absorption bands of the nucleic acids and polynucleotides.

We acknowledge the skillful technical assistance of M. Capecchi.[8]

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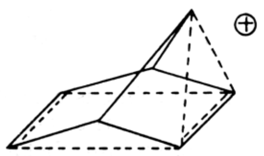
THE 7-NORBORNADIENYL CARBONIUM ION

Sir:

Recent investigations into the solvolysis of a number of norbornenyl derivatives have been characterized by the postulation of non-classical carbonium ions as intermediates. The preparation of a stable bridged carbonium ion from 7-norbornadienyl chloride has now permitted for the first time direct structural evidence to be obtained about these interesting species. Heretofore, structural evidence relating to these carbonium ion intermediates has been inferred from kinetic and product analyses. For example, the remarkable enhancement of the rate of solvolysis of *anti*-7-norbornenyl tosylate compared to the 7-norbornyl derivative has been ascribed to participation of the π electrons of the double bond to give a stabilized non-classical carbonium ion intermediate.[1] More recently, Winstein and Ordronneau[2] have reported that 7-norbornadienyl chloride solvolyzes *ca.* 10^3 faster than *anti*-7-norbornenyl chloride and suggested several possible non-classical structures for the intermediate carbonium ion. We wish to report the preparation and n.m.r. spectrum of this ion.

Treatment of 7-norbornadienol[3] with thionyl chloride in ether gave 7-norbornadienyl chloride,[2] which was dissolved in sulfur dioxide at −80° and slowly added to a similar solution of silver tetrafluoroborate.[4] The silver chloride which precipitated immediately was filtered off leaving a colorless solution. The ultraviolet spectrum at −80° showed no absorption above 330 mμ, the cut-off wave length of liquid sulfur dioxide.

The n.m.r. spectrum of this solution at −10° (Fig. 1) consists of four distinct peaks in the ratio 2:2:2:1 showing partially resolved spin-spin fine structure. We have assigned these peaks to the 7-hydrogen, the bridgehead hydrogens and two *different* pairs of olefinic hydrogens. The peak at 2.4 τ seems to consist of two overlapping triplets suggesting that the normal norbornadiene olefin triplet[5] is split by coupling with *one additional hydrogen* with coupling constant about 5 c.p.s. The above data, which definitely eliminate any symmetrical structure, are consistent with structure I, which was among those structures proposed by Winstein and Ordronneau.[2]



I

The other peaks of the spectrum can be reasonably assigned to: remaining olefin, bridgehead and bridge hydrogens, respectively. For comparison, we have determined the n.m.r. spectrum of 7-norbornadienyl chloride in sulfur dioxide. The olefinic hydrogens appear at 3.2 and 3.4 τ with the lower field peak being an incompletely resolved triplet. The bridgehead hydrogens are at 6.3 and the bridge hydrogen at 5.8.

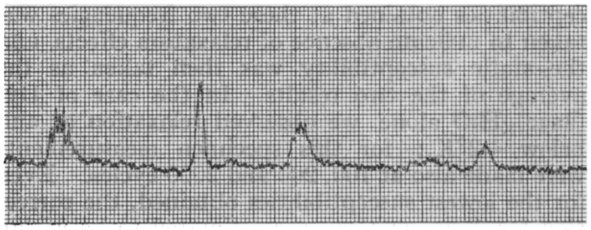


Fig. 1.—N.m.r. spectrum of 7-norbornadienyl fluoroborate in sulfur dioxide at −10°. Peak positions are given in p.p.m. relative to tetramethylsilane as 10.00.

The sulfur dioxide solution appeared to be stable at −10° but became deep brown in color on standing at room temperature for a short period. The absence of skeletal rearrangements was indicated by the exclusive conversion of the carbonium ion to the known 7-norbornadienyl acetate[3] on addition of acetic acid to the sulfur dioxide solution.

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[1] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955).

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MAGNETIC PROPERTIES OF SOME RARE EARTH CHELATES OF ETHYLENEDIAMINETETRAACETIC ACID AND ACETYLACETONE BETWEEN 1.3 AND 77.2°K.[1]

Sir:

In relation to recent studies by Grenthe and Fernelius[2] on the solution stability of a number of rare earth chelates, it was of interest to make a study of the magnetic properties of some of these compounds. The magnetic susceptibilities of the acetylacetonates of Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, and Yb, all of the same general formula $M(acac)_3 \cdot H_2O$ (prepared according to Stites, *et al.*[3]), and ethylenediaminetetraacetates of Pr, Nd and Gd of the formula $Na[M(EDTA)] \cdot 8H_2O$ (obtained from Professor T. Moeller; for preparation see

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[1] The authors wish to thank the Office of Naval Research for financial aid under Contract No. NONR 65624, and the National Science Foundation for support under Grant No. 9928.

[2] I. Grenthe and W. C. Fernelius, *J. Am. Chem. Soc.*, to be published.

[3] J. G. Stites, C. N. McCarthy and L. L. Quill, *ibid.*, **70**, 3172 (1948).

Moeller, *et al.*[4]) were measured between 1.3 and 77.2°K. using the same general method as described by Fritz, *et al.*[5]

The purity of the specimens was 99.9% or better (with respect to content of the rare earth), with the exception of the neodymium chelates, which contained 1% impurity (praseodymium and samarium, both weaker magnetically than the neodymium). Carbon-hydrogen analyses showed in all cases excellent agreement with values calculated for the compositions listed. Measurements were made at four temperatures in the liquid helium range (1 to 4°K.), four in the hydrogen range (10 to 20°K.) and two in the liquid nitrogen range (65 to 77°K.). $CuSO_4 \cdot 5H_2O$ was used for calibration as before.[5] In all cases measurements were made at 400 and 1000 cycles. Agreement of the "dynamic" susceptibilities obtained at these two frequencies was taken to indicate absence of relaxation effects, and the static susceptibility was then taken as the average of the two results. In the case of $Dy(acac)_3 \cdot H_2O$ alone, we observed relaxation at and below 4.2°K.; for this specimen measurements were made also at 100, 200 and 2000 cycles. Even for the lowest susceptibilities obtained, the correction for diamagnetism was estimated to be within the uncertainty of measurement and was not applied.

The data now are being subjected to detailed theoretical treatment following the crystal-field model. Details of the data will be published later, along with the results of the theoretical treatment.

From 1 to 20°K. the data could be fitted by empirical equations of the form of the Curie–Weiss law within about 3% (the precision of the data was about 1%). The constants of these equations are given in Table I, along with the theoretical Curie constants of Van Vleck and Fowler.[6] The large deviations of the empirical "Curie" constants from the high temperature theoretical values indicate mainly that at these low temperatures only some of the low lying multiplets are populated. Some interesting facts become apparent when our results are compared with one another and with earlier measurements on octahydrated sulfates of Pr and Nd,[7] Gd,[8] Dy, Er and Yb.[9,10]

TABLE I

Range °K.	Compound	C (Exptl.)	Δ, °K.	*C* (Van Vleck)
20–1	$Pr(acac)_3 \cdot H_2O$	1.25	11.3	1.64
	$Nd(acac)_3 \cdot H_2O$	1.04	1.1	1.69
	$Gd(acac)_3 \cdot H_2O$	8.0	0.56	7.87
	$Tb(acac)_3 \cdot H_2O$	9.6	0.67	11.81
	$Dy(acac)_3 \cdot H_2O^a$	15.4	1.54	14.0
	$Ho(acac)_3 \cdot H_2O$	10.4	1.67	14.0
20–4	$Er(acac)_3 \cdot H_2O$	8.3	1.7	11.5
4–1		5.9	0.0	
20–3	$Tm(acac)_3 \cdot H_2O$	6.6	0.0	7.2
3–1		11.9	3.3	
20–1	$Yb(acac)_3 \cdot H_2O$	1.3	0.0	2.53
	$Na[Pr(EDTA)] \cdot 8H_2O$	2.4	0.58	1.64
	$Na[Nd(EDTA)] \cdot 8H_2O$	0.73	0.29	1.69
	$Na[Gd(EDTA)] \cdot 8H_2O$	8.3	0.0	7.87

[a] Below 10°K. the data are for the static (zero-frequency) susceptibility calculated using the Debye model.

For praseodymium and neodymium, the temperature dependence of susceptibility is complicated, but in both cases the acetylacetone chelate has a distinctly larger susceptibility than the EDTA complex, and this in turn larger than the sulfate. For gadolinium, the acetylacetonate, the EDTA complex, and the sulfate are all relatively ideal. For erbium, the only member of the series beyond gadolinium for which detailed information about the sulfate is available, the situation is reversed, with the sulfate showing a larger susceptibility than the acetylacetone. Dysprosium acetylacetonate, with the observed relaxation effects, is obviously a special case; the data available for ytterbium sulfate do not permit detailed comparison with the chelate. It is clear, however, that in all cases the magnetic behavior of the acetylacetone complex is definitely different from that of an ordinary hydrated salt.

The change in properties of the compounds of the elements after gadolinium is also apparent through observations on formation constants of rare earth chelates, where the stabilities of the various compounds fit an electrostatic picture of bonding up to gadolinium but fail to do so thereafter.[2] In view of the complicated multiplet structure of the low-lying spectroscopic states of the rare earth ions, considerable detailed theoretical work will be required for a full explanation of the observed magnetic behavior.

The relaxation phenomena observed for $Dy(acac)_3 \cdot H_2O$ in the helium range could be fitted by a simple Debye model[11] at the low frequency end (400 cycles and below). The relaxation time obtained from this model was about 10^{-3} sec., and decreased with increasing temperature.

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[5] J. J. Fritz, R. V. G. Rao and S. Seki, *J. Phys. Chem.*, **62**, 703 (1958).

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[11] See C. G. Gorter, "Paramagnetic Relaxation," Elsevier Publishing Company, Inc., Houston, Texas, 1947.

[12] On leave from University of Lund (Sweden).

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THE CYCLOPROPYL CARBENE

Sir:

The cyclopropyl carbene, a previously unreported species, appeared most intriguing to us for two reasons. First, its addition to olefins should lead to the formation of substituted spiropentanes, a type of compound for which no general method of synthesis is known.[1] Second, it would be of theo-

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[1] *Cf.* D. E. Applequist, G. F. Fanta and B. W. Henrikson, THIS JOURNAL, **82**, 2368 (1960).