

Fig. 1.—N.m.r. spectrum of I in 96% H_2SO_4 . Band positions are in p.p.m. downfield and relative to $(\text{CH}_3)_4\text{Si}$. The spectrum was measured on a 60 Mc. instrument so that the splitting of 0.22 p.p.m. is 13.2 c.p.s.

The n.m.r. spectrum of I (Fig. 1) is particularly satisfying. The H at C-4 is at 9.02 p.p.m. [downfield from $(\text{CH}_3)_4\text{Si}$]. This is farther downfield than the two hydrogens at C-3 and C-5 (7.19 p.p.m.), in accord with the MO estimate that a $+0.33$ charge resides on C-4 but zero charge on C-3 and C-5. The separate bands for the two pairs of methyl groups indicates that the methyl groups do not equilibrate by rapid rotation about the $\text{C}=\text{C}$ bond and that *cis-trans* isomerism is possible in the dienylic cations as had been found in the alkenyl cations.¹ The position of the methyl bands at 2.61 and 2.64 p.p.m. is at slightly higher fields than the 2.95 and 2.97 p.p.m. found for the methyl groups in the 2,4-dimethylpentenyl cation, in accord with the expectation that the positive charge is more diffuse in the dienylic cations.

The n.m.r. spectra of I and II (Fig. 2) are similar in band positions to the spectrum of VI, and to the spectra of the protonated benzene derivatives, confirming that the protonated aromatics are simple aliphatic dienylic cations. Such a view is further supported by the ultraviolet spectrum of I [λ_{max} 397 $\text{m}\mu$ (ϵ 9900)] and II [λ_{max} 395 $\text{m}\mu$ (ϵ 47,000)] which are similar to the spectra of the protonated benzenes^{6,7} and in agreement with the ~ 400 $\text{m}\mu$ λ_{max} predicted by simple MO theory.

The solution of I in H_2SO_4 was produced by H_2SO_4 extraction of 2,6-dimethyl-1,3,5-heptatriene from solution in CCl_4 . The triene was produced in 72% yield by reduction of phorone with LiAlH_4 .⁸ The solution of II was similarly produced from the triene (or mixture of trienes) obtained by addition of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{MgBr}$ to isophorone. The Grignard reagent, though of the allylic type, was formed by the standard procedure, and the yield of triene was perhaps 40%, although contamination by dienylic alcohol and iso-

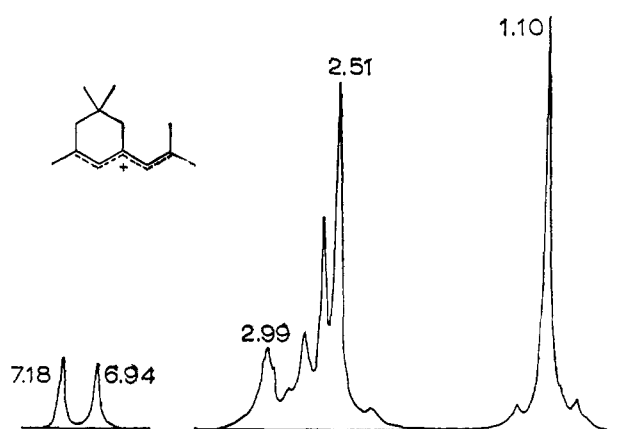


Fig. 2.—N.m.r. spectrum of II in 96% H_2SO_4 .

phorone (removed by treatment with hydroxylamine) prevented accurate estimate of the yield. The solution of V was produced by addition of III to H_2SO_4 , and III was prepared by addition of CH_3MgBr to phorone.⁸ The addition is entirely 1,2 whereas $\text{C}_2\text{H}_5\text{MgBr}$ adds partially 1,4. Fortunately, $\text{C}_2\text{H}_5\text{Li}$ gave 1,2-addition.

The triene derived from I can be quantitatively regenerated from I by rapid dispersal¹ of the H_2SO_4 solution into 10% aqueous NaOH . The n.m.r. spectrum of the triene, initial and recovered, agrees with that expected for 2,6-dimethyl-1,3,5-heptatriene.

There appears to be only one valid report of direct observation of a polyenylic cation (in equilibrium with an aliphatic polyene) higher than dienylic, and this was the complex C-22 tetraenylic cation elucidated by de Vries.⁹ The work reported herein suggests that a wide variety will soon be observed.

Acknowledgment.—We are grateful to the National Science Foundation for providing funds both to support this research and to aid in the purchase of a Varian A-60 n.m.r. spectrometer.

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The Crystal and Molecular Structure of β -Adenosine-2'- β -uridine-5'-phosphoric Acid¹

Sir:

Although the crystal structures of a number of nucleosides and mononucleotides have been determined, no precise single-crystal analyses of the detailed molecular geometry of any dinucleotides or other polynucleotides have been reported. The conformation and packing of such molecules is of significance in connection with hypotheses about the molecular geometry and conformations important in the mechanisms of reactions involving nucleic acids and related species. We were fortunate in obtaining good single crystals of a dinucleoside phosphate, β -adenosine-2'- β -uridine-5'-phosphoric acid (I), from Dr. A. M. Michelson, and have determined its detailed structure by X-ray methods. Although this is not a naturally occurring

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substance, it has many of the structural features of the natural nucleotides. It differs from a dinucleotide in having but one phosphate group, and differs from naturally occurring nucleotides because it has the 2' rather than the 3' linkage of the adenosylribose to the phosphate group.

I crystallizes from aqueous solution as monoclinic prisms, with $a_0 = 9.783 \pm 0.003$, $b_0 = 16.013 \pm 0.007$, $c_0 = 8.718 \pm 0.007$ Å., and $\beta = 90.79 \pm 0.05^\circ$, and belonging to space group $P2_1$. The observed density is 1.56 ± 0.01 g./cm.³; that calculated for two molecules of I ($C_{19}H_{24}N_7O_{12}P$) and eight molecules of water in the unit cell is 1.569. Thus the asymmetric unit appears to contain one molecule of I and four molecules of water. Integrated Weissenberg intensity data were collected with Cu K α from two small crystals about 0.2 mm. in each dimension mounted about c and b , and were estimated both visually and with a microdensitometer. There were 1786 independent diffraction maxima with intensities sufficient to be measured, and an additional 222 below the estimable minimum. After the data had been converted to F^2 in the usual manner, a sharpened three-dimensional Patterson function, with the origin peak removed, was calculated. The position of the phosphate group was readily found, both by classical methods and by an unpublished, rigid-body, computer-search routine which determined the best (least-squares) fit of the vectors of an idealized PO_4 model to the region near the origin, and also the general fit of the vectors between the atoms of the two separate phosphate groups in the unit cell. The average deviation of the positions so found from the "true" positions of the corresponding atoms was slightly less than 0.1 Å.

The structure was solved by interpretation of a three-dimensional Fourier synthesis phased only on the phosphate group (about 24% of the scattering matter). In this first approximation to the electron density distribution in the crystal, it was possible to find eight peaks in reasonable positions for (groups of) atoms bonded to the phosphate. A second approximation to the electron density was then calculated, phasing with these additional atoms also, and the two ribose molecules showed up clearly. Three further similar Fourier's revealed the entire molecule of I and the four water molecules; at this stage, R (the usual discrepancy index) was 26%. Block-diagonal least-squares refinement, first isotropically and then anisotropically, reduced R to 8.8%, including the unobserved reflections. A difference Fourier then revealed clearly the positions of eighteen of the hydrogen atoms, including all of those on carbon atoms and the two on ring nitrogen atoms. It is noteworthy that these are the only hydrogen atoms whose geometry is fixed by that of the "heavy" atoms; some of the other hydrogens showed up as weak peaks, but often not unambiguously. It is possible to locate most of them by consideration of the hydrogen-bonding scheme. Additional least squares, including the hydrogens, reduced R to 6.5%.

The conformation of the molecule as it exists in the crystal is illustrated in Fig. 1. The more important features of the structure are:

(1) The adenine residue is protonated at N_1 by proton transfer from the phosphate group, as in

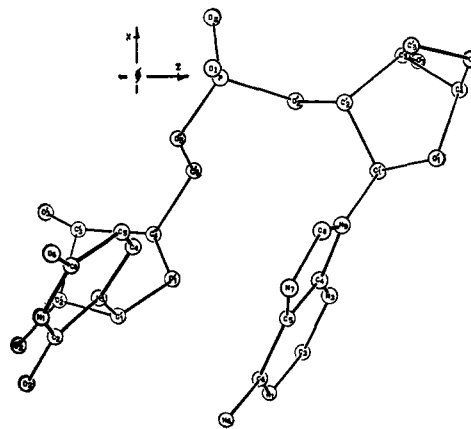


Fig. 1.—The molecule viewed down b . No hydrogen atoms or water molecules are shown. The origin is at the screw axis.

adenosine-5'-phosphate.² The adenine ring is planar, even though the amino group appears to be twisted through about 25° , just as in adenosine phosphate, by its hydrogen-bonding environment. The small departure from planarity of the adenine ring found by Kraut and Jensen was attributed to this twist. The uracil ring is in the keto form, with $C=O$ distances 1.22 and 1.24 Å.

(2) The two ribose rings are in the familiar conformation with four of the atoms very nearly coplanar; however, in that of the uridine residue, it is C_3' which is out of the plane by about 0.60 Å., whereas in the adenosine ribose C_2' is out of the plane of the other four atoms by 0.62 Å.

(3) The dihedral angle made by the two P-O-C planes of the ester linkages is 123° (assuming the 0° angle to be that with the O-C bonds nearly parallel, as in ethylene phosphate). The significance of this angle in phosphate diesters has been discussed in connection with their ease of hydrolysis.³

(4) The torsion angle⁴ about the glycosidic C-N bond, *i.e.*, the dihedral angle between the trace of the plane of the base and the $C_1'-O_1'$ bond, is -55° in the adenosine half and -5° in the uridine. Both of these are in the *anti* range, as for all other nucleotides investigated. The -5° value is the smallest reported; however, it is not characteristic of all uridine nucleotides, for in an unpublished study of barium uridine-5'-phosphate in these laboratories we have found the torsion angle to be -45° . Presumably the -5° value results from the adjustments made to give the best intra- and intermolecular packing. The planes of the base residues in one molecule (Fig. 1) are nearly parallel (deviating by about 15°); their closest approach is about 3.4 Å., although they actually overlap only to a small extent. The angles between the normals to the sugar and base planes are 62 and 69° in the uridine and adenosine residues, respectively. These values are comparable to those in other nucleosides and nucleotides.

(5) Each molecule is hydrogen-bonded to four different neighboring molecules, each by a pair of N-H \cdots O, or N-H \cdots O and O-H \cdots N bonds. In

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(3) (a) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961); (b) E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963).

(4) J. Donohue and K. N. Trueblood, *J. Mol. Biol.*, **2**, 363 (1960).

addition it has nine close water molecule neighbors, most of which are undoubtedly hydrogen-bonded. No hydrogen bonds link bases directly.

(6) The bond distances and angles do not differ significantly from the expected values; the standard errors average about 0.012 Å. and 0.7° for distances and angles not involving hydrogen atoms. The C₁' atom of each sugar is very nearly in the plane of the base to which it is attached (deviation 0.01 and 0.03 Å.), unlike the situation in adenosine phosphate² and 5-fluoro-2'-deoxy-β-uridine.⁵

(5) D. R. Harris and W. M. Macintyre, unpublished work.

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Molecular Structure of a Carborane (1,2-Dicarbaclododecaborane) Derivative, B₁₀Cl₈H₂C₂H₂

Sir:

The carborane^{1,2} B₁₀C₂H₁₂ is usually assumed²⁻⁴ to have very nearly the icosahedral geometry of the B₁₂H₁₂²⁻ ion⁵ (Fig. 1a). However, an X-ray diffraction study⁶ of B₁₀H₁₀C₂(CH₂Br)₂ has supported an ethylene decaborane type of B₁₀C₂ unit (Fig. 1b.). We report here the results of a three-dimensional single crystal X-ray diffraction study of B₁₀Cl₈H₂C₂H₂ which indicates the nearly regular icosahedral arrangement for the B₁₀C₂ structural unit (Fig. 1a).

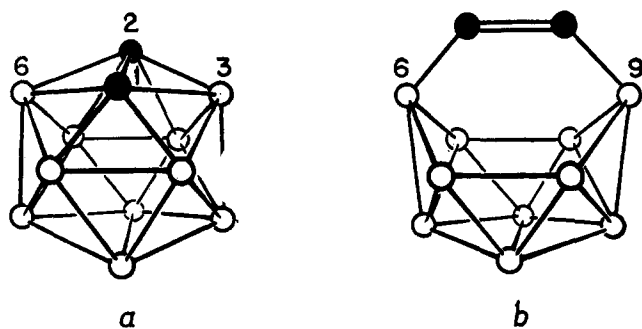


Fig. 1.—a represents the near icosahedral B₁₀C₂ framework in B₁₀Cl₈H₂C₂H₂. Open and black circles indicate, respectively, B atoms and C atoms. Substitution of Cl has taken place at all H atoms of the parent B₁₀C₂H₁₂ except those attached to B₃, B₈, C₁, and C₂. b represents the boron-carbon framework described⁶ for B₁₀H₁₀C₂(CH₂Br)₂.

The crystal symmetry is Pbn_a, and there are eight molecules in a unit cell of dimensions $a = 17.10$, $b = 13.46$, and $c = 13.65$ Å. All B and C atoms were located and distinguished from one another by their electron densities in three-dimensional Fourier series

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(2) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963), footnote 7.

(3) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); *Inorg. Chem.*, **2**, 231 (1963).

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from which the Cl atoms had been subtracted. The present value of $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ is 0.13 for the 1739 observed X-ray diffraction maxima.

Two other features of the structure are of interest here. The C-C distance of 1.68 ± 0.02 Å. is considerably larger than the distance⁷ of 1.43 Å. in B₄H₆C₂(CH₃)₂, which contains two adjacent C atoms in a slightly less strongly electron-deficient environment. Also, substitution of Cl has taken place at all B atoms (4,5,7,8,9,10,11,12) except for the two B atoms (3,6) which are indicated to be most positively charged by both molecular orbital and resonance theories³ of charge distribution.

A comparison⁸ of ¹¹B nuclear magnetic resonance in B₁₀C₂H₁₂ and in B₁₀Cl₁₀C₂H₂ indicates that direct chlorination produces essentially no change in the B₁₀C₂ framework. Also, the thermal stability of carborane up to a temperature of 470°, at which it transforms³ readily and without decomposition to neocarborane,^{8,9} is more easily understood on the basis of the icosahedral structure (Fig. 1a) rather than the ethylene decaborane type of structure (Fig. 1b). However, the possibility that the structure of Fig. 1b is an intermediate in the synthesis of carborane derivatives is not excluded. Further structural studies of carborane and neocarborane derivatives are in progress.

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Decreasing Sorption Effect with Increasing Pressure

Sir:

In a recent article by Cimino, *et al.*,¹ the hypothesis was advanced that the surface of polycrystalline ZnO was very likely conditioned for further H₂ uptake by a rapid initial adsorption of H₂. This initial adsorption is frequently observed^{2,3} with other systems but much less frequently measured. A somewhat similar effect has been observed during the study of the uptake of oxygen by Pr₂O₃. This effect, in general, is a small loss of sorbed gas with an increase in gas pressure. The effect has been noted during "equilibrium" as well as kinetic measurements. Three separate pieces of evidence seem to indicate that the effect is real.

(1) During the course of a general study of the Pr-O system it was noted that in some cases the oxygen content on and/or in the solid PrO_x could be reduced slightly by increasing the oxygen pressure. The effect was observed specifically⁴ during the investigation of

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(3) M. J. D. Low, *Chem. Rev.*, **60**, 267 (1960).

(4) P. A. Faeth and A. F. Clifford, *J. Phys. Chem.*, **67**, 1453 (1963).