$$\vartheta = \frac{3 + 4\dfrac{T}{V}\left(\dfrac{\partial V}{\partial T}\right)_p}{\dfrac{\mathrm{C}e^2}{6R^4V}\left(\dfrac{\partial V}{\partial p}\right)_T - \dfrac{T}{V}\left(\dfrac{\partial V}{\partial T}\right)_p} \qquad (7)$$

$$n = \frac{NCe^2\Delta R^2}{\mathbf{R}TR^3}\left(\frac{1}{2} - \frac{\vartheta}{4}\right)\left(1 + (1 - p)\frac{3\Delta R}{R}\right) \qquad (8)$$

$$\sigma = \frac{1 - \sqrt{1 - 4p(1 - p)(1 - e^n)}}{2(1 - e^n)p(1 - p)} - 1 \qquad (9)$$

ϑ can be calculated if the compressibility coefficient, $\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$, and the cubic expansion coefficient, $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, is known. Equations 5 and 6 have been simplified by assuming that the ϑ value for cesium chloride is equal to the value for rubidium chloride. This is not likely to introduce a serious error, since the values calculated for some other alkali halides indicate little variation in ϑ.[7]

Numerical values for $\Delta\bar{H}$ and $T\Delta\bar{S}$ have been evaluated from equations 5–9, taking for ϑ the value 9.1 given by Hovi for rubidium chloride,[7] and calculating R and ΔR at various temperatures for the unit cell edge interpolation formula given by Wood, Sweeney and Derbes.[2] Results are given in cal./mole in the table, columns 3 and 4, for a solid solution of p mole of cesium chloride with $1-p$ mole % rubidium chloride at the temperature of initial transition. Column 5 gives the simpler expression $\mathbf{R}T \ln p$.

TABLE I

T_m, °K.	p	$\Delta\bar{H}$	$T\Delta\bar{S}$	$\mathbf{R}T \ln p$
735	1.00	0	0	0
711	0.95	4	73	73
668	0.90	14	141	139
628	0.80	54	282	278
488	0.50	251	652	672

These data show clearly that the approximations represented by equation 2 and 3 did not strongly interfere with our previous efforts to determine the heat of transition in cesium chloride.[1] Thus by using equations 1, 4, 5 and 6, a heat of transition around 1.4 kcal./mole is found, as compared with the value 1.55 kcal./mole based on equations 1, 2, 3, 4.[1] The calculated heat of transition is seen to deviate from the experimental value (0.58 kcal./mole) far more than can possibly be explained by a non-ideal mixing of cesium and rubidium atoms.

Data for an accurate evaluation of the remaining correction term (the last term in equation 1), which takes care of the difference in specific heat of high and low cesium chloride, do not exist. When $T_{\mathrm{tr}} - T_{\mathrm{m}}$ is small, however, this term is quite negligible (of the order of magnitude $\Delta c_{\mathrm{p}}(T_{\mathrm{tr}} - T_{\mathrm{m}})^2/2T_{\mathrm{m}}$). From the heat content curves,[3] Δc_{p} is calculated to be 0.173 cal./mole deg. at 745°K., a value which entirely justifies the exclusion of this term from the calculations. Actually an agreement between the observed heat of transition and the heat of transition calculated from the phase diagram cannot be obtained by choosing any reasonable function for Δc_{p}. Therefore (provided that only a negligible amount of rubidium chloride is soluble in low cesium chloride at any temperature) the experimental results appear to be inconsistent.

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[7] V. Hovi, *Acta Metallurgica*, **2**, 334 (1954).

THE n → π* TRANSITION IN NUCLEIC ACIDS AND POLYNUCLEOTIDES

Sir:

The 2600 Å. absorption band of the nucleic acids is often tacitly assumed to be a single electronic band. However, spectroscopic studies suggest that the seemingly simple near-ultraviolet band is actually rather complex, aside from the superposition of pyrimidine and purine bands. First it is clear[1] that the purine absorption band consists of two independent and mutually perpendicularly polarized $\pi \rightarrow \pi^*$ transitions, involving the conjugation electrons of both rings. Secondly, both in the pyrimidines[2] and purines[2–4] there is an $n \rightarrow \pi^*$ transition region on the long wave length side of the strong near ultraviolet $\pi \rightarrow \pi^*$ absorption band, even in aqueous solution. The $n \rightarrow \pi^*$ absorption appears in the N-heterocyclic bases in aqueous solution often as merely a shoulder or poorly resolved inflection in the absorption curve.

The $n \rightarrow \pi^*$ transitions originate in the promotion of a non-bonding (n-orbital) lone-pair electron on a hetero-atom (O or N) to an empty π-antibonding molecular orbital. The $n \rightarrow \pi^*$ transitions are distinguished from $\pi \rightarrow \pi^*$ transitions by several inherent characteristics, of which two are of special interest here: (a) the $n \rightarrow \pi^*$ absorption bands are of intrinsically low intensity, being at most one-tenth as intense as the $\pi \rightarrow \pi^*$ bands; (b) the $n \rightarrow \pi^*$ bands have transition moments polarized out-of-plane, whereas the $\pi \rightarrow \pi^*$ transition moments are polarized in-plane for all pyrimidines and purines. Thus for DNA or other two stranded helical polynucleotides, the transition moment for the $\pi \rightarrow \pi^*$ transition is perpendicular to the molecular helix axis, while the $n \rightarrow \pi^*$ transition moment is parallel to the helix axis.

Dichroic studies on oriented polymer films should reveal the characteristic differences in polarization directly. Accordingly, a series of ultraviolet absorption curves in polarized light were measured using oriented films of various synthetic polynucleotides and nucleic acids. Films were prepared by placing the polymer sample on a quartz disk and dissolving the material in a small droplet of water. This produced a gel which was stroked until the material had air dried. The films were optically clear, and examination under the polarizing microscope revealed several areas of high birefringence. The disks were placed in a Cary Model 14 recording spectrophotometer which had been fitted with Glan Thompson prisms so that the polarized ab-

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(4) M. Kasha, in "The Nature and Significance of n → π* Transitions," "Symposium on Light and Life," Johns Hopkins University Press, Baltimore, Md., 1960.

sorption spectrum could be recorded in the ultraviolet region. Homogeneous areas were selected and the absorption spectrum measured with the electric vector both parallel and perpendicular to the stroking direction. The sign of the birefringence showed that the stroking direction is also the direction of the molecular helix axis.

An example of dichroic absorption results is shown in Fig. 1 for polycytidylic acid, a synthetic polynucleotide. Polycytidylic acid forms a helix[5] in which the cytosine residues are oriented almost perpendicular to the helix axis as shown by its X-ray diffraction pattern and strong negative birefringence. It can be seen that the shape of the ultraviolet absorption curve obtained with the electric vector of the light wave parallel to the helix axis differs markedly from that obtained with the electric vector perpendicular to the helix axis. In the perpendicular case, the two strong peaks at 270 mμ and 225 mμ undoubtedly are $\pi \rightarrow \pi^*$ bands. In the parallel polarization case, a low broad peak is seen with a $\lambda_{\max}$ near 280 mμ. The fact that this peak appears with the light vector parallel to the helix axis establishes the presence of an $n \rightarrow \pi^*$ transition in this region. At higher dichroic ratios, better resolution of this band would be expected. Similar studies have been carried out on several helical polynucleotides including polyinosinic acid, polyadenylic acid and the complex of polyadenylic acid plus polyuridylic acid. Polarized absorption spectra of these materials also show that the shape of the absorption curve depends upon the orientation of the electric vector relative to the helix axis.

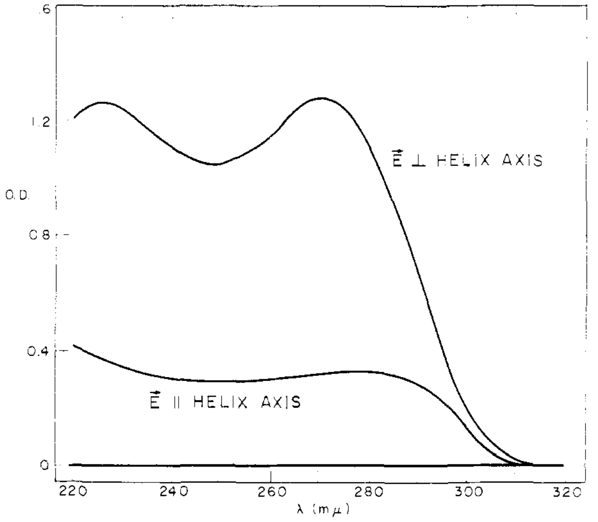

Fig. 1.—Ultraviolet dichroic absorption curves for an oriented film of polycytidylic acid: temp. = 24°, 50% relative humidity.

Oriented spectra of calf thymus DNA with a dichroic ratio of 6.3 at 2600 Å. show a slight displacement of the absorption maximum to longer wave length for parallel polarization compared with perpendicularly polarized absorption, and there is also an alteration in the shape of the band. The two absorption curves for microsomal particle RNA also differ in shape; and there is greater absorption with parallel polarization in the 290–300 mμ region.

Hypochromism in nucleic acids has been interpreted recently by Tinoco,[6] whose treatment gives a quantitative account of the effect in terms of diminution of the transition moment for parallel stacking of $\pi \rightarrow \pi^*$ chromophoric units in the helix. It follows from his treatment that a head-to-tail alignment of transition moments should produce a *hyperchromism*, or increase in absorption intensity, in the formation of a helix. Such an arrangement should be present for the $n \rightarrow \pi^*$ transitions of a helical polynucleotide polymer. Accordingly, we have re-examined the solution absorption spectrum of the random coil-to-helix transitions and have found a hyperchromic region on the long wave length side of the absorption band (Fig. 2). The two stranded helix of polyadenylic + polyuridylic acid (dashed curve) has an increased absorption in the region 280–300 mμ. Several polynucleotide helices are known[7] and our examination of their spectra shows similar hyperchromicity.

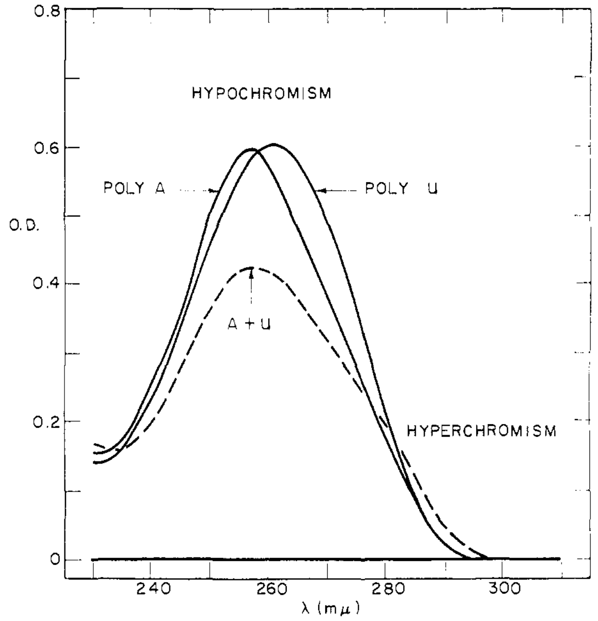

Fig. 2.—Ultraviolet absorption spectra of polyadenylic acid (Poly A), polyuridylic acid (Poly U), and the 1:1 helical complex (A + U). The solutions are in 0.1 *M* NaCl, 0.001 *M* cacodylate buffer at *p*H 6.8, temp. is 23°.

In addition, microsomal particle RNA at neutral *p*H in 0.1*M* NaCl shows a *hypochromism* on the long wave length side of the absorption band when it is denatured by heating to 90° for fifteen minutes, *i.e.*, a loss of the alignment hyperchromism.

The present experiments in the solid state and in solution show the possibility of effecting a partial resolution of the complex near-ultraviolet

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absorption bands of the nucleic acids and polynucleotides.

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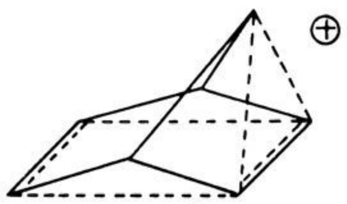
THE 7-NORBORNADIENYL CARBONIUM ION

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]



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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.

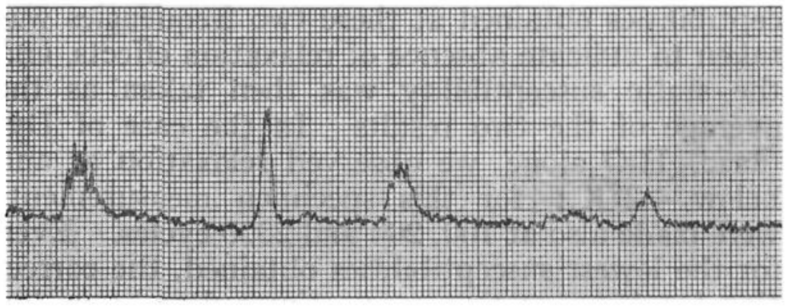

Fig. 1.—N.m.r. spectrum of 7-norbornadienyl fluoroborate in sulfur dioxide at −10°. Peak positions are given in p.p.m. relative to tetramethylsilane as 10.00.

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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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.

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