constants of the cis and trans isomers.[25] Although this fact prevents any quantitative comparison, from Figure 2 it is apparent that the quenching ability of the cis isomers is higher than that of the corresponding trans isomers. Moreover, a change in the ligands seems to cause a larger effect in the cis family.

In conclusion, our data show that the nature of the ligands and the geometrical configuration are very important factors in determining the quenching ability of coordination compounds. Whether the ionic charge also plays an important role should be established by similar, systematic investigations. These, however, are made difficult by the fact that a change in the ionic charge is accompanied by a change in the nature of the ligands.

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(25) Whether this difference originates during the diffusion or the encounter is to be established.

F. Bolletta,* M. Maestri
L. Moggi, V. Balzani
Istituto Chimico "G. Ciamician" dell Universita
40126 Bologna, Italy

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The Karplus Relationship and the Correlation of Two Anomalous ^{13}C-Vicinal ^{1}H Coupling Constants with Bonding Electron Density Distribution Found by Accurate X-Ray Analysis

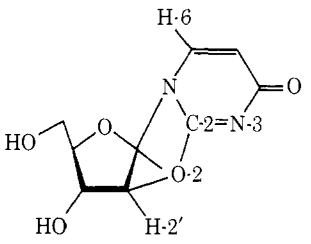
Sir:

Recently,[1] a Karplus-type[2] relationship between the coupling constants for ^{13}C-2 and vicinal ^{1}H nuclei and the magnitudes of the respective torsional angles defined by these two atomic species in uridine, 2,2′-anhydro-1-β-D-*arabino*-furanosyluracil, (**1**) and 2,5′-anhydro-2′,3′-isopropylidenecyclouridine (**2**), was demonstrated. The latter two cyclonucleosides possess conformationally rigid structures as a consequence of their polycyclic fused ring systems and one can therefore be confident in comparing their conformations as observed in the crystalline state with those deduced in solution. To this end X-ray crystallographic analyses of these two cyclonucleosides were carried out so that accurate values for the torsional angles which had previously been estimated from molecular models would be available. In addition to providing the above information these two structural determinations have provided insight into two anomalous coupling constants observed in the ^{13}C nmr spectrum of **2** (with the 2 position of the uracil ring ^{13}C enriched). Finally, this work has provided evidence of a shift of electron density from two bonding orbitals on N-3 of the uracil ring in **1** to the lone-pair orbital of this atom when a hydrogen bond is formed.

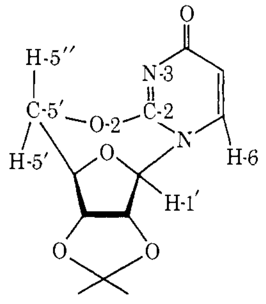
Compound **1** crystallizes in space group $P2_12_12_1$ with unit cell dimensions a = 13.687 (2), b = 18.241 (3), and c = 7.439 (1) Å. Compound **2** crystallizes in space group $P2_1$ with the unit cell dimensions a = 10.344 (1), b = 6.407 (1), and c = 9.077 (1) Å, and β = 93.69 (1)°. Intensity data in the range 3° < 2θ < 60° for the two compounds were collected on a Picker FACS-1 diffractometer with Mo Kα (λ = 0.71069 Å) radiation and a graphite monochromator. The solution of the crystal structure of **1** was accomplished by the straightforward application of the tangent formula[3] whereas that of **2** required the additional use of a translation function.[4,5] The final R indexes were 0.033 and 0.034 for **1** and **2**, respectively.

The relevant torsional angles found by these X-ray analyses are given in Table I along with the corresponding ^{13}C to vicinal ^{1}H coupling constants and the previously estimated torsion angles.[1] Figure 1 shows that, with two exceptions, a Karplus-type relation does exist; the $^3J_{^{13}\text{C-2,H-5'}}$ for **2** lies 2.8 Hz above and the $^3J_{^{13}\text{C-2,H-1'}}$ for **2** falls 1.0 Hz below the curve in Figure 1. The occurrence of these two values may be denoted as anomalies to this Karplus curve.

Table I. Relationships of Vicinal ^{13}C–^{1}H Coupling Constants to Torsion Angle



1



2

Vicinal atoms	$J_{^{13}\text{C},^{1}\text{H}}$, Hz[a]	Torsion angle, deg[b]	Previously estimated[a]	Solvent
C-2–H-6	8.0 (**1**)	180, 177		D_2O
	7.2 (**2**)	−174	~175	$CDCl_3$
C-2–H-1′	3.6 (**1**)	−134, −138	−125	D_2O
	6.6 (**2**)	−175	170	$CDCl_3$
C-2–H-2′	2.0 (**1**)	120, 112	120	D_2O
C-2–H-5′	8.7 (**2**)	−158	175	$CDCl_3$
C-2–H-5″	2.0 (**2**)	−38	50	$CDCl_3$

[a] Reference 1. [b] The estimated standard deviation of these torsional angles is ±2°.

The conformation and dimensions of compounds **1** and **2** differ. The glycosidic torsion angles, O-1′–C-1′–N-1–C-6,[6] are 294.5 and 290.0° for the two independent molecules of **1** and 246.4° for molecule **2**. In general, the chemically equivalent bond distances are similar in **1** and **2**, but many chemically equivalent bond angles differ greatly, particularly in the regions of the uracil–sugar linkages. The distances C-2′–O-2 in the two molecules of compound **1** are 1.460 (2) and 1.462 (2) Å. The similar distance in compound **2**, C-5′–O-2, is 1.458 (3) Å and is therefore equivalent. The exocyclic distances C-2–O-2 in the two molecules of compound **1** are 1.337 (2) and 1.333 (2) Å, whereas this distance has

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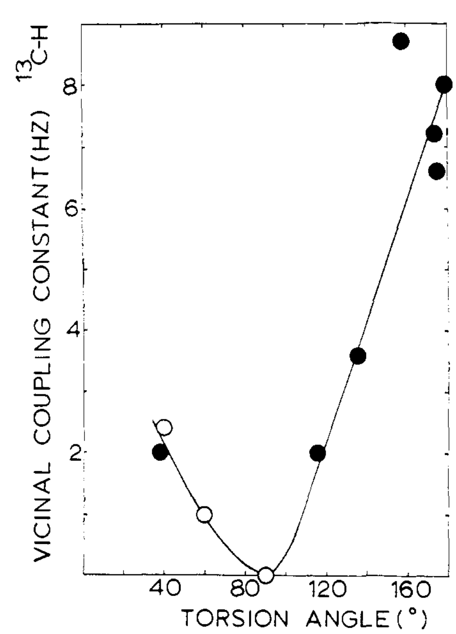

Figure 1. Plot of the coupling constants *vs.* torsion angles. The data presented in Table I are shown in solid circles; the open circle at 60° was obtained from [2-^{13}C]phenyl-5-methyl-1,3-dioxane (R. U. Lemieux and A. J. F. Humphries, unpublished results) and those at 40 and 90° are as previously reported.[1]

been increased to 1.351 (2) Å in molecule **2**. The largest difference, however, is in the interbond angle of atom O-2. In the two molecules of **1** the angles C-2–O-2–C-2′ are 109.4 (1) and 109.3 (1)°, whereas in compound **2** the angle at O-2 (C-2–O-2–C-5′) is increased by 9° to 118.2 (2)°. The variations in conformation and in bond dimensions would require overall different bonding in the two compounds. This different bonding is reflected by the different residual bonding electron densities in the final difference electron density maps, of the cyclonucleosides **1** and **2**, where an explanation for the two anomalous ^{13}C–vicinal ^{1}H coupling constants may be found; see Figure 2.

In Figure 2 the skeletal outlines of the uracil rings and neighboring bonded atoms are superimposed on the final difference electron density sections through the respective pyrimidine rings. It is immediately obvious in comparing the bonding electron density distribution between compounds **1** and **2** that a significant difference between the two uracil rings exists; there is a marked increase in the electron density associated with the C-2–O-2 bond and a marked decrease in the electron density of the C-2–N-1 and C-2–N-3 bonds in **2** compared to those similar bonds in **1**. Electron density has apparently been transferred from the C-2–N-1 and C-2–N-3 bonds into the C-2–O-2 bond in compound **2**. The increased electron density observed in bond C-2–O-2 in compound **2** may account for the abnormally large coupling constant $^{3}J_{^{13}\text{C-2,H-5}'}$ since the nuclear coupling is thought to be transmitted by the bonding electrons.[7] That this electron density is abnormally large for normal C–O bonds may be seen by comparing the electron density observed in other C–O bonds in these structures also shown in Figure 3. In addition, in other accurate crystal-structure analyses in which final difference electron density maps were computed the residual density in the C–O bonds is small.[8–10]

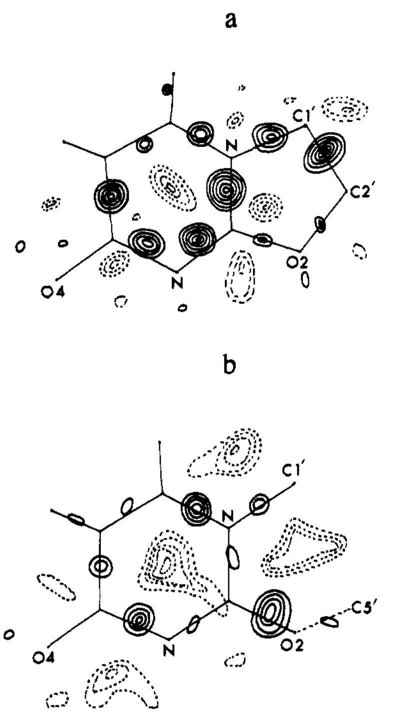

Figure 2. (a) A portion of the final difference electron density map of 2,2′-anhydro-1-β-D-*arabino*-furanosyluracil showing one of the crystallographically independent molecules of the asymmetric unit. (b) A portion of the final difference electron density map of 2,5′-anhydro-2′,3′-isopropylidenecyclouridine. The features shown are greater than three times the estimated standard deviation (0.03 e Å^{-3}). The first contour is at 0.09 e Å^{-3} (and also −0.09 e Å^{-3}) and the contour interval is 0.02 e Å^{-3}. Negative contours are denoted as broken curves.

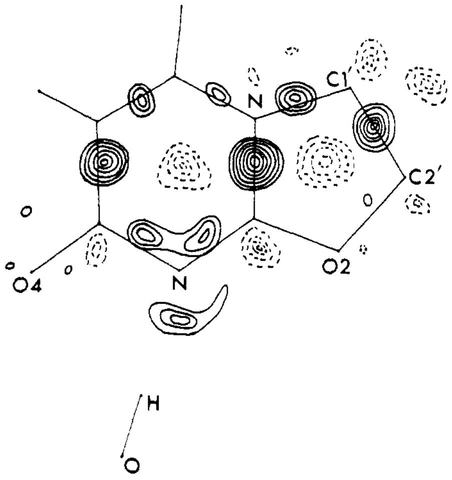

Figure 3. Portions of the final difference electron density map for the second crystallographically independent molecule of 2,2′-anhydro-1-β-D-*arabino*-furanosyluracil.

A possible explanation for this larger than expected coupling in **2** is that the molecular geometry is favorably disposed for overlap of electron density of atom C-2 with the antibonding orbital of C-5′ (of the ribose residue) which lies on the opposite side of C-5′ to the H-5′–C-5′ bond. The coupling of ^{13}C-2 to H-5′ could then

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be transmitted through this system and would not affect the coupling of ^{13}C-2 to H-5″. The large amount of electron density in the C-2–O-2 bond of **2** is extended in this direction as seen on the difference map. The decrease in the residual electron density of the C-2–N-1 and N-1–C-1′ bonds in **2** as compared to that in **1** can account for the anomalously low value for **2** of $^3J_{^{13}\text{C-2,H-1}'}$ (6.6 Hz for a torsional angle of −175°). The residual electron density is decreased in the C-2–N-1 bond but is increased in the N-1–C-6 bond of **2** from that of **1** and the $^3J_{^{13}\text{C-2,H-6}}$ for **2** of 7.2 Hz for a torsion angle of −174° falls closer to the Karplus curve.

The comparison of the residual electron density between compounds **2** and **1** has been made with only one of the independent molecules in the asymmetric unit of **1**. The reason for this particular comparison is that the second independent molecule of **1** forms a hydrogen bond with N-3 of the uracil ring. The formation of this hydrogen bond distorts the electron density in the ring in the manner shown in Figure 3. In this map the only significant change in the electron density distribution involves atom N-3 of the molecule forming a hydrogen bond. Electron density is withdrawn from the bonds N-3–C-2 and N-3–C-4 and resides in the remaining sp^2 orbital on N-3 and is directed toward the proton of the hydrogen bond donor. This work thus also gives evidence of a shift in electron density, from the bonding orbitals of a nitrogen atom to a nonbonding orbital of this atom, as a result of the formation of a hydrogen bond.

These combined results from X-ray diffraction and nmr studies indicate that anomalous bonding electron density can account for non-Karplus-type behavior relating torsional angles to observed coupling constants and therefore care should be exercised in the interpretation of nmr results in cases where anomalous bonding is concerned.

The National Research Council crystallographic programs of Ahmed, *et al.*,[11] were used in the computations. Support for this research came from the National Research Council of Canada (Grant A-172 to R. U. L.) and the Medical Research Council of Canada (Grant MA-3406 to M. N. G. J.). We wish to thank Dr. Brian D. Sykes for valuable discussions regarding the anomalous couplings for compound **2**.

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L. T. J. Delbaere, M. N. G. James*
Department of Biochemistry, University of Alberta
Edmonton, Alberta, Canada

R. U. Lemieux
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

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Reversible Oxygen Adduct Formation in Ferrous Complexes Derived from a "Picket Fence" Porphyrin. A Model for Oxymyoglobin

Sir:

The synthetic challenge of preparing oxymyoglobin and oxyhemoglobin models has both fascinated and frustrated chemists for decades. Many claims of ferrous complexes that reversibly bind molecular oxygen have been made,[1–9] but none have been fully substantiated, some have later proved to be invalid,[10,11] and most have rested on the observation of a single physical parameter, often a change in the visible spectrum, as a criterion of oxygen uptake and reversibility. Low temperature seems to sufficiently retard irreversible oxidation in some systems[8,9,12] to permit the observation of some reversible oxygenation. However, in view of the now well-recognized facile ligand redox reactions of iron complexes,[13] claims of reversible oxygenation which rely solely on the criterion of solution spectral change must be treated with utmost caution. We communicate here the synthesis and full characterization of a crystalline dioxygen[14] complex derived from a specifically designed ferrous porphyrin complex.

Reversible oxygenation of myoglobin and hemoglobin appears to result from a five-coordinate high-spin iron(II) porphyrin immobilized within a hydrophobic pocket.[15] Apparently irreversible oxidation of iron results from either a bimolecular interaction involving two Fe(II) complexes with one O_2 molecule[16] or protonation affording H_2O_2 which subsequently reacts with the Fe(II). Exploiting the concept of biphenyl-type atropisomerism[17] in ortho-substituted meso-tetraphenylporphyrins, we have constructed a "picket fence" porphyrin whose steric bulk on one side creates a nonprotic cavity for the coordination of small ligands while also protecting such ligands from bimolecular reactions.

meso-Tetra(*o*-aminophenyl)porphyrin (H_2TamPP)[18a,b] was prepared by $SnCl_2$ reduction of *meso*-tetra(*o*-nitrophenyl)porphyrin and separated (silica gel chromatography) into its four atropisomers.[19] The slowest

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