A Detailed Analysis of the 7-Norbornadienyl Carbonium Ion Nuclear Magnetic Resonance Spectrum[1]

BY PAUL R. STORY, LAWRENCE C. SNYDER, DEAN C. DOUGLASS, ERNEST W. ANDERSON, AND ROBERT L. KORNEGAY

The use of improved vacuum line techniques gives sulfur dioxide solutions of 7-norbornadienyl fluoroborate of sufficient purity and concentration to permit spin–spin decoupling and computer synthesis analyses of its nuclear magnetic resonance spectrum. These analyses have revealed an earlier interpretation of the spectrum to be inaccurate. We now find that the coupling between the low field olefinic pair of hydrogens (2,3) and the bridge hydrogen (7) has a value of 2.7 c.p.s. Further, it has been demonstrated that the bridge hydrogen (7) is also coupled to the high field olefinic pair of hydrogens (5,6) with $J_{5-7} = J_{6-7} = 1.0$ c.p.s.

Introduction

Winstein and Ordronneau[2] solvolyzed 7-norbornadienyl chloride (1) and found that it was *ca.* 10^3 more reactive than *anti*-7-norbornenyl chloride (2)[3] and *ca.* 10^{14} more reactive than the saturated analog, 7-norbornyl chloride (3).[3] On this basis and by analogy to 2 which solvolyzed with retention of configuration, it
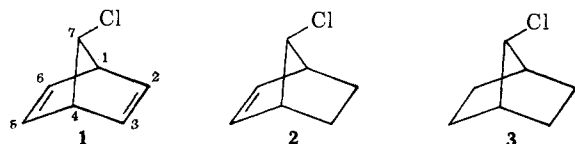
was concluded[2] that the 7-norbornadienyl carbonium ion, which under solvolysis conditions probably existed only as a transient intermediate, was stabilized by nonclassical electron delocalization. Lacking direct structural information, three possible nonclassical structures were proposed.

Subsequently, Story and Saunders,[4] using 7-norbornadienyl chloride (1), made available by a new synthetic procedure,[5] prepared 7-norbornadienyl fluoroborate (4) in liquid sulfur dioxide and observed its n.m.r. spectrum. This spectrum revealed that the 7-norbornadienyl carbonium ion was unsymmetrical and probably possessed the structure depicted in 5. This early spectrum, which exhibited a relatively poor signal-to-

noise ratio, consisted of four multiplets in the area ratio of 2:2:2:1. Only the multiplicity of the lowest field signal could be discerned. However, this multiplet which seemed to consist of two overlapping triplets, revealed some rather vital structural information, *i.e.*, the low field olefinic pair of hydrogens (2,3) was coupled to one additional hydrogen, presumably the bridge hydrogen (7), with $J_{7-2,3} = ca.$ 5 c.p.s.

The examination of spin decoupled spectra has now revealed the earlier interpretation of this multiplet to be in error. An improved synthesis of the fluoroborate 4 has yielded solutions of sufficient purity and concentration to permit a detailed analysis of the entire n.m.r. spectrum. Consequently, all observable couplings present in the molecule have been uncovered using the spin–spin decoupling method. The decoupling tech-

nique used was that suggested by Johnson,[6] which is a modification of the procedure devised by Freeman.[7]

The final value of the couplings and the interpretation of the spectra were checked by a nuclear magnetic resonance spectrum simulation program using an IBM 7090 computer and based on solutions of the appropriate secular equations.

Results

Preparation of 7-Norbornadienyl Fluoroborate (4).—The sulfur dioxide solution of 7-norbornadienyl fluoroborate (4) was prepared generally as described elsewhere[8] by the reaction of 7-norbornadienyl chloride (1) and silver fluoroborate in sulfur dioxide at low temperature. However, in order to obtain a concentrated solution of greater purity, the solution was prepared, filtered, concentrated, and sealed into a sample tube for n.m.r. spectral analysis in an apparatus which was sealed to a high vacuum system and especially constructed for this purpose. It was further found advantageous to prepare the solution at 0.2 M and then concentrate to 0.8 to 1.0 M. The spectra shown here were obtained from a *ca.* 0.9 M solution. A referee has noted that the SO₂ solution may instead contain 7-fluoronorbornadiene complexed with BF₃. We have considered this possibility but we believe that the lack of an observable H–F coupling and the previously reported chemical evidence (ref. 8) favor the fluoroborate.

Analysis of the Spectrum.—The complete spectrum and assignments are shown in Fig. 1. The general features of the spectrum, including the chemical shift values, have been discussed previously.[8]

Obviously too complex for solution by direct inspection, the spectrum was simplified by use of the spin–spin decoupling technique as outlined by Freeman[7] and modified by Johnson.[6] Briefly, the method involved using the Varian integrator as a second oscillator to modulate the field at *ca.* 2 kc. The relatively low amplitude (H₂) 2-kc. side band was followed by the lock-on detector circuit present in the integrator. The 60-Mc. center band was thus filtered out. Decoupling was accomplished by centering upon the 60-Mc. signal to be saturated, a third oscillator with a frequency setting of 2 kc. ± ($\nu_i - \nu_j$), where ν is the chemical shift in c.p.s. of the multiplets (i,j) involved. The amplitude (H₃) of the third oscillator was experimentally determined to bring about the decoupling condition according to

$$\gamma H_3/2\pi \gg |J_{i-j}|$$

The calculated spectra were obtained by use of a nuclear magnetic resonance spectrum simulation program[9] written for an IBM 7090 computer with a

(1) Presented in part before the American Chemical Society Metropolitan Regional Meeting, Newark, N. J., January 23, 1963.

(2) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(3) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(4) P. R. Story and M. Saunders, *ibid.*, **82**, 6199 (1960).

(5) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(6) L. F. Johnson, "Varian Tech. Information Bull. 111," No. 3, 1962, p. 5.

(7) R. Freeman, *J. Mol. Phys.*, **3**, 435 (1960); R. Freeman and D. H. Whiffen, *Proc. Phys. Soc.*, **79**, 794 (1962).

(8) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).
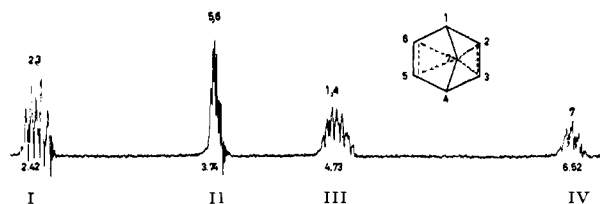
Fig. 1.—High resolution 60 Mc. n.m.r. spectrum of $ca.$ 0.9 M 7-norbornadienyl fluoborate (4) in sulfur dioxide. Peak positions are in p.p.m. relative to tetramethylsilane, internal standard, as 10.0 p.p.m.

$J_{1-2} = J_{3-4} = 6.1$ c.p.s.
$J_{1-3} = J_{2-4} = 1.5$ c.p.s.
$J_{2-3} = 4.6$ c.p.s.

$J_{1-4} = 0.5$ c.p.s.
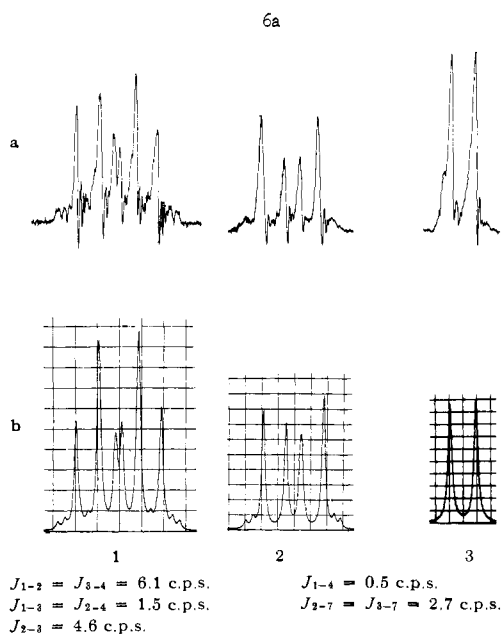$J_{2-7} = J_{3-7} = 2.7$ c.p.s.

Fig. 2.—Analysis of multiplet I at $\tau = 2.42$: row a, experimental spectra; row b, calculated spectra; column 1, normal spectra; column 2, spectra obtained by decoupling H-7 (multiplet IV); column 3, spectra obtained by decoupling H-1 and H-4 (multiplet III).

Stromberg–Carlson 4020 microfilm printer. The program computes the stationary state wave functions and energies and derives n.m.r. line positions and intensities for a system of up to seven nuclei (ABCDEFG) of spin 0.5 with spin–spin coupling. The program prepares and solves secular equations for groups of nuclear states having the same component (F_z) of the total spin in the direction of the applied field (H_1). The position and relative intensity of lines corresponding to a unit change of F_z are computed. The full curve spectrum is obtained by summing Lorentzian lines of half-width (W) at half-height at these positions and with the computed relative intensities.

Decoupled Spectra.—Proceeding on this basis, Fig. 2 shows multiplet I along with the decoupled spectra obtained by perturbing multiplets III and IV. The corresponding calculated spectra and the coupling parameters used to generate them are also shown. An estimated line half-width (W) of 0.25 c.p.s. was used in all calculations.

Examination of the spectra in Fig. 2 reveals that multiplet I is one-half of a typical A_2X_2 pattern generated by hydrogens 1, 2, 3, and 4 and is additionally split by coupling of hydrogens 2 and 3 with H-7. That splitting is given by the spectra in column 3. The parameters used to calculate the A_2X_2 pattern in column 2 were estimated by the use of the equations describing this system set forth by Pople, Schneider, and Bernstein.[10] Note that the complete multiplet,

(9) This program was written by R. L. Kornegay and L. C. Snyder.

$J_{1\,6} = J_{4\,5} = 1.8$ c.p.s.
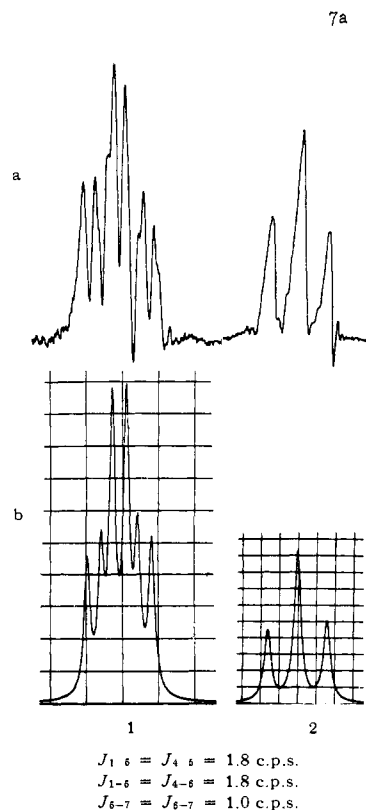$J_{1-5} = J_{4-6} = 1.8$ c.p.s.
$J_{5-7} = J_{6-7} = 1.0$ c.p.s.

Fig. 3.—Analysis of multiplet II at $\tau = 3.74$: row a, experimental spectra; row b, calculated spectra: column 1, normal spectra; column 2, spectra obtained by decoupling H-7 (multiplet IV).

both calculated and experimental, is slightly unsymmetrical suggesting a little A_2B_2 character. The values obtained in this way were refined by the iterative computational procedure already described. Hydrogens 2 and 3 were found not to be coupled to hydrogens 5 and 6. In a separate experiment, multiplet I was reduced to a singlet by simultaneously decoupling hydrogens 1 and 4 and hydrogen 7 with the aid of an additional audiooscillator in what might be termed a "triple resonance" experiment.

The multiplet II at $\tau = 3.73$ is shown in Fig. 3 and at first glance appeared to be a straightforward A_2X_2 pattern indicating that hydrogens 5 and 6 are coupled only to the bridgehead hydrogens (1,4). However, the decoupling experiment illustrated in column 2 shows hydrogens 5 and 6 to be one-half of a special case A_2X_2 pattern where $J_{AX} \cong J'_{AX}$ and J_{AA} and J_{XX} have little or no effect on the spectrum. Coupling with H-7 results in the six lines observed in column 1. Decoupling H-1 and H-4 resulted in a poor doublet (not shown).

The reason for the complexity of the two remaining multiplets now becomes apparent. The bridgehead hydrogens (1,4) and the bridge hydrogen (7) are coupled to all other hydrogens in the molecule resulting in 36 expected lines for the former and 18 for the latter. The multiplet assigned to the bridgehead hydrogens (1,4) is treated in Fig. 4. Spectrum Ia is distorted somewhat by the very slow sweep rate used to show its features more clearly. It is also unsymmetrical because of some A_2B_2 character as indicated in multiplet I. Uncoupling multiplet I reveals approximately two triplets due to coupling with H-7 and hydrogens 5 and 6.

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, p. 140.

8a

$J_{1-2} = J_{3-4} = 6.1$ c.p.s.
$J_{1-3} = J_{2-4} = 1.5$ c.p.s.
$J_{2-3} = 4.6$ c.p.s.
$J_{1-4} = 0.5$ c.p.s.
$J_{1-7} = J_{4-7} = 2.8$ c.p.s.
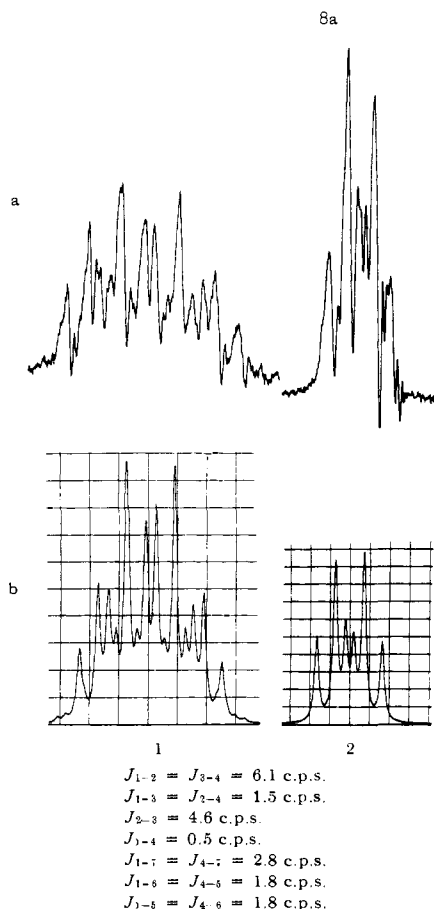$J_{1-6} = J_{4-5} = 1.8$ c.p.s.
$J_{1-5} = J_{4-6} = 1.8$ c.p.s.

Fig. 4.—Analysis of multiplet III at $\tau = 4.73$: row a, experimental spectra; row b, calculated spectra; column 1, normal spectra: column 2, spectra obtained by decoupling H-2,3 (multiplet I).

A rough triplet was obtained by simultaneously decoupling multiplets I and IV.

The bridge hydrogen (7) multiplet simplified surprisingly to the 5-line spectrum shown in column 2. This result requires that J_{2-7} have approximately the same value as J_{1-7}. The triple resonance experiment shown in 3 gives the value of J_{1-7}.

Discussion

Detailed analysis of the 7-norbornadienyl carbonium ion n.m.r. spectrum has served to confirm, with some modification, the structure originally proposed[4] for the ion. We eventually hope to obtain a more quantitative understanding of the structure and n.m.r. parameters from a molecular orbital description. For such a description, a minimum basic set of orbitals must include at least the π-molecular orbitals of the two double bonds and a set of four hybrid orbitals (ζ) from the 2s and 2p atomic orbitals at C-7. We expect that three directed hybrid orbitals (ζ_{C-1}, ζ_{C-4}, and ζ_H) should be taken from C-7 toward C-1, C-4, and the hydrogen at C-7. We call the remaining hybrid orbital (ζ_O) the *open hybrid*. Qualitatively, the mixing of the open hybrid (ζ_O) with the π-molecular orbitals of the double bonds is the nonclassical interaction. A particularly complex problem is the determination of the linear combination of C-7 2s and 2p atomic orbitals which form ζ_H and ζ_O. This hybridization will depend on the amount of charge transfer from the ethylenic bonds to ζ_O. The term ζ_O will be used in this discussion to emphasize the lack of information concerning this orbital and, moreover, that it probably differs appreciably from a normal p-orbital. The present analysis helps

8b

(3)

1   2

$J_{1-7} = J_{4-7} = 2.8$ c.p.s.
$J_{2-7} = J_{3-7} = 2.7$ c.p.s.
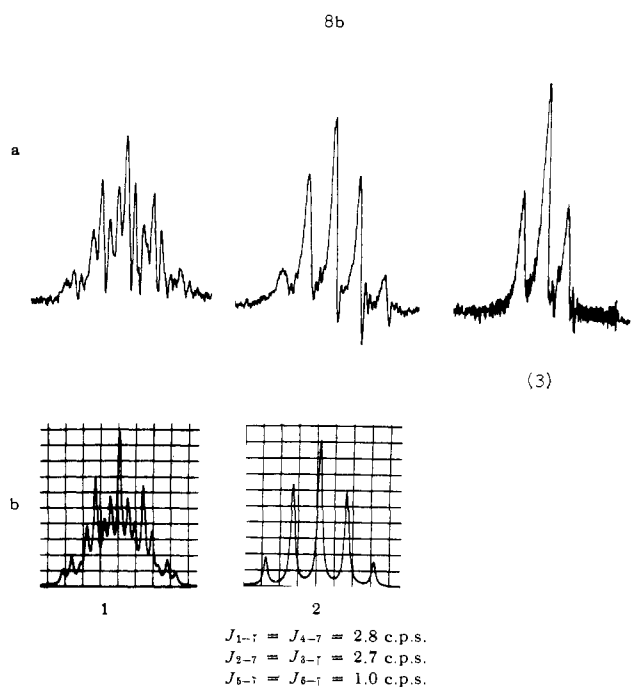$J_{5-7} = J_{6-7} = 1.0$ c.p.s.

Fig. 5.—Analysis of multiplet IV at $\tau = 6.52$: row a, experimental spectra; row b, calculated spectra; column 1, normal spectra; column 2, spectra obtained by decoupling H-5,6 (multiplet II); 3, triple resonance spectrum obtained by decoupling multiplets I and II simultaneously.

to fill in the qualitative picture of electron delocalization. As pointed out earlier,[8] the extent and nature of participation by the 5-double bond in electron delocalization is unclear. Since the unexpected coupling ($J_{7-5,6} = 1.0$) observed between the bridge hydrogen (7) and the upfield olefinic pair of hydrogens (5,6) probably arises by overlap of the open hybrid orbital (ζ_O) at C-7 with the 5-double band π-system, a revision of the current picture of the carbonium ion may be in order. Winstein and Ordronneau[2] found that 7-norbornadienyl chloride (1) was about 800 times more reactive than *anti*-7-norbornenyl chloride (2). For this reason, it has been assumed, from the time of the original n.m.r. spectrum of the ion, that any extra charge delocalization takes place between the two olefinic pairs of carbons although it was recognized that at least part of the greater reactivity of the diene 1 may be due to a ground-transition state effect.[8]

The bridge hydrogen (7) in norbornadiene has been shown not to couple with the olefinic hydrogens.[11] However, close examination of 7-norbornadienyl chloride (1) has revealed that the bridge (7) hydrogen is coupled to *one* olefinic pair of hydrogens with $J = 0.8$ c.p.s. Coupling with the other pair (lower field) of hydrogens was not observable. It cannot be determined at this point whether the coupled pair of hydrogens is *cis* or *anti* to the bridge hydrogen (7). By analogy to the [2.1.1]bicyclic investigation by Meinwald,[12] however, the *anti* pair is considered more likely as shown in 6 since this arrangement would


6
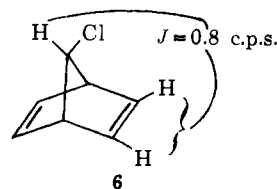
(11) F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959).
(12) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

allow the small lobe of the carbon hydrogen sp^3 orbital to overlap the π-orbital system of the double bond.

These facts probably rule out coupling through the carbon–carbon bonds in the carbonium ion and suggest actual, but unequal, open hybrid ($\mathfrak{z}_0$) orbital overlap to both sides of the one-carbon bridge so that **7** may be a more accurate presentation of the ion. No coupling was discovered between the two pairs of olefinic hydrogens in the carbonium ion. It should be remembered, however, that lack of an observable coupling constant does not, by any means, rule out carbon–carbon bond formation. On the other hand, some liason must

7
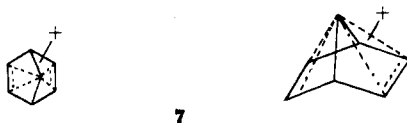
exist between hydrogens to permit an observable coupling. All observable coupling constants are displayed in **8**. The coupling of the bridgehead hydrogens, $J_{1-4} = 0.5$ was estimated rather roughly from the undecoupled multiplet I. It will be noticed that the chosen value splits the small "outside" lines a sufficient amount and only serves to broaden the "inside" lines of the A_2X_2 pattern as required.

8
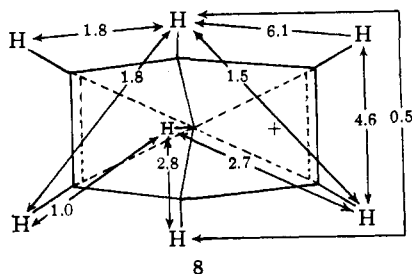
Multiplet I at $\tau = 2.42$, which has been shown to consist of one-half of an A_2X_2 pattern additionally split into two overlapping pattern by coupling with the bridge hydrogen (7), was originally interpreted as two overlapping triplets[4,8] by analogy to several 7-substituted norbornadienes.[5,8,13] The olefinic hydrogens of all 7-substituted norbornadienes examined in this Laboratory generate, approximately, a special case A_2X_2 triplet. Norbornadiene[11] itself, gives a six-line A_2X_2 pattern for the olefinic hydrogens, but appears as a triplet except on close examination.

All of the coupling constants in the carbonium ion, except those involved in the A_2X_2 type multiplets involving hydrogens 1, 2, 3, and 4, are first-order observables and were measured directly from the appropriate spectra. That part of the spectrum involving only first-order constants will not be affected by a sign change. However, a coupling constant sign ambiguity does exist and only the absolute values are given here. Relative signs of the coupling constants are now under consideration employing Freeman's procedure.[14] There is one exception to the relative sign ambiguity. Multiplets I and III are sensitive to a change in sign of J_{1-2} or J_{1-3}. The constant most likely to be negative is J_{1-3}.[15] On the other hand, J_{1-2} is more likely to be positive. However, no satisfactory solution to the spectrum could be found if J_{1-2} and J_{1-3} were permitted to be of opposite sign. Consequently, J_{1-2} and J_{1-3}, whether positive or negative, must be of the same sign.

In this and previous papers, the 7-norbornadienyl carbonium ion (**5**) has been discussed in terms of nonclassical structures even though n.m.r. evidence taken

alone would not differentiate between a nonclassical structure such as **5** or a corresponding rapidly equilibrating mixture of classical ions; *i.e.*, the resonance structures, of which **5** is a hybrid, are, instead, in equilibrium with each other. The n.m.r. spectrometer would then see an average of these structures which could reasonably be expected to generate the observed spectrum.[16] The nonclassical structure **5** has been favored because of other evidence. For example, the greatly enhanced reactivity of 7-norbornadienyl chloride[2] is difficult to explain in terms of classical ions since none of the possible classical ions would, in the light of present knowledge, be expected to have any great stability. Even if it is argued that electron delocalization occurs only in the transition state leading to a carbonium ion intermediate, it becomes difficult to explain the comparative stability of the fluoroborate salt **4** in terms of classical ions.

It should also be noted that the evidence so far accumulated does not rigorously establish that the species observed by n.m.r. is actually a fluoroborate salt. Other structures have been considered. For example, the n.m.r. evidence alone might not distinguish between the fluoroborate **4** structure and a boron trifluoride complex of 7-fluoronorbornadiene. However, we believe that the sum total of information, including the chemical evidence reported earlier,[8] favors the fluoroborate representation.

It is also true that the multiplet representing the olefinic hydrogens (2,3) of the presumed carbonium ions is shifted downfield considerably less than might be expected. We have previously offered a rationalization of the high field H-7 position which may also be applicable to the olefinic hydrogens (2,3). Alternatively, the relatively small chemical shift may be caused by only partial ionization of the fluoroborate salt which may exist partially or wholly as a tight ion pair.

At any rate the fluoroborate **4** exhibits considerably more carbonium ion character than the chloride **1**. It is almost certainly not a free carbonium ion.

Experimental

(16) The nonclassical structure **7** cannot be translated into a corresponding set of classical ions unless it is argued that the 7-hydrogen in one of the possible classical ions
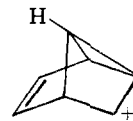
is coupled to the olefinic hydrogens. Preliminary findings argue against this coupling. It is simpler to suppose that the coupling arises in another of the possible classical ions, namely
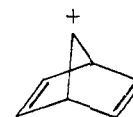
However, if it is held that coupling occurs directly between the 7-hydrogen and the olefinic pair it must come about by a nonclassical interaction since we already know that the C-7 bridge does not move from one side of the molecule to the other faster than about twice per second.

(13) P. R. Story and S. R. Fahrenholtz, *J. Org. Chem.*, **28**, 1716 (1963).
(14) R. Freeman, *J. Mol. Phys.*, **4**, 385 (1961).
(15) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

Sulfur dioxide was Matheson anhydrous reagent and was distilled through a 24-in. column packed with phosphorus pentoxide and glass helices into a reservoir connected to the high vacuum system where it was stored until used.

7-Norbornadienyl chloride (1) was prepared as described previously[8] and purified by g.p.c. immediately before use. A 10 ft. × ³/₈ in., 10% didecyl phthalate on Chromosorb-W column was used at 130°.

Silver fluoroborate was obtained from Chemical Procurement Laboratories, Inc., and dried as described earlier.[8]

Preparation of 7-Norbornadienyl Fluoroborate (4).—Anhydrous silver fluoroborate 0.344 g. (1.77 mmoles), was placed, *via* a side arm, into a reaction vessel containing a stirring bar and sealed to a high vacuum system capable of attaining *ca.* 10⁻⁵ mm. After the side arm was sealed and the chamber was evacuated, the fluoroborate was heated for *ca.* 30 min. to 50–75° by means of an air heater to remove any trace of moisture. The salt was pumped-on for an additional 1.5 hr. A tube containing 0.2025 g. (1.60 mmoles) of 7-norbornadienyl chloride (1) was connected to the same system. This container was cooled, after flushing with argon, in liquid nitrogen and evacuated. After evacuation was complete the container was allowed to warm to room temperature.

The reaction vessel was then cooled by means of a Plexiglas jacket through which cold nitrogen was passed and the chloride 1 was distilled into a chamber directly above the main reaction chamber and separated from it by a break seal. Sulfur dioxide was distilled into this chamber after transfer of the chloride 1 was complete to give a total volume of *ca.* 1 ml.

Sulfur dioxide was also distilled into the reaction chamber to a volume of 6.5 ml. This mixture was stirred and cooled to −70°. The chloride 1 was introduced all at once by breaking the seal with a magnetic bar stored in a side arm. The upper part of the reaction vessel was flushed with additional sulfur dioxide and the total volume of solution was brought to 8 ml. Silver chloride precipitated immediately upon addition of 1. Stirring was continued for 30 min. while the temperature was maintained at −70°.

Approximately 4 ml. of this solution was removed by breaking a seal located below the surface of the solution and leading to a side arm which had been evacuated. The decanted solution was filtered by a fine porosity glass disk located in the side arm and situated so that the solution was filtered vertically through it. The filtration required *ca.* 30 min. To speed up this process, dry argon was introduced into the reaction chamber to create a greater pressure differential. The volume of filtered solution, which was colorless to this point, was reduced to slightly less than 1 ml. to give a solution approximately 0.8 to 1.0 *M* in fluoroborate **4**. The concentrated solution, which had become slightly yellow, was passed by means of another break-seal connection through a medium porosity filter into an n.m.r. sample tube and sealed off for analysis.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGE WASHINGTON UNIVERSITY, WASHINGTON 6, D. C.]

2-Phenyl-2,1-borazarene and Derivatives of 1,2-Azaboracycloalkanes

BY DAVID G. WHITE

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1-Methyl-2-phenyl-1,2-azaborolidine (IV), the first example of a 1,2-azaboracycloalkane, has been obtained by (a) the reaction of (allylmethylamino)phenylchloroborane (III) with lithium aluminum hydride and (b) by the slow addition of N-methylallylamine to a hot, dilute solution of trimethylaminephenylborane (V) in diglyme. The latter method also afforded 2-phenyl-1,2-azaboracyclohexane (IIa) from 3-butenylamine and V. When refluxed under nitrogen with 30% palladium-on-charcoal, IIa was slowly dehydrogenated to 2-phenyl-2,1-borazarene (Ib). The relative inertness of Ib toward oxidation and solvolysis indicates that the 2,1-borazarene ring is aromatically stabilized.
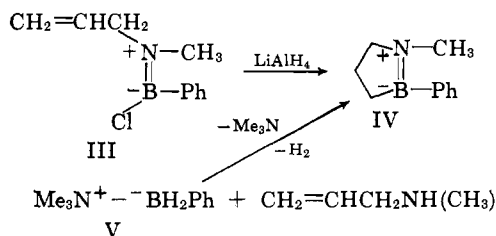
2,1-Borazaronaphthalene, 10,9-borazarophenanthrene, and numerous derivatives of these compounds have been studied extensively, chiefly by M. J. S. Dewar and co-workers. Their heteroaromatic character is demonstrated by their ultraviolet spectra, their readiness to undergo typical electrophylic substitution reactions, and the resistance of the boron-nitrogen link to solvolysis.[1] However, neither the benzene analog, 2,1-borazarene (Ia), nor any of its simple derivatives have been prepared. Dewar and Marr have reported the preparation of 2,3-diphenyl-6-(2-carbomethoxyethyl)-2,1-borazarene, but this was obtained by a method that does not appear to be of general utility.[2] It occurred to the present author that the dehydrogenation of a 1,2-azaboracyclohexane (II) might serve as a useful route to the 2,1-borazarene ring system, and this paper describes the synthesis of 2-phenyl-2,1-

Ia, R = H, R′ = H
b, R = H, R′ = Ph

IIa, R = H. R′ = Ph

borazarene (Ib) by this procedure.

No 1,2-azaboracycloalkanes have been previously described. Therefore an initial study was undertaken to prepare a five-membered cyclic aminoborane of this type, namely 1-methyl-2-phenyl-1,2-azaborolidine (IV). This compound has been obtained in two ways. The first scheme involved the prior formation of (allylmethylamino)phenylchloroborane (III) by the straightforward reaction of phenyldichloroborane with N-methylallylamine, with the use of an equivalent amount of triethylamine to facilitate the elimination of hydrogen chloride. The procedure was that which has been employed to prepare a number of aminophenylchloroboranes derived from saturated secondary amines.[3] A 36% yield of IV was then obtained by adding III to a dilute ether solution of lithium aluminum hydride, followed by the introduction of trimethylammonium chloride and benzene, and heating to about 80°. The infrared spectrum of IV showed the absence

CH₂=CHCH₂
      N—CH₃   LiAlH₄   N—CH₃
      B—Ph   ———→   B—Ph
      Cl   —Me₃N   IV
      III   —H₂

Me₃N⁺—⁻BH₂Ph + CH₂=CHCH₂NH(CH₃)
       V

of olefinic and B–H absorption and the presence of an intense peak at 1512 cm.⁻¹, which can be assigned to the stretching vibration of a boron–nitrogen bond with π-bond character.[4]

The reaction described above is thought to involve the intermediate formation (after the addition of

(1) See P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962), for a review of these and other heterocyclic organic boron compounds and for the rules of nomenclature which are in use.

(2) M. J. S. Dewar and P. A. Marr. *J. Am. Chem. Soc.*, **84**, 3782 (1962).

(3) K. Niedenzu and J. W. Dawson, *ibid.*, **82**, 4223 (1960).

(4) See, for example, G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).