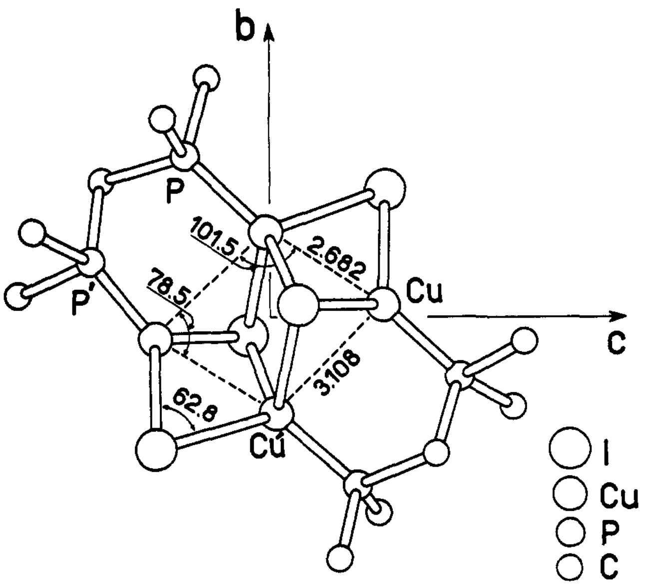

Figure 1. The molecule viewed along the cystallographic *a* axis. Only the first carbon atom of each phenyl group is shown.

of copper atoms, with Cu–Cu distances of 2.682 (7) and 3.108 (7) Å and angles at copper atoms of 101.5 (2) and 78.5 (2)° as shown in Figure 1. Such an arrangement has been already found in the structure of $Cu_4[SC(NH_2)_2]_9(NO_3)_4$[3] where rectangles of copper atoms bridged by thiourea groups are connected by other thiourea groups to form an infinite chain. However, whereas two Cu–Cu distances are 2.707 (5) Å, the other distances are above 4 Å. As already noticed,[4] the copper–copper distances depend markedly on the nature of the bridging ligand. On each of the short sides of the parallelogram two copper atoms are bridged asymmetrically by one iodine atom (Cu–I = 2.512 (7) and Cu'–I = 2.632 (6) Å) whereas on each of the long sides they are bridged by a DPM molecule, with equal copper–phosphorus bond lengths (2.22 Å). In addition, each of the other two iodine atoms, above and below the plane of the parallelogram, bridges three metal atoms with distances Cu–I 2.721 (6), 2.737 (5), and 2.784 (5) Å, the distance with the fourth copper atom being 3.340 (6) Å. In our knowledge, a tricoordinate iodine atom is rather unusual, the resulting geometry being a distorted pyramid with the iodine atom at the apex and three copper atoms in the triangular basis. The Cu–I–Cu angles are 58.9, 68.7, and 83.6°. The Cu atom (see Figure 1) has a roughly trigonal coordination polyhedron (the sum of the angles around Cu is 350°) bonding one phosphorus and two iodine atoms, whereas Cu' has a distorted tetrahedral geometry, bonding one phosphorus and three iodine atoms.[5] This result is similar to that found in other polynuclear complexes[6] possessing copper atoms with different geometries in the same compound.

Both P atoms have a distorted tetrahedral geometry (angles ranging from 104 to 119° and from 106 to 121° around P and P', respectively) with expected values for the Cu–P bond lengths. The bite P–P' is 3.08 (1) Å, the angle PCP' being 113°.

The analogous chlorine derivative appears to be also dimeric from molecular weight measurements in chloroform and dichloroethane solutions and gives nonconducting solutions in dichloroethane.[1] These results suggest the compounds to have the same structure in the solid state and in solutions of slightly polar solvents. However, in solutions of appreciably polar solvents they undergo a dissociation in ionic species of lower molecular weight, in agreement with the values of the conductivity in acetone solutions.[7]

Acknowledgment. Support of this work by the C.N.R. is gratefully acknowledged.

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(4) R. Mason, *et al.* (*J. Chem Soc., Chem. Commun.*, 446 (1972)) have recently reported a cluster of Cu(I) where four copper atoms are arranged in a distorted butterfly structure.

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(6) J. M. Guss, R. Mason, K. M. Thomas, G. VanKoten, and J. G. Noltes, *J. Organometal. Chem.*, **40**, C79 (1972); V. Albano, P. L. Bellon, G. Ciani, and M. Monassero, *J. Chem. Soc., Dalton Trans.*, 171 (1972), and references therein.

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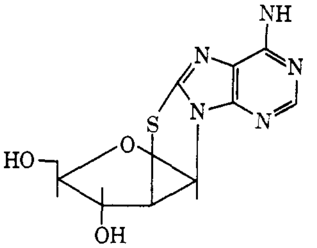
Synthesis of Cyclouridine Oligonucleotides Forming a Double Stranded Complex of Left-Handedness with Cycloadenosine Oligonucleotides

Sir:

Previously we have reported the synthesis and properties of single stranded oligonucleotides having 8,2'-*S*-cycloadenosine (A^s) (I).[1-3] It was found that these



I

oligomers had a left-handed stacked conformation despite their D-ribose backbone by criteria of nmr and CD and that they could not form double stranded complexes with poly (*U*). Since it was reported that L-ApA- having left-handed stacking could form triple helical complexes with poly (U),[4] the cause of the failure to obtain complexes from A^spA^s and poly (U) has to be interpreted. In this communication, we report the synthesis of oligonucleotides containing 6,2'-anhydro-6-oxy-1-β-D-arabinofuranosyluracil (U^o) (II) and the formation of a double stranded complex of $(U^o)_8$ with $(A^s)_8$.

Starting from 1-β-D-arabinofuranosyl-5-bromouracil (III), compound II was obtained by an elegant method

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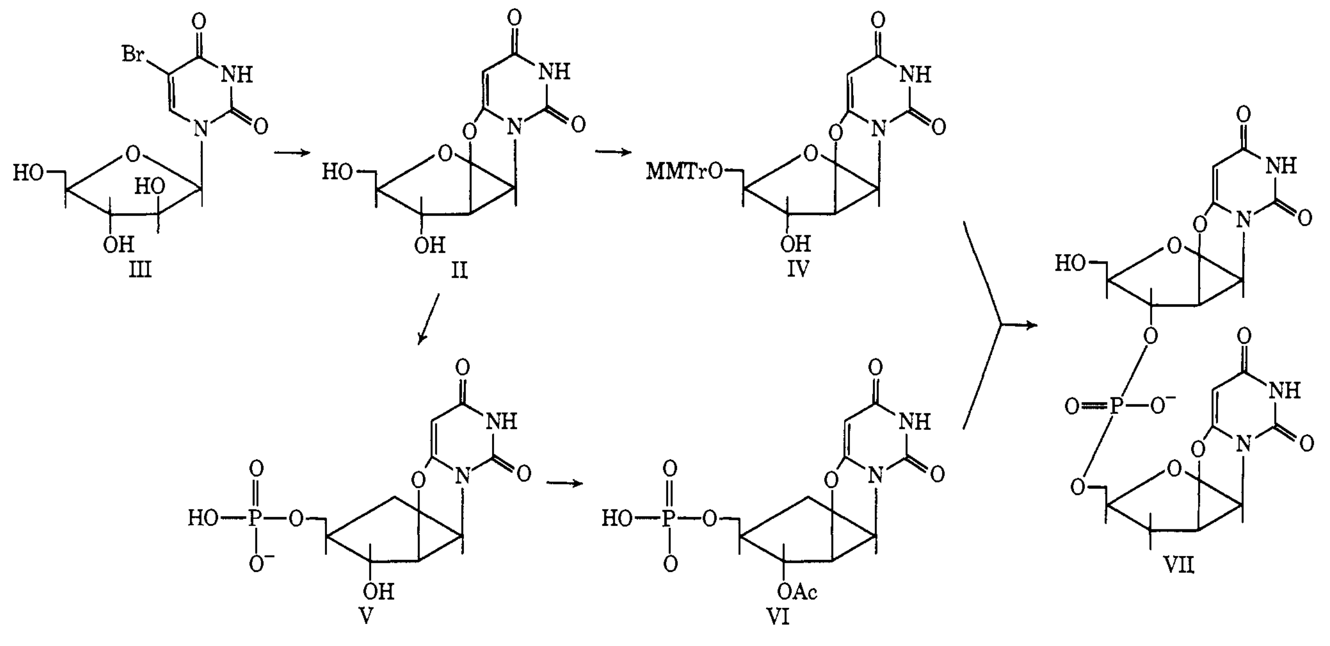
(1) M. Ikehara, S. Uesugi, and M. Yasumoto, *J. Amer. Chem. Soc.*, **92**, 4735 (1970); M. Ikehara and S. Uesugi, *ibid.*, **94**, 9189 (1972).

(2) S. Uesugi, M. Yasumoto, M. Ikehara, K. N. Fang, and P. O. P. Ts'o, *J. Amer. Chem. Soc.*, **94**, 5480 (1972).

(3) M. Ikehara, S. Uesugi, and J. Yano, *Nature (London), New Biol.*, **240**, 16 (1972).

(4) I. Tazawa, S. Tazawa, L. M. Stempel, and P. O. P. Ts'o, *Biochemistry*, **9**, 3499 (1970).

Chart I



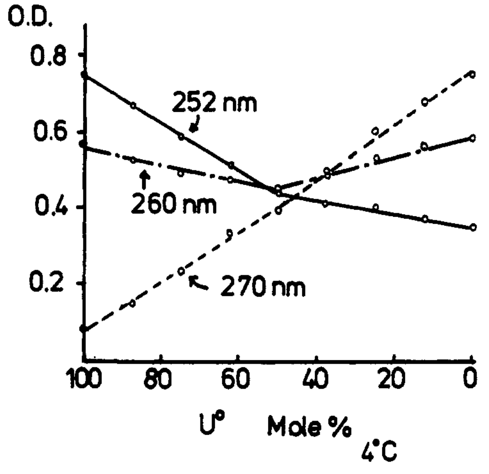


Figure 1. Mixing curves of $(\mathrm{pU}^\circ)_8$ and $(\mathrm{pA}^s)_8$ taken at 4° in 0.01 *M* phosphate buffer (pH 7.3) in the presence of 0.1 *M* KF: O---O, taken at 252 nm; –·–O–·–O–, at 260 nm; and O—O, at 270 nm.

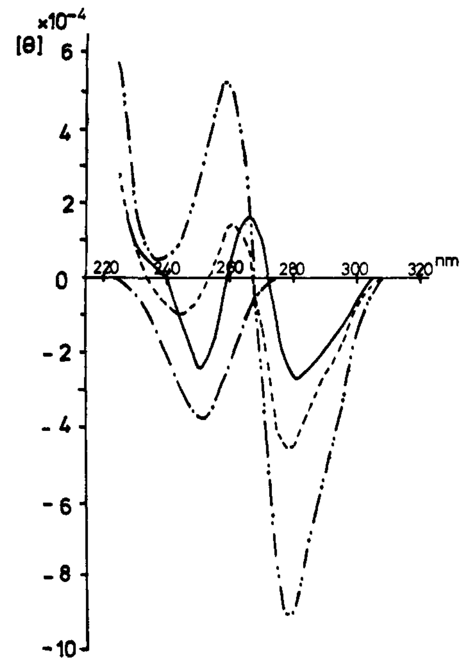


Figure 2. CD spectra of $(\mathrm{pU}^\circ)_8$, $(\mathrm{pA}^s)_8$, and $(\mathrm{pU}^\circ)_8 \cdot (\mathrm{pA}^s)_8$ taken at 4° in 0.01 *M* phosphate buffer (pH 7.3) in the presence of 0.1 *M* KF: ——, 1:1 complex of $(\mathrm{pU}^\circ)_8$ and $(\mathrm{pA}^s)_8$; ------, calculated sum of $(\mathrm{pU}^\circ)_8$ and $(\mathrm{pA}^s)_8$; –·–·–·–, $(\mathrm{pU}^\circ)_8$; –··–··–, $(\mathrm{pA}^s)_8$.

of Fox, *et al.*[5] (Chart I). Compound II was converted to 5′-monomethoxytrityl derivative (IV) and 5′-monophosphate (V) by phosphorylation with phosphoryl chloride in trimethyl phosphate.[6] Yields were 71 and 70%, respectively. Compound V was protected at 3′-OH by acetylation to give VI. Compounds VI (pyridinium salt) and IV were condensed using dicyclohexylcarbodiimide (DCC) as the activating reagent in anhydrous pyridine. By chromatography on a DEAE-cellulose column 6,2′-anhydro-6-oxy-1-β-D-arabinofuranosyluracilphosphoryl-(3′,5′)-6,2′-anhydro-6-oxy-1-β-D-arabinofuranosyluracil ($\mathrm{U}^\circ\mathrm{pU}^\circ$) (VII) was obtained in a yield of 70%. The structure of compound VII was confirmed by elemental analysis, spectral properties [$\lambda_{\max}^{\mathrm{pH}\,7}$ 253 nm (ϵ 1.68×10^4), $\lambda_{\max}^{\mathrm{pH}\,3}$ 253 nm (ϵ 1.76×10^4), and $\lambda_{\max}^{\mathrm{pH}\,11}$ 255 nm (ϵ 1.25×10^4)], and hydrolysis with snake venom phosphodiesterase to give U° and pU° in 1:1 ratio. The CD spectrum of $\mathrm{U}^\circ\mathrm{pU}^\circ$ was identical with that of U°, showing that $\mathrm{U}^\circ\mathrm{pU}^\circ$ had almost no stacking of the bases. We next polymerized pU° (V) employing DCC as the reagent. The polymerized mixture was applied to a DEAE-cellulose column and oligonucleotides having chain lengths of 2–10 were separated. $(\mathrm{pU}^\circ)_2$ was dephosphorylated by alkaline phosphatase and identified as $\mathrm{U}^\circ\mathrm{pU}^\circ$ synthesized above. Uv absorption profiles of a mixture of $(\mathrm{pU}^\circ)_8$ with $(\mathrm{pA})^s{}_8$[2] in various ratios taken at 252, 260, and 270 nm are shown in Figure 1. This experiment clearly indicated that $(\mathrm{pU}^\circ)_8$ and $(\mathrm{pA}^s)_8$ formed a complex of 1:1 ratio as in the case of poly U

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[5] B. A. Otter, E. A. Falco, and J. J. Fox, *J. Org. Chem.*, **33**, 3593 (1968).

[6] M. Yoshikawa, T. Kato, and T. Takenishi, *Bull. Chem. Soc., Jap.*, 42, 3505 (1969).

and poly A.[7] As shown in Figure 2, the CD spectrum of this complex has a peak at 267 and troughs at 250 and 281 nm. Comparing it with the B-band region of CD spectrum of single stranded $(pA^s)_8$, which had a trough at 281 and a peak at 259 nm, one can presume that $(pA^s)_8$ in the complex also has a left-handed helix. Accordingly, the duplex $(pA^s)_8 \cdot (pU^o)_8$ may well possess a left-handed helical conformation.

This is the first case that oligonucleotides of cyclonucleosides constitute a double helical complex. Both nucleosides A^s or U^o have almost the same torsion angle of $\phi_{CN} = -122°$ [8] and the bases are rigidly fixed at the syn–anti region by the cyclo bonds. If we set these two strands in antiparallel fashion, bases in both strands situate in a position favorable for the hydrogen bonding. Since $(pA^s)_n$ could not form complexes with poly U and $(pU^o)_n$ could not form complexes with poly A, it seemed that the torsion angle of the bases have to be identical to form a double stranded complex. In the case of $(pA^s)_8 \cdot (pU^o)_8$ the direction of the helical turn would be determined by $(pA^s)_8$ which has a strong tendency toward left-handed stacking,[2] and $(pU^o)_8$ stays in a favorable position along the helix by the hydrogen bonding between A^s and U^o residues. We may suggest, therefore, that the torsion angle of bases in mononucleotides of nucleic acids is an important factor to determine the direction of the helical turn and the identity of the torsion angles in the two strands is essential for stable double helical structures.

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(7) G. Felsenfeld and A. Rich, *Biochim. Biophys. Acta*, **26**, 457 (1957).

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Probable Nonexistence of Xenon Monofluoride as a Chemically Bound Species in the Gas Phase

Sir:

The long-range interaction between Xe and F may be expressed as the sum of two terms:[1] (a) the induction energy due to the permanent quadrupole moment of the F atom and the polarizability of the Xe atom and (b) the dispersion attraction due to the polarizabilities of the two atoms. Assuming no *chemical* attraction between Xe and F, the long range terms will yield an attractive potential well similar to that found[2] for Xe–Ne, where the bond distance r_e(Xe–Ne) is 3.8 Å and the dissociation energy D_e is 0.15 kcal/mol.

However, following the discovery of XeF_2, XeF_4, and XeF_6 during the past decade, many workers have assumed[3] that XeF is a chemically bound species, with a dissociation energy of ~20 kcal/mol. This assumption is based in large part on the electron spin resonance (esr) experiments of Falconer and Morton.[4] They reported the esr spectrum of XeF in crystals of XeF_4 subjected to γ radiation at 77°K. Furthermore, kinetic studies have suggested the existence of XeF as an intermediate in water oxidation[5] and in NO and NO_2 oxidation[6] by XeF_2. Finally, it is thought[7,8] that the decomposition of both $XeF^+OsF_6^-$ and $FXeOSO_2F$ involves the XeF radical.

In the present communication we report the results of *ab initio* electronic structure calculations on the lowest $^2\Sigma^+$ and $^2\Pi$ states of XeF. This study is the logical extension of our earlier work[9,10] on the krypton fluorides. The chosen basis set of Slater-type functions centered on Xe and F is shown in Table I. The properties of the F atom basis are well understood.[9–11] For the ^1S ground state of the Xe atom, the present basis yields a self-consistent field (SCF) energy of −7232.1204 hartrees, which may be compared to the numerical Hartree–Fock results of Mann,[12] −7232.14 hartrees, and Fischer,[13] −7232.153 hartrees. In either case, it is seen that the present basis set for xenon yields an SCF total energy within 1 eV of the nonrelativistic Hartree–Fock limit.

Table I. Basis Set of Slater Functions, $r^{n-1}e^{-\zeta r}$, for Calculations of Xenon Fluorides

Atom	Type	Orbital ζ	Atom	Type	Orbital ζ
Xe	1s	55.110	Xe	3d	20.469
	1s	36.545		3d	11.964
	2s	26.283		4d	7.727
	2s	22.451		4d	5.233
	3s	14.881		4d	3.379
	3s	12.067		5d	2.0
	4s	7.620		5d	1.2
	4s	5.566		4f	3.5
	5s	3.518		4f	2.5
	5s	2.173	F	1s	11.011
	2p	30.678		1s	7.917
	2p	21.424		2s	3.096
	3p	13.721		2s	1.946
	3p	10.709		2p	6.165
	4p	7.422		2p	3.176
	4p	5.036		2p	1.612
	5p	3.516		3d	4.0
	5p	2.016		3d	2.0
				4f	3.0

The present calculations were carried out using the

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