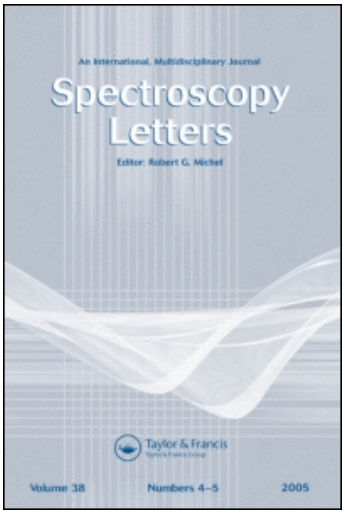

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CNDO/2 Calculations for Hydroxy Stretching Bands of Intramolecular Hydrogen Bonds in *cis*-Cyclohexane-1,3-Diol and *cis*-3-Aminocyclohexanol

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CNDO/2 CALCULATIONS FOR HYDROXY STRETCHING BANDS OF INTRAMOLECULAR HYDROGEN BONDS IN cis-CYCLOHEXANE-1,3-DIOL AND cis-3-AMINOCYCLOHEXANOL

Key Words: Intramolecular Hydrogen Bond, CNDO/2 Calculation

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ABSTRACT

CNDO/2 calculations are used to predict the hydroxy stretching frequency and intensity of the intramolecular hydrogen bonds in the title compounds. The predictions are compared with experimental data.

INTRODUCTION

Many IR studies [1-7] have been reported because the hydroxy stretching band, ν_{OH} band, of intra-

molecular hydrogen bonding in alicyclic alcohols in dilute CCl_4 solutions gives very useful information on the molecular conformation, but few molecular orbital studies for this ν_{OH} band have been reported in literature. Therefore, we carried out CNDO/2 calculations [8] for the title compounds.

CALCULATIONS

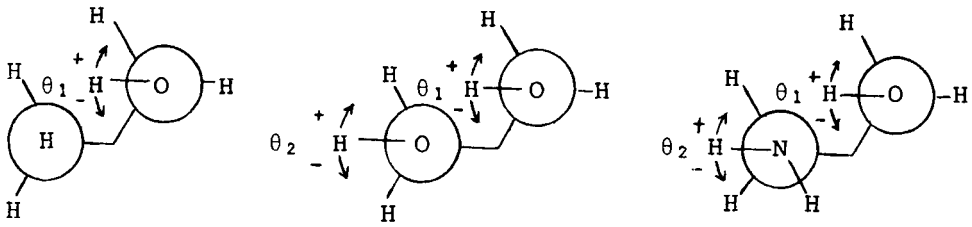
On the basis of available data [9] on analogous compounds, we adopted the geometries shown in Table 1 for cis-3-substituted cyclohexanols. The cyclohexane ring was assumed to take the chair form and for the

TABLE 1

Bond lengths (Å) and angles (°) [9] of the molecules used in the CNDO/2 calculations

Geometry			
R_{C-C}	1.54 Å	∠COH	109°
R_{C-H}	1.09	∠CNH	112.2
R_{C-O}	1.43	∠HNH	105.8
R_{O-H}	0.96	∠CCC = ∠CCH =	
R_{C-N}	1.47	∠HCH = CCO =	
R_{N-H}	1.01	∠CCN	109.47

sake of simplicity, a C_4-C_5-C_6 moiety in this ring was substituted with H atoms, while the other moieties were retained. The angles θ_1 and θ_2 for the model compounds (A)-(C) were estimated by minimum energy geometry using the CNDO/2 method [8].



(A) (B) (C)

For the purpose of comparison, calculations of the angles for (B) and (C) were performed for structures with non-hydrogen bonded and intramolecular hydrogen bonded conformations. The force constant K and the dipole moment derivative $|\partial\mu/\partial R_{OH}|$ values for the obtained geometries were calculated similarly as described previously [10] using the CNDO/2 method [8].

RESULTS AND DISCUSSION

The values obtained from the CNDO/2 calculations are given in Table 2, together with corresponding experimental values. In general, the CNDO/2 calcula-

TABLE 2

Optimum OH bond lengths, force constants, frequency shifts, and dipole moment derivatives of cis-3-substituted cyclohexanols by CNDO/2 calculations (experimental values in parentheses)

No	Substituent	θ_1 °	θ_2 °	R_{OH} Å	K mdyn Å^{-1}	$\Delta\nu_{OH}$[a] cm^{-1}	$\frac{\nu_f-\nu_b}{\nu_f}$	$10^{10}\left\|\frac{\partial\mu}{\partial R_{OH}}\right\|$ e.s.u.
A	H	+120	-	1.0306	16.713	0 (0)	0 (0)	0.970 (1.005)[d]
B_1	OH	+120	0	1.0307	16.703			0.995
B_2	OH	-25	-4	1.0427	15.124	265 (75)[b]	0.048 (0.021)[b]	1.298 (1.772)[e]
C_1	NH_2	+120	0	1.0308	16.703			1.021
C_2	NH_2	-21	+12	1.0486	13.845	490 (256)[c]	0.090 (0.071)[c]	2.241 (2.321)[e]

[a] $\Delta\nu_{OH} = \nu_f - \nu_b$, where ν_f and ν_b are frequencies of free and intramolecular hydrogen-bonded ν_{OH} bands, respectively, but when only the free ν_{OH} band was observed, $\Delta\nu_{OH} = 0$. [b] Ref. 1. [c] Ref. 14. [d] The frequency and integrated intensity of the OH stretching band of cyclohexanol in dilute CCl_4 solution are 3623 cm^{-1} and 0.45 x 10^4 mol$^{-1}\cdot$l$\cdot$cm^{-2}, respectively. [e] The values were estimated using A_{OH} - $\Delta\nu_{OH}$ relationships [3], where A_{OH} is the integrated intensity of the OH stretching band; because cis-cyclohexane-1,3-diol may coexist at conformational equilibrium, diaxial OH $\rightleftharpoons$ diequatorial OH, and the OH stretching band of cis-3-aminocyclohexanol is overlapped by the NH stretching band, accurate values of their A_{OH} are difficult to estimate.

tions overestimate the optimum OH bond length R_{OH}^{o} and the K values [8, 10, 11]. The OH stretching frequency, the ν_{OH} value, which was calculated from the K value by the usual method, is almost twice the observed value [10, 12, 13]. However, it seems reasonable that the values of the calculated R_{OH}^{o} and OH stretching frequency shift $\Delta\nu_{OH}$ increase with increasing hydrogen bond strength due to intramolecular hydrogen bonding in (A)-(C). In addition, the calculated $(\nu_f-\nu_b)/\nu_f$ and $|\partial\mu/\partial R_{OH}|$ values agree reasonably well with the corresponding experimental values both in magnitude and order.

In conclusion, the CNDO/2 method predicts fairly reasonable values for $(\nu_f-\nu_b)/\nu_f$ and $|\partial\mu/\partial R_{OH}|$ of the ν_{OH} band in the system examined.

EXPERIMENTAL

The calculations were performed with an IBM 370/158 computer. IR spectra were recorded with a JASCO DS-403G grating spectrometer.

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