

Figure 2. Stereodrawing of the $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anion. The long W—O(phosphate) bonds have been drawn as lines; the even longer V—O(phosphate) bonds are not shown. Although the differences are not significant on the basis of their esd's, the P—O bond lengths appear to be sensitive to the number of metal atoms to which the oxygen atoms are bound: 1.54 (2) and 1.56 (2) Å for the two oxygens that are bonded to three tungsten atoms vs. 1.52 (2) and 1.52 (2) Å for the two that interact with only two tungsten atoms. The V=O bond lengths are 1.61 (2) and 1.63 (2) Å for V(1) and V(2), respectively; the V—O—V bonds vary from 1.79 (2) to 1.87 (2) Å.

band, generally ascribed to M—O—M corner vibrations, to overlap with the 800-cm^{-1} M—O—M edge vibration.¹⁰

The ^{31}P NMR spectrum of $\gamma\text{-PV}_2\text{W}_{10}\text{O}_{40}^{5-}$ shows a single line at -14.56 ppm while the precursor $\text{PW}_{10}\text{O}_{36}^{7-}$ has a single (solid state) resonance at -12.5 ppm. The ^{183}W NMR spectrum (Figure 1B) shows a three-line 4:4:2 pattern with the high-frequency line (-106.2 ppm) substantially broadened^{14a} by scalar coupling to the quadrupolar relaxed ^{51}V . Decoupling of ^{51}V sharpens this line, and $^2J_{\text{WOW}}$ values establish the expected connectivity and assignment.¹¹ Nevertheless, the high symmetry of the anion, and resultant paucity of ^{183}W features, left some doubt in the formulation so an X-ray crystal structure determination was made.

The structure is shown in the stereoperspective of Figure 2¹² and unequivocally establishes the γ -nature of the compound.

The tungsten atoms exhibit typical distorted octahedral coordinations with short W=O (terminal) bonds, 1.69–1.74 Å, long W—O (phosphate) bonds, 2.34–2.43 Å, and intermediate W—O—M bonds, 1.85–2.00 Å for M = W and 1.82–1.86 Å for M = V. The exceptionally long V—O (phosphate) bonds, 2.70 (2) and 2.64 (2) Å for V(1) and V(2), respectively, place the coordinations of the vanadium atoms in between the 6-fold distorted octahedron expected for the γ -isomer and that of a truly isolated 5-fold square prism. The vanadium atoms are also unique in the sense that their VO_n polyhedra are joined together by a single shared edge, which is the only shared edge joining adjacent M_3O_{13} units in the complex.

(10) Better resolved IR spectra are obtained from the tetra-*n*-butylammonium salt where the M—O—M corner vibration is evident at 874 cm^{-1} . Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207–216.

(11) ^{183}W NMR data (5 °C) -137.1 (2 W, $^2J_{\text{WOW}} = 23.7 \pm 0.2$, 6.4 ± 0.2 Hz), -121.1 (4 W, $^2J_{\text{WOW}} = 17.0 \pm 0.2$, 6.6 ± 0.2 , $^2J_{\text{POW}} = 1.28$ Hz), -106.2 ppm (4 W, $^2J_{\text{WOW}} = 22.7 \pm 2$, 17.2 ± 2 Hz).

(12) Crystal structure information: $\text{Cs}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$, FW = 3419.98. Monoclinic, space group $C2/c$. At -100 °C, $a = 32.151$ (8) Å, $b = 18.343$ (4) Å, $c = 17.637$ (4) Å, $\beta = 120.78$ (1)°, $V = 8936.2$ Å³; $D_x = 5.084$ g cm⁻³; $\mu = 307.2$ cm⁻¹. Data were collected on a Syntex P3 diffractometer with the crystal cooled to -100 °C (graphite monochromator, MoK α radiation, $\lambda = 0.71069$ Å). Intensity data for 7855 reflections were collected by using the ω -scan technique ($4^\circ < 2\theta < 50^\circ$; scan width of 1.0° ; variable scan rate of $5.0\text{--}15.0^\circ\text{ min}^{-1}$). On the basis of ψ -scan data, empirical absorption corrections ranging from 0.56 to 1.00 were applied. Following solution (heavy-atom technique) and isotropic refinement, DIFABS (Wacker, N.; Stuart, P. *Acta Crystallogr., Sect. A* **1983**, *A39*, 159) indicated that further absorption corrections were necessary and these were applied: 0.80–1.15. Full-matrix, least-squares refinement of 372 variables (W, Cs, V, and P with anisotropic thermal parameters; O with isotropic) using 5193 reflections for which $I > 3.0\sigma(I)$ converged at $R = 0.047$. Three of the Cs^+ ions are in partially occupied sites with water molecules occupying these sites when Cs^+ does not; the occupancies were included in the refinement. The final difference map had a number of peaks in the range $1.0\text{--}1.2\text{ e } \text{Å}^{-3}$ which were located near heavy atoms. All computer programs used are local modifications of the programs supplied by the Enraf-Nonius Corp. (Frenz, B. A. "Computing in Crystallography"; Schenk, H.; Olthof-Hazehamp, R., van Koningsveld, H., Bassi, G. C. Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71).

Isolation and identification of this thermodynamically unfavored isomer from a well-defined precursor defect anion again demonstrate the utility of these species in the synthesis of novel heteropolyanion systems. Furthermore, a synthetic scheme that produces a less favored isomer allows entry into other species which are thermodynamically downhill. The facile reaction with VO_2^+ (coupled with the monitoring of reactions by ^{51}V NMR) suggests that poorly defined precursor anions may be identifiable from final products.

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Registry No. $\text{Cs}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$, 100513-51-7; $\text{Cs}_7[\text{PW}_{10}\text{O}_{36}]$, 100513-52-8; VO_2^+ , 18252-79-4.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and selected bond distances and angles (13 pages). Ordering information is given on any current masthead page.

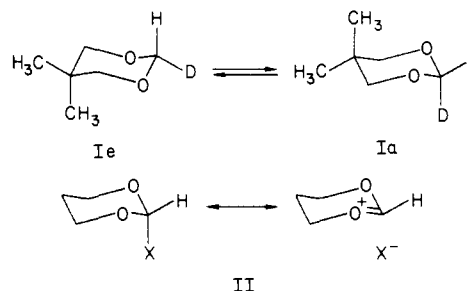
Deuterium Isotope and Anomeric Effects in the Conformational Equilibria of Molecules Containing CHD—O Groups

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We have recently shown that the deuterium in a CHD group in cyclohexane- d_1 or cyclohexane- d_{11} prefers the equatorial over the axial position by 6.3 ± 1.5 cal/mol.¹ We now report that the deuterium in 5,5-dimethyl-1,3-dioxane-2- d_1 (I) prefers the



equatorial position by about 50 cal/mol. This remarkably large

(1) Anet, F. A. L.; Kopelevich, M. *J. Am. Chem. Soc.*, in press.

equilibrium isotope effect is understandable in terms of $n-\sigma^*$ hyperconjugation (no-bond resonance) of a type which is also responsible, in large part,² for the anomeric effect.³ The latter is a stabilization of an axial vs. an equatorial electronegative substituent, as in II. The bond to the axial substituent is weakened and lengthened, whereas the adjacent C–O bond is changed in an opposite fashion.⁴ The weakening of the axial bond, albeit in reduced form, should exist even when X = H in II. The anomeric effect is responsible for stereoselective reactions in carbohydrates,³ and, more generally, in ketals.⁵ The same electronic feature is responsible also for the conformational dependence of the α C–H stretching frequencies in ethers.⁶

The 1,3-dioxane structure is well suited for the purpose of detecting a deuterium isotope perturbation originating from an anomeric effect, since a CHD group in the 2-position is flanked by two oxygens, thus doubling the energy difference of the effect. Also, such compounds are easy to synthesize and their conformational properties are well established.⁷

We chose the 5,5-dimethyl derivative of 1,3-dioxane since the methyl groups are sufficiently well isolated from the C-2 position so that intrinsic isotope effects⁸ can be safely neglected in applying Saunders' isotopic perturbation method.⁹ The 500-MHz ¹H NMR spectrum of I showed a 1:1 doublet with a separation of 0.0194 ppm for the methyl groups. Taken together with the methyl axial-equatorial chemical shift difference of 0.470 ppm,¹⁰ this gives a $|\Delta G^\circ|$ value of 49 ± 3 cal/mol for the isotope effect at room temperature. The isotope effect is so large that direct integration of the two peaks for the C-2 proton of I under slow inversion conditions (-70°C) can be used.¹¹ The ratio of the

integrals was measured to be 0.88 ± 0.02 with the axial site more populated than the equatorial site. This corresponds to deuterium favoring the equatorial position by a ΔG° of 52 ± 10 cal/mol at -70°C , in agreement with the isotopic perturbation value and with the expected near-zero entropy contribution to ΔG° .

The CH stretching frequencies in 1,3-dioxane-2,4,4,5,5,6,6-*d*₇ (III) are reported to be 2828 and 2990 cm^{-1} ,⁷ giving a zero point energy (ZPE) contribution of 65 cal/mol to ΔG° in that compound. In I itself, the C–D stretching bands in the infrared occur at 2081 and 2131 cm^{-1} , corresponding to a slightly higher ZPE contribution of 85 cal/mol. Additionally, bending vibrations must be considered. In cyclohexane-*d*₁,¹ it appears that the angle bending force constants are the same for axial and equatorial CH bonds but that the bending frequencies are a little higher for the axial than for the equatorial CH bond because of differences in the 1,4 and 1,5 non-bonded interactions for the two types of protons. Thus, in cyclohexane-*d*₁, bending contributions (-6 cal/mol) partially cancel the stretching contributions (12 cal/mol).¹ In the 1,3-dioxane system, the ZPE contribution from bond stretching is also larger than the observed isotope effect, and thus a bending contribution of about -30 cal/mol is needed.¹²

Previously observed, but puzzling and unexplained, deuterium isotope chemical shift effects in some cyclic ethers are most probably of an equilibrium type resulting from conformational differences in C–H bond strengths α to an oxygen atom.¹³

Further calculations on I and the parent 1,3-dioxane using molecular mechanics calculations are in progress,¹⁴ and deuterium equilibrium isotope effects in other 1,3-dioxanes and their isotopomers are under investigation.

Acknowledgment. The 500-MHz spectrometer was purchased through funds provided in part by the National Science Foundation.

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(3) For reviews, see: (a) Lemieux, R. U. *Pure Appl. Chem.* **1971**, *25*, 527–548. (b) Eliel, E. L. *Acc. Chem. Res.* **1970**, *3*, 1–8. (c) Zefirinov, N. S.; Shekhtman, N. M. *Russ. Chem. Rev. (Engl. Transl.)* **1979**, *40*, 315–329. (d) "Anomeric Effect, Origin and Consequences"; *ACS Symp. Ser.* **1979**, No 87. (e) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer Verlag: Berlin, 1983. The effect in I, with deuterium as the substituent, is actually a reverse anomeric effect.

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(7) Riddell, F. G. *The Conformational Analysis of Heterocyclic Compounds*; Academic Press: New York, 1980. The deuterated compound, I, was prepared from 2-methoxy-5,5-dimethyl-1,3-dioxane (Eliel, E. L.; Nader, F. W. *J. Am. Chem. Soc.* **1970**, *92*, 584–590) by reduction with $\text{LiAlD}_4\text{-AlCl}_3$ according to the procedure of: Eliel, E. L.; Nader, F. W. *J. Am. Chem. Soc.* **1970**, *92*, 3045–3050.

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(9) (a) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558–2559. (b) Anet, F. A. L.; Basus, V. J.; Hewitt, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945–3946 and references therein.

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Photocyclization Strategy for the Synthesis of Antitumor Agent CC-1065. Synthesis of the B and C Unit Fragments

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The potent antitumor antibiotic CC-1065 (**1**), which is composed of three essentially planar benzo[1,2-*b*:4,3-*b'*]dipyrrole units connected by amide bonds, has been the subject of a number of synthetic efforts in recent years.^{1–4} Much of this research has

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