peptide atoms. Statistically, the difference in the C_3–C_4–C_5 bond angles of the two pyrrolid-2-ones is not significant at the 99% probability level (2.58σ).[13] Hydrogen bonding occurs in ribbons among the carboxamide groups of molecules related by the screw axis in the *c* direction. Each water molecule interacts with three amide molecules—two with O_1 and one through H_1. The observed and final calculated structure factors for both of these compounds have been deposited with ASIS.[14]

Acknowledgments. We express appreciation to F. Grabiner for the collection of the data for L-pyrrolid-2-one-5-carboxamide, to D. Mayers for preparing the carboxamide crystals, and to NIH and ARPA for partial support.

(13) G. H. Stout and L. H. Jensen, "X-ray Structure Determination," MacMillan, Toronto, 1968, p 420.

(14) These tables have been deposited as Document No. NAPS-01065 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to CCMIC–NAPS.

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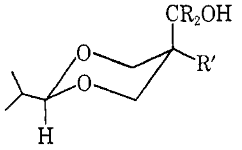
Effect of Dipolar and Bond Eclipsing Forces on Intramolecular Hydrogen Bonds

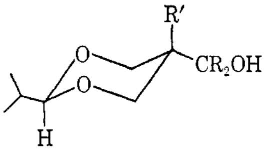
Sir:

Intramolecular hydrogen bonding is a well-known and well-reviewed[1] topic in chemistry. However, little is known regarding its interplay with other intramolecular interactions, such as bond eclipsing and dipole forces. We present here specific instances where bond eclipsing, acting in opposition to an intramolecular hydrogen bond, is shown to reduce the population of the hydrogen-bonding conformation; and where the combination of eclipsing and dipolar forces depopulates the hydrogen-bonded conformation further to the point where, in some instances, the bond cannot be perceived at all.

cis-5-Hydroxymethyl-2-isopropyl-1,3-dioxane (**1a**) has been shown,[2] by infrared spectroscopy, to be devoid of intramolecular hydrogen bonding[3] even though its lower homolog, 5-hydroxy-2-isopropyl-1,3-dioxane, shows only intramolecularly bonded and *no* free OH.[2,4]



1a, R = R' = H
b, R = H; R' = CH_3
c, R = CH_3; R' = H



2a, R = R' = H
b, R = H; R' = CH_3
c, R = CH_3; R' = H

We have now synthesized[5] compounds **1b**, **1c**, **2b**, and **2c**; their salient OH stretching frequencies in the infrared are shown in Table I.[6]

Table I. Hydroxyl Group Stretching Frequencies[a]

Compd	$\tilde{\nu}_{\text{free}}$, cm^{-1}	$\tilde{\nu}_{\text{bonded}}$, cm^{-1}
1a	3640	*b*
2a	3640	*b*
1b	3641	*b*
2b	3642	*b*
1c	3622 3639[c]	3571 (weak)
2c	3616	*b*
5	3623	*b*
6	3640	3530
7	3641	*b*

[a] Recorded on a Perkin-Elmer 521 double-beam grating spectrophotometer using matched 10-cm quartz cells. The concentration of substrate was 5.0 × 10^{-4} *M* in spectral grade CCl_4. The spectra were calibrated using the absorption peaks of *cis*-cyclohexane-1,2-diol at 3626 and 3588 cm^{-1}. [b] Absent. [c] Shoulder.

Compound **1b**, like **1a**, shows no intramolecular hydrogen bond at all.[3] The tertiary carbinol **1c** does display an intramolecularly bonded OH band, albeit a very weak one, along with much free OH, the latter apparently distributed over two different rotational conformations.

In **1c**, either the carbinol methyl groups or the oxygen atom may point into the ring; only in the latter situation is intramolecular hydrogen bonding possible. Three lines of evidence suggest that it is, in fact, the oxygen which points inward. First, it has been calculated[7] that the methyl-inside conformation is destabilized by 2.3 kcal/mol. Secondly, and in contrast to all the other cases, the major stretching frequency for unbonded OH in **1c** (3622 cm^{-1}) is in poor agreement with that calculated[6] (3605–3617 cm^{-1}). Thirdly, and most significantly, the chemical shift (proton nmr, 60 MHz, measured in CCl_4 solution relative to TMS) of the carbinol methyl group in **1c** changes dramatically, from 82.7 to 68.7 Hz, upon dilution from *ca.* 1 *M* to 5.5 × 10^{-3} *M*. We ascribe this to a change from the predominantly "OH-outside" con-

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(1) (a) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, New York, N. Y., 1960, Chapter 5; (b) M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

(2) E. L. Eliel and M. K. Kaloustian, *Chem. Commun.*, 290 (1970); E. L. Eliel, paper presented at the International Symposium on Conformational Analysis, Brussels, Belgium, Sept 11, 1969.

(3) Similar results have been observed by (a) P. Laszlo, personal communication, Oct 7, 1969; R. Dratler and P. Laszlo, *Tetrahedron Lett.*, in press; (b) J. Delmau, personal communication, Nov 5, 1969. Both Laszlo and Delmau worked with an unbiased system (5-methyl-5-hydroxymethyl-1,3-dioxane, analogous to **1b**/**2b** without the 2-isopropyl group). Laszlo has adduced spectral evidence that this compound does, in fact, exist predominantly in the CH_2OH axial conformation (analogous to **1b**). Unpublished work from our laboratory (R. Enanoza) confirms that in the **1b** $\rightleftharpoons$ **2b** chemical equilibrium, **1b** predominates by 0.68 kcal/mol.

(4) S. A. Barker, J. S. Brimacombe, A. B. Foster, D. H. Whiffen, and G. Zweifel, *Tetrahedron*, 7, 10 (1959).

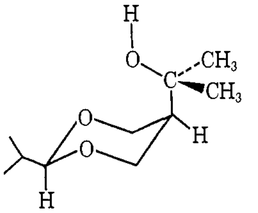
(5) Preparation of **1b** and **2b** by Mr. R. Enanoza involved condensation of 2-methylene-1,3-propanediol (kindly donated by Professor J. P. Fleury, Mulhouse, Switzerland) with isobutyraldehyde followed by oxymercuration–demercuration according to H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, **89**, 1522, 1524, 1525 (1967). The stereoisomers were separated by preparative glpc. Treatment of pure *cis*- and *trans*-5-carbomethoxy-2-isopropyl-1,3-dioxane[2] with 2 equiv of MeMgI gave **1c** and **2c**, respectively, in good yields. Elemental and spectral analyses for all new compounds were in agreement with the postulated structures.

(6) Except in the case of **1c**, the stretching frequencies for the unbonded OH in the compounds in Table I were within the range calculated according to L. Joris, P. v. R. Schleyer, and E. Osawa, *Tetrahedron*, **24**, 4759 (1968), for the largest number of possible rotational isomers. In the case of **1c**, shown to be mainly in conformation **3**, prediction according to Schleyer's rules is not possible.

(7) See E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968), footnote 43.

formation, which is stabilized by *inter*molecular hydrogen bonding in concentrated solution, to the predominantly "OH-inside" conformation, more stable on steric grounds, in dilute solution where association plays no part.[8]

That **1c** exists largely with the OH over the ring and yet forms an intramolecular hydrogen bond only to a slight extent must mean that the predominant conformation in dilute solution is **3** rather than **4**. Since $\Delta\bar{\nu}$ is 51–68 cm^{-1} (depending on the choice of reference for free OH; see Table I), pointing to a moderately strong hydrogen bond,[1b] there must be a strong opposing force to keep the population of the hydrogen-bonded conformation so low. We see this force in a combination of eclipsing and dipolar interactions: in **4** there is both H–O–C$_\alpha$–C$_5$ and partial O–C$_\alpha$–C$_5$–C$_4$, Me–C$_\alpha$–C$_5$–C$_4$, and Me–C$_\alpha$–C$_5$–H eclipsing, as well as a repulsion of the near-parallel dipoles of C$_\alpha$–O–H and of the ring oxygen which is *not* hydrogen bonded.



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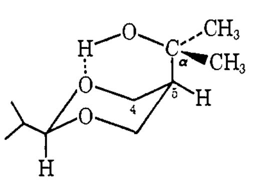

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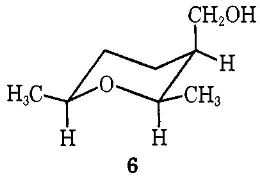
In order to sort out the two factors, we synthesized[9] 3-hydroxymethyltetrahydropyran (**5**) and its *r*-2,*cis*-**6**-dimethyl homologs (**6**, **7**). In these compounds, dipolar factors are absent, since there is only one ring oxygen which would be involved in the intramolecular hydrogen bond, if any; eclipsing factors, however, are similar to those in **1a**. Compound **5** did not display an intramolecular hydrogen bond; this may well be due to its being very predominantly in the equatorial conformation (analogous to **7**, minus the Me groups). There was, however, a clear indication of a strong intramolecular hydrogen bond in **6** (Table I). The difference between **6** and **1a** supports the hypothesis that unfavorable dipole interactions do inhibit hydrogen bonding in **1a**.[10]



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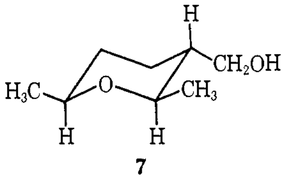

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Nevertheless we believe that eclipsing forces make a strong contribution to the absence of hydrogen bonding in **1a**, **1b**, and **5** and its weakness in **1c**. Three lines of evidence lead to this conclusion. First, the axial conformation of **5** should be destabilized *vis-à-vis* the equatorial by *less* than 1.65 kcal/mol, the corresponding value in cyclohexylcarbinol,[11] even in the absence of hydrogen bonding. The hydrogen bond should overcome this energy disadvantage sufficiently to produce a palpable amount of the bonded conformation, unless there are other factors interfering with the hydrogen bond. Secondly, it has been calculated[3a,10] that dipolar factors alone do not suffice to explain the complete absence of bonding in **1a** and **1b**. Thirdly, and most significantly, the intensity ratio of the bonded and unbonded OH stretching frequencies in **6**, *ca.* 1:1, is nearly the same as in the acyclic analog 3-methoxypropanol (**8**), CH$_3$OCH$_2$CH$_2$CH$_2$OH.[12] Hydrogen-bond formation in **8** requires conformational "freezing" about the four bonds shown; in contrast, formation of an intramolecular hydrogen bond in **6** involves conformational rigidity about two bonds only (C$_5$–C$_\alpha$ and C$_\alpha$–O). Thus, in the absence of opposing factors, **6** should show a much more populous hydrogen-bonded conformation than **8**. That this prediction is not borne out by experiment suggests bond eclipsing as a factor complicating hydrogen bonding in **6**. Model considerations show that **8**, in contrast, can form an intramolecular hydrogen bond in a nearly perfectly staggered, cyclohexane-like conformation.

Acknowledgment. We acknowledge support of this work under a National Science Foundation Science Development Grant.

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[8] The large observed shift is not just due to a change in magnetic anisotropy of the medium. That change may be gauged by the change in carbinol methyl shift in **2c** upon dilution (71.2 to 68.7 Hz) and a similar shift of about 3 Hz in the isopropyl methyl shift in both **1c** and **2c**.

[9] Reduction of 3-formyl-5,6-dihydro-2H-pyran (C. W. Smith, Ed., "Acrolein," Wiley, New York, N. Y., 1962, p 149) with lithium aluminum hydride followed by hydrogenation over Pt gave **5**, identical in ir and nmr spectra with an authentic sample (J. Falbe and F. Korte, *Chem. Ber.*, 97, 1104 (1964)); Sadtler spectra 1074 (nmr) and 28058 (ir). Dimerization of crotonaldehyde (F. E. Bader, *Helv. Chim. Acta*, **28**, 225 (1953); A. Losse, *Chem. Ber.*, **100**, 1266 (1967)) followed by crystallization at −78° from pentane gave 2,6-dimethyl-3-formyl-5,6-dihydro-2H-pyran, presumed to be the *cis* isomer. LiAlH$_4$ reduction and hydrogenation over 5% Pd on charcoal gave a mixture of *ca.* 44% of **6** and 56% of **7** which was separated by preparative glpc.

[10] Professor Laszlo has kindly informed us (personal communication, April 9, 1970; see also ref 3a) that calculation of dipole interactions gives an amount of repulsive energy insufficient to account for the observed phenomena. Underestimation of intramolecular dipolar interactions by calculations based on Coulomb's law seems to be typical; for a similar situation with regard to the "rabbit-ear effect," see E. L. Eliel, *Kem. Tidskr.*, **81** (6/7), 22 (1969).

[11] E. L. Eliel, D. G. Neilson, and E. C. Gilbert, *Chem. Commun.*, 360 (1968).

[12] A. B. Foster, A. H. Haines, and M. Stacey, *Tetrahedron*, **16**, 177 (1961).

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Insertion Reactions Involving Isocyanide Ligands in Platinum Alkyl and Aryl Complexes

Sir:

We wish to report recent studies involving reactions of methyl isocyanide with platinum(II) alkyl and aryl compounds.

When 1 mol of methyl isocyanide is added to a slurry of *trans*-[(C$_6$H$_5$)$_3$P]$_2$Pt(R)X [for (R)X = (CH$_3$)I, (C$_6$H$_5$)Cl, (C$_6$H$_5$)Br, or (C$_6$H$_5$)I] in benzene, an immediate change in color from white to yellow is observed. From these reactions a product is obtained which on crystallization at 25° gives white or pale yellow crystals of a 1:1 adduct [(C$_6$H$_5$)$_3$P]$_2$Pt(R)X·CNCH$_3$. These compounds are soluble in chloroform and dichloromethane, but not soluble in hydrocarbon solvents. They can be formulated as five-coordinate platinum complexes, or, more likely, as the ionic four-coordinate platinum complexes, *trans*-[(C$_6$H$_5$)$_3$P]$_2$Pt(CNCH$_3$)R$^+$X$^-$.