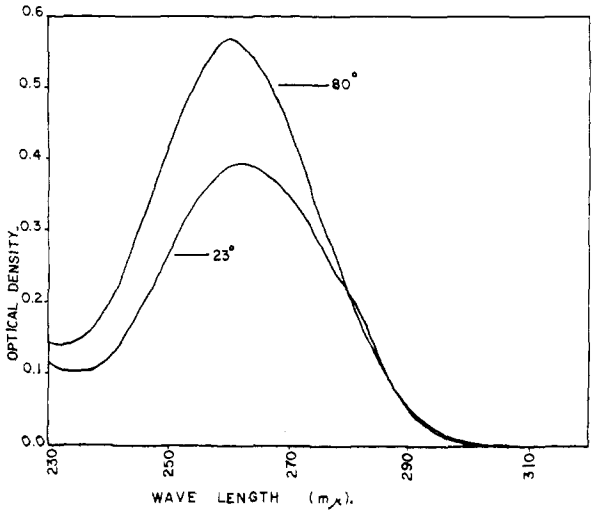

Fig. 1.—Ultraviolet absorption spectra of poly-(dAT), native and denatured by heating. The spectra were taken at the given temperatures. The solution is in 0.002 *M* LiCl, pH 7.

hence is out-of-plane with respect to the nucleotide bases. The assignment as a $n \rightarrow \pi^*$ transition is deduced from the out-of-plane moment.[3] The authors also mention polarized spectra of poly-(A + U), but do not draw conclusions sufficient to aid in assigning the transition.

In this note, evidence is presented contradictory to this assignment, for a closely related system. An alternant copolymer of deoxyadenylic and deoxythymidylic acids (poly-(dAT)) has been synthesized and described.[4] The spectrum (Fig. 1) of this material in solution also shows a shoulder at 280 mμ, which is hyperchromic with respect to the heated (denatured) polymer. The close similarity of this spectrum to that of poly-(A + U) is not surprising since poly-(A + U) and poly-(dAT) have very similar spatial structures, both close to that of DNA,[5,6] and since thymine differs from uracil only by a methyl group.

By the analysis used by Rich and Kasha, this hyperchromic shoulder in the poly-(dAT) spectrum would also be assigned as out-of-plane and therefore a $n \rightarrow \pi^*$ transition.

In order to test this assignment, polarized spectra of oriented streaks of poly-(dAT) have been measured. Poly-(dAT) has higher molecular weight, and hence can be better oriented, than available samples of poly-(A + U). Streaks were made by placing a drop of concentrated poly-(dAT) solution (lithium form), containing about 1% glycerol, on a quartz slide, and stroking it while viewing between crossed polarizers, until good (negative) birefringence was seen. Spectra were taken in a Cary model 14 spectrometer, with a Glan prism polarizer set parallel or perpendicular to the direction of stroking. Appropriate blank spectra, with the polarizer and an empty quartz plate, were also taken. Correction was made for the scattering of

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(4) H. K. Schachman, J. Adler, C. M. Radding, I. R. Lehman and A. Kornberg, *J. Biol. Chem.*, **235**, 3242 (1960).

(5) A. Rich and D. R. Davies, *J. Am. Chem. Soc.*, **78**, 3548 (1956).

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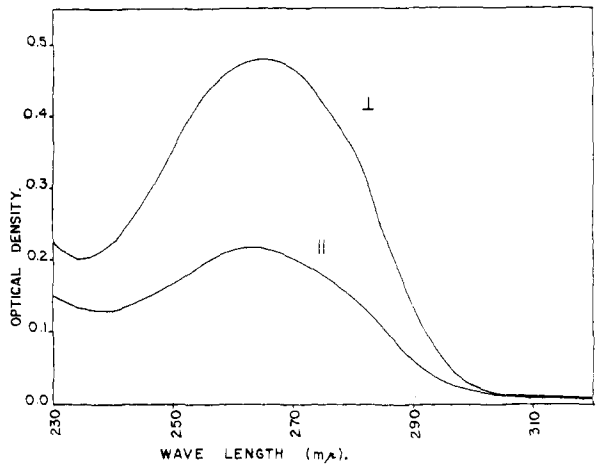

Fig. 2.—Polarized ultraviolet absorption spectra of an oriented streak of poly-(dAT). The polarizations are indicated relative to the direction of streaking. Spectra taken at 23°, 60% relative humidity.

the poly-(dAT) streak by taking the optical density at 320 mμ as equal to zero, and subtracting this constant amount at all wave lengths. The sample was at room temperature (23°) and about 60% relative humidity. Under these conditions, fibers of poly-(dAT) show an X-ray diffraction pattern very like the B form of DNA.[6]

The spectra thus obtained (Fig. 2) give a dichroism ($\epsilon_\perp/\epsilon_\parallel$) of 2.3 at the peak, and closely similar values over the whole band. More precisely, the dichroism is 2.2 at 290 mμ, 2.5 at 280 mμ, 2.4 at 270 mμ, 2.3 at 260 mμ and 2.2 at 250 mμ. If the shoulder at 280 mμ had the inverse dichroism to the main peak, the measured dichroism at that wave length would necessarily drop well below 2.0. One is forced to conclude that the 280 mμ shoulder has closely the same perpendicular polarization as the main peak, and most probably also represents a transition in the plane of the bases. It is thus highly unlikely to be an $n \rightarrow \pi^*$ transition. The nature of the transition is being investigated.

Since poly-(dAT) and poly-(A + U) have similar structures and spectra, this result also casts some doubt on the assignment of the 280 mμ band in poly-(A + U). Apparently the presence of a hyperchromic band is not of itself a sufficient criterion for the assignment of a $n \rightarrow \pi^*$ transition.

I am greatly indebted to Prof. R. L. Baldwin for a gift of poly-(dAT), and for valuable discussions on its properties.

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RECEIVED AUGUST 2, 1961

DENSITY OF LIQUID URANIUM[1]

Sir:

The density of pure liquid uranium was determined by using the Archimedean method, from its melting point (1406°K.) to about 1900°K.

(1) Supported by the National Science Foundation under Grant 15540, and lately by the U. S. Atomic Energy Commission under Grant AT-(30-1)2082.

TABLE I

°K.	D of liquid uranium in g./cm.³ Natural	U^{238}	U^{235}	U^{233}	Atomic volume, cm.³/g. at.	Cubical coef. of expansion for natural uranium, T^{-1} °K. × 10^6
1406 m.p.	17.898	17.905	17.678	17.528	13.301	57.60
1500	17.801	17.807	17.582	17.432	13.374	57.92
2000	17.284	17.291	17.072	16.927	13.774	59.65
2500	16.768	16.774	16.562	16.421	14.198	61.49
3000	16.252	16.258	16.052	15.916	14.649	63.44
4200 b.p.	15.01 ± 0.04	15.02	14.83	14.70	15.86 ± 0.04	69
D_0	19.350	19.357	19.112	18.949		
α	-10.310×10^{-4}	-10.330×10^{-4}	-10.200×10^{-4}	-10.110×10^{-4}		

Three runs were made using different type sinkers and crucibles to avoid or minimize chemical contamination effects. The sinkers and crucibles used were a ZrO_2-coated molybdenum sinker and a Al_2O_3 crucible in run 1, a pure Al_2O_3 sinker and a Al_2O_3 crucible in run 2, and a ZrO_2-coated molybdenum sinker and a pure ThO_2 crucible in run 3. No noticeable chemical reaction was observed. All materials performed satisfactorily, those of run 3 being the best. All the measured values fitted the same straight line. The uranium (from Davison Chemical Co.) contained 0.220% U^{235} and its actual uranium content was 99.9 wt.%. Impurities, in p.p.m., were: Fe and Ni, 200; O, 150; C, 90; Cu and Si, 50; N, 25; Al, 20.

The equation of the density of liquid uranium, determined by the method of least squares, is $D_{\text{liq.}}$ in g./cm.³ $= 19.356 - 10.328 \cdot 10^{-4}\ T$, with a probable error of ±0.078%.

Details of our general method of density measurement, electrical heating, temperature control and surface tension correction are given in another publication.[2]

In recent papers[3,4] it was shown that the temperature range of liquid metals, *i.e.*, the range from the melting to the critical point, is far greater than for any other type of substance. It extends, in view of their elementary and atomic nature, far beyond the thermal limits of existence of any other solid or liquid; even the stablest of the latter dissociate into atoms at about 5000–6000°K. In contrast, the refractory metals such as Re, Ta and W *will be liquids* up to a critical temperature of about 20,000, 22,000, and 23,000°K., respectively.

It also was shown[3,4] that one can construct a liquid temperature range diagram of metals demonstrating the relationship between liquid (and saturated vapor) density *vs.* temperature over the whole liquid temperature range, from the melting point to the critical point, by using the theorem of corresponding states of van der Waals, the law of rectilinear diameter of Cailletet and Mathias and experimental data on heats and entropies of vaporization, vapor pressure and particularly experimental liquid density data over as wide a temperature range as possible. Density measurements have been carried out, at this Institute, on a large number of metals from their melting points to their boiling points, such metals as Pb,[2] Ag,[5] Cu, Sn, and In.

It is clear now, from a study of the temperature range diagram of liquid metals, that liquid density is a straight line function of temperature far beyond the metal's normal boiling point, because the saturated vapor density of metal, which according to the law of rectilinear diameter causes deviation from linearity, assumes significant values only *substantially* above the normal boiling point. Thus, we can estimate the density of liquid uranium at its normal boiling point with reasonable accuracy.

T. W. Richards in his classical work[6] on the atomic volumes of separated lead isotopes proved F. Soddy's concept of the equality of atomic volumes of isotopes with a high degree of precision. Thus, we can calculate from our data the liquid densities of pure U^{235}, U^{233} and U^{238}. The coefficients of the density equation $D_T = D_0 + \alpha T$ and density values for set temperatures for the three isotopes and the natural U-mixture are given in Table I.

(2) A. D. Kirshenbaum, J. A. Cahill and A. V. Grosse, *J. Inorg. & Nucl. Chem.*, in press (1961).

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(4) A. V. Grosse, *J. Inorg. & Nucl. Chem.*, in press (1961).

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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. ABNORMAL SPLITTING OF ETHYL GROUPS DUE TO MOLECULAR ASYMMETRY. II.[1]

Sir:

Diethyl sulfite,[2–5] acetaldehyde diethyl acetal,[3] and cyclopropylcarbinyl ethyl ether[3] offer striking examples of the magnetic non-equivalence of the methylene hydrogens in compounds of the type $R—CH_2—O—XR_1R_2R_3$ (with R = CH_3 and X = S, C, P, etc.). Thus, the nuclear magnetic resonance (n.m.r.) spectra of such methylene protons are often typical of AB rather than A_2 systems.[6,7]

(1) Supported in part by the Office of Naval Research.

(2) H. Finegold, *Proc. Chem. Soc.*, 283 (1960).

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(6) *Cf.* P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

(7) (a) J. A. Pople, W. G. Schneider and H. Bernstein, "High-resolution Nuclear Magnetic Resonance Spectra," McGraw-Hill Book Co., Inc., New York, 1959, pp. 98, 119–123; (b) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., Chap. 2–3.