Intramolecular O-H··· π Interaction Studies in Homoallyl Alcohols

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Some acyclic. mono- and bi-cyclic homoallyl alcohols exhibit bands due to more than one type of bonded species in the O-H stretching region. which have been assigned to specific bonded conformations.

INTRAMOLECULAR O-H··· π interactions, which exist in some unsaturated alcohols and are observed as a shift of the band due to the O-H stretching vibration to lower frequencies, have been used as a means of configurational and conformational studies in such systems.[1] In the present study, the existence of internal interactions in the homoallyl alcohols (I),[2] (II),[3] and (III) have been utilized in establishing the degree of conformational mobility in these *trans*-decalin systems. Any mobility should result in more than one steric relationship between the interacting groups, giving rise to more than one band in the bonded OH stretching region. Based on the study of (I)—(III) the stereochemistry of hydrogen bonding in isopulegol (IV), neoisopulegol (V), and but-3-en-1-ol (VI) has been assigned.

Both (I) and (II) exhibit a principal band due to $v_{(OH)b}$ (bonded OH) at 3 596 cm^{-1} and a weak band at 3 575 cm^{-1} (Figure 1). It can be seen that there is a
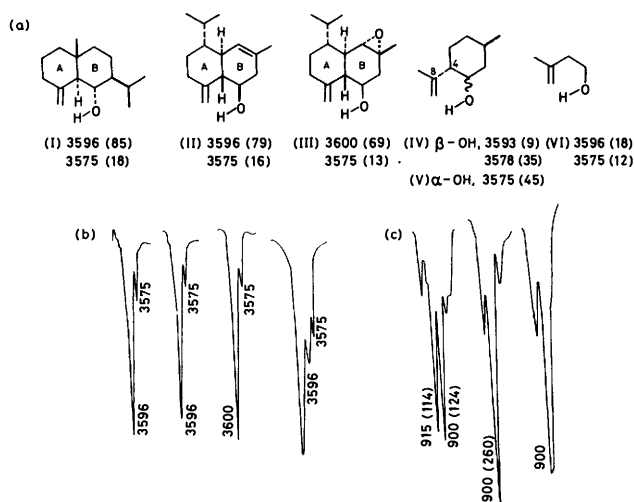

FIGURE 1 (a) Band positions (cm^{-1}) due to $v_{(OH)b}$ in (I)—(VI) (ε in parentheses). (b) Bands (cm^{-1}) due to v_{OH} in (I)—(III) and (VI). (c) Bands (cm^{-1}) due to $\delta_{=CH_2}$ in (I)—(III) (ε in parentheses)

torsion angle deviation [4,5] of 5 and 16° at the A–B bridgehead in (I) and (II), respectively, from that necessary for a smooth diequatorial fusion. This strain should be largely accommodated by distortion around the different atomic centres in the carbocyclic systems.[4] One can therefore, expect (I) to adopt predominantly a

chair–chair form (Ia) and (II) a chair–half-chair form (IIa). The principal band at 3 596 cm^{-1} can then be assumed to arise from the same relative bonding conformations (Ia) and (IIa) (Figure 2).

The weak band at 3 575 cm^{-1} for (I) and (II) is suggestive of a steric relationship between the interacting groups, requiring a greater O-H··· π orbital collinearity, since the bands due to internal interactions are at still lower frequencies. A scrutiny of molecular models (Dreiding) reveals that this condition is met only in the flexible forms for ring A with a pseudorotational angle [6] (θ) of 60°, as in (Ib) and (IIb). For (III), the bands at 3 600 and 3 575 cm^{-1} should arise from conformations similar to (IIa) and (IIb) respectively, since 1,2-epoxycyclohexane is known to adopt very much the same conformation as cyclohexene.[7]

For (I), another flexible form (Ic; θ 120°), more favourable than (Ib), is possible (Figure 2). In both (Ib and c), there is one ethane-like eclipsing interaction. The additional strain in (Ib) is the non-bonded 1,4-methyl–hydrogen interaction. In (Ic), the steric relationship between the interacting groups is very much the same as in (Ia), and hence, it is expected to absorb at the same position due to $v_{(OH)b}$, *i.e.* at 3 596 cm^{-1}, rendering its identification impossible.

Of the monocyclic analogues of (I), (IV) is known to exhibit [8] two bands due to $v_{(OH)b}$ at 3 593 and 3 578 cm^{-1}, while its epimer (V), exhibits only one band at 3 575 cm^{-1}. The acyclic alcohol, but-3-en-1-ol (VI) has been found to exhibit two bands at 3 575 and 3 596 cm^{-1} in the present studies. All compounds (IV)—(VI) can exist in two distinct conformations as shown in Figure 2. In (IVa) and (VIa) the steric relationship between the interacting groups is very much the same as in (Ia) and hence the band around 3 596 cm^{-1} is assignable to this form. In (IVb)—(VIb) the steric relationship through the contiguous atomic centres, H,O,α-C, β-C, and C=C is the same and hence could be ascribed to the band around 3 575 cm^{-1}. In (IVb)—(VIb) one can discern a better overlap of OH with the π-orbitals and hence the lower frequencies of the bonded hydroxy in these.

Significantly, while (IV) exists in two conformations (IVa and b), (V) is entirely present as (Va). This can be traced to two factors: (i) the strength of hydrogen

[1] M. Oki, H. Iwamura, T. Onada, and M. Iwamura, *Tetrahedron*, 1968, **24**, 1905 and references cited here.

[2] A. M. Shaligram, A. S. Rao, and S. C. Bhattacharyya, *Tetrahedron*, 1962, **18**, 969.

[3] R. Seshadri, P. S. Kalsi, K. K. Chakravarti, and S. C. Bhattacharyya, *Tetrahedron*, 1967, **23**, 1267; S. V. Tirodkar, S. K. Paknikar, and K. K. Chakravarti, *Science and Culture*, 1969, **35**, 27.

[4] N. L. Allinger, J. A. Hirsch, M. A. Miller, and T. J. Tyminski, *J. Amer. Chem. Soc.*, 1968, **90**, 5773.

[5] G. Chiurodoglue, 'Conformational Analysis,' Academic Press, New York, 1971.

[6] N. L. Allinger, J. Allinger, and M. A. Darooge, *J. Amer. Chem. Soc.*, 1964, **86**, 4061.

[7] M. Hanack, 'Conformation Theory,' Academic Press, New York and London, 1965.

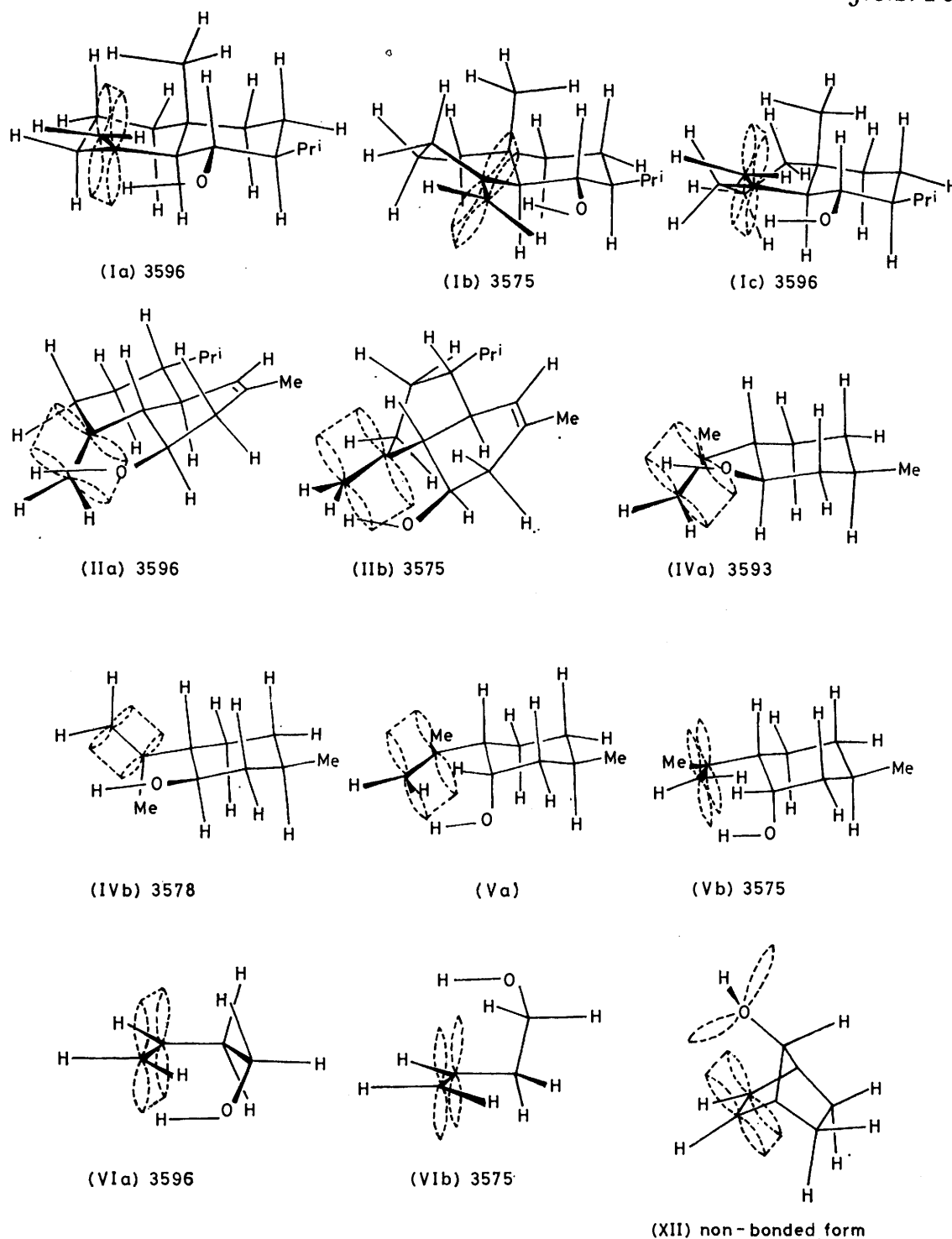[8] T. Shishibori, *Bull. Chem. Soc. Japan*, 1968, **41**, 1170.

Figure 2 Stereochemistry of hydrogen bonding in (I)—(VI) and (XII)

bonding and (ii) the preferred isopropenyl rotamer, *i.e.* that in which there is a gauche relationship between 4-H and the double bond along the C(4)–C(8) axis, due to greater hyperconjugation [9] stability, which governs the conformer populations. In (IV) these two factors are in conflict with each other in both conformers (IVa or b).

Hence, both conformers are present. In (V) these two factors act in conjunction with each other in stabilising conformer (Vb). For (VI), the preferred conformations around the sp^2–sp^3 centres, as shown in (VIa and b), is the same as in but-1-ene.[10]

The present assignment of the stereochemistry of

[9] F. G. Riddell and M. J. T. Robinson, *Tetrahedron*, 1971, **27**, 4163.

[10] A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Amer. Chem. Soc.*, 1962, **84**, 2748.

hydrogen bonding in (IV) and (V) amounts to a revision of the earlier assignments by Shishibori *et al.*[8] Previous work [11] on but-3-en-1-ol (VI) reports only one band at 3 596 cm⁻¹, which was not assigned to any specific conformer.

Modification of the Band due to δ(=CH₂) *in* (I).— Compound (I), with an angular methyl group exhibits two

(i) *Steric strain.* The decrease in the bonded species as one goes from (VII) [1] to (IX) [1] is due to increasing steric strain (decreasing θ) (Figure 3).

(ii) *Steric environment.*[12] The bonding form seems to be stabilized more when the hydroxy-group is in a secondary than in a tertiary steric environment. Thus, (Xa) [1] is populated more than (Xb), although the latter
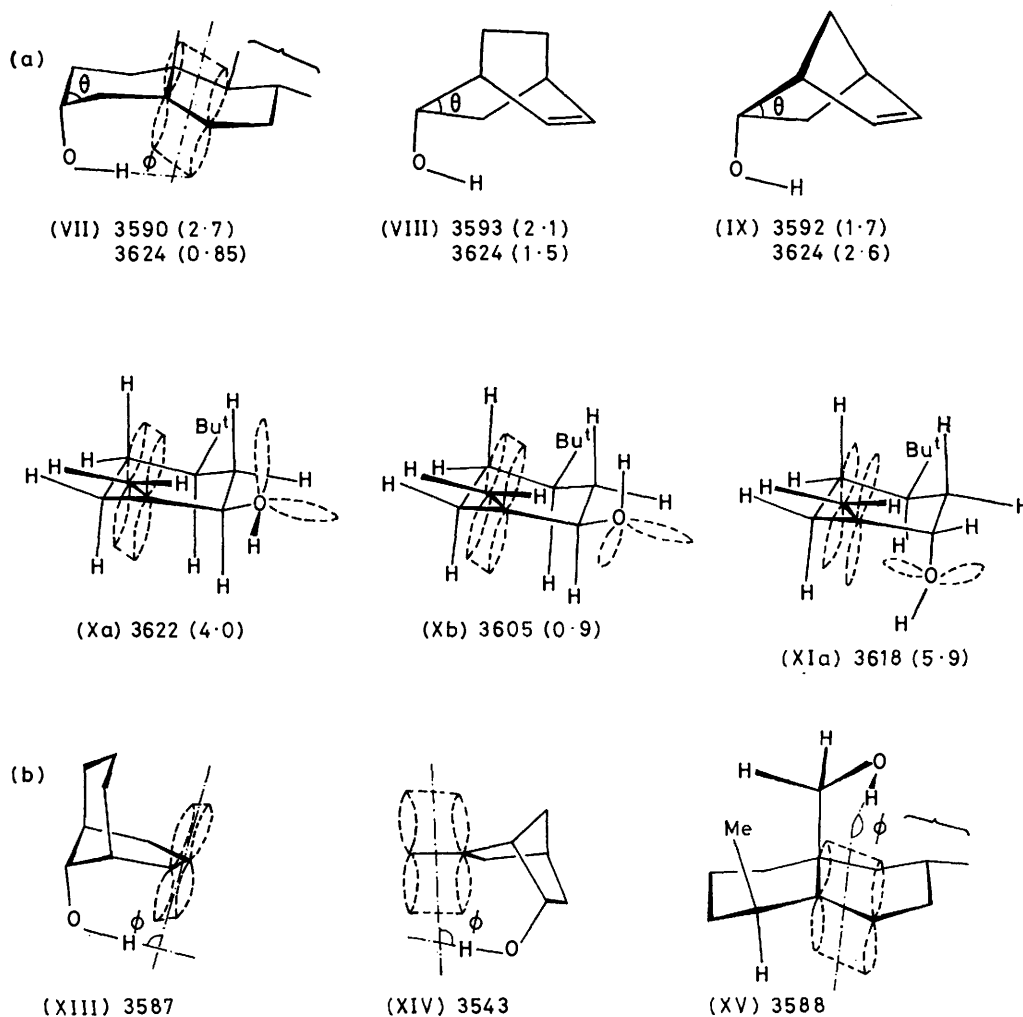

(VII) 3590 (2·7)
     3624 (0·85)

(VIII) 3593 (2·1)
      3624 (1·5)

(IX) 3592 (1·7)
     3624 (2·6)

(Xa) 3622 (4·0)

(Xb) 3605 (0·9)

(XIa) 3618 (5·9)

(XIII) 3587

(XIV) 3543

(XV) 3588

FIGURE 3   (a) Band positions (cm⁻¹) due to v_{OH} in (VII)—(XI) ($10^{-3} A/1$ mol⁻¹ cm⁻² in parentheses).   (b) Band positions (cm⁻¹) due to $v_{(OH)^b}$ in (XIII—(XV)

bands at 900 and 915 cm⁻¹, while (II) exhibits only one band at 900 cm⁻¹ with a much greater E_a value (Figure 1). While the available evidence shows (solvent studies) that the twin bands in (I) should be traced to different conformers of ring A, a qualitative strain analysis warrants a large dihedral angle strain at the bridgehead to push ring A into existing in a 1 : 1 chair-flexible equilibrium.

Population of the Bonded Species versus Free Hydroxy-groups.—Compounds (I)—(III) exhibit bands due only to $v_{(OH)^b}$ and none due to $v_{(OH)^f}$. It appears that the following factors govern the $v_{(OH)^b}$: $v_{(OH)^f}$ ratio.

is the more strongly bonded species (Figure 3). Further, (XI) [1] exists entirely as (XIa) due to favourable aspects of factors (i) and (ii).

(iii) The severity of repulsions between π electrons and the lone pair electrons of the hydroxy-oxygen [13] in the non-bonding conformation apparently depends on the distance and direction between the interacting groups. The total bonding in (XII) [14] should be largely determined by this factor. However, (VII)—(IX) [1] show free hydroxy, since such a large interaction does not

[11] M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan,* 1959, **32**, 567.

[12] L. Joris, P. v. R. Schleyer, and D. Oswa, *Tetrahedron,* 1968, **24**, 759 and references cited here.
[13] R. Baker and L. K. Dyall, *J. Chem. Soc.,* 1971, **10**, 1972.
[14] R. K. Bly and R. S. Bly, *J. Org. Chem.,* 1963, **28**, 3165.

exist in the non-bonding conformation. From molecular models, it appears that the size of the interaction in (I)—(III) should be somewhere in between that in (XII) and (VII).

The strength of the hydrogen-bonding is principally governed by the degree of collinearity of O–H with π orbitals.[15] Thus, as one goes from (XIII)[1] to (XIV),[16] an increase in the angle ϕ increases the strength of the hydrogen bonding. Between (XIII) and (VII) even the increased distance of one of the sp^2 carbons from hydroxy hydrogen in (VII) does not alter the strength of the hydrogen bonding, since the angle ϕ remains the same in both. However, the calculated[1] overlap integral (S) gives different values for (XIII) and (VII), since ϕ is neglected as a parameter.

The difference between $v_{(OH)b}$ and that expected for the free hydroxy-group in the same steric environment in the absence of bonding ($\Delta v_{(OH)}$) is taken as the measure of the strength of the hydrogen bonding.[1] It is possible for two compounds to have different $\Delta v_{(OH)}$ values but the same value for (S). So, relation between them may not be valid always. For example, in a linear plot[1] of $\Delta v_{(OH)}$ against S^2, compounds (VII) and (XV)[1] do not lie on the same position in spite of their overlap integrals being adjacent (angle ϕ is also the same in both), because $\Delta v_{(OH)}$ is not the same for primary and secondary hydroxy-groups.

Conclusions.—The introduction of an sp^2 centre in cyclohexane systems has considerable stereochemical

consequence[17] and results in the reduction in the energy barrier between the chair and flexible forms compared with cyclohexane itself. Intramolecular hydrogen bonding studies can be effectively used in detecting conformational preferences in a variety of suitably constituted unsaturated systems.

In acyclic unsaturated systems intramolecular OH $\cdots \pi$ interaction studies can be used in determining the conformational preferences around the sp^2–sp^3 centres[18] by comparing the frequency of $v_{(OH)b}$ with that obtained in a suitable cyclic system.

EXPERIMENTAL

All the compounds studied were g.l.c. and t.l.c. pure and had physical constants in agreement with those in the literature.

I.r. spectral measurements were carried out on a Perkin-Elmer 237B grating i.r. spectrophotometer. In the OH stretching region the measurements were carried out at concentrations at and below 0.5M using an LiF window in a 5 cm cell. Carbon tetrachloride (AnalaR) was used as solvent. The measurements in the O–H stretching region may be in error by ± 3 cm^{-1}.

[15] C. G. Cannon, *Spectrochimica Acta*, 1957, **10**, 341.
[16] L. Joris and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1968, **90**, 4599.
[17] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Interscience, New York, 1965.
[18] C. J. Karabatsos and D. J. Fenoglio, ' Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, Wiley–Interscience, New York, 1970, p. 167.