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AN ABNORMALLY WEAK HYDROGEN BOND IN A DIOL WITH A 0^{o} DIHEDRAL ANGLE. BREAKDOWN OF THE OH....OH SPECTRAL SHIFT-DIHEDRAL ANGLE RELATIONSHIP

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Infrared spectral shifts ($\Delta\upsilon$) due to intramolecular hydrogen bonding have been used to obtain information concerning the conformation of many organic molecules.[2] In particular, O-H .....O $\Delta\upsilon$'s for 1,2-diols have been reported to be dependent on the O-C-C-O dihedral angles (ϕ), and quantitative $\Delta\upsilon$-ϕ relationships have been proposed.[2-5] These relationships have been evaluated by using data from a number of compounds with assumed torsional angles including the isomeric <u>cis</u>-2,3-norbornane diols (e.g., I, $\Delta\upsilon = 103$ cm^{-1}),[6] expected to have $\phi = 0^{o}$. Since it is now apparent that the norbornane skeleton is not as rigid as formerly believed,[7] ϕ may well be significantly greater than 0^{o}. Furthermore, Tichý and Kniežo[8] have recently reported the apparently anomalous behavior of compounds with ϕ's expected to be in the 0 to 30^{o} range.

We therefore elected to examine the behavior of noradamantane-3,4-diol (II),[9] a rigid, tricyclic molecule, where ϕ must be fixed effectively at an angle very near 0^{o}. We anticipated an unusually <u>high</u> $\Delta\upsilon$, but, instead $\Delta\upsilon$ proved to be remarkably <u>low</u>, 37 cm^{-1}.[10] Consequently, we have reexamined the validity of the ϕ-$\Delta\upsilon$ relationship.

Since experimentally determined dihedral angles for the diols of interest are not available for comparison with the corresponding $\Delta\upsilon$ values, they have been evaluated using quantitative conformational analysis.[11,12] In view of the lack of data concerning the force field for the interaction of 1,2-diols, 1,2-dimethyl substituted hydrocarbons were employed as models to approximate the repulsive interactions between adjacent O-H groups. This approximation is reasonable since OH and CH_3 groups have similar van der Waal's radii. Further, it was hoped that electronic contributions involved in 1,2-diol hydrogen bonds would be constant or at least proportional. The dimethyl compounds generally gave ϕ's only a few degrees larger than those calculated for the parent hydrocarbons. A plot of ϕ for dimethyl substituted hydrocarbons vs. $\Delta\upsilon$ for the corresponding diols is given in Figure 1 (data in Table 1). While a general trend of increasing $\Delta\upsilon$ with decreasing ϕ is indicated, there is widespread scatter with no linear relationship demonstrated. Similarly, $H_3C....CH_3$ nonbonded distances (R) were calculated and compared with $\Delta\upsilon$'s for the corresponding diols; no correlation was observed.

Tichý and Kniežo[8] suggested that eclipsing strain when ϕ is low may force the OH...O proton out of the plane, reducing hydrogen bonding. Apparently, this factor is responsible for the anomalously low $\Delta\upsilon$ for II. The scatter of points in Figure 1 demonstrates that $\Delta\upsilon$ is not just a simple function of dihedral angle; other structural factors, e.g., the central C-C bond length and the OCC angles, may be involved. Furthermore, many systems are not as rigid as previously believed[13] (e.g., VI, VII and X), and therefore the HO-C-C-OH functionality will contribute heavily to the conformation actually adopted by the molecule. Were it possible to

Fig.1. Plot of calculated dihedral angles (ϕ) for 1,2-dimethylhydrocarbons vs. the OH...O infrared spectral shifts ($\Delta\upsilon$) for the corresponding diols. (See Table 1 numbering).

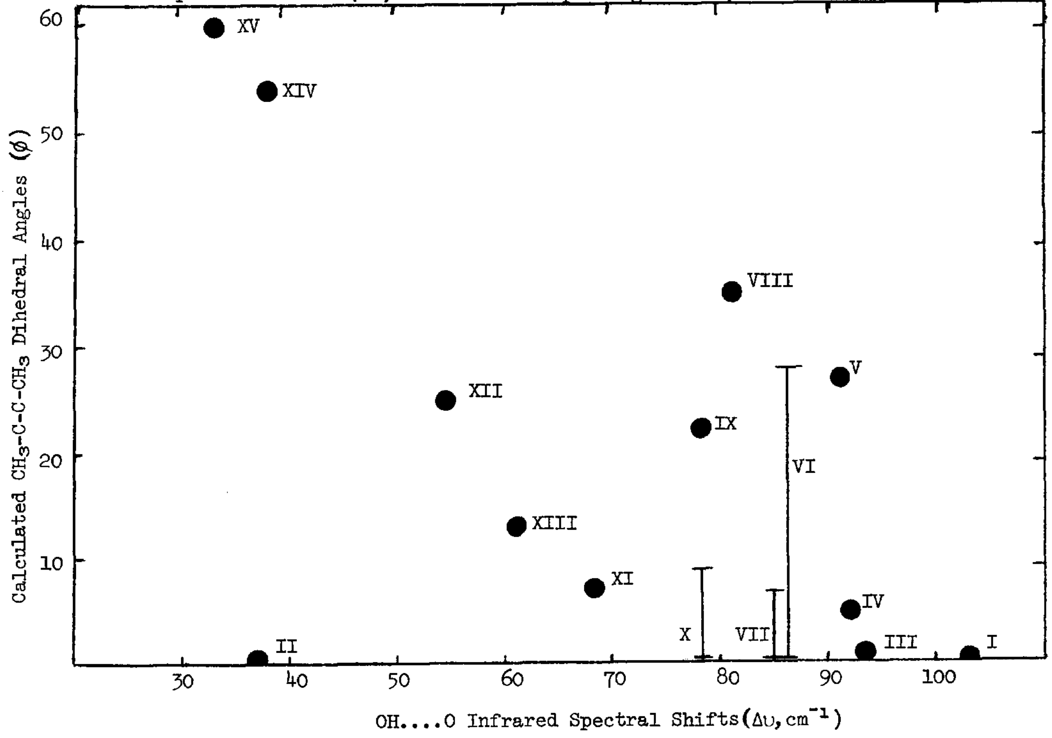
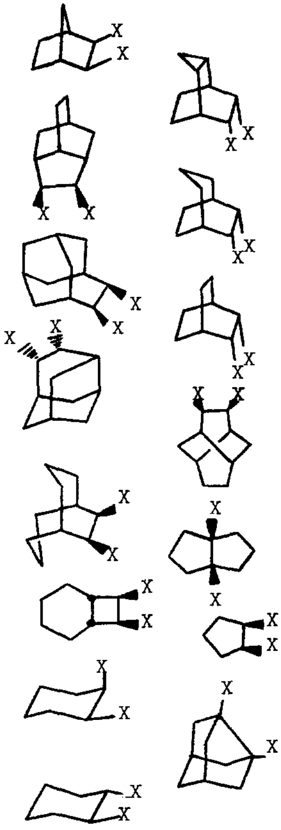


Table 1. Infrared OH...O Spectral Shifts(Δυ) For 1,2 Diols and Calculated Dihedral Angles (ϕ) and Nonbonded Distances (R) For 1,2-Dimethylhydrocarbons



Compound	Δυ(X = OH) cm^{-1}	ϕ(X = CH_3)[a,b] degrees	R(X = CH_3)[b,c] Å
(I)	103[d]	0.5	2.89
(III)	93[e]	1	2.90
(IV)	92[f]	5	2.89
(V)	91(87)[g]	27	2.91
(VI)	86(89)[h]	0-29[i]	2.83-2.90
(VII)	85(83)[j]	0-7[i]	2.84-2.89
(VIII)	81[k]	35	3.00
(IX)	78[l]	22	2.89
(X)	78[m]	0-9[i]	2.83-2.84
(XI)	68[n]	7	2.92
(XII)	54[o]	25	2.88
(XIII)	61[p]	13	2.83
(XIV)	38[q]	54	3.07
(II)	37[r]	0	2.99
(XV)	33[q]	60	3.10

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[a] CH_3-C-C-CH_3 dihedral angle. [b] Calculated using a quantitative conformational analysis program with a force field described previously: ref. 12. [c] $CH_3 \ldots CH_3$ nonbonded distance. [d] Ref. 6. [e] This compound was obtained from Dr. J. Daub, whom we thank. υ_{OH} = 3633, 3541 cm^{-1}. [f] M. Tichý and J. Sicher, Tetrahedron Lett., 4609 (1969). [g] J. Braband, M. Mühlstädt and G. Mann, Tetrahedron, 26, 3667 (1970). [h] P. v. R. Schleyer, E. Funke and S. H. Liggero, J. Amer. Chem. Soc., 91, 3965 (1969). [i] Flexible systems where a range of CH_3-C-C-CH_3 dihedral angles yield similar calculated enthalpies; ref. 13. [j] Refs. 2 and 4. [k] This compound was obtained from Dr. D. Lenoir, whom we thank. υ_{OH} = 3629, 3548 cm^{-1}. [l] Ref. 8. [m] υ_{OH} = 3630, 3552 cm^{-1}. [n] This compound was obtained from Dr. W. T. Borden, whom we thank. υ_{OH} = 3624, 3556 cm^{-1}. [o] E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally and F. T. Wallenberger, J. Amer Chem. Soc., 81, 6472 (1959). [p] Ref. 3. [q] L. P. Kuhn, J. Amer. Chem. Soc., 76, 4323 (1954). [r] υ_{OH} = 3614, 3577 cm^{-1}.

determine ϕ accurately for the diols, it does not follow that the parent hydrocarbon will prefer the same conformation.

We conclude that the spectral shift-dihedral angle relationship should be used with considerable reservation to determine conformations of diols.

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