Further work on this reaction needs to be done before the mechanism is understood. The chemistry taking place here may have some relation to that supporting the remarkable conclusion reported by Williams and Hunt,[5] namely, that more than one NH_3 is transferred from Co(III) for each act of electron transfer between Co(II) and Co(III) ammines.

Acknowledgment. Financial support for this research by the Atomic Energy Commission, Grant No. AT 04 3 326, is gratefully acknowledged.

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[5] T. J. Williams and J. P. Hunt, *J. Amer. Chem. Soc.*, **90**, 7213 (1968).

James Dee White, James C. Sullivan, Henry Taube
Department of Chemistry
Stanford University, Stanford, California, and
Argonne National Laboratories, Argonne, Illinois
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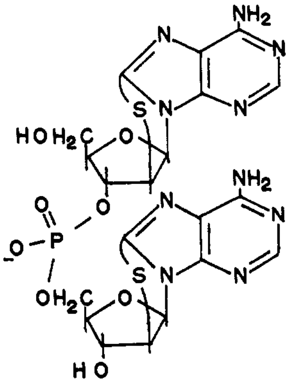
A Highly Stacked Dinucleoside Monophosphate Derived from Adenine 8-Cyclonucleosides

Sir:

Many purine 8-cyclonucleosides have been synthesized[1] and some of their physical properties were investigated.[2] In contrast to the ordinary purine nucleoside, all β-cyclonucleosides of this series have large positive Cotton curves in ORD and CD measurements around major absorption bands due presumably to an unusual interaction between transition moments of the base and the sugar, which were fixed together with anhydro linkages.

We now synthesized a dinucleoside monophosphate (I) (A^spA^s) from 8,2′-anhydro-8-mercapto-9-β-D-arabinofuranosyladenine[3] (A^s) linked with 3′-5′-phosphodiester linkage and an unusual strong stacking of two adenine rings in A^spA^s was found. Moreover, A^spA^s forms a left-handed helical structure opposite to the right-handed one in adenylyl-(3′-5′)-adenosine (ApA).

Compound I was synthesized from 5′-*O*-trityl-N^6-dimethylaminomethylene-8,2′-anhydro-9-β-D-arabinofuranosyladenine 3′-phosphate and N^6,O^2-dibenzoyl-8,-2′-anhydro-8-mercapto-9-β-D-arabinofuranosyladenine using DCC as condensing agent, followed by removal of protecting groups, in a yield of 70%.[4]



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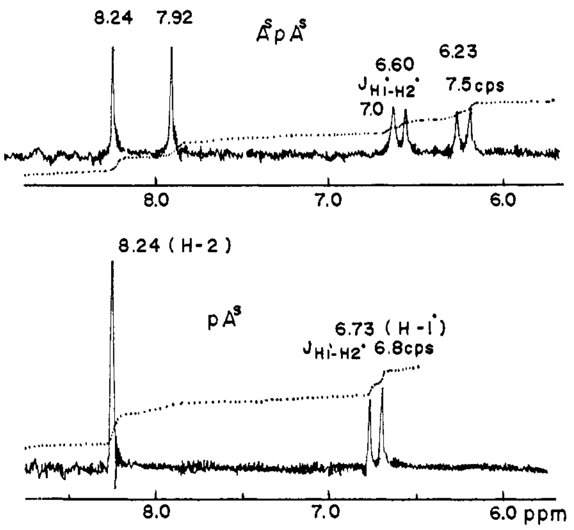

Figure 1. Nmr spectra of A^spA^s and pA^s.

The structure of this compound was confirmed by elemental analyses, optical properties, and desulfurization with Raney nickel to afford 2′-deoxyadenylyl-(3′-5′)-2′-deoxyadenosine, which was identified with an authentic sample.[5]

Ultraviolet absorption properties of A^spA^s [$\lambda_{\max}^{\text{pH 1}}$ 276.5 nm (ε 42,000), $\lambda_{\max}^{\text{pH 7}}$ 271 nm (ε 38,000), $\lambda_{\max}^{\text{pH 13}}$ 271.5 nm (ε 35,800)] showed a large hypsochromic shift of maxima (5 nm) compared to those of the monomer and had a hypochromicity of 15% calculated from ε at $\lambda_{\max}$. A small shift of absorption maxima (1 nm) was reported in the case of ApA and hypochromicity was 10%.[6]

As shown in Figure 1, nmr[7] of this compound in D_2O solution (sodium salt, 0.05 *M*) showed signals of H_2 (8.24 and 7.92 ppm) and $H_{1'}$ (6.60 ppm, $J_{1'-2'}$ = 7.0 cps; 6.23 ppm, $J_{1'-2'}$ = 7.5 cps). Ts'o, *et al.*,[8] reported that ApA (in D_2O, 0.02 *M*) gives also two groups of signals due to H_2 and H_8 (8.50, 8.36 and 8.64, 8.60, respectively), as well as signals of $H_{1'}$ (6.38 and 6.25). They could assign each signal to 3′-linked and 5′-linked nucleosides according to a general rule that the shielding effect of the ring current caused shift of the signal toward high magnetic field. We have examined CPK molecular models of A^spA^s and found that 5′-linked H_2 must be shielded by the ring current of the 3′-linked adenine. Therefore, a signal of 8.24 ppm is assigned to H_2 of the 3′-linked nucleoside and 7.92 ppm to the 5′-linked one. The shift of the H_2 signal compared to that of the monomer (disodium salt, 0.1 *M* in D_2O) was 32 cps toward high magnetic field and this was far greater than that observed in ApA. Although intermolecular interaction of the monomer at the observed concentration is highly probable, the difference in the chemical shift between the A^spA^s and the unassociated monomer can be substantially higher than that shown here.

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[1] M. Ikehara, *Accounts Chem. Res.*, **2**, 47 (1969), and references cited therein.

[2] M. Ikehara, M. Kaneko, K. Muneyama, and H. Tanaka, *Tetrahedron Lett.*, 3977 (1967); M. Ikehara and M. Kaneko, *Chem. Pharm. Bull.*, **15**, 1261 (1967); M. Ikehara and M. Kaneko, *J. Amer. Chem. Soc.*, **90**, 497 (1968).

[3] M. Ikehara and H. Tada, *Chem. Pharm. Bull.*, **15**, 94 (1967).

[4] Unpublished experiments by M. Yasumoto.

[5] S. A. Narang, T. M. Jacob, and H. G. Khorana, *J. Amer. Chem. Soc.*, **87**, 2988 (1965).

[6] M. M. Warshaw and I. Tinoco, Jr., *J. Mol. Biol.*, **13**, 54 (1965).

[7] Nmr spectra were taken in D_2O solution at the concentration indicated in the text. The chemical shift was presented in δ using tetramethylsilane as external standard.

[8] P. O. P. Ts'o, N. S. Kondo, M. P. Schweizer, and D. P. Hollis, *Biochemistry*, **8**, 997 (1969).

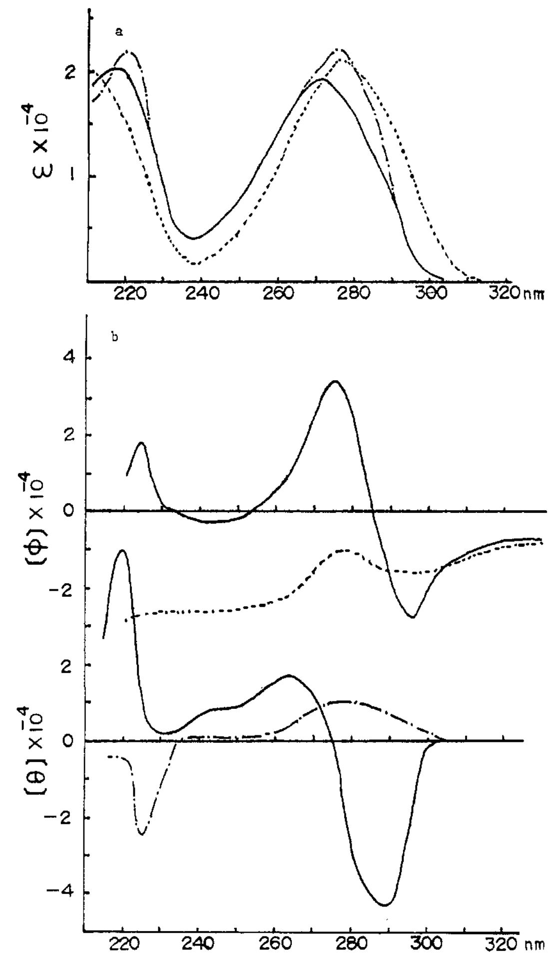

Figure 2. Uv absorption (a) and ORD and CD (b) curves of $\mathrm{A^{s}pA^{s}}$ and $\mathrm{pA^{s}}$. Solid lines are curves of $\mathrm{A^{s}pA^{s}}$ measured at pH 6.9 (in 0.01 *M* phosphate buffer and 0.08 *M* $\mathrm{KClO_4}$ solution) and dotted lines are at pH 1 (0.1 *M* $\mathrm{HClO_4}$). Broken lines are curves of $\mathrm{pA^{s}}$ measured at pH 7 (in 0.1 *M* phosphate buffer). ϵ, $[\phi]$, and $[\theta]$ are given per nucleotide residue.

ORD and CD curves of $\mathrm{A^{s}pA^{s}}$ are shown in Figure 2 together with uv absorption spectra. The first positive Cotton band of the monomer around 280 nm splits to a pair of a large negative (290 nm) and a positive band (264 nm). The second small positive band at 250 nm of the monomer also splits to a negative (260 nm) and a positive (245 nm) band, though the negative band may be cancelled by a large positive 264-nm band. Presumably the second positive band at 220 nm of $\mathrm{A^{s}pA^{s}}$ is also caused by the splitting of the negative band at 225 nm of the monomer. Thus far, all Cotton bands of the monomer $\mathrm{A^{s}}$ split to pairs of negative and positive bands in $\mathrm{A^{s}pA^{s}}$. This splitting may be interpreted by the exciton theory presented by Tinoco, *et al.*[9] They observed a drastic change of Cotton curves in ApA from the monomer and interpreted it by interaction of two adjacent transition moments of the base. Stacking of two adenines in $\mathrm{A^{s}pA^{s}}$ could be thus safely deduced from the splitting bands shown here.

The base moieties of both nucleoside units in $\mathrm{A^{s}pA^{s}}$ should be fixed at α_{CN}[10] nearly equal to $-108°$ by nucleosidic and anhydro linkages[2] and if these nucleosides are linked together with phosphodiester in 3′-5′ direction, two bases have to be in the position as shown in Figure 3 deduced from the result of nmr measurements. If we construct a model of $\mathrm{A^{s}pA^{s}}$ fitting this requirement, a conformation having a *left-handed* screw axis seems to be the most favorable one. This conformation is unique in $\mathrm{A^{s}pA^{s}}$, because dinucleoside phosphates from β-D-ribonucleosides give a *right-handed* screw axis.[11] Although final assignment of the left-handed screw axis must await further investigation, this model satisfactorily explained the physical properties of the $\mathrm{A^{s}pA^{s}}$. The strong stacking tendency of $\mathrm{A^{s}pA^{s}}$ might be due to restricted rotation of base moieties around nucleosidic linkages so that free energy of $\mathrm{A^{s}pA^{s}}$ is minimized relative to that of ApA. An alternate explanation that sulfur atoms in position 8 attract each other and stabilize the stacked conformation may be excluded because 5′,5′-pyrophosphate synthesized from $\mathrm{A^{s}}$ does not stack at all, though the pyrophosphate from 5′-AMP could stack well.[13]

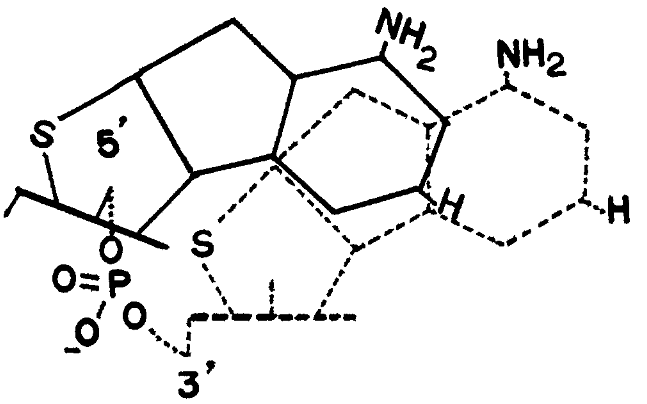

Figure 3. Schematic representation of $\mathrm{A^{s}pA^{s}}$. Solid line is 5′-linked nucleoside and dotted line shows 3′-linked nucleoside. Furanose ring is drawn as a line, in which 3′ means 3′-OH and 5′ means 5′-OH. Note that 3′-OH's are in the left end of the furanose ring and 5′-OH's in the middle.

Further investigations of oligonucleotides involving cyclonucleosides are in progress.

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[9] I. Tinoco, Jr., *J. Amer. Chem. Soc.*, **86**, 297 (1964).

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

(11) Tazawa, *et al.*,[12] synthesized dinucleoside phosphate from L-adenosine and reported its left-handed screw axis.

(12) I. Tazawa, S. Tazawa, L. M. Stempel, and P. O. P. Ts'o, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. BIOL-74.

(13) Unpublished experiments by K. Yoshida.

* To whom correspondence should be addressed.

Morio Ikehara,* Seiichi Uesugi, Mitsugi Yasumoto
Faculty of Pharmaceutical Sciences, Osaka University
Toyonaka, Osaka, Japan
Received March 24, 1970

Aromaticity *via* Cyclopropyl Conjugation. On the Electronic Structure of Spiro[2.4]hepta-4,6-diene

Sir:

The significance of the delocalization of the electrons of the carbon–carbon bonds of suitably oriented cyclopropanes into proximate π systems has been the subject of recent interest.[1] We wish to report that for a favorably structured molecule such delocalization may result in aromatic character. The preferred geometric

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(1) For leading references see (a) S. W. Staley, *J. Amer. Chem. Soc.*, **89**, 1532 (1967); (b) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964); (c) M. Y. Lukina, *Russ. Chem. Rev.*, 419 (1962).