trum[5] included singlets at δ 0.65 (3 H) for the C-19 methyl, 0.92 (3 H) for the C-18 methyl, 1.58 (3 H) for $CH_3C{=}C$, and 2.13 (3 H) for the C-21 methyl. Crystallization from pentane gave material mp 88–89°, which contained $<5\%$ of the 17α form by vpc.

The tetracyclic ketone **12** was submitted to ozonolysis to give the triketone **13** which, without purification, was treated so as to induce intramolecular aldol condensation. Preparative tlc of the product on silica gel (40% EtOAc in pentane) gave (45% overall yield from **12**) a crystalline product which contained 85% of the 17β (**14**) and 15% of the 17α isomer. Two recrystallizations gave *dl*-progesterone, mp 182–185°, undepressed on admixture with authentic material,[10] mp 182–185.5°. The solution ir, nmr, and mass spectra of the former specimen were identical with the respective spectra of the latter as well as of natural progesterone. It is to be noted that many of the yields recorded in this paper have not yet been optimized.

Acknowledgments. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research.

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A Correlation of Some Structural Parameters of Pyrimidine Nucleosides. A Nuclear Magnetic Resonance Study

Sir:

A number of workers have drawn attention to the apparent correlation between the nature of the sugar-ring puckering and the sugar–base torsion angle (ϕ_{CN}) of crystalline nucleosides as determined by X-ray studies.[1-3] Prestegard and Chan[4] described correlations between the chemical shift of the H_6 hydrogen and the $J_{1'2'}$ coupling constant of pyrimidine nucleosides which suggest that this torsion angle–ring puckering relationship may exist in aqueous solution as well. Wilson and Rahman[5] pointed out that there may in some cases be a mutual relation between ring puckering and the nucleoside conformation about the exocyclic $C_{4'}$–$C_{5'}$ bond. It was to investigate the possibility of the existence of this latter relationship in aqueous solution that the present pmr study of a variety of pyrimidine nucleosides was initiated. Our data demonstrate that the gauche–gauche conformation is favored if the ribose, or deoxyribose, is in the $C_{3'}$ endo conformation and less favored if the sugar is puckered $C_{2'}$ endo.

The nucleosides were purchased from Calbiochem and the Sigma Chemical Co.; 0.1 *M* aqueous (D_2O) solutions containing 0.05 *M* internal reference (2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionic acid sodium salt) were lyophilized three times. Spectra were obtained at 220 MHz (23°) and analyzed using LAME.[6] The spectral assignments were carried out by comparison of the shift data in the ribose and deoxyribose series with consideration of published work.[4,7] Some of the data for the correlation were taken from the literature. The literature sources are indicated in the caption of Figure 2.

The $J_{1'2'}$ and $J_{3'4'}$ couplings provide a means of monitoring the average conformation of the sugar ring. They can be related, *via* the Karplus equation,[8] to the dihedral angles $\phi_{1'2'}$ and $\phi_{3'4'}$ in the relevant HCC′H′ fragments (Figure 1). Smith and Jardetzky[9] have estimated the dihedral angles and corresponding coupling constants for a number of possible puckered conformations of ribose and deoxyribose rings. From their table we can make the following qualitative predictions: (a) with increasing proportion of the $C_{3'}$ endo (and/or $C_{2'}$ exo) conformation $\phi_{3'4'}$ and $J_{3'4'}$ increase whereas $\phi_{1'2'}$ and $J_{1'2'}$ decrease and (b) the reverse of (a) is the case for increasing proportion of the $C_{2'}$ endo (and/or $C_{3'}$ exo) conformation.[10]

Newman projection formulas along the $C_{4'}$–$C_{5'}$ bond are shown in Figure 1. Clearly, in the gauche–gauche rotamer in which the 5′ hydroxyl lies above the sugar ring the magnitudes of the vicinal coupling constants $J_{4'5'B}$ and $J_{4'5'C}$[11] are predicted by the Karplus equation to be small (*ca.* 2 Hz), since the coupled nuclei are in a gauche configuration ($\phi_{4'5'B}$ and $\phi_{4'5'C}$ = 60°). However, if the 5′ hydroxyl lies off the ring in either the trans–gauche or gauche–trans rotamer, the 4′ hydrogen is trans to one methylene hydrogen (ϕ = 180°) and the corresponding vicinal J is predicted to be large (*ca.* 10 Hz). Thus any perturbation resulting in a *decrease* in the proportion of the gauche–gauche rotamer should be manifest in an increase in the observed *sum* of $J_{4'5'B} + J_{4'5'C}$.[12]

In Figures 2 and 3 we have plotted this sum *vs.* $J_{3'4'}$ and $J_{1'2'}$, respectively. Clearly, a good correlation exists for the nucleosides indicated by ×. Further, we note that the sum decreases smoothly with increasing $J_{3'4'}$, but increases with increasing $J_{1'2'}$. Both trends are consistent with a correlated decrease in the gauche–gauche population with an increasing proportion of the $C_{2'}$ endo (and/or $C_{3'}$ exo) conformation in this series of ribo- and deoxyribonucleosides. The molecules on the correlation lines have the following common structural features: (a) they are β anomers, (b) they have a C—H and C═O at the ortho positions of the base, and (c) they most certainly exist in their anti conformation in solution.[13-26]

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[10] Endo means the atom is located on the same side of the plane defined by $C_{1'}$, $O_{1'}$, and $C_{4'}$ as the $C_{4'}$–$C_{5'}$ bond. Exo means that it is found on the opposite side.

[11] In the spectral analyses the 4′ and 5′ hydrogens are treated as an ABC subsystem, hence the subscripts B and C.

[12] We realize that the actual rotamers about the $C_{4'}$–$C_{5'}$ bond may be somewhat distorted from the ϕ = 60° values due to O–O repulsion. Qualitatively identical trends are predicted on a distorted rotamer model. Further, since an absolute assignment of the magnetically nonequivalent methylene hydrogens cannot be made at this time, the sum of the two vicinal couplings must be used as a qualitative measure of the relative rotamer populations.

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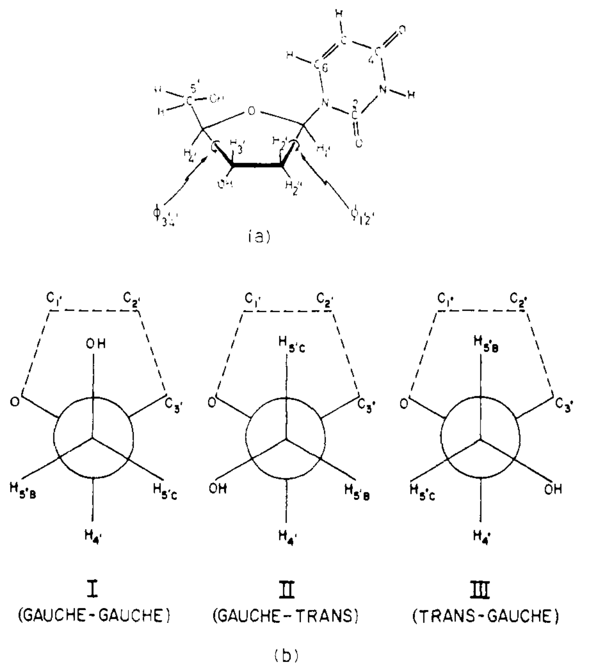

Figure 1. (a) Structure of 2′-deoxyuridine indicating the dihedral angles $\phi_{1'2'}$ and $\phi_{3'4'}$; (b) possible rotational isomers around the $C_{4'}$–$C_{5'}$ bond of a nucleoside.

It is interesting to note that the approximate data for poly-U[19] fall near to both correlation plots. However, points for the α anomer of pseudouridine do not correlate. Further, the points for O and β-RCA (in which a bulky keto group lies in close proximity to the ribose ring[15,16,26]) and AU and AC (in which an aza nitrogen replaces the C_6–H group) lie distant from the curves. It is apparent that in the compounds which fall off the line the $C_{2'}$ endo pucker is not probable. A possible rationalization of the deviations may be based on anomalous nonbonded interactions between such keto groups or aza nitrogens and the sugar ring.

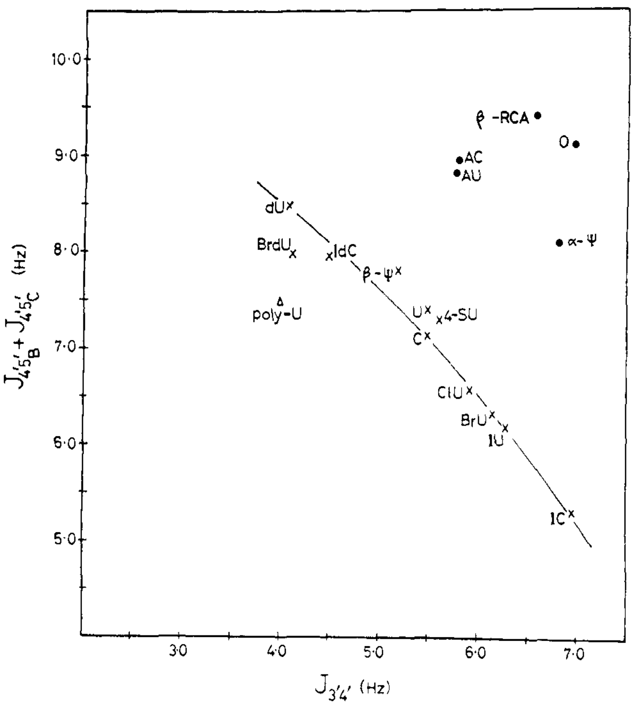

Figure 2. Plot of $J_{4'5'B} + J_{4'5'C}$ vs. $J_{3'4'}$ for a series of pyrimidine nucleosides. Abbreviations: U, ClU, BrU, and IU for uridine[13] and its 5-substituted halo derivatives; dU and BrdU for the analogous deoxy derivatives; C, IC, and IdC for cytidine, 5-iodo-, and 5-iododeoxycytidine; 4-SU, 4-thiouridine;[14] O, orotidine;[15] β-RCA, 1-(B-D-ribofuranosyl)cyanuric acid;[16] AU, 6-azauridine; AC, 6-azacytidine; α-ψ and β-ψ, α- and β-pseudouridine;[17,18] poly-U, polyuridylic acid.[19] References where given are to the data source.

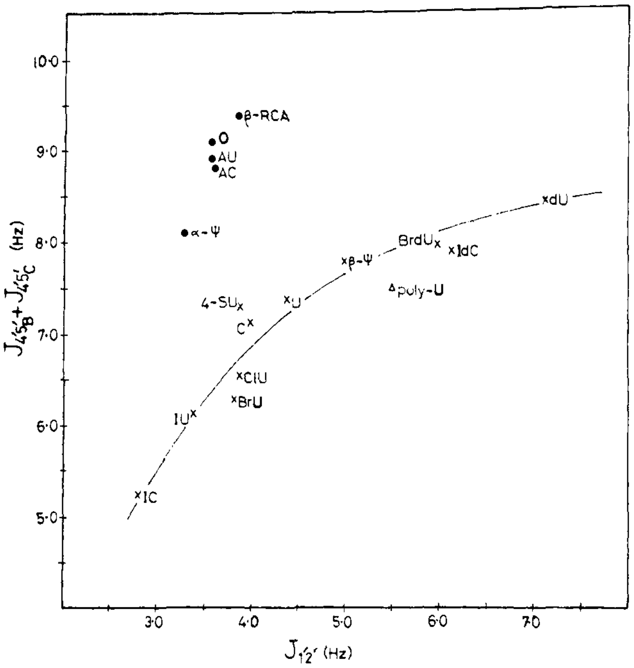

Figure 3. Plot of $J_{4'5'B} + J_{4'5'C}$ vs. $J_{1'2'}$ for a series of pyrimidine ribo- and deoxyribonucleosides. Abbreviations as in Figure 2.

X-Ray data[1-3] indicate that the gauche–gauche conformation is most commonly observed for crystalline nucleosides with *either* the $C_{2'}$ endo or $C_{3'}$ endo structures. However, in the two instances with $C_{3'}$ exo sugars (thymidine[27] and deoxyadenosine[28]) the gauche–trans conformation is observed. In addition, Rahman and Wilson[23] have noted that in crystalline 5-iodouridine the molecules exist in two nonequivalent environments, those in one exhibiting a $C_{3'}$ endo-gauche–gauche con-

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formation, those in the other, a $C_{2'}$ endo-trans–gauche conformation.[29]

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(29) NOTE ADDED IN PROOF. A correction (*ca.* 1 Hz) for the effect of the electronegativity differential between 2′-H and 2′-OH should be applied to the $J_{1'2'}$ values of dU, IdC, and BrdU. A much smaller correction (<0.5 Hz) might be required for the corresponding $J_{3'4'}$ values. These corrections would shift the three points to the *left* in Figure 3 and to the *right* in Figure 2 but do not affect our qualitative conclusions. Further, since submission of this article we have analyzed spectra for thymidine (T), dihydrouridine (diHU), and arabinouridine (aU). Data for T and diHU correlate, although the latter does not have feature b in common with the correlating nucleosides. However, aU does not correlate; this suggests that the stereoconfiguration of the sugar is important insofar as the correlation is concerned.

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Emission from Tungsten Carbonyl Complexes

Sir:

Dissociative decay is a major deactivation pathway for electronic excited states of metal carbonyls.[1] Other facile nonradiative processes include reactions of coordinated ligands other than CO[1–3] and internal conversion where photoreaction quantum yields are less than unity.[4–6] In this communication we report the observation of emission from $W(CO)_5(L)$ compounds where L is a ketone, ether, amine, or pyridine. This is the first report of a radiative deactivation pathway for metal carbonyl complexes.

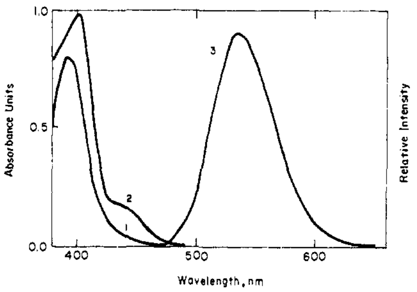

Figure 1. Room temperature absorption spectra of $Mo(CO)_5$(cyclohexylamine), curve 1, and $W(CO)_5$(cyclohexylamine), curve 2. Spectra recorded for $\sim 10^{-4}$ *M* isooctane solutions using 1-cm path cells. Curve 3 shows 77°K emission from $W(CO)_5$(cyclohexylamine). No emission could be seen from $Mo(CO)_5$(cyclohexylamine).

Preparation of the $W(CO)_5(L)$ compounds was achieved by photolysis of $W(CO)_6$ in the presence of the entering ligand.[1] Infrared spectra in the carbonyl region are in agreement with previously published data.[7] The uv–vis spectra of the complexes studied are similar, with a prominent feature being an intense absorption in the vicinity of 400 nm. Room-temperature emission from the complexes could not be detected, but upon cooling to 77°K all of the complexes exhibited an emission maximum between 510 and 545 nm.[8] The emission spectra show little or no structure and there is some overlap of the emission and absorption bands. Figure 1 shows typical emission and absorption spectra. Table I gives emission maxima as well as low-energy absorption maxima for a number of $W(CO)_5(L)$ species

Table I. Emission and Absorption Maxima for Some $M(CO)_5(L)$ Complexes

Compound	Absorption max, nm	Emission max, nm
$W(CO)_5(NEt_3)$	465, 428, 402	533
$Mo(CO)_5(NEt_3)$	393	*c*
$W(CO)_5(NHEt_2)$	438, 402	533
$Mo(CO)_5(NHEt_2)$	393	*c*
$W(CO)_5$(cyclohexylamine)	438, 402	533
$Mo(CO)_5$(cyclohexylamine)	393	*c*
$W(CO)_5$	436[a]	533
$W(CO)_6$	314, 334, 353[b]	*c*
$Mo(CO)_6$	313, 332, 347[b]	*c*
$W(CO)_5$(acetone)	406, 450	538
$W(CO)_5$(ethyl ether)	418, 456	533
$Mo(CO)_5$(ethyl ether)	407	*c*
$W(CO)_5$(pyridine)	440, 385	510
$W(CO)_5(S\text{-}Et_2)$	412, 386	545
$Mo(CO)_5(S\text{-}Et_2)$	377	*c*

[a] Reference 9. [b] Reference 13. [c] None detectable.

We have also found weak emission from $W(CO)_5$ itself. Tungsten pentacarbonyl was produced in a methylcyclohexane glass at 77°K by photolysis of $W(CO)_6$ as previously reported.[9,10] The 533-nm emission, however, could not be detected until the excess CO was removed. The lack of emission before removing the trapped CO is probably related to the fact that regeneration of $W(CO)_6$ can be achieved *via* long-wavelength photolysis of the $[W(CO)_5 + CO]$ in the low-temperature glass.[11] The CO in the cage may be weakly interacting as an O-bonded ligand or in a π-type configuration. We have not been able to detect emission from complexes with L = olefins or acetonitrile.

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