One very interesting aspect of the electron affinity of the allyl radical is the comparison of the resonance energy in the radical and anion. The resonance energy of the allyl radical is given as 9.6 ± 1.5 kcal/mol by Golden, Rodgers, and Benson[32] and is only slightly less than its electron affinity. If the electron affinity of the undelocalized vinyl methyl radical $CH_2{=}CH{-}CH_2\cdot$ is known, the resonance energy, RE, of the allyl anion may be calculated. It is given by

$$\begin{aligned}\mathrm{RE}(CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2^-) &= \mathrm{RE}(CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2\cdot)\\ &\quad + \mathrm{EA}(CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2\cdot) - \mathrm{EA}(CH_2{=}CH{-}CH_2\cdot)\end{aligned}$$

We estimate the electron affinity of the undelocalized vinyl methyl radical, $CH_2{=}CH{-}CH_2\cdot$, as ≤7.8 kcal/mol.[33] This gives the resonance stabilization of the allyl anion as ≳14.5 kcal/mol.

This is greater than the resonance energy of the allyl radical, a result which might be expected since electron repulsion will be more important in the anion and delocalization should play an important role in promoting correlation.

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(34) NOTE ADDED IN PROOF. Recent work by P. Kebarle (Alberta) resolves the discrepancy between the acidity of acetonitrile reported in Ref. 31 and that inferred in this work (P. Kebarle, personal communication).

Application of Photoelectron Spectroscopy to Intramolecular Hydrogen Bonding. 5. The X-Ray Photoelectron Spectra of *cis*- and *trans*-2-Substituted Cyclanols

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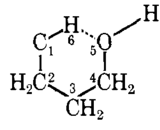
Abstract: The technique of x-ray photoelectron spectroscopy has been used to determine the binding energy shifts in the 1s orbitals of the heavy atom termini of an intramolecular H bond relative to those in a geometric isomer whose structure precludes H-bond formation. When E_B shifts could be detected, the electron donor atom becomes harder to ionize and the electron acceptor atom easier to ionize on H-bond formation. Such shifts cannot simply be a consequence of changing geometric isomers, since these changes produce no such shifts in the absence of H bonding. The direction of the shifts is qualitatively predicted by existing ab initio calculations on related systems, although such calculations do not take account of excited-state electron distributions. A CNDO/2 potential model based charge shifts within the molecule fails to account for the observed results.

Recently the phenomenon of H bonding has been studied by several sophisticated computational techniques.[1-7] Except for extended Hückel methods[2a] (EHT), calculations on H-bonded systems using semiempirical[2] and ab initio methods[3-7] agree on the general charge redistributions occurring on H-bond formation. For example, in 1,3-propanediol[3b] (**1**), the



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intramolecular H bond results in a Mulliken population[8] increase on O(1), O(5), and C(2), and a decrease on H(6) and the C(4) methylene unit. This trend of population redistribution appears to be a general phenomenon of both inter-[4a,5,6] and intramolecular H bonds, although calculations on the latter appear to be limited to relatively few systems.[3,4b] Interestingly however, the ab initio calculations on dimers involving electronegative first-row elements[6,7] invariably indicate that all orbitals associated with the electron donor atom become stabilized, while those associated with the electron acceptor atom become destabilized on H-bond formation. A similar observation has been made for an intramolecular system[3b] and has been discussed as being a general feature of electron donor–acceptor complex formation.[6,7]

It has been suggested[3a,b] that x-ray photoelectron spectroscopy[9] (ESCA) might serve as a useful tool for investigating changes in the 1s orbital ionization energies arising from H-bond formation. We[10] and others[11] have reported the use of UV photoelectron spectroscopy in probing changes in the ionization potentials (IP) of valence orbitals of H-bonded systems. Such studies demonstrated that the IP of the donor electron pair increases, while that of the proton donor atom decreases, and have been analyzed[10b,11a] in terms of the effect of the H bond on the ground and ion states. We wish now to report that we have determined the binding energy shifts (ΔE_B) of the 1s orbitals of the proton and electron donor atoms involved in intramolecular H bonding. Further, in subsequent sections we will analyze the results in terms of existing ab initio calculations and CNDO/2 potential models.

Experimental Section

Binding energies were determined using a McPherson Model 36 ESCA spectrometer to analyze x-ray photoemitted electrons resulting from Mg $K\alpha_{1,2}$ radiation (1253.6 eV). Samples were studied as vapors introduced along with a calibrating gas mixture of Ne, N_2, and CO_2. Each reported binding energy represents the average of at least four sequential determinations and are reported with a precision of better than 0.03 eV. Experimental data were least-squares analyzed with an ELSPEC program[12] assuming Gaussian peaks. Routine IR and NMR spectra were determined on a Perkin-Elmer 421 grating spectrophotometer and Varian Associates A-60 spectrometer, respectively.

The 2-aminocyclanols and 2-methoxycyclanols were synthesized as previously reported.[10a,b]

***trans*-2-Methoxy-1-(*N*,*N*-dimethylamino)cyclopentane (5)** was prepared by dissolving 2.60 g (0.02 mol) of *trans*-2-(*N*,*N*-dimethylamino)cyclopentanol (4)[10a] in 100 mL of dry DME containing 8 mL of anhydrous HMPA. To the stirring solution at room temperature was added 1.5 g (0.036 mol, 57% suspension) of NaH portionwise and then the mixture was stirred at reflux for 8 h to ensure complete anion formation. Subsequent cooling and dropwise addition of 2.84 g (0.02 mol) of CH_3I at room temperature was followed by stirring overnight. To the resulting mixture was added 200 cm^3 of H_2O and the brown mixture was extracted with several 50-mL portions of pentane. The combined pentane extracts were washed with 50 mL of H_2O, dried over $MgSO_4$, and the solvent was removed through a Vigreux column. Distillation of the residue afforded 1.5 g (50%) of a colorless liquid: bp 52–53 °C (9 mm); IR ($CHCl_3$) 2955, 2870, 2830, 2780, 1458, 1445, 1362, 1343, 1090, 1065, and 1030 cm^{-1}; NMR ($CDCl_3$) δ 1.87–1.50 (m, 6 H), 2.27 (s, 6 H, -$N(CH_3)_2$), 2.33–2.67 (m, 1 H, -CHN<), 3.30 (s, 3 H, OCH_3), and 3.48–3.73 (m, 1 H, -CHO). Anal. Calcd for $C_8H_{17}NO$: C, 67.08; H, 11.96; N, 9.78. Found: C, 66.97; H, 11.78; N, 9.93.

***cis*-2-Methoxy-1-(*N*,*N*-dimethylamino)cyclopentane (8).** To 100 mL of freshly distilled dry HMPA was added 2.60 g (0.02 mol) of *cis*-2-(*N*,*N*-dimethylamino)cyclopentanol (7)[13] and 1.5 g (0.036 mol, 57% suspension) of NaH and the mixture stirred at room temperature for 1 h. To this was added 2.84 g (0.02 mol) of CH_3I in 15 mL of dry HMPA over a 20-min period, and the mixture was stirred an additional 1 h. After dilution with 100 mL of H_2O, the solution was extracted with ten 50-ml portions of pentane which were combined, washed with water, and dried over $MgSO_4$. Removal of solvent through an 18-in. column packed with glass helices and distillation of the residue yielded 1.8 g of colorless liquid which proved by GLC analysis (18 × ⅛ in. Carbowax 20M on Chromosorb W 60/80 at 120 °C) to contain 12% of the starting alcohol. This mixture, not separable by distillation, was mixed with 50 mL of anhydrous ether containing 0.3 g of benzoyl chloride. After 10 min, the mixture was poured into 10 mL of saturated aqueous K_2CO_3 and shaken vigorously until the upper layer was no longer turbid. Separation of the ethereal layer, drying over $MgSO_4$, removal of solvent, and distillation of the residue afforded 1.2 g (42%) of a colorless liquid: bp 58 °C (10 mm); IR ($CHCl_3$) 2965, 2900, 2835, 2790, 1463, 1445, 1365, 1353, 1140, 1125, 1093, and 1072 cm^{-1}; NMR ($CDCl_3$) δ 1.88–1.53 (m, 6 H, ring methylene), 2.07–1.92 (m, 1 H, >CHN<), 2.27 (s, 6 H, $N(CH_3)_2$), 3.28 (s, 3H, OCH_3), and 3.76–3.55 (m, 1 H, >CHOR). Anal. Calcd for $C_8H_{17}NO$: C, 67.08; H, 11.96; N, 9.78. Found: C, 67.10; H, 11.94; N, 9.56.

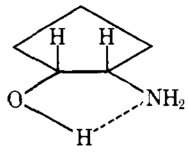
Results and Discussion

O_{1s} and N_{1s} binding energies for a series of 1,2-disubstituted cyclopentanes and hexanes were determined. The binding energies (E_B) and binding energy shifts (ΔE_B) relative to internal calibrants CO_2 and N_2 are presented in Table I along with the structures of the compounds. Although there exists some uncertainty regarding the absolute binding energies for CO_2[9,14] and N_2,[9,15] the values of ΔE_B can be determined much more precisely and are therefore of more concern to the present study.

From Table I, one can see the general effect of increasing ring substitution on the E_B of the 1s electrons. It is interesting to notice that a substitution of a 2-OH group on *N*,*N*-dimethylaminocyclopentane (2) to form 4 or 7 increases the E_B (N_{1s}) value, but by different amounts for the two isomers. Conversely, substituting a 2-(*N*,*N*-dimethylamino) group on cyclopentanol (9) to form 4 or 7 reduces the E_B (O_{1s}) for both isomers with E_B (O_{1s}) cis < E_B (O_{1s}) trans.

In order to facilitate comparison between the trans and cis isomers within a series, the change in ΔE_B values ($\delta\Delta E_B$) in passing from trans to cis are presented in Table II.

Inspection of the data of Table II shows that in the relatively rigid 2-hydroxycyclopentylamines (aminocyclopentanols), changing from trans to cis isomers increases the E_B (N_{1s}) and concomitantly decreases the E_B (O_{1s}) values. We believe this observation to be a direct consequence of intramolecular H bonding present in the latter series,[10a] but precluded in the former by geometric restrictions. For *cis*-2-aminocyclopentanol (6), IR data[10a] is consistent with the formation of an OH···N rather than an NH···O H bond[17] as in structures 19 and 20, respectively. Certainly for the (*N*,*N*-dimethylamino)cyclopentanes (4 and 7) only structure 19 is possible for 7 and the E_B shifts monitored parallel those for 3 and 6. That such shifts are not simply attributable to changes in orbital interactions or the relative orientation of the two functional groups can be illustrated by comparing the E_B values of *trans*- and *cis*-2-methoxy-(*N*,*N*-dimethylamino)cyclopentane (5 and 8). While we assume the substituent effects approximate those present in 4 and 7, in neither compound is H bonding possible and the experimental $\delta\Delta E_B$ values show that *both* the N_{1s} and O_{1s} electrons are slightly easier to ionize in the cis isomer.



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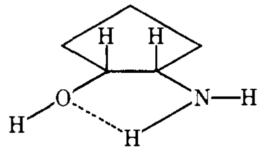

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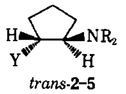
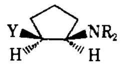
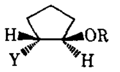
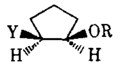
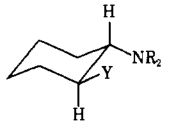
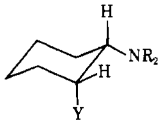
Table I. Binding Energies (E_B) and Binding Energy Shifts (ΔE_B) (in eV) Referred to O_{1s,CO_2} (541.28) and N_{1s,N_2} (409.93)[a,b]

Compound		E_B (O_{1s})	ΔE_B (O_{1s})[c]	E_B (N_{1s})	ΔE_B (N_{1s})[d]
 *trans*-**2**–**5**	**2**, Y = H; R = CH_3			404.47	-5.46
	3, Y = OH; R = H	538.48	-2.80	404.94	-4.99
	4, Y = OH; R = CH_3	538.34	-2.94	404.64	-5.29
	5, Y = OCH_3; R = CH_3	538.00	-3.28	404.52	-5.41
 *cis*-**6**–**8**	**6**, Y = OH; R = H	538.06	-3.22	405.13	-4.80
	7, Y = OH; R = CH_3	537.89	-3.39	404.90	-5.03
	8, Y = OCH_3; R = CH_3	537.93	-3.35	404.45	-5.48
 *trans*-**9**–**12**	**9**, Y = H; R = H	538.48	-2.80		
	10, Y = H; R = CH_3	538.10	-3.18		
	11, Y = OH; R = CH_3[e]	538.39	-2.89		
	12, Y = OCH_3; R = CH_3[e]	538.10	-3.18		
 *cis*-**13**–**14**	**13**, Y = OH; R = CH_3[e]	538.35	-2.93		
	14, Y = OCH_3; R = CH_3[e]	538.05	-3.23		
 *trans*-**15**–**16**	**15**, Y = OH; R = H	538.15	-3.13	404.95	-4.98
	16, Y = OH; R = CH_3	537.86	-3.42	404.76	-5.17
 *cis*-**17**–**18**	**17**, Y = OH; R = H	538.03	-3.25	405.01	-4.92
	18, Y = OH; R = CH_3	537.87	-3.41	404.77	-5.16

[a] Reference binding energies are those of G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, 2, 295 (1973). [b] ΔE_B values have a precision of 0.03 eV or better. [c] ΔE_B (O_{1s}) = E_B (O_{1s}, compound) − E_B (O_{1s}, CO_2). A negative value for ΔE_B indicates a lower binding energy for the compound than for the reference. [d] ΔE_B (N_{1s}) = E_B (N_{1s}, compound) − E_B (N_{1s}, N_2). [e] Only one oxygen band was observed for these compounds, which infers that the ionization energy for both oxygens is equivalent.

Table II. Differences in O_{1s} and N_{1s} Binding Energies ($\delta\Delta E_B$) Resulting from H-Bond Formation[a,b]

Compounds	$\delta\Delta E_B$ (O_{1s}), eV[b]	$\delta\Delta E_B$ (N_{1s}), eV[c]
trans- and *cis*-2-aminocyclopentanol (**3**–**6**)	0.42	−0.19
trans- and *cis*-2-(*N*,*N*-dimethylamino)-cyclopentanol (**4**–**7**)	0.45	−0.26
trans- and *cis*-2-aminocyclohexanol (**15**–**17**)	0.12	−0.06
trans- and *cis*-2-(*N*,*N*-dimethylamino)-cyclohexanol (**16**–**18**)	−0.01	−0.01
trans- and *cis*-2-methoxy(*N*,*N*-dimethylamino)cyclopentane (**5**–**8**)	0.07	0.07
trans- and *cis*-2-methoxycyclopentanol (**11**–**13**)	0.04	
trans- and *cis*-1,2-dimethoxycyclopentane (**12**–**14**)	0.05	

[a] $\delta\Delta E_B = E_B(\text{trans}) - E_B(\text{cis})$. [b] A positive $\delta\Delta E_B$ indicates a shift to lower binding energy, while a negative $\delta\Delta E_B$ indicates a shift to higher binding energy in passing from the trans to cis isomer.

A similar but less pronounced shift attributable to H bonding is observed in passing from *trans*- to *cis*-2-aminocyclohexanol (**15** and **17**), while in the *N*,*N*-dimethylamino analogues (**16** and **18**) there is apparently no shift. IR studies show that intramolecular H bonding exists in all four compounds[10b] and molecular models of these indicate that the OH···N distance for the trans and cis isomers is roughly the same. The small E_B shifts noted in passing from **15** to **17** may be related to a larger H-bond interaction in the latter, but the situation is more ambiguous than in the cyclopentanes, so discussion concerning compounds **15**–**18** should be limited at this time.

IR and UV PES studies[10b] conclusively show the existence of an intramolecular H bond in *cis*-2-methoxycyclopentanol (**13**), but the experimental E_B (O_{1s}) values for both **13** and its trans isomer (**11**), in which H bonding is precluded, are virtually the same. Oddly enough the values from Table I show that ΔE_B (CH_3O_{1s}) $\simeq$ ΔE_B (HO_{1s}), since only a single oxygen ionization was detected (fwhm = 1.4 eV) for each isomer. Cyclopentanol (**9**) appears to be more difficult to ionize than methoxycyclopentane (**10**) by roughly 0.4 eV as expected[16] and the fwhm for each is roughly 1.4 eV. If H bonding has the same general effect on binding energies in **13** as it does in the *cis*-aminocyclanols, its occurrence should reduce the E_B of the HO_{1s}, and raise the E_B of the CH_3O_{1s} electrons to values intermediate between those of **9** and **10**. This is in fact what is observed, but it remains unclear why the non-H-bonded trans isomer (**11**) should have the same E_B (O_{1s}) values as its cis isomer (**13**). There must be two different oxygen 1s ionizations concealed by the narrow peak for each isomer, but apparently the resolution is insufficient to separate them, or to detect subtle shifts.

Comparison of Experimental E_B and Computations. As mentioned previously, the number of quality calculations concerning intramolecularly H-bonded systems is limited;[3,4b] however, the generalities of the results compare favorably with those on intermolecular H bonding.[4a,5-7] In both series, ab initio studies[6,7,3b,18] show that H bond formation decreases the energy of the 1s orbital of the electron donor atom, and increases the same of the electron acceptor. Energy decreases on the electron pair donor sometimes, but not always, exceed the increases on the acceptor.[6b] This has been rationalized as being a consequence of lessened "effective" electron-electron repulsion on the electron donor and increased effective repulsion on the electron acceptor[7] and is projected to be a general finding in electron donor-acceptor complexes.[6b,7] Our results if analyzed under the assumptions of Koopmans' theorem[19] seemingly are in accord with some aspects of the ab initio calculations. In particular, on H-bond formation, the energy required to ionize the electron donor atom increases, while that required to ionize the electron acceptor hydroxyl oxygen decreases. In the amino alcohols where H-bonding differences between isomers can be detected by conventional IR techniques, Table II shows that the $\delta\Delta E_B$ values for the electron donor nitrogen are less than those of the acceptor oxygen. Of course both ab initio calculations and Koopmans' theorem ignore differences in the ion states which may contribute heavily to the ionization process.

It should be mentioned that virtually all calculations concerning H bonding[2b-7] indicate that the Mulliken populations[8] of both the electron donor and acceptor termini of the H bond increase, the former at the expense of the atoms immediately bonded to it. If these Mulliken population changes are indicative of the major contribution to the binding energy shifts arising from H-bond formation, then one might well expect that both the electron donor and acceptor atoms should shift in the same direction. Since experiment does not verify this speculation, other effects of more importance must be operative. Kollman and Allen suggest[7] that these population analyses actually oversimplify the charge-density shifts, and that charge-density plots give a much better analysis of the actual charge redistribution resulting from H-bond formation.[20] The electron distribution analyses of Yamabe and Morokuma[4a] nicely illustrate this point.

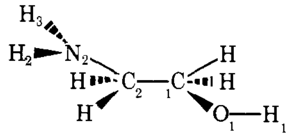
In analyzing the ESCA E_B values two general methods have been found to be of utility. The first method has been discussed by Siegbahn et al.[9] and involves an electrostatic approach as given in the equation

$$E_i = E_o + kq_i + \sum_{j \neq i} (q_j/r_{ij}) \qquad (1)$$

where E_i and E_o are the observed and reference binding potentials, q_i and q_j represent the charges on atoms i and j, and r_{ij} represents the distance between atoms i and j.[21] In the second method, developed by Davis, Shirley, and Thomas[22] and used in the present study, the electrostatic potential energy of an electron at a nucleus

$$e^2 \left\langle \sum_i 1/r_i \right\rangle - e^2 \sum_j Z_j/R_j$$

is calculated. Here r_i and R_j refer respectively to the distance between the parent nucleus and the ith electron, and to the distance between the nucleus and the jth other nucleus with charge Z_j. Based on CNDO wave functions, the shift in electrostatic potential (ΔV) at a particular nucleus in two molecules can be related to the binding energy shift, i.e., $\delta\Delta E_B \simeq -\Delta V$.[22,23] From the above approaches, it is clear that while the binding energy of an electron is dependent upon the charge at that atom, there exists no *quantitative* correlation between binding potential and atomic charge, since the E_B values are determined by local potentials dependent upon the entire molecular environment. It is not surprising then that the changes in E_B noticed in the 2-aminocyclopentanols and attributed to H bonding cannot be simply related to the charge shifts experienced by the heavy atom termini of the H bond which, according to Mulliken population analysis, should be gaining electrons. However, in order to test if a correlation exists between E_B and the calculated local potential in these systems, we have calculated[23] these values for two conformations of 2-aminoethanol (**21** and **22**). Although it has been shown[17b] that the most stable computed conformation for 2-aminoethanol is the g'Gg' structure **23**, here the five-membered ring should constrain the aminoethanol unit to be close to the conformations of **21** and **22**.[24] The results qualitatively agree with ab initio computations on related systems as far as Mulliken populations are concerned and show **22** to be more stable than **21**[25] by 0.35 kcal/mol. As well this CNDO/2 approach predicts that the lone pair orbitals centered mainly on oxygen and nitrogen should become easier and harder to ionize, respectively, in agreement with our earlier experimental data.[10a,b] However, the most pertinent result of the above calculations is that the CNDO/2 potential model[22] predicts that on H-bond formation the 1s electrons of the electron donor and acceptor atoms should become easier and harder to ionize, respectively, contrary to what is experimentally observed. The shortcomings of the use of point-charge potentials with respect to lone pairs have been pointed out by Davis, Shirley, and Thomas[22] and such a model is apparently inappropriate for H-bonded systems.[4b,20]



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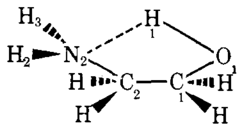
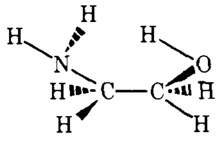


22



g'Gg' **23**

Neither the ab initio nor point-charge potential calculations when applied to ionization processes take account of electron redistribution accompanying ionization.[16,26] The possible influence of the H bond on the ground state and ion state of the same molecular geometry has been discussed[10b,11a] and, since the experimental ionization energy is simply the energy required to interconvert the two states, the effect of the H bond on both must be considered. Unfortunately we have no detailed knowledge of the potential curve of the ion states as a function of H-bond distance,[10b] but it might be anticipated that they would be quite different from the ground-state potential curve, depending upon which atom is ionized.

Conclusions

From the above study, one can deduce the following points:

1. H-bond formation can induce relatively large shifts in the E_B values of the heavy atom termini of the bond. Such shifts cannot simply be a consequence of changing geometric isomers, since trans to cis changes produce no such shift in the absence of H bonding. In cases in which shifts could be detected, the electron donor atom becomes harder, and electron acceptor atom easier to ionize on H-bond formation. Shifts in the former are smaller than those in the latter, although this may not be a general observation when more cases are studied.

2. Ab initio calculations[6,7] on inter- and intramolecular H-bonded species predict the directions of the observed shifts. Since such calculations performed on a variety of systems do not take account of excited-state electronic reorganization accompanying ionization, it is surprising that such an accurate relationship exists.

3. The CNDO/2 potential model, used successfully by Shirley et al.[22] in a variety of systems to account for changes in binding energy for various molecules, appears to be insufficient to treat H-bonded systems. This may arise from conceptual difficulties in the point-charge model for treating lone pairs,[22] or from the inaccuracy of the Mulliken populations (which are calculated simply from the molecular orbital coefficients)[8] in reflecting the charge redistribution accompanying H-bond formation.[7,20]

Acknowledgment. The support of the University of Alberta and the National Research Council of Canada is gratefully acknowledged.

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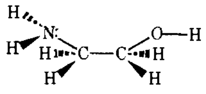
(23) The program used was a standard CNDO/2 package modified at the Lawrence Berkeley Laboratory as described in ref 22, and was kindly supplied by Professor R. G. Cavell. Although the approach is similar to that of eq 1, it is not identical and incorporates no empirical parameters outside the CNDO/2 approach. Standard bond lengths and angles given by J. A. Pople and M. Gordon [*J. Am. Chem. Soc.*, **89,** 4253 (1967)] were assumed.
(24) The choice of the orientation of the O–H bond in **21** is arbitrary and its only significance is that it is non-H-bonded and gauche to the methylene unit. Clearly the amino group may prefer to be gauche to its methylene unit as well, but we have chosen the eclipsed conformation to probe those charge distributions actually arising from H-bond formation, and not from rotations about bonds.
(25) Rotation about the C(1)–C(2) bond produces conformations of differing energy in the absence of H bonding. In fact, our calculations on **22** and its non-H bonded conformation **22a**, in which only the O–H bond has been reoriented 180°, show population shifts similar to but reduced in magnitude to those between **21** and **22**. Although their energies are nearly equal, the CNDO/2 computed potentials for **22** and **22a** parallel those for **22** and **21**.



22a

(26) On the expectation that ion state relaxation should be important for H-bonded systems, we have attempted to use a relaxation potential model (RPM) to calculate the excited-state effect of removal of a core electron. Such computations[16a] give results which parallel those obtained using only the ground state of the molecule. We feel, however, that the limitations imposed by the present CNDO/2 calculations with respect to orbital occupancy should invalidate RPM calculations for systems containing lone pairs of similar energies.

High-Pressure High-Resolution Nuclear Magnetic Resonance. Pressure Dependence of the Ring Proton Chemical Shifts of Substituted Benzenes

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Abstract: Pressure dependence of the ring proton chemical shifts of 1,4-disubstituted benzenes relative to the internal benzene has been measured in *n*-hexane up to 2000 kg cm^{-2} using a 100-MHz high-resolution spectrometer. The observed displacement of the proton resonance to high field, with increasing pressure, has been interpreted in terms of the substituent steric effect, which hinders partly the approach of medium molecule to the resonating proton ortho to the substituent.

Most of the liquid organic compounds, when compressed to a pressure region of the order of 10^3 kg cm^{-2}, are forced to lose 10–15% of their volumes at 1 atm with the resultant contraction of intermolecular separations. This contraction intensifies the contacts between medium molecules and hydrogen atoms which are located normally on the surfaces of the organic molecules, giving rise to change in the so-called medium effect on the proton magnetic resonance. The high-pressure high-resolution proton NMR[1,2] thus appears to be a very attractive means for studying the behavior of the organic molecule under high pressure. In preceding papers, we reported the high-resolution NMR experiments under the increased pressures up to 2000 kg cm^{-2} carried out on a standard high-resolution spectrometer[1b,d,e] operating at 60 MHz with some observations on the pressure dependence of proton chemical shifts of organic compounds.[1b,d] The results were qualitatively discussed in terms of the pressure effect on the intermolecular interactions. Since we are using the internal referencing system throughout this experiment with a reference compound dissolved in a sample solution and subjected to the influence of the same high pressure, the only detectable pressure effect is the difference of the pressure effects on the chemical shifts between the sample and reference compounds, to which we refer hereafter as the "relative pressure shift", $\delta\Delta$. Although the relative pressure shifts of the proton resonances are shown to be generally small[1b,d] and are the order of magnitude 1–5 × 10^{-2} ppm under the increased pressures up to 2000 kg cm^{-2}, our technique to measure the shifts with a considerable accu-