Table I. Metal Ion Catalysis of Trimetaphosphate Formation from Protonated and Unprotonated Polyphosphate End Groups

Metal ion	β_T[a]	k^H, min^{-1} [b]	k, min^{-1} [c]
None	0	2.1	0.3
Mg	0.2	2	14
	0.6	4	21
Ca	0.4	3	52
	0.6	~5	~120
Ni	0.4	9	62

[a] Metal ion to phosphate ratio as described in text. [b] Moles of trimetaphosphate formed per minute from 1 mole of protonated end groups. [c] Moles of trimetaphosphate formed per minute from 1 mole of unprotonated end groups.

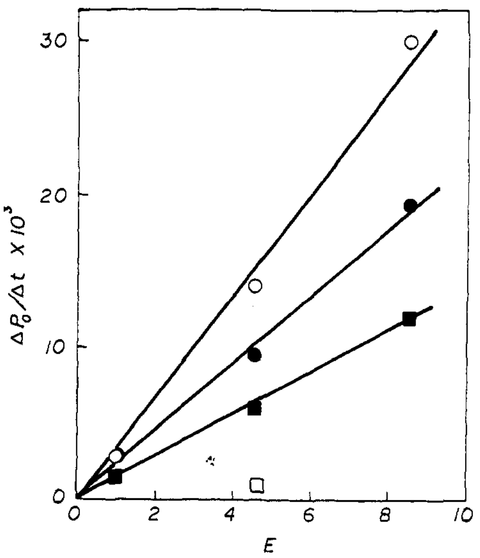

Figure 1. Dependence of the initial rate of formation of trimetaphosphate, $\Delta P_0/\Delta t$, on the per cent end groups. P_0 = moles of trimetaphosphate per 100 g-atoms of total phosphorus. ○: Ca^{2+}, β_T = 0.4, pH 7.0; ■: Mg^{2+}, β_T = 0.4, pH 6.5; ●: Ni^{2+}, β_T = 0.2, pH 7.5; □: no added metal ion, pH 7.0.

than two orders of magnitude are observed. (2) Hydrogen ion, a catalyst itself, inhibits the metal ion catalysis. The evidence on which these conclusions are based is as follows.

The initial rates of formation of trimetaphosphate from three samples of tetramethylammonium polyphosphate (TMAPP) of different chain lengths were determined at 66° in 0.2 *M* TMACl as a function of pH and β_T, the stoichiometric ratio of equivalents of metal ion to gram-atoms of phosphorus. The initial concentration of TMAPP was 0.02 monomole/l. In order to avoid complications known to arise from heterogeneous catalysis,[6] special precautions were taken to prevent conditions which would lead to phase separation. The polyphosphate samples were characterized by potentiometric acid–base titration of the weak acid end groups; their number-average degrees of polymerization were 23, 46, and 200. The degradation products, ortho- and trimetaphosphate, were identified by ion-exchange chromatography and determined quantitatively by an automated technique using Technicon Autoanalyzer components. Figure 1 shows the effects of Mg^{2+}, Ca^{2+}, and Ni^{2+} on the initial rate of trimetaphosphate formation for the three chain lengths. The abscissa is *E*, the concentration of end groups, expressed as mole per cent end group phosphate relative to total phosphate. The results show clearly that the rate of trimetaphosphate formation is directly proportional to the concentration of end groups.

The acid-catalyzed formation of trimethaphosphate has been related directly to the binding of protons to the reactive sites at both interior and end phosphate groups.[2] However, even though the divalent metal ions are bound much more strongly to interior groups than is hydrogen ion,[9] they catalyze only the reaction occurring at the chain end. This conclusion is a departure from the proposal recently made by other workers who infer that, in the presence of divalent metal ions, trimetaphosphate splits out from sites in the chain interior.[5]

Very little has been reported on the effect of pH on the metal ion catalyzed reaction.[3] Our observations show that this reaction is decelerated by decreasing pH exactly in the pH range where the state of protonation of the end groups changes with pH. Over this range of pH, the observed rate can be clearly separated into two contributions, one from the protonated end groups, the other from the unprotonated end groups. (Because the divalent metal ions affect the acid strength of the end groups,[10] the degree of protonation had to be determined from titrations made in the presence of metal ion.) The effects of several metal ions on the specific rate constants for the protonated and unprotonated end groups are listed in Table I. It can be seen that the metal ion catalysis is very pronounced for the unprotonated end groups, but very small for the protonated end groups. It is clear from these data that while hydrogen ion acts as a catalyst in the absence of metal ion, it inhibits the metal ion catalysis.

These findings as well as further results involving the rather complex and specific dependence of the catalysis on the extent of metal ion binding are open to a number of interpretations. The subject will be treated more fully in a future article.

Acknowledgment. This work was supported by Grant GM-12307 from the National Institutes of Health, Public Health Service.

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(9) See listing of stability constants for various cation complexes of polyphosphate: J. Bjerrum, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 199.

(10) J. R. Van Wazer and D. Campanella, *J. Am. Chem. Soc.*, **72**, 655 (1950).

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The Carbon-13 Nuclear Magnetic Resonance Spectrum at −150° of the 2-Norbornyl Cation and Its Relationship to the 7-Norbornenyl and 7-Norbornadienyl Cations[1]

Sir:

Recently we reported the ^{13}C spectrum of the 2-norbornyl cation at −70° in SbF_5–SO_2 solution.[2] At this

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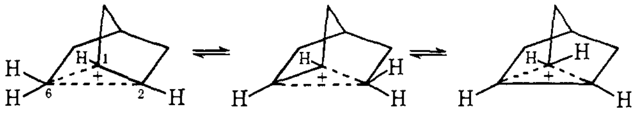
(1) Stable Carbonium Ions. XCV. Presented in part at the XXIst National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969; part XCIV: G. A. Olah, A. T. Ku, and J. Sommer, submitted for publication.

(2) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969).

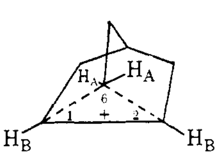
temperature, a three-resonance ^{13}C (and ^{1}H) spectrum is obtained due to the equilibrium **1a** ⇄ **1b** ⇄ **1c** (*via* 1,2-hydrogen shifts) being fast relative to the nmr time scale. The data obtained were shown to be compatible only with the nonclassical formulation of the ion as shown in **1**.



1a **1b** **1c**

At −150° we found it possible to sufficiently slow down the rate of this equilibrium to enable observation of the proton spectrum of the nonclassical ion as a static species.[3] This result together with Raman spectral data[4] showed the structure of the 2-norbornyl ion is most aptly described as corner-protonated nortricyclene with approximate equivalence of the 6-1, 6-2, and 1-2 bond distances.

In the "frozen-out" proton spectrum, the four protons associated with the protonated cyclopropane ring give two resonances of equal area at δ 3.05 and 6.59. Assignment of these protons to either H_A or H_B in **2** was not, however, possible on the basis of this spectrum although a tentative assignment of the bridging protons (H_A) to the high-field peak (δ 3.05) was made on the basis of a presumed analogy between this ion and the 7-norbornenyl cation,[3] which was also suggested by Winstein based on comparison of the pmr spectra.[5]



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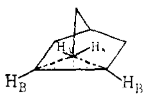
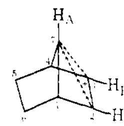
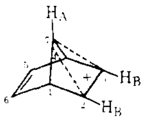
We have now confirmed this assignment by obtaining the ^{13}C spectrum at −150° and wish also to report the ^{13}C spectra of the 7-norbornenyl and 7-norbornadienyl cations which show these ions indeed to be analogs of the 2-norbornyl cation.[6]

The ^{13}C indor spectrum[7] at −70° was obtained by observing the effects of irradiation on the ^{13}C satellites in the proton spectrum of the ion. These satellites could not be observed at −150° due to a poor signal-to-noise ratio at this temperature. Enhancement of the ^{12}C-proton resonance (due to a collapse of the ^{13}C satellites and possibly a nuclear Overhauser effect) was, however, obtained at −150° on irradiation at 25.1 MHz. The low-field proton resonance (at δ 6.59) was enhanced on irradiation at 70 ± 2 ppm while the higher field proton resonance (at δ 3.05) was enhanced on irradiation at 173 ± 2 ppm. We were unable to obtain the C–H coupling constants and peak multiplicities in this manner but since the weighted *average* of these shifts has to give rise to the three-carbon resonance at 101.8 ppm (observed in the equilibrating ion at −70°) the 70-ppm shift has to be assigned to two cyclopropane-type carbon atoms and the 173-ppm shift to one bridging carbon atom *i.e.*, $(2 \times 70 + 173)/3 = 104$ ppm.

To extend the comparison of the 2-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations, we have determined the ^{13}C indor spectra for the two latter ions[8-10] and the results are summarized in Table I.

Table I. Proton and Carbon-13 Nmr Data[a] for the 2-Norbornyl, 7-Norbornenyl, and 7-Norbornadienyl Cations

		
H_A, 3.05 H_B, 6.59 C_A, 173 C_B, 70 $J_{CH_A} + J_{CH_B} = 320$ Hz[b]	H_A, 3.25[c] H_B, 7.04[c] C_A, 162.2[e] C_B, 68.7 $J_{CH_B} = 194$ Hz[d]	H_A, 3.24[c] H_B, 7.48[c] C_A, 152.7 ppm[e] C_B, 75.8 ppm $J_{CH_A} = 220 \pm 5$ Hz $J_{CH_B} = 200 \pm 5$ Hz

[a] Proton shifts are in parts per million from internal tetramethylsilane. Carbon-13 shifts are in parts per million from carbon disulfide. [b] From −70° 100-MHz proton spectrum in SbF_5–SO_2 solution; other values at −150° in SbF_5–SO_2ClF–SO_2F_2 solution. [c] From spectra obtained at −60° in 4:1 *M* FSO_3H–SbF_5 solution (diluted 1:1 by volume with SO_2). [d] J_{CH_A} could not be determined due to overlapping peaks in the proton spectrum. [e] Other shifts: 7-norbornenyl, C_1 138.0 ppm ($J = 160$ Hz); $C_{5,6}$ 171.5 ppm ($J = 130$ Hz); 7-norbornadienyl, C_1 132.6 ppm ($J = 176$ Hz), $C_{5,6}$ 68.9 ppm ($J = 180$ Hz).

A corner-protonated cyclopropane ring can be seen to be common to all three ions. This common structural feature and the resultant similar charge distribution is reflected in the correspondence between the carbon and proton chemical shifts associated with the cyclopropane ring in the three ions. This similarity allows us to estimate the magnitude of J_{CH_A} in the norbornyl cation. We would expect that J_{CH_B} in the three ions would be of similar magnitude as a result of a similar charge distribution and hybridization associated with the CH_B bonds. Therefore taking a value of 195 Hz for J_{CH_B} in the norbornyl cation, and knowing that the sum of J_{CH_A} and J_{CH_B} is 320 Hz,[2] leads to a value of 125 Hz for J_{CH}. This is considerably lower than the 220 Hz observed for J_{CH_A} in the 7-norbornadienyl cation. This difference can be rationalized since there is an obvious dissimilarity between the orientation of the C–H_A bonds in the two ions. This would be expected to result in a higher s character for this bond in the 7-norbornadienyl ion and hence a larger carbon–hydrogen coupling constant. In fact, the coupling constant of 125 Hz estimated for J_{CH_A} in the 2-norbornyl cation is that expected for sp^3 hybridization and is in agreement with our pre-

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(3) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3956 (1969).

(4) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968).

(5) S. Winstein, Abstracts, XXIst National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.

(6) The 7-norbornenyl and 7-norbornadienyl cations were generated in 4:1 *M* FSO_3H-SbF_5 solution (diluted with SO_2) from the corresponding alcohols. We thank Professor H. G. Richey for providing these precursors.

(7) For experimental details of the indor method used, see A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).

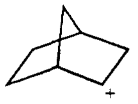
(8) The proton spectra of these ions were identical with those described previously.[9]

(9) (a) M. Brookhart, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3133, 3135 (1966); (b) R. K. Lustgarten, M. Brookhart, and S. Winstein *ibid.*, **89**, 6350 (1967); (c) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967); (d) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966); (e) P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962).

(10) The nonclassical nature of these ions is well established both from proton nmr and stereochemical studies. For a recent review see S. Winstein, *Quart. Rev.* (London), **23**, 141 (1969).

vious estimate based on the ^{13}C spectrum of trimethylaluminum dimer.[3]

We conclude from these studies that there is a close relationship between the charge distribution in the nonclassical 2-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations. Furthermore, in all these cations the positive charge resides mainly at the cyclopropane-type carbon atoms rather than at the bridging carbon. In valence-bond terms this work thus provides evidence that in the 2-norbornyl cation the major contributing resonance structures are thus **3** and **4**, and not **5**. The unimportance of canonical form **5** to the mesomeric structure means that **2** is a better representation of the 2-norbornyl cation than the usual formulation **6** using three dashed lines.[11]



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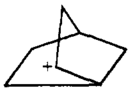

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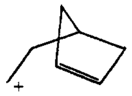

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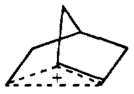

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In summary from our recent results, it can be concluded that the 2-norbornyl cation has: (1) the nonclassical structure which is best described as corner-protonated nortricyclene with approximate equality of the C_1–C_2, C_2–C_6, and C_1–C_6 bond distances; and (2) a charge distribution in which the positive charge is localized predominantly at C_1 and C_2 and not at the bridging, C_6, position.

Acknowledgment. Support of the work by the National Science Foundation and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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(11) For a discussion, see G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

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Tin-119m Mössbauer and Nuclear Magnetic Resonance Study of Dicyclopentadienyltin(II)

Sir:

Dicyclopentadienyltin(II)[1] (I) is one of the two[2] true examples of tin(II) derivatives containing only carbon and hydrogen.[3] In addition it is, with its Pb(II) homolog,[1b,4] with which it shares the angular sandwich structure in the gas phase,[5] one of the two examples of main group elements so bonded. This communication reports some results of our investigation of this remarkable compound.

The Sn^{119m} Mössbauer resonances of I (IS = 3.73 ± 0.06; QS = 0.65 ± 0.06 mm/sec) and of trimethylcyclopentadienyltin(IV)[6] (II) (IS = 1.05 ± 0.06; QS = 1.20 ± 0.06 mm/sec) run at 77°K *vs.* a $BaSn^{119m}O_3$ source (New England Nuclear Corp.) fall on opposite sides of that of β-tin,[7] and on this basis we confirm the valence state as tin(II).[8] The easily resolvable QS shown by II is observed in only one other class of compounds containing only tin, carbon, and hydrogen, the organotin(IV) acetylenes (IS = 1.15–1.24; QS = 1.05–1.48 mm/sec).[9,10] It has been suggested that electric field gradients (efg) in pyramidal, three-coordinate, inorganic tin(II) materials arise from inequalities in the tin internuclear distances rather than from the p character of the lone pair electrons,[11,12] but in I, with equivalent distances, it is possible to carry out a calculation based on a model in which point electron pairs are placed at intermediate positions (1.21 Å[5]) along the ring–tin axes (125° angle at tin[5]). From the magnitude of the QS, this model locates the lone pair along the bisecting *z* axis at 1.2 Å from the tin nucleus.[13,14]

I is transformed slowly at ambient temperatures (DMF is a catalyst) to a material with IS = 0.72 ± 0.06 mm/sec, presumably

$$n(C_5H_5)_2Sn \longrightarrow [(C_5H_5)_2Sn]_n \qquad (1)$$

The conversion can be followed by Sn^{119m} Mössbauer spectroscopy; it is 90% complete in 5 days. Exposure to air produces dicyclopentadienyltin(IV) oxide

$$\begin{tikzcd} n(C_5H_5)_2Sn(II) \arrow[dr, "air"] & & (2a) \\ & {[(C_5H_5)_2SnO]_n} & \\ {[(C_5H_5)_2Sn]_n} \arrow[ur, "air"] & & (2b) \end{tikzcd}$$

These transformations 1 and 2a are complex, since they must involve simultaneously (i) oxidation of tin(II) to tin(IV); (ii) change in the mode of attachment of the C_5H_5 ligand from the angular sandwich[5] to the locally connected, but stereochemically nonrigid, puckered cyclopentadiene ring;[15] (iii) change in the nature of the

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(1) (a) E. O. Fischer and H. Grubert, *Z. Naturforsch.*, **11b**, 423 (1956); (b) L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).

(2) Dihydrodibenzostannepin has been prepared by a difficult route: H. G. Kuivila and F. Beumel, *J. Am. Chem. Soc*,, **80**, 3250 (1958). Di(9-phenahthryl)tin has been studied by Sn^{119m} Mössbauer spectroscopy, but the sample used had apparently polymerized: V. I. Baranovskii, B. E. Dzevitskii, L. M. Krizhanskii, and B. I. Rogozev, *J. Struct. Chem.* (USSR), **7**, 754 (1966).

(3) Compounds of the formula R_2Sn, known for over a century as representatives of this class, have recently on the basis of chemical [W. P. Neumann, *Angew. Chem.*, **75**, 225 (1963)], nmr [W. P. Neumann and J. Pedain, *Ann. Chem.*, **672**, 34 (1964)], Sn^{119m} Mössbauer [V. I. Goldanskii, V. Ya. Rochev, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **156**, 909 (1964)], and structural [D. H. Olsen and R. E. Rundle, *Inorg. Chem.*, **2**, 310 (1963)] evidence been reformulated as tin(IV).

(4) E. O. Fischer and H. Grubert, *Z. Anorg. Allgem. Chem.*, **286**, 237 (1956).

(5) A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometal. Chem.*, **7**, 97 (1967).

(6) H. P. Fritz and C. G. Kreiter, *ibid.*, **1**, 323 (1964).

(7) In the absence of an accepted standard reference compound to which Sn^{119m} IS measurements can be referred, a wide spread of values for β-tin is to be found in the literature. The IS is commonly quoted as *ca.* 2.65 mm/sec with respect to SnO_2 at ambient temperature.

(8) The IS of β-tin is taken as the dividing line between the two valences, all tin(IV) compounds falling below and all tin(II) above; see J. J. Zuckerman in "Mössbauer Effect Methodology," Vol. III, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, p 15; and D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, **8**, 1771 (1969).

(9) For the compound $(CH_3)_3SnC{\equiv}CC{\equiv}CC_2H_5$, QS = 1.80 ± 0.05 mm/sec.[10]

(10) B. I. Rogozev, V. S. Zavorodnii, L. M. Krizhanskii, and A. A. Petrov, *Zh. Obshch. Khim.*, **38**, 2064 (1968).

(11) J. D. Donaldson and B. J. Senior, *J. Inorg. Nucl. Chem.*, **31**, 881 (1969).

(12) This leads to the prediction of sign inversions in the principle axis of the efg for tin(II) salts, contrary to recent measurements: N. E. Erickson, private communication, 1969.

(13) This trigonal-planar electrostatic model would be applicable as well to the localized σ-bonded situation, and so does not serve to specify the solid-state structure of I.

(14) N. W. G. Debye and J. J. Zuckerman, unpublished results.