μ is more tightly bound to the surface than the species which absorbs at $4.8\,\mu$.

These observations are consistent with the hypothesis that absorption at $4.8\,\mu$ is due to linear carbonyl-like species, and absorption at $5.2\,\mu$ is due to a bridged species. It is not unreasonable to expect that relatively more high Miller-index faces are exposed on small particles than on large particles and that the average distance between adjacent pairs of metal atoms is greater on high-index faces than on low-index faces. The relative stabilities and numbers of bridged and linear species on a given crystal face will depend, *inter alia*, on the distribution of distances between neighboring metal atoms on that face. It is obvious that for sufficiently large distances between metal atoms, bridged species will not form. Thus we suggest that the variation in the relative intensities of the bands at 4.8 and $5.2\,\mu$ arises because at lower metal concentrations the average particle sizes tend to be smaller, and the crystal faces with interatomic spacings unfavorable for the bridged species become more numerous. Further, our results to not support Blyholder's[5] contention that on large crystals (of these metals) with well-developed planes there will be a relative increase in the high-frequently band.

Samples were prepared by making a slurry from 1 g of Cabosil and 20 ml of aqueous ammonium chloropalladite, drying the mixture while stirring, and heating the residue to decompose the palladium salt. This impregnation sequence was repeated until the required metal concentration was obtained, and the number of impregnations used was chosen to vary the metal particle dispersion as desired. One-inch diameter circular disks weighing approximately 85 mg were compressed from the impregnated silica at about 40 tons in.$^{-2}$ pressure. These were dried, oxidized, and reduced in an *in situ* cell.[6] Typically, the transmission of the dried disks was about 40% at $4.75\,\mu$.

Spectra were obtained with a Grubb Parsons "Spectromaster." Work continues on this system in this laboratory.

(5) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964); see also J. T. Yates' communicated comments on ref 5, *ibid.*, **68**, 2777 (1964).

(6) This cell and other relevant material will be described in a subsequent paper.

(7) Communications regarding this note should be sent to this author.

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Calorimetric Measurement of Transition Enthalpies in the Polynucleotide System Poly A–Poly U

Sir: The synthetic polynucleotides polyriboadenylic acid (poly A) and polyribouridylic acid (poly U) are able to associate in aqueous solution to a double-stranded helical complex poly(A + U) and a three-stranded poly(A + 2U) complex.[1] In heating the solutions, these highly ordered systems convert to partially ordered structures or to randomly coiled forms. For an equimolar mixture of the two polymers, the regions of temperature over which the different conformations exist (within a limited pH range) depend on the concentration of cations in the solution.[2]

The transition enthalpies ΔH of thermal structural conversions of this cooperative type can be determined by accurate measurements of the temperature course of the heat capacity using an adiabatic calorimeter.[3,4] The characteristic behavior of the transition curves obtained by ultraviolet absorption measurements is reflected in the corresponding temperature course of the heat capacity data (Figures 1 and 2). According to the phase diagram given by Stevens and Felsenfeld, the first peak of the heat capacity *vs. T* curve in Figure 2 refers to the conversion of poly(A + U) to poly(A + 2U), and poly A,[5] the second one, is caused by the dissociation of the poly(A + 2U) complex. Since poly A is forming an intramolecular secondary structure in the course of these reactions, the measured transition enthalpies are reduced ΔH values because of heat released in the partial helix formation of poly A. Therefore, an extrapolation to about 95° is necessary, where poly A is assumed to exist completely in the randomly coiled conformation.[6]

The combination of the results obtained from the calorimetric measurements carried out for different cation concentrations (in order to vary the conversion temperature T_c) and at neutral pH yields the extrapolated $\Delta H°$ values for the transitions of both the complexes into the completely randomly coiled polymers

$$\Delta H°(A + U) = 8.5 \pm$$
$$0.5\ \text{kcal/mole of base pair (Figure 3)}[7]$$

(1) R. F. Steiner and R. F. Beers, Jr. "Polynucleotides," Elsevier Publishing Co., Amsterdam, 1961.

(2) C. L. Stevens and G. Felsenfeld, *Biopolymers*, **2**, 293 (1964).

(3) Th. Ackermann in "Experimental Thermodynamics," Vol. I, Butterworth and Co. Ltd., London, in press, Chapter 12.

(4) Th. Ackermann, *Z. Elektrochem.*, **62**, 411 (1958).

(5) H. T. Miles and J. Frazier, *Biochem. Biophys. Res. Commun.*, **14**, 129 (1964).

(6) M. Leng and G. Felsenfeld, *J. Mol. Biol.*, **15**, 455 (1966).

$\Delta H^{\circ}(\text{A} + 2\text{U}) = 12.5 \pm$

0.5 kcal/mole of (A + 2U) residue

The heat of conversion of the double-stranded poly-(A + U) into the three-stranded complex was found to be

$\Delta H_c{}^{\circ} = 4.5 \pm 0.5$ kcal/mole of (A + 2U) formed

and the enthalpy change for the addition reaction poly(A + U) + poly U = poly(A + 2U) is

$\Delta H(\text{addition}) = -4.0 \pm$

0.1 kcal/mole of (A + 2U) formed[8]

We are trying to reduce the margin of error for the extrapolated values in further measurements. The influence of polymer concentration on the ΔH values is about to be investigated.

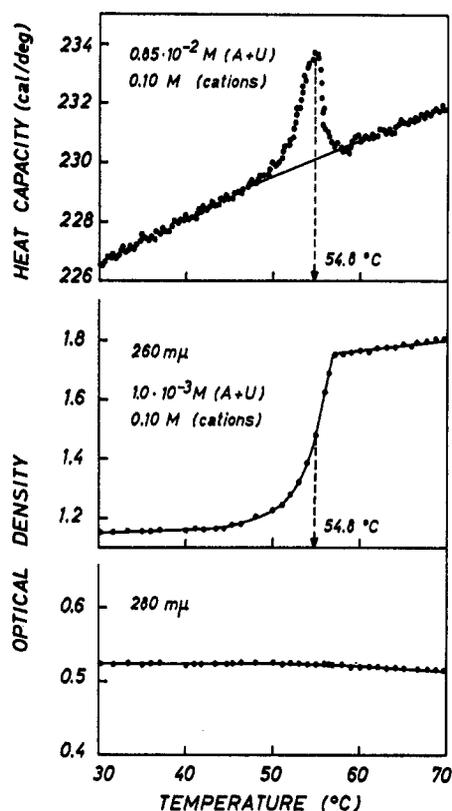The results of the calorimetric measurements will

Figure 1. The conversion of an equimolar mixture of poly A and poly U in aqueous salt solution. The total concentration of cations is 0.10 M; 0.01 M citrate buffer, pH 6.8. (The change in optical density at 260 mμ refers to the transition reaction poly(A + U) = poly A + poly U, and poly(A + 2U) = poly A + 2 poly U. The change in optical density at 280 mμ refers to the formation and dissociation of the three-stranded poly(A + 2U) complex. See ref 2.)
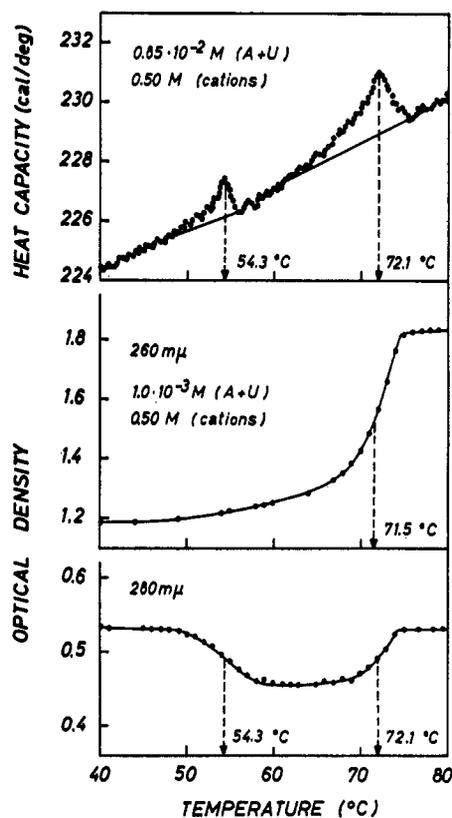

Figure 2. The conversions of an equimolar mixture of poly A and poly U in aqueous salt solution. The total concentration of cations is 0.50 M; 0.01 M citrate buffer, pH 6.8. (See Figure 1.)

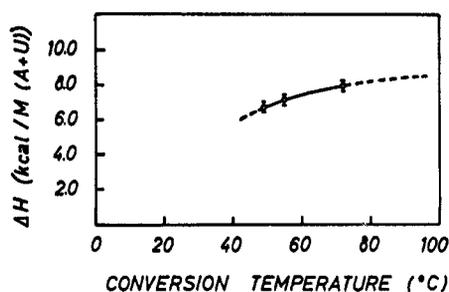Figure 3. The enthalpy change ΔH for the helix–coil transition of poly(A + U) at pH 6.8 for different conversion temperatures, i.e., different concentrations of cations.

provide us with information about the energetic interactions (stacking energy) in the ordered polynucleotide structures. The polymers were purchased from Miles Laboratories. The dried products were mixed 1:1 in aqueous salt solutions containing 0.01 M citrate buffer,

(7) See M. A. Rawitscher, P. D. Ross, and J. M. Sturtevant, J. Am. Chem. Soc., 85, 1915 (1963).

(8) See P. D. Ross and R. L. Scruggs, Biopolymers, 3, 491 (1965).

pH 6.8. All concentrations are given in moles per kilogram of the pure solvent. The weight of every solution prepared for the calorimetric measurements was about 200 g. The heating rate was 0.06°/min.

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Hybridization, Conjugation, and Bond Lengths. An Experimental Test[1]

Sir: The reasons for decreased lengths and increased strengths of single carbon–carbon bonds in "conjugated" molecules such as butadiene and diacetylene are the subjects of a longstanding controversy.[2] The shortening of these bonds has been attributed to: (1) the introduction of double-bond character by conjugation[3a–h] as in $CH_2=CHCH=CH_2 \leftrightarrow \dot{C}H_2CH=CH\dot{C}H_2$; (2) decreased repulsions in unsaturated molecules;[4a,b] (3) changes in hybridization,[5] and to various combinations of all three effects.[3e] Dewar and Schmeising[5b,c] have plotted single-bond lengths against the mean per cent s character in the orbitals composing the bond, and have obtained a straight line which can be expressed as[6]

$$l = 1.692 - 0.0062 \times s \tag{1}$$

(*l* is the bond length; *s* is the mean per cent s character). Equation 1 fits available data within experimental error (± 0.004 A).[7]

To separate the effect of hybridization[8] from that of conjugation, an experiment was designed in which the bond lengths of a series of single bonds with varying per cent s character would be measured precisely by X-ray diffraction crystallography. In order to exclude conjugation and keep the bond environment constant, a series of *bis*-bridgehead hydrocarbons was chosen.

(I)   (II)
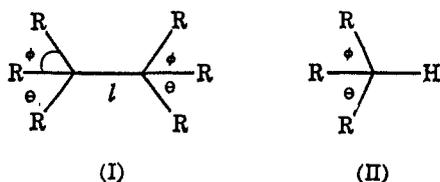
Theoretical considerations,[9] J_{13CH} measurements,[10–12] and several chemical properties,[10,13] show that decreasing the angles θ and ϕ increases the s character in the central bond of I, and in the C–H bond of II.

In fact, a rather accurate estimate of this per cent s character may be obtained from the carbon-13 to hydrogen coupling constant in the nmr of II ($J_{13CH} = 5 \times \%s$). By a suitable selection of compounds, it is theoretically possible to synthesize a series of dimers with hybridization at the central bond covering the range 25% to 42%s.[11,13b]

Thus far, three structures of this type have been investigated by X-ray methods: 1-biapocamphane (III), 1-binorbornane (IV), and 1-biadamantane (V).[7]

28% s character[14a,c,15]   28% s character[14a,b,16]

(III)   (IV)

25% s character[14,16]

(V)
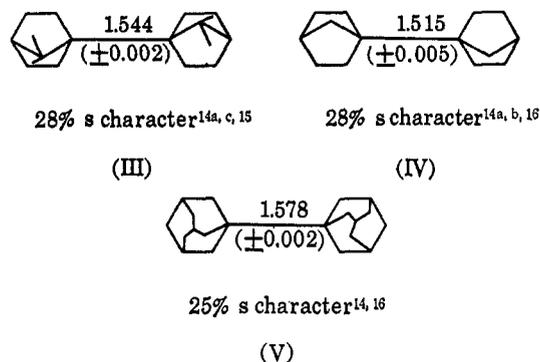
(1) This work was supported by the Army Research Office (Durham) under Grant No. DA-ARO-D-31-124-G-602.

(2) (a) D. R. Lide, Jr., *Tetrahedron,* **17,** 125 (1962); (b) R. S. Mulliken, *ibid.,* **17,** 247 (1962); (c) B. P. Stoicheff, *ibid.,* **17,** 135 (1962); (d) O. Bastiensen and M. Traeteberg, *ibid.,* **17,** 147 (1962); (e) L. S. Bartell, *ibid.,* **17,** 177 (1962); (f) I. Fisher-Hjalmars, *ibid.,* **17,** 235 (1962). See also the discussion section, pp 247–266.

(3) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 299; (b) G. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 174–185; (c) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 247; (d) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 247; (e) currently, Mulliken,[3f] Wilson[3g] and others[2,3h] attribute bond shortening to a combination of conjugation and hybridization; (f) R. S. Mulliken, *Tetrahedron,* **6,** 68 (1959); (g) E. B. Wilson, Jr., *ibid.,* **17,** 191 (1962); (h) B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.,* **33,** 418 (1960).

(4) (a) L. S. Bartell, *ibid.,* **32,** 827 (1960); (b) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Am. Chem. Soc.,* **61,** 1868 (1939).

(5) (a) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron,* **5,** 166 (1959); (b) *ibid.,* **11,** 96 (1960); (c) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 53.

(6) Equation 1 is our expression of the Dewar and Schmeising plot.

(7) See ref 2a for discussions of accuracy of bond length measurements. Our bond lengths were determined with a precision of $\pm$ 0.005 A or less, as computed by standard least-squares techniques, and as confirmed by the internal consistency of other C–C bond lengths. This is somewhat better than usual, probably because of centrosymmetry, the absence of atoms heavier than carbon, low R factors (4–6%) and low and almost spherical temperature factors (2.2–4.6 A²). While absolute errors are difficult to evaluate, and are probably appreciable, our arguments are based solely upon comparisons of bonds situated in similar environments and measured in the same way.

(8) We do not attempt to distinguish between the hybridization postulate (3) and the bond repulsion proposal (2). Indeed, they are not entirely independent.

(9) C. A. Coulson, "Valence," Clarendon Press, Oxford, 1962, p 255.

(10) W. Muller and O. E. Pritchard, *J. Chem. Phys.,* **31,** 768 (1959).