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 un-

3   4   5
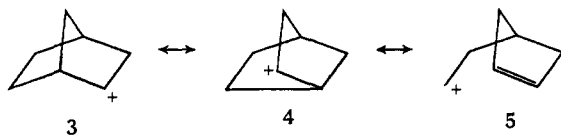
importance of canonical form **5** to the mesomeric structure means that **2** is a better representation of the 2-norbornyl cation than the usual formulation **6** using three dashed lines.[11]

6
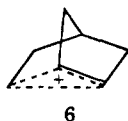
In summary from our recent results, it can be concluded that the 2-norbornyl cation has: (1) the nonclassical structure which is best described as corner-protonated nortricyclene with approximate equality of the C_1–C_2, C_2–C_6, and C_1–C_6 bond distances; and (2) a charge distribution in which the positive charge is localized predominantly at C_1 and C_2 and not at the bridging, C_6, position.

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

George A. Olah, Anthony M. White
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
Received August 5, 1969

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) homo-

(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 R₂Sn, 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).

log,[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}O₃ 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

$$n(C_5H_5)_2Sn \longrightarrow [(C_5H_5)_2Sn]_n \qquad (1)$$
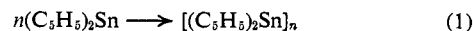
The conversion can be followed by Sn^{119m} Mössbauer spectroscopy; it is 90% complete in 5 days. Exposure to air produces dicyclopentadienyltin(IV) oxide

$$n(C_5H_5)_2Sn(II) \qquad (2a)$$
$$\xrightarrow{\text{air}} [(C_5H_5)_2SnO]_n$$
$$[(C_5H_5)_2Sn]_n \qquad (2b)$$
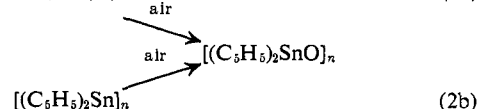
These transformations 1 and 2a are complex, since they must involve simultaneously (i) oxidation of tin(II) to tin(IV); (ii) change in the mode of attachment of the C_5H_5 ligand from the angular sandwich[5] to the locally connected, but stereochemically nonrigid, puckered cyclopentadiene ring;[15] (iii) change in the nature of the

(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 SnO₂ 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 (CH₃)₃SnC≡CC≡CC₂H₅, 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.
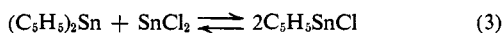(13) This trigonal-planar electrostatic model would be applicable as well to the localized σ-bonded situation, and so does not serve to specify the solid-state structure of I.
(14) N. W. G. Debye and J. J. Zuckerman, unpublished results.

C_5H_5 ligand from delocalized to diene type; and (iv) change from centrally σ bonding (pseudo-π) to localized σ bonding of the rings.

Nmr spectra of tin(II)[1b] and tin(IV) cyclopentadienyls[6,16] have been recorded. The C_5H_5 protons in II are downfield of I. In cyclopentadienyliron derivatives the Fe[57] Mössbauer IS and nmr τ values are related linearly such that an increase in IS of 0.3 mm/sec is accompanied by an increase of nearly one τ unit, taking the extremes of the scale.[17] For tin an increase in IS of 2.7 mm/sec is accompanied by a *decrease* of a few hundredths of a τ unit. Recalling the difference in signs of the fractional change in the nuclear charge radii for iron and tin,[18] these observations are corroboratory. The large substituent-induced nmr shifts for iron (τ 3.92–5.87),[17] are not seen in the various organotin(IV) cyclopentadienyls (τ 4.05–4.13),[6] nor in the small shift (barely a few cycles at 60 MHz) accompanying the change in tin valence state.

The single sharp resonances of the C_5H_5 protons have been interpreted in terms of stereochemically nonrigid cyclopentadienyltin(IV) systems, and temperature-variable spectra have been reported for several compounds.[16b,19] The observation of spin-spin coupling shows that the processes occurring are *intra*molecular. The nmr spectrum of I[1b] [$J(Sn^{117,119}-C-H^1) = 15.9$ Hz] is unchanged at $-90°$, where crystallization takes place from most suitable solvents, but the tin satellites disappear at 125° in xylene (the C_5H_5 signal remains sharp), denoting the onset of dissociative processes. Other *inter*molecular processes are brought about by exchange with tin(II) chloride and trimethyltin(IV) chloride.

$$(C_5H_5)_2Sn + SnCl_2 \rightleftharpoons 2C_5H_5SnCl \qquad (3)$$

$$(C_5H_5)_2Sn + (CH_3)_3SnCl \rightleftharpoons C_5H_5SnCl + (CH_3)_3SnC_5H_5 \qquad (4)$$

No satellites are observed on the sharp C_5H_5 singlets, even at $-80°$. The position of the equilibrium in (4) can be established from the methyltin proton resonance relative to the two pure methyltin species.

Information concerning the conformational integrity of I with phase comes from ir and Mössbauer spectra in solution, which are very similar to those for the solid; the ir can be used to rule out a diene-type cyclopentadienyl ring in either phase.[20] No peaks above the parent ion are seen in the mass spectrum, where the most prominent peak is the monotin fragment at 184 ($C_5H_5Sn^+ = 100\%$) followed by 119 ($Sn^+ = 13\%$). This behavior differs from that of the σ-cyclopentadienyls such as $C_5H_5CuP(C_2H_5)_3$ which does not show the $C_5H_5Cu^+$ peak[21] and from that of ferrocene and other π-bonded species where prominent parent ions are seen (*vs.* 249 [$(C_5H_5)_2Sn^+ = 4.6\%$]) but resembles the vanadium and nickel examples.[22] Like both ferrocene and nickelocene, I gives rise to fragments at 158 ($SnC_3H_3^+ = 3.7\%$) and 144 ($SnC_2H^+ = 3.0\%$). The former, presumably a cyclopropenium tin ion, has been previously observed with cyclopentadienyl–transition metal compounds.[22]

(22) M. I. Bruice, *Advan. Organometal. Chem.*, **6**, 273 (1968).

P. G. Harrison, J. J. Zuckerman
Department of Chemistry
State University of New York at Albany
Albany, New York 12203

The Carboxyl Carbon Isotope Effect on the Enzymatic Decarboxylation of Glutamic Acid

Sir:

Heavy-atom isotope effects have been used to study the mechanisms of a number of chemical reactions,[1–4] but little use has been made of heavy-atom isotope effects in biochemical systems. Seltzer, Hamilton, and Westheimer reported only a very small carbon isotope effect on the enzymatic decarboxylation of oxalacetic acid.[5] Other studies of heavy-atom isotope effects have provided little useful information about mechanism because of unexplained variations of isotope effect from experiment to experiment.[6–8] The extreme sensitivity of isotope effects to contamination requires that such measurements be made and reported with great attention to experimental technique.

We have measured the carboxyl carbon-13 isotope effect on the decarboxylation of glutamic acid catalyzed by an enzyme from *E. coli*.[9] The isotope effect is $k^{12}/k^{13} = 1.0172$ at 37°, pH 4.7. Isotope effects of this type can provide much useful information about the correctness of the Michaelis–Menten mechanism and about the nature of the decarboxylation transition state.

For each experiment freshly prepared solutions of 0.01 M L-glutamic acid in 0.1 M pyridine hydrochloride buffer, pH 4.7, were freed of CO_2 by bubbling CO_2-free nitrogen through the solutions for 30 min. The air in each reaction flask was displaced with nitrogen before

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(15) As observed in solid π-$C_5H_5Fe(CO)_2]_2Sn(C_5H_5)_2$: B. P. Biryukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Commun.*, 119 (1968); *Zh. Strukt. Khim.*, **10**, 95 (1969).

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(3) W. H. Saunders, Jr., in "Techniques of Organic Chemistry," Vol. VIII, Part 1, 2nd ed, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1961, Chapter 9.

(4) H. Simon and D. Palm, *Angew. Chem. Intern. Ed. Engl.*, **5**, 920 (1966).

(5) S. Seltzer, G. A. Hamilton, and F. H. Westheimer, *J. Am. Chem. Soc.*, **81**, 4018 (1959).

(6) K. R. Lynn and P. E. Yankwich, *Biochim. Biophys. Acta*, **56**, 512 (1962); **81**, 533 (1964).

(7) J. L. Rabinowitz, G. D. Chase, and L. F. Kaliner, *Anal. Biochem.*, **19**, 578 (1967).

(8) J. L. Rabinowitz, J. S. Lafair, H. D. Strauss, and H. C. Allen, Jr., *Biochim. Biophys. Acta*, **27**, 544 (1958).

(9) For our previous work on this enzyme, see M. H. O'Leary, *Biochemistry*, **8**, 1117 (1969).