) Shepperd Chemical Co., Cincinnati, Ohio.

(18) Bio-Beads S-XI, Bio-Rad Laboratories, Richmond, Calif.

(19) K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

(20) Ion analyses were done by atomic absorption and expressed in parts per million.

Ethylbenzenium Ions and the Heptaethylbenzenium Ion[1a]

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received December 30, 1974*

Abstract: A series of ethyl-substituted benzenium ions has been prepared under stable-ion conditions by protonation or electrophilic ethylation of the corresponding arenes. The series culminates in the heptaethylbenzenium ion (**1**-Et), and the physical and chemical properties of **1**-Et were investigated. The ions were studied by ^{1}H NMR and ^{13}C NMR spectroscopy, and the ^{13}C NMR spectra were compared with the analogous methyl-substituted benzenium ions. The carbon chemical shifts are interpreted in terms of charge distribution and are consistent with a regional charge distribution model but not the total or π charges calculated by the ab initio method. $^{1}J_{CH}$ values for C_1 in the benzenium ions indicate a high degree of strain in the hexa-substituted species relative to the less substituted members. The highly crowded ion **1**-Et appears to have several anomalously deshielded carbon resonances in the C_6–C_1–C_2 fragment.

The ability of aromatic compounds to undergo ring protonation in strongly acidic media to form arenium ions is one of the best known aspects of stable-ion chemistry.[2] The structures of these ions have been determined by a variety of spectroscopic methods including uv spectroscopy,[2] ^{1}H NMR spectroscopy,[2,3] and in recent years ^{13}C NMR spectroscopy.[3c-e,4]

The most intensely studied arenium ions have been the methyl-substituted benzenium ions; ^{1}H NMR spectra have been reported for all isomeric ions from the p-methylbenzenium ion[3c] to Doering and Saunders' heptamethylbenzenium ion (**1**-Me).[3a] The charge distributions in several of these ions have been discussed in relation to the carbon-13 chemical shifts of the ring carbon atoms[3c,4a,b] and, in the earlier literature, to the proton chemical shifts.[2]

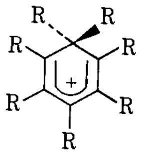
We have now extended our studies and prepared a series of ethyl-substituted benzenium ions including the heptaethylbenzenium ion (**1**-Et). The physical and chemical data for **1**-Et are discussed in relation to those for **1**-Me.[3a] The question of steric-induced strain in highly substituted benzenium ions is one of continuing interest; it has been suggested on the basis of ^{1}H NMR spectral parameters that the hexamethylbenzenium ion (**2**-Me) is distorted, relative to less substituted derivatives, with the C_1–CH_3 group forced pseudo-axial.[2,5] Since one-bond ^{13}C–^{1}H coupling ($^{1}J_{CH}$) magnitudes are known to be dependent upon strain,[6] this seemed a logical technique with which to investigate this problem. Steric factors could be more important in ethyl-substituted benzenium ions, and the carbon-13 chemical shifts and $^{1}J_{CH}$ values are compared with the methyl-substituted analogs and discussed in relation to charge distribution and ring strain.

Ethylbenzenium ions are of particular importance, because the aluminum chloride catalyzed liquid phase ethylation of benzene is one of the largest scale manufacturing processes. The red-oil layer produced in this reaction con-

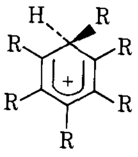
Table I. ^{1}H NMR Chemical Shifts[a] for the Ethyl-Substituted Benzenium Ions

Ion	Proton chemical shifts and multiplicities[a]				
	$H_{2,6}$	$H_{3,5}$	H_1	CH_2	CH_3
1-Et[b]				C_1–CH_2, q, 2.46; $C_{2,3,4,5,6}$–CH_2, 2.75, 2.86, overlapping q	C_1–CH_3, t, 0.17; $C_{2,3,4,5,6}$–CH_3, 0.98, 1.08, 1.23, overlapping t
2-Et[b]			4.43, broad t	C_1–CH_2, dq, 2.43; $C_{2,3,4,5,6}$–CH_2, q, 2.84	C_1–CH_3, t, 0.20; $C_{2,3,4,5,6}$–CH_3, t, 1.18
3[c]	9.44, d	8.47, d	5.13, broad	3.60, q	1.73, t
4[d]	H_6, 8.86, d	H_3, 7.95 H_5, 7.85, d	4.68, broad	3.20, q	1.33, t
5-Et[d]		7.67	4.48, broad	2.96, q	C_4–CH_3, t, 1.31; $C_{2,6}$–CH_3, t, 1.26

[a] Proton chemical shifts are relative to internal (capillary) Me_4Si; the resonances are singlets except where shown, d = doublet, t = triplet, q = quartet. [b] In SO_2 at −40°. [c] Data taken from ref 3c. [d] In HF–SbF_5–SO_2 at −60°.



1, R = Me, Et

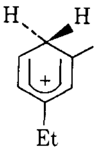


2, R = Me, Et

tains polyolefin catalyst complexes as well as ethylbenzenium tetrachloroaluminates which tie up substantial amounts of the $AlCl_3$ in the form of the catalytically inactive $AlCl_4^-$ counter ion. To maintain sufficient reaction rates, up to 25 w/w % of $AlCl_3$ is required since only a small amount (<1%) is present in the "free" state. A comparative study of ethylbenzenium ions with the "red-oil" complex layer of benzene ethylation was thus of additional interest.

Results and Discussion

Preparation of Ethylbenzenium Ions. Protonation and Electrophilic Ethylation. The basicities of ethyl-substituted benzenes are very similar to their methyl-substituted analogs,[7] and accordingly their behavior in superacid media is very similar. The protonation of ethylbenzene in HF-SbF_5-SO_2ClF has been reported previously by Olah and coworkers; at −100°, the static (nonexchanging) ion **3** was observed by ^{1}H NMR spectroscopy (Table I).[3c] 1,3-Diethylbenzene readily protonates in HF-SbF_5-SO_2 at −78° to give the 2,4-diethylbenzenium ion (**4**, Table I), but 1,2- and 1,4-diethylbenzene only rapidly equilibrate with the superacid at −78°, as observed for the corresponding xylenes.[2,3b] 1,3,5-Triethylbenzene, under the same conditions, affords the 2,4,6-triethylbenzenium ion (**5**-Et, Table I). The more basic hexaethylbenzene can be protonated in HSO_3F-SbF_5-SO_2 at −78° to the hexaethylbenzenium ion (**2**-Et, Table I); **2**-Et can also be prepared as the tetrachloroaluminate salt by the addition of gaseous HCl to aluminum chloride and hexaethylbenzene in carbon tetrachloride.



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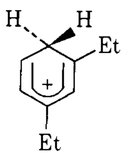

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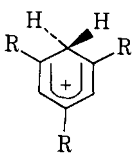
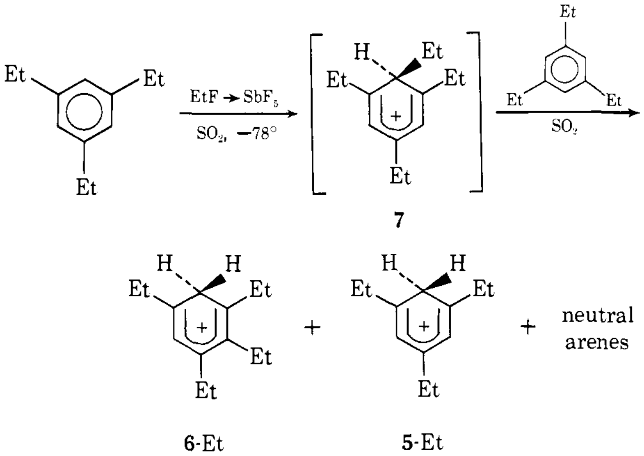


5, R = Me, Et

When a solution of 1,3,5-triethylbenzene in SO_2 was added to a solution of ethylfluoroantimonate (EtF → SbF_5)[8] in SO_2 at −78°, two ions were formed in approximately equal concentrations together with smaller amounts of neutral arenes. The total concentration of neutral arenes was similar to the concentration of each ion, as determined from the ^{1}H NMR spectrum. The ions were identified, from the ^{1}H NMR and ^{13}C NMR spectra, as **5**-Et and the 2,3,4,6-tetraethylbenzenium ion (**6**-Et). This reaction is assumed to involve the initial formation of the 1,2,4,6-tetraethylbenzenium ion (**7**) which subsequently loses a proton to the solvent followed by competitive protonation and ethylation of the excess 1,3,5-triethylbenzene, forms **6**-Et by successive hydride shifts, or directly transfers a proton intermolecularly to the excess 1,3,5-triethylbenzene.[9] **7** cannot be detected in the reaction mixture,[10] suggesting that this ion is much less stable than **6**-Et and **5**-Et. 1,2-, 1,3-, and 1,4-diethylbenzene, under the same conditions, give a complex mixture of ethylated benzenes and very small concentrations of benzenium ions.

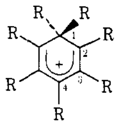
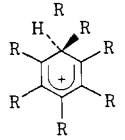
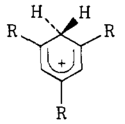
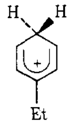
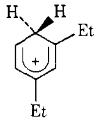
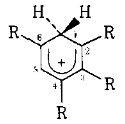


The experimental procedures for ion preparations are described in the Experimental Section, and the ^{13}C NMR data for the ethylbenzenium ion series are given in Table II.

The Heptaethylbenzenium Ion (1-Et). When a 10% solution of hexaethylbenzene in carbon tetrachloride at 10° is treated with equimolar amounts of aluminum chloride and ethyl chloride and the mixture stirred 1 hr, a dark-colored solid separates. The ^{1}H NMR spectrum of an SO_2 solution of this solid at −70° (Table I) showed three sets of signals; a shielded triplet at δ 0.17 (6 H) and three overlapping triplets and quartets between δ 1.2-1.4 (15 H) and 2.4-2.8 (14 H), respectively (a small quartet at δ 3.5 was shown to be due to unreacted ethyl chloride). The spectral data are consistent with the heptaethylbenzenium ion structure **1**-Et; the shielded triplet is assigned to the methyl protons of the C_1 geminal ethyl groups. The ^{13}C NMR spectrum (Table II) is also consistent with this structure.

1-Et can also be prepared as the hexafluoroantimonate salt by the addition of hexaethylbenzene to an equimolar quantity of ethylfluoroantimonate (EtF → SbF_5)[8] in SO_2 at

Table II. Carbon-13 Chemical Shifts[a] and $^1J_{CH}$ Values[a] for the Ethyl- and Methyl-Substituted Benzenium Ions

		Carbon-13 chemical shifts and $^1J_{CH}$ values[a]				
Ion		C_1	C_2, C_6	C_3, C_5	C_4	Additional
	(1-Et)[b]	70.1	203.8	148.6	198.2	C_1–CH_2, 27.3; $C_{2,6}$–CH_2, 35.4; $C_{3,5}$–CH_2, 22.9; C_4–CH_2, 28.6; C_1–CH_3, 9.9; $C_{2,6}$–CH_3, 14.8; $C_{3,5}$–CH_3, 13.4; C_4–CH_3, 15.6
	(1-Me)[c]	56.6	197.7	139.2	191.1	C_1–CH_3, 21.5[i]; $C_{2,6}$–CH_3, 23.9[i]; $C_{3,5}$–CH_3, 14.6; C_4–CH_3, 23.7
	(2-Et)[d]	58.2 $^1J_{CH}$ = 135.5	198.6	145.2	195.8	$C_{1,4}$–CH_2, 27.6[i]; $C_{2,6}$–CH_2, 28.2[i]; $C_{3,5}$–CH_2, 20.6; C_1–CH_3, 6.3; $C_{2,4,6}$–CH_3, 13.6; $C_{3,5}$–CH_3, 13.0
	(2-Me)[e]	57.7 $^1J_{CH}$ = 134.2	193.8	139.5	191.9	C_1–CH_3, 20.5; $C_{2,4,6}$–CH_3, 23.3; $C_{3,5}$–CH_3, 14.5
	(5-Et)[f]	49.8 $^1J_{CH}$ = 121.6	199.2	130.8 $^1J_{CH}$ = 168.8	198.3	$C_{2,6}$–CH_2, 32.1; C_4–CH_2, 34.3; $C_{2,4,6}$–CH_3, 12.1
	(5-Me)[f]	51.9 $^1J_{CH}$ = 122.8	194.0	133.9 $^1J_{CH}$ = 169.9	194.3	$C_{2,6}$–CH_3, 25.2; C_4–CH_3, 27.6
	g	54.5	194.2	135.4	194.2	$C_{2,4,6}$–CH_3, 27.5
	h	53.3	196.0	135.0	196.0	
	(3)[h]	48.3	180.4	137.5	209.7	
	(4)[f]	48.5	C_2, 207.0[i] C_6, 172.8	133.5, 133.9	200.5[i]	C_2–CH_2, 34.4; C_4–CH_2, 35.1; $C_{2,4}$–CH_3, 12.0, 12.4
	(6-Et)[b]	50.4	196.5	C_3, 144.6 C_5, 131.8	195.9	$C_{2,6}$–CH_2, 28.6, 29.9; C_4–CH_2, 31.6; C_3–CH_2, 20.1; C_4–CH_3, 15.1; $C_{2,6}$–CH_3, 13.9; 13.3; C_3–CH_3, 12.2
	(6-Me)[f]	53.9	C_2, 190.1[i] C_6, 192.7[i]	C_3, 141.1 C_5, 135.1	190.4[i]	$C_{2,6}$–CH_3, 24.4, 23.8; C_3–CH_3, 13.6; C_4–CH_3, 26.8

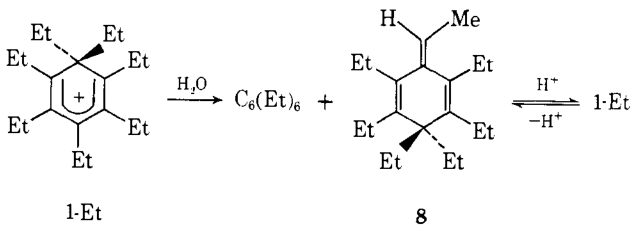
[a] Chemical shifts are in parts per million relative to internal (capillary) Me_4Si; coupling constants are in hertz. [b] In SO_2 at −70°. [c] Data from ref 4c. [d] In HSO_3F–SbF_5–SO_2 at −65°. [e] Chemical shifts from ref 4b; the $^1J_{CH}$ value is unpublished datum of G. A. Olah and G. Liang. [f] In HF–SbF_5–SO_2 at −65°. [g] Data from ref 4a, converted to external Me_4Si using $\delta_{CS_2}(Me_4Si)$ 193.7 ppm. [h] Data from ref 3c, converted to external Me_4Si using $\delta_{CS_2}(Me_4Si)$ 193.7 ppm. [i] Relative assignment uncertain.

−78°. The ^1H NMR spectrum of the product is almost identical with that of the tetrachloroaluminate salt described above.

Warming a solution of the tetrachloroaluminate salt of **1**-Et in SO_2 to room temperature (with removal of SO_2) gave a thick oil, the ^{13}C NMR spectrum of which exhibited intense signals at δ 15.6, 22.2, and 139.0 (hexaethylbenzene) and weaker signals for **1**-Et. Further heating resulted in complete decomposition of **1**-Et, indicating that **1**-Et tetrachloroaluminate loses ethyl chloride to reform hexaethylbenzene. In contrast, the tetrachloroaluminate salt of the heptamethylbenzenium (**1**-Me) is stable under these conditions and did not eliminate methyl chloride;[3a] the greater stability of the latter ion results from the methyl cation being a poorer leaving group than the ethyl cation.

Quenching a solution of **1**-Et in SO_2 with water and extraction with pentane gave a yellow crystalline material, the ^1H NMR spectrum of which indicated the presence of hexaethylbenzene and 1,1,2,3,5,6-hexaethyl-4-ethylidenecyclohexa-2,5-diene (**8**)[11] in the ratio 2:1. If a solution of these compounds in pentane is extracted with 10 *N* hydrochloric acid, pure hexaethylbenzene can be isolated from the pentane, while neutralization of the acid layer with sodium bicarbonate solution at 0° again gives a crystalline mixture of hexaethylbenzene and **8** almost identical (by ^1H NMR) with that described above. Analogous results were observed previously upon quenching **1**-Me.[3a]

Addition of chlorosulfuric acid to a solution of **1**-Et in SO_2 enabled it to be warmed above room temperature (with removal of SO_2). The ^1H NMR spectrum of this solution shows considerable broadening at 37°, while further heating to 58° results in the shielded triplet (δ 0.17), coalescing with the other methyl signals. At 70°, the ^1H NMR spectrum consists of only a triplet at δ 1.1 and a quartet at δ 2.9. This change in the spectrum is reversible and by analogy with the observed methyl migration in **1**-Me[12a,b] is due to rapid intramolecular ethyl group migration.[12c] A limited amount of decomposition of **1**-Et is also evident at this temperature, as shown by the irreversible appearance in the ^1H NMR spectrum of quartets at δ 4.85 and 3.72 and triplets at δ 1.67 and 1.60. The deshielded set of signals are coincident with those of an added sample of ethyl chlorosulfate and suggest that **1**-Et transethylates the solvent at this temperature. **1**-Et can indeed be prepared by ethylating hexaethylbenzene with ethyl chloro(fluoro)sulfate in the presence of HF-SbF_5 or SbF_5 as catalyst. The identity of the other product is not known; sustained heating of **1**-Et in $ClSO_3H$ at temperatures above 70° results in complete decomposition to a viscous polymeric material.

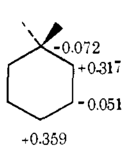


$$C_5(Et)_6 + EtSO_3Cl + HF\text{–}SbF_5 \xrightleftharpoons{ClSO_3H} \text{1-Et } SbF_6^-$$

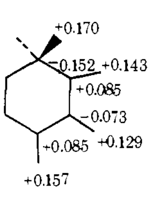
We have also examined several of the red-oil complex layers produced in the ethylation of benzene as well as samples of industrial ethylations. The viscous red layer formed by mixing benzene with a large excess of ethyl chloride and aluminum chloride does indeed contain **1**-Et and **2**-Et, as shown by the ^1H NMR spectrum of a solution in SO_2. A sample obtained from the Dow Chemical Co.'s ethylation process exhibited similar but broadened resonances when examined as a solution in SO_2. Evidently this system is still undergoing exchange reactions even at low temperature.

Charge Distribution and Steric-Induced Strain in Benzenium Ions. The ^{13}C NMR data for the series of ethyl- and methyl-substituted benzenium ions are summarized in Table II. The ring-carbon shifts are characteristic of benzenium ions, showing the upfield shift of C_1 due to the change in hybridization from sp^2 to sp^3. The strong deshielding of the C_2, C_4, and C_6 resonances are indicative of extensive positive charge localization at positions ortho and para to the protonation site, while the C_3 and C_5 chemical shifts are only moderately deshielded from the neutral arenes, e.g., hexaethylbenzene ($C_{1\text{-}6}$ = 139.0) and 1,3,5-triethylbenzene ($C_{1,3,5}$ = 143.9; $C_{2,4,6}$ = 124.6), indicating minimal positive charge development at these positions.[13] Recent ab initio and earlier semiempirical molecular orbital calculations for the parent benzenium ion[14] predict that there is slightly greater positive charge localized at the para carbon relative to each ortho carbon. If relative charge density was the only factor influencing the chemical shifts, the ortho carbon would be expected to be more shielded than the para carbon. However, in all cases except **5**-Me, the carbon shifts of C_2 and C_6 are slightly deshielded relative to C_4. Nevertheless, it is reasonable to suggest that more charge is localized at C_4 than at C_2 or C_6, because C_2 and C_6 are bonded to an additional alkyl substituent; the sp^3-hybridized C_1-carbon and alkyl substitution typically leads to deshielding of the substituted carbon atom.[15] Further substitution at C_1, e.g., **1**-Et, **2**-Et, **1**-Me, and **2**-Me, results in increased deshielding of C_2 and C_6.

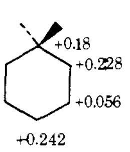
The ab initio calculations predict an alternation in sign of the π charges (**9**) and total charges (**10**) of the ring carbon atoms in the parent benzenium ion,[14] with negative charge at the meta carbons. The ^{13}C NMR results are more consistent with the regional charge[16] distribution pattern (**11**) in which some positive charge is developed at the meta positions in addition to the positive charges at the ortho and para positions; the meta carbon resonances in **1**-Et, **1**-Me, **2**-Et, and **2**-Me are all moderately deshielded from the neutral arenes. A ^{13}C NMR study of the parent benzenium ion would clearly be of importance in resolving this point but so far only a partial, poorly resolved spectrum has been obtained and work is continuing on this project in these laboratories.



9 (π charges)[14]

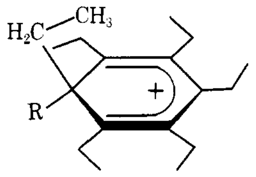


10 (total charges)[14]

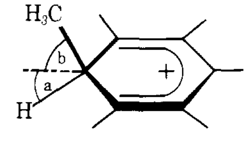


11 (regional charges)[16]

The methyl protons of the C_1-ethyl groups in **1**-Et and **2**-Et resonate at extremely high field (**1**-Et, δ 0.17; **2**-Et, δ 0.20), consistent with the forced adoption of a conformation as in **12** where the methyl group is subjected to the strong anisotropic shielding from the pentadienyl fragment. The corresponding methyl carbons also resonate at high field, particularly **2**-Et (δ 6.3). It had earlier been suggested, on the basis of the long-range proton-proton coupling constants (e.g. **5**-Me, $^6J_{C_4\text{-}CH_3,H_1}$ = 3.5 Hz; **2**-Me, $^6J_{C_4\text{-}CH_3,H_1}$ = 2.0 Hz),[2,3b] and the ^1H NMR shifts of H_1 that the C_1-CH_3 group in **2**-Me was forced pseudo-axial and, correspondingly, H_1 was forced pseudo-equatorial,[2,5,17] i.e., **13.**



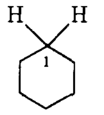
12, R = H, Et



13, b > a

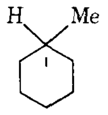
We have measured the $^1J_{CH}$ values for C_1 in **2**-Me and **5**-Me, and **2**-Et and **5**-Et (Table II); the approximately 10% increase in $^1J_{CH}$ for **2** relative to **5** is indicative of a significantly greater degree of s character, hence strain, at C_1. Methyl substitution normally leads to small changes in $^1J_{CH}$ values in unstrained systems, e.g., compare **14** and **15.** The earlier ^1H NMR data,[2,5] combined with the $^1J_{CH}$ values determined in this study, are consistent with **2**-Et and **2**-Me, and presumably **1**-Et and **1**-Me, being strained relative to the less substituted benzenium ions. These systems should thus provide a means of testing whether strain affects carbon chemical shifts. Several previous studies of moderately strained systems have failed to detect any anomalies in the shifts of the sp^3-hybridized carbons that could be attributed to strain.[15,19] In contrast, two studies of sp^2-hybridized carbons in strained systems have shown that strain causes an upfield shift of these resonances.[20]

A comparison of the C_1 resonances in **5**-Me, **2**-Me, and **1**-Me (Table II) is at first sight surprising; as anticipated from consideration of the α-substituent effect of a methyl group,[15] C_1 in **2**-Me is deshielded from that of **5**-Me, but C_1 in **1**-Me is more *shielded* than **2**-Me. Although it would be tempting to attribute this effect to strain, a comparison of the corresponding C_1 shifts in cyclohexanes **14**–**16** shows nearly identical trends.[21] The C_1 resonance in **2**-Et relative to **5**-Et shows the anticipated deshielding due to an ethyl substituent[15] and follows the relative shifts of **14** and **17.** However, C_1 in **1**-Et is deshielded by 11.9 ppm over C_1 in **2**-Et and, although no data are available for 1,1-diethylcyclohexane, this additional deshielding is certainly large by comparison with the difference between **2**-Et and **5**-Et. Two further unexpected deshieldings are observed in **1**-Et; the $C_{2,6}$-CH_2 groups are substantially deshielded (δ 35.4) with respect to the C_1- and C_4-CH_2 groups, a result completely unpredictable from the corresponding methyl shifts of **1**-Me



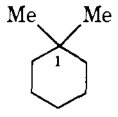
14

(δ_{C_1} = 27.7 ppm[18a]; $^1J_{CH}$ = 125.0 Hz[18b])



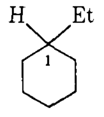
15

(δ_{C_1} = 33.7 ppm[18a]; $^1J_{CH}$ = 126.5 Hz[18c])



16

(δ_{C_1} = 30.6 ppm[18a])



17

(δ_{C_1} = 40.6 ppm[18d])

to **5**-Me, while the methyl carbon of the C_1-ethyl in **1**-Et is also deshielded relative to that in **2**-Et, the reverse of the proton chemical shifts (Table I). The resonance positions of the sp^2-hybridized carbons $C_{2,6}$ in **1**-Et, **2**-Et and **1**-Me, **2**-Me could be affected by small charge distribution changes, and no reliable conclusion can therefore be drawn.

These results are in accord with the previous conclusions[15,19] that strain does not introduce detectable changes in the chemical shifts of sp^3-hybridized carbon atoms. However, the unexpected deshielding of several carbon atoms in or attached to the C_6-C_1-C_2 fragment of the highly crowded ion **1**-Et suggests that the steric proximity of neighboring groups (as opposed to the strain inherent in certain bicyclic ring systems) could cause strong deshielding of the carbon resonances of the groups which are involved, an interesting facet of ^{13}C NMR spectroscopy worthy of further investigation.

Experimental Section

All compounds used in this study were commercial samples of the highest purity. Antimony pentafluoride was triply distilled and fluorosulfuric acid doubly distilled before use. The ethyl fluoride-antimony pentafluoride complex in SO_2 was prepared as described in the literature.[8a]

Preparation of Ions. The protonation of arenes with 1:1 HF-SbF_5 in SO_2 at $-78°$ has been described previously,[3c,4d] and an analogous procedure was employed for 1,3-diethylbenzene, 1,3,5-triethylbenzene, 1,3,5-trimethylbenzene, and 1,2,3,5-tetramethylbenzene to form **4**, **5**-Et, **5**-Me, and **6**-Me, respectively. Hexaethylbenzene was protonated with 1:1 HSO_3F-SbF_5 in SO_2 at $-78°$ under identical conditions to form **2**-Et.

Heptaethylbenzenium Ion (1-Et) and Hexaethylbenzenium Ion (2-Et). Aluminum chloride (1.1 g, 0.087 mol) and ethyl chloride (0.5 g, 0.070 mol) were added to a solution of hexaethylbenzene (2.0 g, 0.087 mol) in anhydrous CCl_4 (30 ml) at 10°. After stirring for 30 min, **1**-Et tetrachloroaluminate separated out at the top of the solution as a viscous red liquid which was removed by precooled pipet and dissolved in SO_2. Small impurities of ethyl chloride and CCl_4 were detected by ^1H NMR and ^{13}C NMR spectroscopy. An alternative procedure for the protonation of hexaethylbenzene is analogous to that described above using an excess of hydrogen chloride gas bubbled directly into the CCl_4 solution (instead of ethyl chloride) at 0°. The tetrachloroaluminate salt of **2**-Et is obtained as a red oil and was studied as described for **1**-Et.

Reaction of 1,3,5-Triethylbenzene with EtF → SbF_5. 1,3,5-Triethylbenzene (200 mg) in SO_2 at $-78°$ was added dropwise, with rapid shaking, to an equimolar solution of EtF → SbF_5 in SO_2 at $-78°$. The deep-red solution was transferred immediately to a precooled NMR tube.

Nuclear Magnetic Resonance Spectra. ^1H NMR spectra were obtained using a Varian Associates Model A56/60A NMR spectrometer equipped with a variable-temperature probe. External Me_4Si (capillary) was used as reference.

^{13}C NMR spectra were obtained using a Varian Associates Model XL-100 NMR spectrometer equipped with a broad-band decoupler, Fourier transform accessory, and a variable-temperature probe. Chemical shifts were measured from external (capillary) 5% ^{13}C-enriched Me_4Si. Coupling constants were obtained directly from the ^{13}C NMR spectra in the gyro-gate mode.

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(9) By analogy with the similarity of the basicity constants for 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene, this cannot be ruled out; see ref 7.

(10) No aliphatic $>CH(CH_2CH_3)$ can be detected either by ^1H NMR or ^{13}C NMR spectroscopy.

(11) The ^1H NMR spectrum of **8** is identical with that reported for an authentic sample: see V. G. Shubin, A. A. Tabatskaya, B. G. Derendaev, D. V. Korchagina, and V. A. Koptyug, *J. Org. Chem. USSR* (*Engl. Transl.*), **7**, 2079 (1971).

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(16) Regional charge is defined as the charge on carbon plus the charge on the attached hydrogens: see A. Streitwieser, Jr., and R. G. Jesaitis in "Sigma Molecular Orbital Theory", O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 197.

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(21) Although there are obvious differences between these two series of compounds, there are intrinsically no substituent effect differences introduced by the change **14** to **16** or **5**-Me to **1**-Me.