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Protonation of Benzocyclobutene with Superacid: Cram's Phenonium Ion (Spiro[5.2]octa-5,7-diene-4-yl Cation) Revisited[1]

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Abstract: Protonation of benzocyclobutene under superacidic ($HF\text{-}SbF_5/SO_2ClF$) stable ion conditions was found to be a new independent route to Cram's phenonium ion. On the basis of the observed ^{13}C NMR data, total chemical shift difference (TCSD) criteria, *ab initio* theoretical and IGLO chemical shift calculations, and comparison with relevant models, the phenonium ion is indeed a spirocyclopropylbenzenium ion (spiro[5.2]octa-5,7-diene-4-yl cation) with a 4π cyclohexadienyl system and additional cyclopropylcarbinyl delocalization. It can not be characterized as a nonclassical Freudenberg type ion which should contain a hypercoordinate sp^2 carbon and display 6π aromatic nature. In an attempt to prepare a *de facto* nonclassical phenonium ion 2-fluoro(tetrafluoro)benzonorbornene, containing a strongly deactivated aromatic ring, was ionized under long lived stable ion conditions, but it gave instead the corresponding tetrafluorobenzonortricyclyl cation. On the basis of the observed ^{13}C NMR data, TCSD, and comparison with its parent analog this ion too is of predominantly spirocyclopropylbenzenium ion nature.

Introduction

In 1949 Cram reported in a series of papers[2] that optically active *threo-* and *erythro*-3-phenylethyl-2-tosylates undergo acetolysis with nearly 50% phenyl migration and a remarkable degree of configurational retention. To account for these results Cram originally proposed structure **1**, the phenonium ion, formed directly by π-participation, as the intermediate involved. A similar symmetrical intermediate has also been invoked to rationalize the results of isotopic scrambling in the related Friedel-Crafts reactions of ^{14}C-labeled β-phenylethyl chloride.[3] Since the postulation of the bridged phenonium ion (**1**) its structure has been extensively investigated[4] and was initially a major subject of the so called classical−nonclassical carbocation debate.[5] Carbocations with too few electrons to allow a pair for each "bond", i.e., containing ground state delocalized σ-electrons (as defined by Bartlett[6a]) came to be known as nonclassical, a term first used by Roberts.[6a] In order to clarify the terms classical and nonclassical Olah in 1972 suggested[6b] the simple differentiation between trivalent carbenium ions (classical ions) and penta-(or higher)-coordinate carbonium ions (nonclassical ions). A more comprehensive definition was offered by H. C. Brown and P. v. R. Schleyer in 1977:[6c] "A classical carbocation is a positively charged species which can adequately be represented by a single Lewis structure involving only two-electron−two-center bonds. Traditionally π-conjugated cations, such as allyl and cyclopropenyl, are included in this category. A nonclassical carbocation is a positively charged species which cannot be represented adequately by a single Lewis structure. Such a cation contains one or more carbon or hydrogen bridges joining the two electron deficient centers. The bridging atoms have coordination numbers higher than usual, typically five or more for carbon and two or more for hydrogen. Such ions contain two electron-three (or multiple) center bonds including a carbon or hydrogen bridge."

A number of alternative structures have been used to depict the phenonium ion, **2**−**10**.[3b,7−14] Brown,[8] in a general challenge to nonclassical ions proposed that the solvolytic evidence could be accommodated by rapidly equilibrating open (**2**) or partially π-bridged (**3**) ions. In latter studies with Schleyer[15] involving 3-aryl-2-butyl and 2-arylethyl systems Brown accepted the symmetrical fully bridged structure (**1**) as best representing the intermediate involved in these systems. Although not stated as such in Cram's original work[2] phenonium ions have also been regularly termed "nonclassical". This dates back to a series of papers by Winstein[12,16] in 1952 where the use of dotted-lines to represent the three-membered ring and the term "nonclassical" was first used in connection with the phenonium

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(1) (a) Presented in part, and dedicated with friendship and admiration, at the symposium honoring D. J. Cram on occasion of his 75th birthday; UCLA, Los Angeles, March, 1994. (b) Stable Carbocations. 293. For part 292, see: Reddy, V. P.; Olah, G. A.; PraSash, G. K. S. *J. Org. Chem.* **1993**, *58*, 7622.

(2) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863, 3871, 3875.

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(4) For review, see: Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 27.

(5) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440 and references cited therein.

(6) (a) Bartlett, P. D. *Nonclassical Ions.* (b) Olah G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808. (c) Brown, H. C. (with commentary by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum Press: New York, 1977; p 49.

(7) (a) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6877. (b) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284.

(8) (a) Brown, H. C.; Morgan, K. J.; Chloupek, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 2137. (b) Brown, H. C.; Bernhiemer, R.; Kim, C. J.; Schepple, S. E. *J. Am. Chem. Soc.* **1967**, *89*, 370.

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(10) Brown, H. C.; Kim, C. J. *J. Am. Chem. Soc.* **1971**, *93*, 5765.

(11) (a) Roberts, J. D.; Regan, C. M. *J. Am. Chem. Soc.* **1953**, *75*, 2069. (b) Heck, R.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 3432. (c) Winstein, S. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol III, p 966.

(12) Winstein, S.; Brown, M.; Schrieber, K. C. Schlesinger, A. H. *J. Am. Chem. Soc.* **1952**, *74*, 1140.

(13) Schoeller, W. W.; Dahm, J. *Tetrahedron* **1973**, *29*, 425, 3237.

(14) Cram, D. J. *J. Am. Chem. Soc.* **1958**, *74*, 2129.

(15) Brown, H. C.; Kim, C. J.; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5244.

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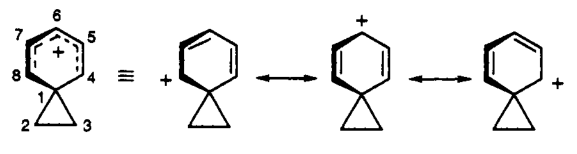

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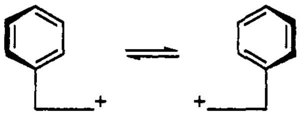

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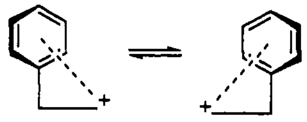

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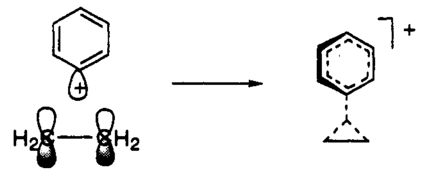

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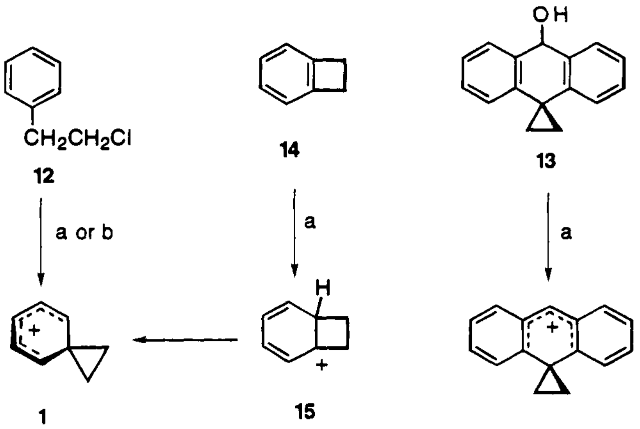
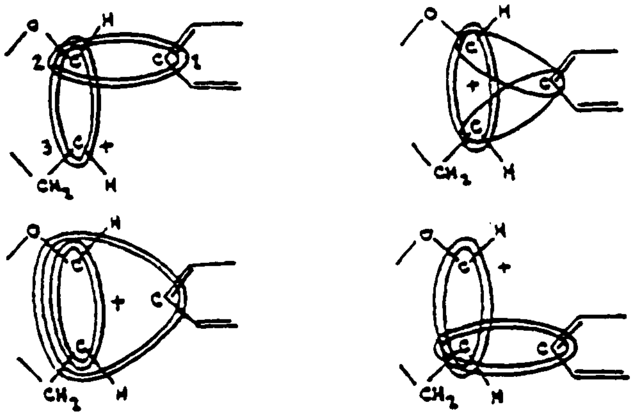
Scheme 1



[a] (a) HF-SbF$_5$/SO$_2$ClF, −80 °C; (b) SbF$_5$/SO$_2$ClF, −80 °C.

ion. On the basis of this suggestion (but without direct evidence for any σ-delocalized bonding) the nonclassical nature of the phenonium ion was entrenched in the literature, and various nonclassical depictions appeared (**4**−**10**),[3b,9−14] all of which include "dotted-line" structures for the cyclopropane ring and some an intact aromatic ring. A number of these structures (**4**−**6**) invoke $\pi\sigma$-delocalized cyclopropane bonds even though the *ipso* carbon is only tetravalent. The structures **7**−**9** are, in present bond depiction terms, essentially equivalent to **11** which better illustrates the three-center−two-electron (3c−2e)[17] bond. Such a structure may be envisioned as arising from insertion of the vacant p-orbital of the phenyl cation into the π-bond of ethylene, the cylindrical symmetry of the cationic orbital allowing both planar and orthogonal conformations. Such a structure was indeed first proposed as early as 1927 by Freudenberg[18] in a remarkable, but rarely quoted and not readily accessible paper, discussing 1,2-phenyl migrations in a pinacolin rearrangement. He used dotted lines to represent charge delocalization in bridged tetramethylcatechol cation, cautioning, however, to fully realize their meaning. The nature of the bridged ion was depicted in a molecular orbital picture, amazing in its foresight, showing a three centered, bridged "phenonium ion".



In 1970, Olah and Porter[9b] first reported that long lived phenonium ions could be prepared by ionization of β-phenylethyl chloride under superacidic stable ion conditions (SbF$_5$[7a,9b] or HF-SbF$_5$[7b] in SO$_2$ClF, −78 °C). The proton−proton coupling constants observed for the methylene carbons in a derivative unsymmetrically substituted in the aromatic ring[7a] established the bisected structure of this phenonium ion derivative and thus by analogy the bisected conformation of **1**. Most importantly the observed ^{13}C chemical shift observed for the *ipso* carbon of **1**[9b] established its sp^3 nature. This clearly indicates the classical nature of the phenonium ion, according to both Olah's and Brown−Schleyer's definitions, although obviously cyclopropylcarbinyl type delocalization of the cyclopropyl ring is also involved besides arenium ion like π-delocalization. Consequently it was generally agreed[6a,b,15] that no controversy exists over the true structure of the phenonium ion. This view remained since.

Recently Sieber, Schleyer, and Gauss[19] reported a restudy of the "accurate structure" of Cram's phenonium ion by theoretical methods. Using the high level GIAO theoretical method on MP2(fu)/6-31G* optimized geometry they calculated the observed chemical shifts of the phenonium ion with good accuracy. They concluded based on their calculations that half of the positive charge is delocalized to the two CH$_2$ groups and that the C−C bond lengths in the six-membered ring are nearly equal (1.401 ± 0.018 Å), but those in the three-membered ring differ by 0.2 Å (1.426 *vs* 1.625 Å). They suggested that "the phenonium ion is *nonclassical* with considerable 6π-aromatic character and is most clearly represented by the structure **7**".

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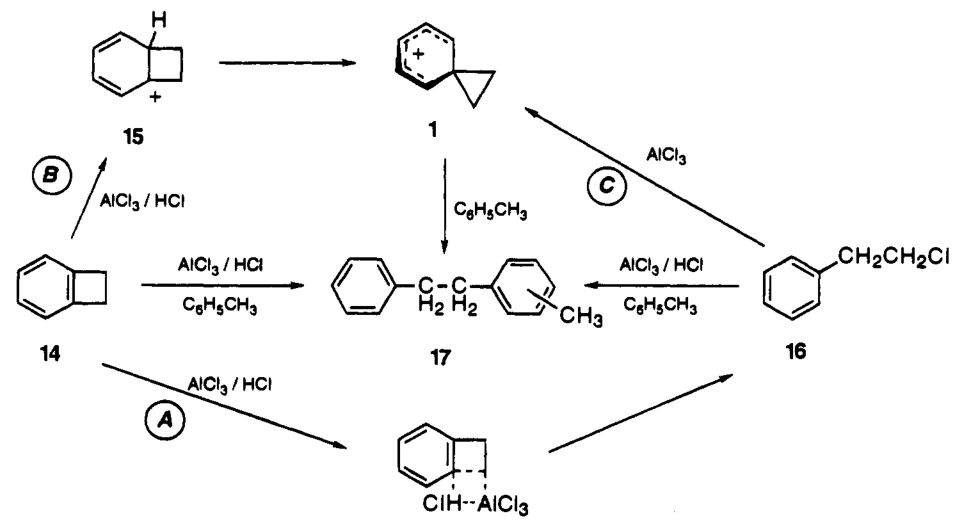
(16) (a) Winstein, S.; Morse, B. K. *J. Am. Chem. Soc.*, **1952**, *74*, 1133. (b) Winstein, S.; Trifin, D. *J. Am. Chem Soc.* **1952**, *74*, 1154.

(17) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987; Chapter 5.

(18) Freudenberg, K. *Sitzungber. Heideb. Akad. Wiss.* **1927**, *10*, 3.

(19) Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987.

Scheme 2



In this paper we report new studies related to Cram's phenonium ion, namely the protonation of benzocyclobutene under superacidic conditions. This route to the phenonium ion is independent of ionizations with π-participation using β-phenylethyl systems. Based on our extended experimental NMR studies and theoretical calculations we conclude that Cram's phenonium ion is, as concluded previously, a spirocyclopropylbenzenium ion (spiro[5.2]octa-5,7-diene-4-yl cation) containing a 4π cyclohexadienyl system and additional cyclopropylcarbinyl delocalization. It cannot be characterized as a nonclassical ion which should contain a hypercoordinate cation and display 6π aromatic nature. In an attempt to prepare a nonclassical, Freudenberg type phenonium ion, we also studied ionization of 2-fluoro(tetrafluoro)benzonorbornene but observed only the respective benzonortricyclyl cation which is also classical in nature.

Results and Discussion

Originally Cram's phenonium ion was suggested on the basis of solvolysis studies of β-phenylethyl systems.[2] After superacidic stable ion chemistry was developed[20] allowing preparation of long lived carbocations, the phenonium ion was prepared by Olah[7,9b] by ionization of β-phenylethyl chloride (fluoride) (**12**) in SbF_5/SO_2ClF solution at low temperature. Alternatively, Winstein and Eberson[21] found ionization of 9-spirocyclopropyl-9,10-dihydroanthracene (**13**) also leads the respective phenonium ion. We report now a third independent route of generating the phenonium ion by protonation of benzocyclobutene (**14**) under stable ion conditions with superacidic HF-SbF_5 in SO_2ClF solution at −90 °C.

Protonation of benzocyclobutene (**14**) with HF-SbF_5 in SO_2ClF at −90 °C gives rise to a carbocation displaying a ^{13}C NMR spectrum identical to that previously obtained for the phenonium ion.[9b] Presumably initial protonation to **15** is followed by rearrangement to **1**. The protonation of benzocyclobutene was previously studied by theoretical calculations.[22] It was found that protonation at the pseudo-*meta* (β) positions leads to a more stable Wheland complex than is obtained on protonation of the pseudo-*ortho* (α) sites in agreement with the Mills–Nixon[23] effect and some experimental studies.[24] However, in the study[22] protonation at the pseudo-*ipso* carbons was not considered. We have undertaken more extensive calculations on the protonation of benzocyclobutene (see Experimental Section for details) and find that at the *ab initio* MP2/6-31G*//RHF/6-31G* level **15** is a stable minimum 30 cal mol^{-1} lower in energy than the β-protonated isomer and 9.0 kcal mol^{-1} higher in energy than **1**. On geometry optimization at the MP2/6-31G* level, however, **15** ceases to be a minimum and collapses to the phenonium ion (**1**).

In the light of these results the mechanistic conclusions on the Friedel–Crafts alkylation reactions of benzocyclobutene (**14**) and 2-tolylethyl chlorides reported by Schwartz *et al.*[25] and electrophilic substitutions of **14** reported by Lloyd and Ongley[26] are open to reinterpretation. Schwartz found that reaction of both benzocyclobutene and 2-phenylethyl chloride with toluene under Friedel–Crafts conditions ($AlCl_3/HCl$) yielded identical mixtures of 1-phenyl-2-tolylethanes in both cases and thus proposed that a common intermediate was involved in both cases. Several possible mechanisms were considered,[25] but it was concluded that under the reaction conditions employed benzocyclobutene is directly converted to 2-phenylethyl chloride (**16**) before reaction with the aromatic hydrocarbon, as illustrated in Scheme 2, path A. Central to their arguments[25] was that **15** should be unable to rearrange to **1** due to unfavorable twisting in the transition state and that the intermediacy of **15** was precluded due to lack of methyl rearrangement, due to what were predicted to be rapid 1,2-hydride shifts in the presumed intermediate cyclobutyltoluenium ions, on reaction of 1-chloro-2-*p*-tolylethane and 1-chloro-2-*m*-tolylethane under similar conditions (Scheme 3).

Firstly it is clear from our observation of **1** on protonation of **14** and that **15** collapses to **1** on MP2/6-31G* geometry optimization, that rearrangement of **15** to **1** is in fact remarkably facile. Secondly that the two chlorotolylethanes show no methyl rearrangement under the $AlCl_3$ catalyzed conditions is fully consistent with our observation that β-arylethyl systems give rise to phenonium ions and not cyclobutylarenium ions on ionization with SbF_5. Even if a cyclobutylarenium ion were the first intermediate formed it is clear from our results that it would immediately collapse to the more stable phenonium ion

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(20) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(21) Eberson, L; Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 3506.

(22) Eckert-Maksic, M; Maksic, Z. B.; Klessinger, M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 285.

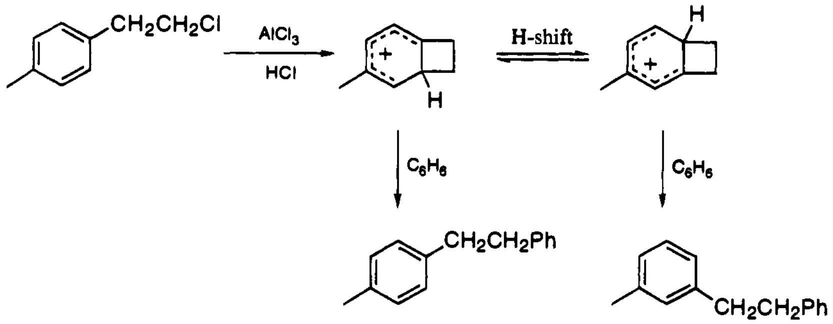
(23) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2150.

(24) See ref 21 refs 2–10 therein.

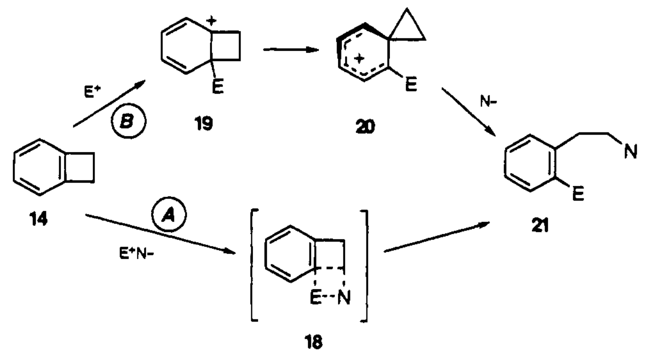
(25) Schwartz, L. H.; Landis, J.; Lazarus, S. B.; Stoldt, S. H. *J. Org. Chem.* **1972**, *37*, 1979.

(26) Lloyd, J. B. F.; Ongley, P. A. *Tetrahedron* **1965**, *21*, 245.

Scheme 3



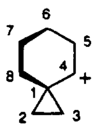
Scheme 4



without a concomitant 1,2-hydride shift. A 1,2-hydride shift in **15** should in fact be relatively slow due to the delocalized nature of the positive charge. These results have no bearing on the possible intermediacy of **15** in the transformation of **14** to **17**. We suggest that the experimental results are fully accommodated by the route shown in Scheme 2, paths B and C.

Similarly, the formation of ring opened products on electrophilic substitution of **14**, previously ascribed[26] to ring opening via a multicentered transition state (**18**) (Scheme 4, path A), may be ascribed to a mechanism involving collapse of a cyclobutylbenzenium ion (**19**) to a phenonium ion (**20**) and its subsequent nucleophilic ring opening to **21**, as illustrated in Scheme 4, path B.

Considering the NMR data for **1**, most instructive is the ^{13}C NMR chemical shift observed for the *ipso* carbon at δ 60.8 indicative of sp^3 hybridization. For comparison the *ipso* carbon of the saturated analog of **1**, the spiro[2.5]oct-4-yl cation (**22**),[27] has a ^{13}C NMR shift: δ 95.0. It is inconceivable that the observed shielding of nearly 35 ppm could be in accord with an sp^2 carbon which would be involved in Sieber *et al.*'s proposed nonclassical cation (**7**) which was suggested[19] to possess 6π-aromatic character and hence an sp^2-*ipso* carbon.



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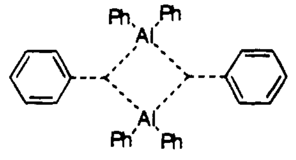

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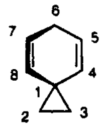

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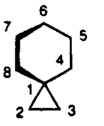

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This carbon should be even further deshielded if it bears partial positive charge as suggested by structure **7**/**11**. An organometallic model for a bridging phenyl group, which has been established by X-ray structural[28] and NMR studies,[29] to be engaged in 3c−2e bonding, is dimeric triphenylaluminium (**23**). The bridging pentacoordinated *ipso* carbons of **23** display chemical shifts at δ 121.3 at −92 °C, indicative of their aromatic nature. Further, comparison of the ^{13}C NMR shift for the bridging carbon in the 2-norbornyl cation at δ 21.1 (−159 °C)[5] and that observed for the bridging pentacoordinated methyls in dimeric trimethylaluminium at δ −5.63 (−75 °C)[29] suggest that the *ipso* carbon for **7** might be even slightly more deshielded than those of **23**. The ^{13}C shifts for the carbons in the cyclohexadienyl ring of ion **1** also resemble strongly those of the benzenium ion.[30] The close analogy between the chemical shifts demonstrates the benzenium ion like charge distribution in the phenonium ion (**1**), i.e., that positive charge is mainly centered at the *ortho* and *para* carbons and further confirms the sp^3 character of the *ipso* carbon.

Concerning the structural nature of **1**; as discussed by Olah in 1972,[6b] in all carbocations there is a gradation of the degree of delocalization. While limiting trivalent carbenium (classical) and hypercoordinated carbonium (nonclassical) ions can be differentiated, *de facto* it is more appropriate to discuss the *degree of classical/nonclassical nature* of any particular ion. To this end an excellent tool for determining the overall degree of classical/nonclassical nature is the method, developed jointly by Olah, Schleyer *et al.*, of "Total Chemical Shift Difference" (TCSD),[31] being the difference of the sum of all ^{13}C NMR shifts of the carbocation in question and its corresponding neutral

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(27) Olah, G. A.; Fung, A. P.; Rawdah, T. N.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 4646.

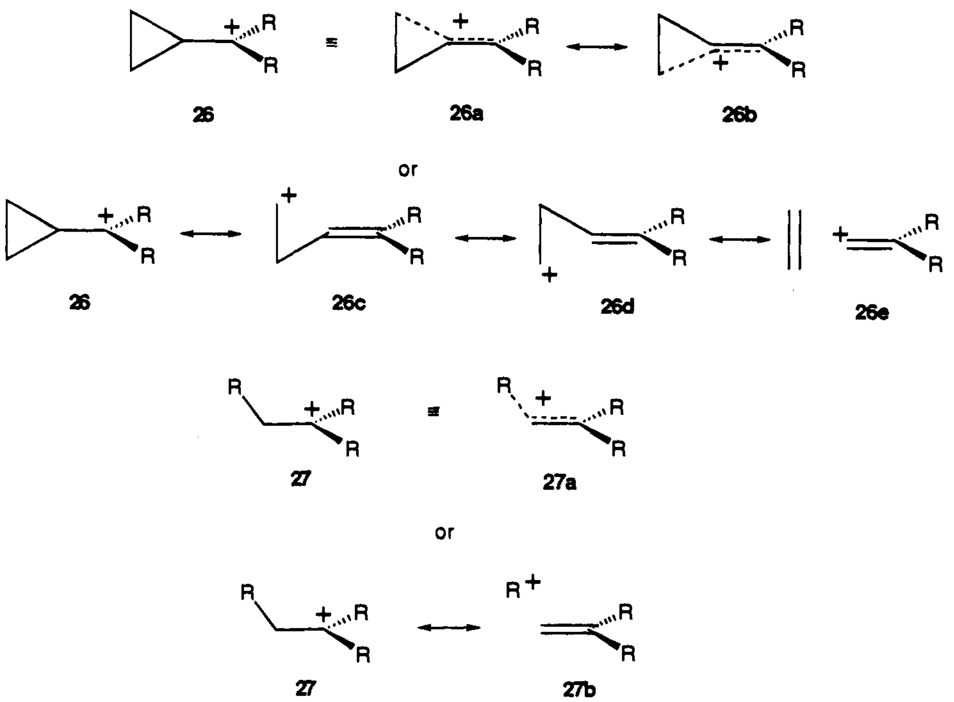
(28) Malone, J. F.; McDonald, W. S. *Chem. Commun.* **1967**, 444.

(29) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217.

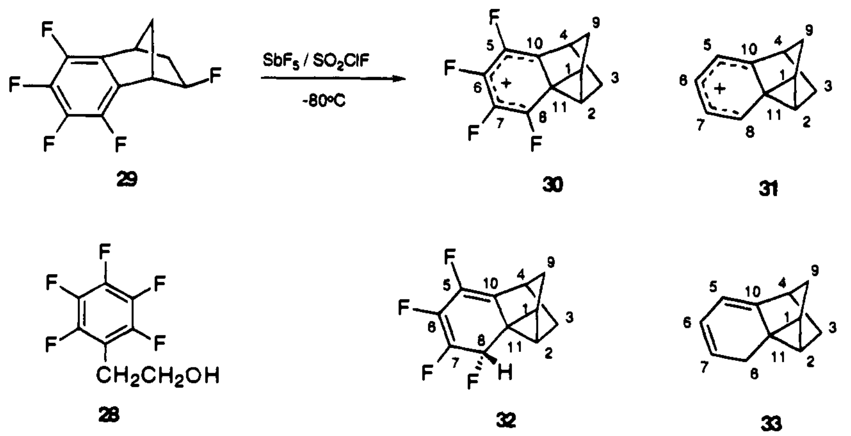
(30) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kellt, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034.

(31) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

Chart 1



Scheme 5



hydrocarbon parent. TCSDs of 350 ppm or greater indicate predominantly classical structure, values below 200 ppm imply structures with considerable nonclassical character. TCSDs between these values indicate borderline cases. These differences in overall chemical shifts represent in good part hybridization changes from sp^3 to sp^2 and the deshielding effect of the unit positive charge. It is important to bear in mind that the TCSD ranges are approximate by their arbitrary nature and are based on experimental observations. Nonetheless their substantial orders of magnitude allow generally reliable overall conclusions to be reached.

It is of substantial interest to apply the TCSD approach to the phenonium ion, which was not previously reported. This was probably due to the fact that although the required hydrocarbon analog (**24**) is known,[32] its ^{13}C NMR shifts have not been reported. However as theoretical calculations of NMR chemical shifts have now achieved generally high reliability we have calculated the ^{13}C NMR shifts at the *ab initio* IGLO DZ//MP2/6-31G* level of theory (see Experimental Section). This level is sufficiently accurate for such a relatively simple ground state molecule and bearing in mind that the TCSD is assessed in terms of hundreds of ppm and thus errors of a few ppm should not affect the overall evaluation. The calculated TCSD between **1** and **24** is 376 ppm strongly indicating that **1** is predominately classical in nature.

A suitable model for the cyclopropylcarbinyl ion nature of **1** is the saturated analog **22** which we prepared and observed previously.[27] As with **24**, ^{13}C NMR chemical shifts do not appear to have been reported for the parent neutral hydrocarbon, spiro[2.5]octane (**25**).[33] We have calculated the ^{13}C NMR shifts for **25** (Table 1) in an identical fashion to **24**, in order to obtain an estimate of the TCSD for **22**. The sum of the calculated ^{13}C NMR chemical shifts for **25** (IGLO DZ//MP2/6-31G*) is 134 ppm. Not unexpectedly, on the basis of its calculated TCSD, 381 ppm, **22** also displays principally classical character. As can be seen from the resonances of the cyclopropyl carbons of **22** (Table 1), which are considerably deshielded, positive charge is delocalized into the cyclopropane ring. The chemical shifts of the methylene carbons of the cyclopropane ring of **1** bear a strong quantitative resemblance to those of **22**. However, ion **22** lacks the delocalized π-system of **1** thus C1 of **22**

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[32] DeMeijere, A. *Chem. Ber.* **1974**, *107*, 1684.

[33] Shortridge, K. W.; Craig, R. A.; Greenlee, K. W,; Derefer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1948**, *70*, 946.

Table 1. Observed and/or Calculated (IGLO/DZ) ^{13}C Chemical Shifts for the Phenonium Ion (**1**), Spiro[2.5]oct-4-yl Cation (**22**), and Spiro[2.5]octane (**25**)[a]

	1	**22**			**25**
	exp[b]	exp[c]	MP2[d]	RHF[e]	MP2[d]
C1	60.8	95.0	108.4	58.4	4.2
C2	59.8	54.5	20.4	72.9	12.6
C3	59.8	51.5	38.9	44.2	12.0
C4	170.8	201.1	158.1	263.3	26.5
C5	137.8	43.8	20.0	34.1	16.3
C6	159.9	21.0	12.1	10.3	16.8
C7	137.8	19.2	12.4	11.8	16.3
C8	170.8	29.3	24.5	20.0	26.5

[a] Chemical shifts in ppm relative to TMS. [b] Reference 9b. [c] Reference 27. [d] IGLO/DZ//MP2/6-31G*. [e] IGLO/DZ//RHF/6-31G*.

accommodates a greater amount of positive charge than it does in **1**, hence it is more deshielded. We have also subjected **22** to IGLO study at the DZ level using both MP2/6-31G* and RHF/6-31G* optimized geometry and although the calculated shifts (Table 1) are in relatively poor agreement with those observed (the ^{13}C NMR shift of the formal cationic site is under and over estimated, respectively, at each level) both the theoretical geometries predict a C2−C3 bond length intermediate between ordinary C−C and C=C bond lengths at 1.401 Å (MP2/6-31G*) and 1.375(RHF/6-31G*). Similarly the C1−C2 bond length is longer than a normal C−C bond at 1.689 Å (MP2/6-31G*) and 1.676(RHF/6-31G*). Thus it can be seen that even in a system in which aromaticity is clearly not possible shortening and lengthening respectively, of bond distances due to cyclopropyl delocalization can arise and hence we attribute the calculated[19] near equivalency of the bond lengths in **1** (actually the C1−C4, C1−C8 bond lengths are calculated to be marginally longer than the others in the six membered ring) not to "substantial aromatic character" but rather to cyclopropylcarbinyl delocalization. The phenonium ion is thus best depicted as **1** and not as **7**.

Sieber *et al.*'*s*[19] principal argument for suggesting that the phenonium ion possesses nonclassical structure (**7**) was based on the calculated degree of positive charge delocalized into the cyclopropane ring, the nonequivalence of the three-membered ring bonds lengths and the near equivalence of the six-membered ring bond lengths, suggestive of 6π-aromatic character, especially when compared with the nonequivalent bond lengths (calculated) of the essentially classical benzenium ion.[19] However these calculated data are easily rationalized once the cyclopropylcarbinyl nature of ion **1** is taken into account. That **1** should exhibit cyclopropylcarbinyl character is in accord with the canonical contributors **1a** and **1c**. It has been well recognized that cyclopropyl groups adjacent to incipient carbocationic sites are particularly adept at delocalizing positive charge. Indeed their ability to stabilize positive charge is akin to that of the phenyl group.[34] The nature of the delocalization of positive charge into the cyclopropyl ring has been extensively explored and thorough reviews have appeared.[34]

The parent cyclopropylmethyl and 1-methylcyclopropylmethyl cations have been shown to display nonclassical character[34] (as indicated for **26**, R = R′ = H by its TCSD value of 231 ppm[31]). The related secondary and tertiary derivatives, on the other hand, are of classical nature with TCSDs of 400−600 ppm depending on the individual case.[31] However these ions are still capable of substantial hyperconjugative charge delocalization, analogous to charge delocalization in the allyl cation. Although the delocalizing ability of adjacent cyclopropyl rings is often depicted with dotted-line structures (**26a**,**26b**)[35] showing σ-delocalized bonds and C2 rendered pentacoordinate, this depiction is analogous to what may be drawn for classical aliphatic cations in order to illustrate their hyperconjugative stabilization (**27a**).

It is by virtue of its strained (bent), electron rich, πσ-bonds that the cyclopropyl group is better able to donate electron density to, and thus stabilize, the vacant carbocationic p-orbital. In certain cases the degree of delocalization can be sufficient that rearrangement to a cyclobutyl cation occurs.[36] As indicated by structures **26a**,**b** the strong hyperconjugative (homoallylic) delocalization results in partial double bond character between C1 and C2 and a decrease in bond order between C2 and C3 (also C2 and C4) and thus C1−C2 bond lengths intermediate between single and double, and C2−C3 (C2−C4) bond lengths longer than normal, should be expected such as those predicted by Sieber *et al.*'*s* calculations.[19] All alkyl cations, except CH_3^+, must be considered to involve varying degrees of σ-delocalization (C−H or C−C hyperconjugation) and thus could be said to possess nonclassical character although they are not considered as such.

A Freudenberg type or nonclassical phenonium ion might arise from a β-arylethyl derivative if the ability of the aryl ring to engage in π-participation was greatly diminished thus allowing σ-participation of the C1−Cα bond. In an attempt to effect this we ionized under stable ion conditions β-pentafluorophenylethyl alcohol (**28**) and 2-fluoro(tetrafluoro)benzonorbornene (**29**), which possess highly fluorinated aryl groups.

Only a complex mixture was observed (^{13}C NMR) on reacting **28** with SbF_5 or FSO_3H in SO_2ClF at −80 °C. However, on reacting a solution of fluoride **29**, which possesses more favorable geometry for phenonium ion formation,[37] in SO_2ClF with SbF_5/SO_2ClF at −80 °C, a highly symmetrical ion was obtained. On the basis of the observed chemical shifts and multiplicities (Table 2) we found, however, this ion to be of the nortricyclic structure **30** which can be viewed as a phenonium ion.

Such nortricyclic ions (e.g., **31**) have been previously observed to be the sole products on ionization of the parent benzonorbornen-2-yl system and certain other substituted derivatives.[38] The ^{13}C NMR spectrum observed was well reproduced by calculation at the highest practical level of theory available to such a large molecule, IGLO DZ//RHF/6-31G* (Table 2). We have also calculated at the same level the chemical shifts for the analogous hydrocarbon **32** and the parent analogs **31** and **33** (Table 2). Although the chemical shifts are well reproduced, due to the modest level of theory employed the ensuing calculation based conclusions should be regarded as tentative. At this level of theory the structures of the fluorinated (**30**) and parent (**31**) ions are almost identical suggesting that these two ions posses similar classical phenonium ion character. A change to C11−C1/C11−C2 σ-bond delocalization in **30** would be expected to lead to dissimilar C11−C1/C11−C2 bond lengths between the two.

This conclusion is supported by the observed chemical shifts for **30** and **31** which, taking into account the effect of the fluorine atoms on the six-membered ring carbons, bear a striking resemblance to one another with the notable exception of C10. Importantly in both these benzonortricyclyl ions the chemical

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Table 2. Observed and Calculated (IGLO/DZ//RHF/6−31G*) ^{13}C Chemical Shifts for the Tetrafluorobenzonortricyclyl Cation (**30**) and Benzonortricyclyl Cation (**31**) and Calculated (IGLO/DZ//RHF/6-31G*) ^{13}C Chemical Shifts for Their Precursors **32** and **33**[a]

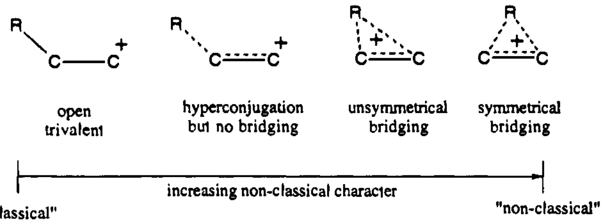
	30		**32**	**31**		**33**
	exp[b]	RHF[c]	RHF[c]	exp[b]	RHF[c]	RHF[c]
C1	95.6 (d, 192)	78.0	22.5	96.1 (d, 190)	75.0	20.4
C2	95.6 (d, 192)	78.8	18.0	96.1 (d, 190)	75.2	20.4
C3	49.5 (t, 142)	44.3	31.9	51.2 (dd, 139, 142)	44.1	29.1
C4	36.7 (d, 160)	31.9	25.9	39.1 (d, 161)	32.4	27.5
C5	139.2 (d, 265)	137	130.5	131.8 (d, 165)	120.3	109.7
C6	158.3 (d, 298)	179	139.7	152.6 (d, 164)	171.4	125.1
C7	142.2 (d, 258)	137	133.3	125.2 (d, 173)	126.8	121.5
C8	172.3 (d, 298)	187	61.7	165.5 (d, 179)	176.9	17.0
C9	49.5 (t, 142)	44.5	123.8	51.2 (as C3)	44.2	29.1
C10	164.4 (s)	175.6	14.0	193.8 (s)	203.0	141.8
C11	67.8 (s)	48.8		84.1 (s)	56.9	10.7

[a] Chemical shifts in ppm relative to TMS. [b] Coupling constants (J(CF) or J(CH) in parentheses. [c] IGLO/DZ//RHF/6-31G*.

shift for the C11 (*ipso*) carbons is similar to that observed in **1** and indicative of an sp^3 hybridized carbon. The chemical shifts and the large C−F coupling constants of the remaining carbons in the six-membered ring of **30** are indicative of substantial charge delocalization to these carbons and its benzenium ion nature. This is supported by the calculated charge distributions for **30** and **31** which also display the observed benzenium type distribution although the C8 carbon in **30** is predicted to accommodate a greater share of the charge at the expense of C10 compared to **31**. This may account for the difference in chemical shift for this carbon (C10) in **30** and **31**. The C1/C2 carbons in **30** are also calculated to bear somewhat more of the positive charge than they do in **31**. Overall it would appear that despite the four electron withdrawing fluorine atoms attached to the aromatic ring of **29** it is still able to engage in π-participation to give a phenonium ion not unlike **1** and **31**. The similar nature of these ions is further borne out by the difference between the total chemical shift of the observed ions **30** and **31** and the calculated chemical shifts for their respective precursors **32** and **33** which are 438 ppm for **30** and 434 ppm for **31**.

Conclusions

We have obtained Cram's phenonium ion (**1**) by the independent route of protonation of benzocyclobutene, under superacidic stable ion conditions. After consideration of the ^{13}C NMR data as well as the Total Chemical Shifts Difference between **1** and **24** and comparison of these data with those of suitable model compounds we further ascertain our previous conclusion that the phenonium ion is *de facto* a spirocyclopropylbenzenium ion (spiro[2.5]octa-5,7-diene-4-yl cation) which can be considered as a cyclopropylcarbinyl cation with the carbenium center being part of a classical cyclohexadienyl cation (benzenium ion). The ion does not contain a pentacoordinate carbonium center, thus it should not be classified as nonclassical. We feel that it is timely to recognize that as all carbocations are delocalized by varying degrees of π- and σ-conjugation/hyperconjugation it is increasingly becoming unnecessary to label carbocations as classical or nonclassical. The terms classical (i.e., trivalent carbenium) and nonclassical (i.e., higher coordinate carbonium) ions define only the limits of a spectrum that all carbocations fall within. This spectrum (Figure 6) ranges from one extreme of localized trivalent ions, through conjugation or hyperconjugation, where there is little change in carbocation geometry to partially bridged ions in which there is significant but unequal bonding to a second atom, to the other extreme of symmetrical bridging involving hypercoordinate carbon.



As π-conjugation is considered a classical interaction it seems unnecessary to suggest that hyperconjugation be described as nonclassical stabilization. Based on extensive spectroscopic evidence[20] including TCSD[31] ions stabilized by such interactions are still predominantly classical in nature. As all carbocations are delocalized to varying degrees use of the prefixes "classical" and "nonclassical" should be more discriminate and only relating to the limiting subcatagories, keeping in mind that these are really trivalent carbenium ions and five (or higher) pentacoordinate carbonium ions, respectively. We do not name boranes/carboranes, organometallics etc. as nonclassical, even if they are bridged (higher coordinate), or for this reason trivalent alkylboranes, etc. as classical. As suggested by Brown years ago,[39] the indiscriminate use of dotted-line structures is also unnecessary and should be limited to true *bridged* ions involving 2e−3c (or multicenter) bonding. Instead of depicting σp-delocalization (hyperconjugation) in terms of dotted line structures it can be more clearly depicted using resonance contributors, with only Lewis type 2c−2e bonds (e.g., **26**, **26c**, **26d**, **26e**), wherein hypercoordinated structures are not invoked and the overall predominantly trivalent nature of the ions is more readily discernible than in the dotted line depictions of the type **26a**,**b**. By none of the discussed criteria, experimental results or theoretical/structural considerations can Cram's phenonium ion be considered a nonclassical carbonium ion, containing hypercoordinate carbon.

Experimental Section

Benzocyclobutene was prepared according to the reported literature procedure.[40] Doubly distilled SbF_5, FSO_3H, and SO_2ClF were used for the preparation of the ions. ^{13}C NMR spectra were obtained on a Varian Unity-300 instrument equipped with a variable-temperature probe.

2-Fluoro(tetrafluoro)benzonorbornane (29). To a solution of tetrafluorobenzonorbornadiene[41] (200 mg, 0.93 mmol) in CH_2Cl_2 (3 mL) in a Nalgene bottle and cooled to 0 °C was added anhydrous HF (ca. 1 mL). The ensuing mixture was capped and stirred for 4 h at 0 °C and then quenched by the dropwise addition of a saturated solution of sodium bicarbonate (15 mL). The organic phase was diluted to 20mL with CH_2Cl_2 and washed successively with saturated sodium bicarbonate (2 × 10 mL) and brine (2 × 10 mL). The methylene chloride solution was dried ($MgSO_4$) and evaporated, and the residue was chromato-

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graphed (silica gel; eluant:hexane) to afford **29** (152 mg, 70%): ^{1}H NMR δ 1.70–2.20 (m, 4H), 3.65 (s, 1H), 3.85 (s, 1H), 4.80 (dd, 1H); ^{13}C NMR δ 29.5, 37.0 (d, J(CF) = 21 Hz), 38.9, 46.2, 92.7 (d, J(CF) = 195 Hz), aromatic carbon peaks were ill defined; ^{19}F NMR δ −143.6 (1F, pseudo triplet, J = 20 Hz), −145.4 (1F, pseudo triplet, J = 20 Hz), −156.9 (1F, pseudo triplet, J = 20 Hz), −158.3 (1F, pseudo triplet, J = 20 Hz), −171.7 (1F, symmetric multiplet); MS(CI) *m/z* (rel intensity) 234 (100), 214 (8), 188 (35), 187 (22), 169 (17), 166 (9), 138 (9); HRMS (CI) [M]$^+$. Calcd for $C_{11}H_7F_5$ 234.0468, found 234.0466.

Carbocation Preparation. To a solution of the appropriate precursor (ca. 30 mg) in SO_2ClF (ca. 0.25 mL) in a 5 mm NMR tube and cooled to −78 °C (dry ice/acetone slurry) was added a precooled solution of the required superacid (see text) in SO_2ClF (1:1, ca. 0.25 mL). The ensuing mixture was vigorously stirred (Vortex agitator) with periodic cooling prior to transfer to a precooled (see text) NMR instrument.

Method, Basis Set, and Geometry. IGLO calculations were performed according to the reported method.[42] Huizinaga[43] Gaussian lobes for the DZ basis are as follows: C or O, 7s 3p contracted to [4111, 21]; H, 3s contracted to [21]. Geometries were optimized by using Spartan[44] or GAUSSIAN92[45] programs on an IBM RISC/6000 Model 560 computer.

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Supplementary Material Available: Calculated optimized structures for **15**, **24**, **30**, **31**, **32**, and **33**, and calculated optimized structures and chemical shifts for **22** and **25** (see text for theoretical levels used) (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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