Ring Strain and Hydrogen Bond Acidity

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The ability of strained hydrocarbons to act as hydrogen bond donors has been explored with a hybrid HF-DFT ab initio method, B3LYP, and the 6-31G* and 6-311++G** basis sets. The results have been correlated with geometrical parameters (number of three- and four-membered rings, bond angles, and hydrogen bond distances), electronic characteristics of the complexes and isolated monomers (electron density at the bond critical points, atomic charges, and dipolar magnetization), and other properties (gas-phase acidities and atomic volume and energy). The results have been rationalized on the basis of a simple strain model and compared to nonsaturated hydrocarbons with donor C−H groups.

Introduction

Hydrogen bond (HB) acidity is defined as the ability of a given compound to act as an HB donor.[1] Even though in some cases this property has been considered to be parallel to the acidity,[2,3] a number of examples show the opposite relationship, as seen in the halogen acids where the acidity increases with the size of the halogen atom while the HB acidity decreases.[4]

The HB acidity is related to the presence of an electronegative atom directly bound to the hydrogen involved in the HB. Some cases have been described where the electronegative atom transmits its effect through more than one bond as in the case of halogenated methanes[5,6] or aldehydes.[7,8] Carbon atoms with sp[2] and sp hybridization are able to generate moderate HBs.[9]

In general, carbon atoms with sp[3] hybridization not surrounded by electronegative atoms are not good HB acceptors or donors. A special case of saturated hydrocarbons is that of cyclopropanes and other hydrocarbons containing three-membered rings in which a certain aromatic character[10] is observed, as indicated by their capabilities to accept HBs.[11]

In this article, the abilities of several saturated strained hydrocarbons to act as HB donors has been calculated and compared to other nonsaturated hydrocarbons. Their HB acidity has been correlated with the presence of three- and four-membered rings and geometrical parameters that define the ring strain.

Methods

The HB complexes formed by the hydrocarbons shown in Figure 1 and ammonia have been studied. The compounds have been selected on the basis of the increasing number of three-membered rings around a C−H group (**1**−**3**), C−H groups simultaneously involved in three- and four-membered rings (**4**, **5**), and finally compounds with C−H groups in one or several four-membered rings (**6**−**9**). As reference saturated hydrocarbons, methane (**10**) and isobutane (**11**) have been used. Finally, other compounds (**12**−**15**) able to use their C−H groups to form HBs have also been considered.

The geometry of the monomers and the complexes has been fully optimized with the GAUSSIAN94[12] program using the standard 6-31G*[13] and 6-311++G**[14] basis sets and the hybrid Hartree−Fock/density functional method (Becke3LYP).[15] This level of calculation yielded results similar to those from MP2 calculations.[16,17] In all cases, the nature, as a minimum, of the monomers and complexes has been established at the B3LYP/6-31G* level by verifying that the corresponding frequencies are all positive.

The interaction energies, taking into account the inherent basis set superposition error (BSSE), $E_{I+BSSE}(AB)$ have been calculated with eq 1:

$$E_{I+BSSE}(AB) = E_I(AB) + E_{BSSE}(AB) \tag{1}$$

where $E_I(AB)$ corresponds to the difference between the energy of the complex and the sum of the energies of the

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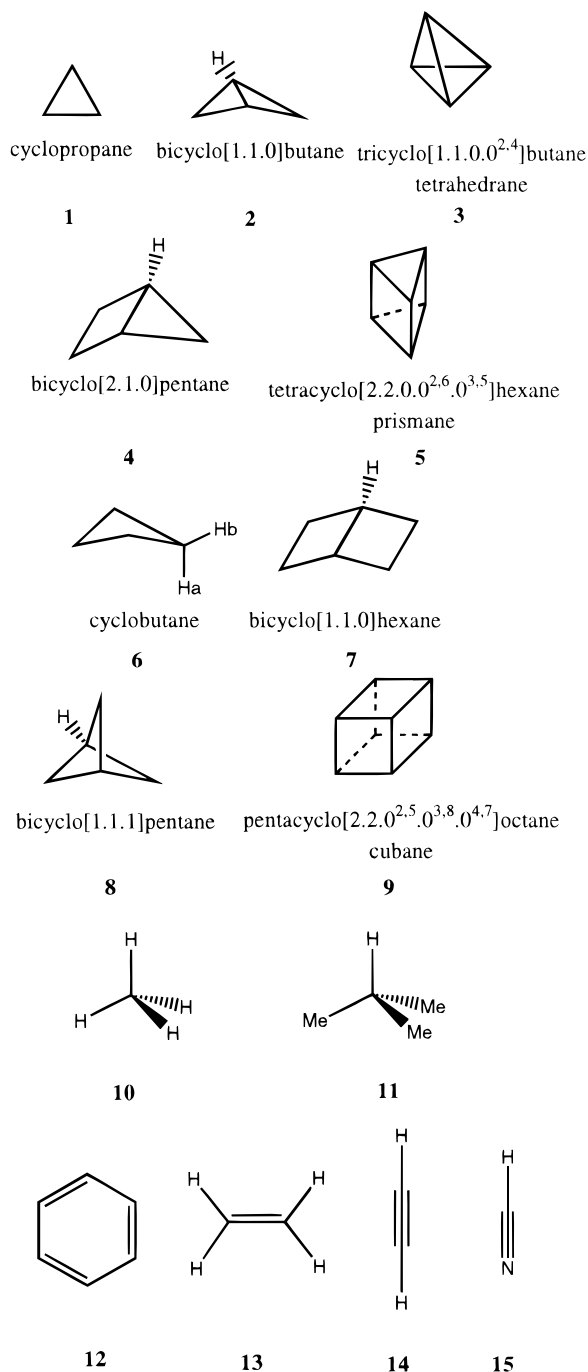(17) Gonzalez, L.; Mó, O.; Yánez, M.; Elguero, J. *THEOCHEM* **1996**, *371*, 1.

Figure 1. Compounds considered as HB donors. The hydrogens involved in the interaction are shown for the cases where all the hydrogens are not identical. **6a** and **6b** stand for the C–H bonds involving hydrogen atoms Ha and Hb of cyclobutane.

isolated monomers (eq 2):

$$E_I(AB) = E(AB)_{AB} - [E(A)_A + E(B)_B] \qquad (2)$$

The BSSE has been calculated using the Boys–Bernardi counterpoise technique[18] and eq 3:

$$E_{BSSE}(AB) = E(A)_A - E(A)_{AB} + E(B)_B - E(B)_{AB} \qquad (3)$$

where $E(A)_{AB}$ represents the energy calculated for mono-

mer A using its geometry in the complex and the complete set of basis functions used to described the dimer and $E(A)_A$ represents the energy for monomer A using its geometry in the complex and its basis set.

The gas-phase acidities of each C–H group in the monomers have been calculated as the difference in energy between the neutral molecule and the corresponding anion including the zero point energy correction at the B3LYP/6-311++G** level of calculation.

The topological properties of the electronic charge density and the atomic charges have been characterized using the atoms in molecules (AIM)[19] methodology with the AIMPAC program package[20] at the B3LYP/6-311++G** level. An electron density of 0.001 e au^{-3} has been used to define the atomic volume. Using the AIM formalism, we have located the bond critical points [i.e., points where the electron density function, $\rho(\mathbf{r})$, is minimum along the bond path and maximum in the other directions) because the values of the charge density and its Laplacian at these critical points give useful information regarding the strength of the linkages. The Laplacian of the density, $\nabla^2\rho(\mathbf{r})$, identifies regions of space wherein the electronic charge is locally depleted [$\nabla^2\rho(\mathbf{r})$ > 0] or built up [$\nabla^2\rho(\mathbf{r})$ < 0]. The former situation is typically associated with interactions between closed-shell systems [ionic bonds, hydrogen bonds, and van der Waals molecules (VDW)], whereas the latter characterizes covalent bonds, where the electron density concentrates in the internuclear region.[19] Other alternative methodologies as the one denominated electron location function[21] (ELF) have been described to characterized the different kinds of bonds but have not been considered in this work. From these considerations, the difference between covalent bonds [$\rho(\mathbf{r}) \sim 10^{-1}$] and HBs [$\rho(\mathbf{r}) \sim 10^{-2}$] is clear, but that between HBs and VDW complexes [$\rho(\mathbf{r}) \sim 10^{-3}$] is not because there is a continuum of situations between typical VDW complexes like Ne···HF and typical HBs such as N$_2$···HF.[19]

Results and Discussion

The hydrogen bonds where the C–H group acts as an HB donor have been thoroughly studied in recent years[22,23] and have been accepted by the scientific community as a source of stabilization, especially in cases where other stronger HBs are not present.[24] In this article, we intend to explore the source of the HB acidity strengthening of the C–H group on the basis of the studies of Allen et al., who found C–H···O=C HBs in the Cambridge Structural Database (CSD), in which the C–H groups belong to cyclopropanes.[25]

Experimental data are available for two of the complexes studied here, as shown in Table 1. The best method used here, B3LYP/6-311++G**, systematically provides HB distances 0.06 Å shorter than the experimental ones, which can be considered as acceptable

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Table 1. Hydrogen Bond Distances (H···N) (in Å) for HB Complexes between the Compounds Indicated and NH₃. Available Experimental Data (14 and 15) Have Been Included

compd	B3LYP/ 6-31G*	B3LYP/6-311++G**	compd	B3LYP/ 6-31G*	B3LYP/6-311++G**	exptl (ref 27)
1	2.653	2.650	**8**	2.735	2.683	
2	2.481	2.529	**9**	2.723	2.681	
3	2.321	2.410	**10**	2.770	2.739	
4	2.652	2.640	**11**	2.844	2.759	
5	2.538	2.573	**12**	2.528	2.568	
6a	2.781	2.735	**13**	2.582	2.594	
6b	2.809	2.761	**14**	2.148	2.262	2.330
7	2.810	2.732	**15**	1.987	2.089	2.156

results. These differences could be due to the dynamic average value of the experimental data, whereas the calculated ones correspond to the bottom of the minimum. In the case of the water dimer, the predicted effect of the third-order anharmonicity might alter the interoxygen distance by 0.13 Å.[26]

One of the properties used, especially in crystallography, to characterize an HB refers to the comparison of the HB distance with the sum of the van der Waals radii of the atoms involved. In this case, depending on the radius set, the sum is equal to 2.6 Å using the values proposed by Pauling and 2.72 Å using those proposed by Bondi.[28]

The results obtained for the complexes of methane **10** and isobutane **11** with ammonia are almost identical to the sums of Pauling's van der Waals radii, which indicates an almost purely van der Waals interaction. These results are in agreement with previous reports indicating that methane is a very poor HB donor.[29−32]

The presence of three-membered rings on the HB donor group produces a shortening of the HB distance. Thus, in the series **11 → 1 → 2 → 3**, where in each step an additional three-membered ring is included around the C−H donor group, a 0.12 Å shortening of the HB distance is observed in each step. The effect due to the presence of four-membered rings is smaller.

Using all the data corresponding to cyclic hydrocarbons (**1−9**), a general equation can be obtained relating the HB distance calculated at the B3LYP/6-311++G** level with the number of three- and four-membered rings around the C−H donor group:

$$\text{HB distance} = 2.785 - 0.127(\text{number three-membered rings}) - 0.034(\text{number four-membered rings}) \quad (4)$$

$$r^2 = 0.988, \quad n = 10$$

Equation 4 provides an excellent qualitative model to evaluate the HB bond distance between these compounds and ammonia. In addition, the constant term, 2.785 Å, provides a good estimation of the value of the isobutane (**11**)−ammonia complex. This complex has been used as a nonstrained model of these compounds.
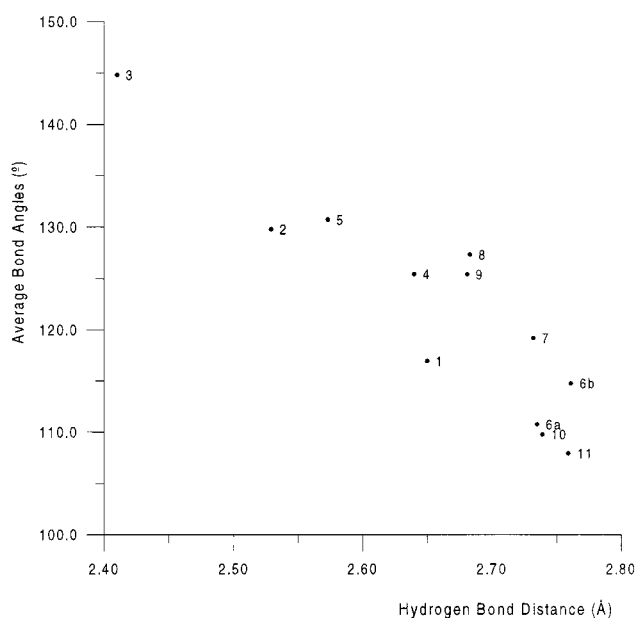
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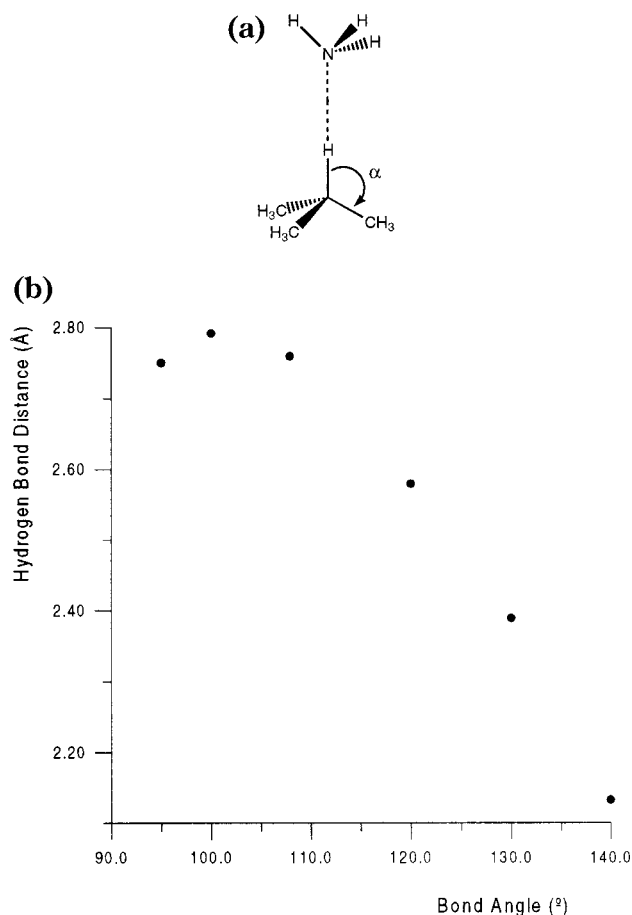

Figure 2. Calculated HB distances (H···N) versus the average bond angles of the hydrogen involved in the HB at the B3LYP/6-311++G** level.

A relationship can also be found between the HB distance and the average bond angles of the donor C−H group. The corresponding plot (Figure 2) shows that, for the series **11 (10) → 1 → 2 → 3** that includes isobutane, methane, and all the compounds with only three-membered rings, a good linear correlation can be obtained. For the remaining compounds containing four-membered rings, an acceptable linear correlation can be obtained excluding the complex with **6a**. One of the geometrical characteristics of these two groups is that although there is a small dispersion in the bond angles for each case in the first group, the dispersion is much larger in the second one.

Following the above idea, a simple model where the three HCC bond angles are simultaneously varied can be generated for isobutane (Figure 3). The corresponding HB distances obtained as a function of the bond angle α are shown in the same figure. A linear correlation is obtained for medium and large bond angles. For angles smaller than 100°, groups approach too close to the HB C−H donor group, altering the observed trend.

Comparison of the HB complexes of **1−9** with those of reference compounds **12−15** indicates that the presence of two three-membered rings as in **2** provides complexes of strengths similar to those of benzene **12** and ethene **13**. Additional strain as in the case of tetrahedrane **3** produces HB distances intermediate between those of C_{sp^2}−H and C_{sp}−H (**14**). In any case, the present HB distances are longer than those of more polar molecules as for **15**.

The corrected interaction energies are gathered in Table 2. The comparison of the compounds containing only three-membered rings shows a reinforcement of the interaction energy of 1.6, 2.0, and 2.4 kJ mol⁻¹ when the series **11 → 1 → 2 → 3** is considered. In the case of compounds with only four-membered rings, the energies are very small (less than 2 kJ mol⁻¹ in all the complexes) and no trend based on the number of these rings is observed.

(a)

(b)

Figure 3. (a) Schematic representation of the strain model between isobutane and ammonia. (b) HB distance versus bond angle in the model shown in Figure 3a calculated at the B3LYP/6-311++G** level.

Table 2. Corrected Interaction Energies (kJ mol^{-1}) for HB Complexes between the Compounds Indicated and NH$_3$

compd	B3LYP/ 6-31G*	B3LYP/6-311++G**	compd	B3LYP/ 6-31G*	B3LYP/6-311++G**
1	−3.35	−2.28	8	−2.56	−1.46
2	−6.22	−4.32	9	−2.36	−1.52
3	−9.14	−6.71	10	−2.17	−1.17
4	−3.03	−1.72	11	−1.36	−0.69
5	−4.62	−3.12	12	−5.61	−4.16
6a	−2.03	−1.33	13	−4.67	−3.42
6b	−1.81	−1.02	14	−17.97	−13.94
7	−1.75	−0.83	15	−34.56	−26.83

The calculated interaction energies follow a second-order polynomial correlation with the HB distances, as indicated in Figure 4. The corresponding equation is

$$E_{\text{I+BSSE}} = -(432 \pm 26) + (313 \pm 21)(\text{HB distance}) - (57 \pm 4)(\text{HB distance})^2$$

$$r^2 = 0.993, \quad \text{SD} = 0.6255, \quad n = 16 \tag{5}$$

A correlation similar to eq 5 is obtained for the energy values of the isobutane···ammonia strained model previously mentioned.

In a recent article,[33] we explored the relationship between ring strain and the carbon acidity of some of the
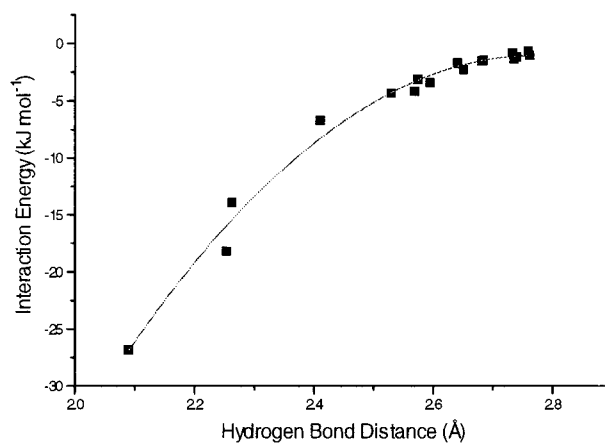
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Figure 4. Interaction energy versus hydrogen bond distances calculated at the B3LYP/6-311++G* level.

Table 3. Gas-Phase Acidity (kJ mol^{-1}) Calculated at the B3LYP/6-311++G Level, Taking into Account the Zero Point Energy Correction**

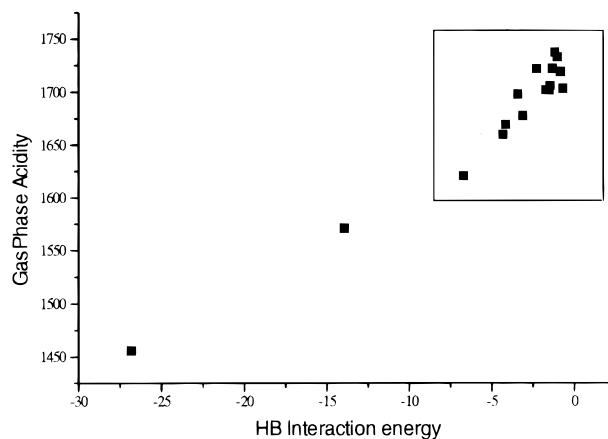| compd	acidity	compd	acidity
1	1721.88[a]	8	1705.65[a]
2	1659.79[a]	9	1701.63[a]
3	1620.59[a]	10	1737.24[a]
4	1702.02	11	1703.45
5	1677.53	12	1669.41
6a	1722.06	13	1697.91[a]
6b	1732.89	14	1570.80[a]
7	1718.99	15	1455.82[a]

[a] Taken from ref 31.

Figure 5. Gas-phase acidity (kJ mol^{-1}) versus the HB interaction energy of the complexes with NH$_3$ (kJ mol^{-1}). The square contains compounds **1−13**.

donors considered in this article. Using the calculated data of the previous article together with new calculations (Table 3), the possible relationship of thermodynamic carbon acidity and the HB acidity in the gas phase has been examined. The plot of the two properties (Figure 5) clearly shows a parallel trend, even though a more detailed analysis of these two properties (only for the strained hydrocarbons) shows a poorer correspondence.

It has been shown that the AIM analysis is a powerful tool to describe HBs.[34,35] In the present case, the AIM analysis has been carried out on the complexes to

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Table 4. Electron Density $\rho_{HB_{cp}}$ (e au^{-3}) and Laplacian $\nabla^2\rho$ (e au^{-5}) at the Hydrogen Bond Critical Points Calculated with the AIM Methodology at the B3LYP/ 6-311++G Level**

compd	$\rho_{HB_{cp}}$	$\nabla^2\rho$	compd	$\rho_{HB_{cp}}$	$\nabla^2\rho$
1	0.0084	0.0213	**8**	0.0079	0.0201
2	0.0092	0.0242	**9**	0.0089	0.0249
3	0.0122	0.0350	**10**	0.0072	0.0180
4	0.0084	0.0218	**11**	0.0072	0.0176
5	0.0094	0.0248	**12**	0.0096	0.0253
6a	0.0074	0.0184	**13**	0.0092	0.0237
6b	0.0070	0.0175	**14**	0.0160	0.0482
7	0.0073	0.0184	**15**	0.0231	0.0664

characterize the interaction and on the isolated proton donor monomers to study possible relationships between the properties of the monomers and the complexes.

The calculated electron densities at the HB critical points, $\rho_{HB_{cp}}$, show small values close to those of van der Waals complexes, as expected for these weak interactions (Table 4). In addition, the positive value of the Laplacian at those points, $\nabla^2\rho$, confirms that they correspond to open shell interactions, as is generally found for HBs.

The values of the electron densities have been correlated in the literature with the interaction energies[36,37] and the HB distance[38] for other HB systems. Here, similar relationships are observed:

$$E_{I+BSSE} = (5.8 \pm 1.5) - (686 \pm 242)\rho_{HB_{cp}} - \\ (31627 \pm 8264)\rho_{HB_{cp}}{}^2 r^2 = 0.993, \quad n = 16 \tag{6}$$

$$\text{HB distance} = -(0.554 \pm 0.002)\ln\rho_{HB_{cp}} \, r^2 = 0.977, \\ n = 16 \tag{7}$$

Because an excellent linear relationship is found between the electron density in the HB critical point and the value of the Laplacian, eq 8, the previous relation-

$$\nabla^2\rho = -(0.0045 \pm 0006) + (3.138 \pm 0.009)\rho_{HB_{cp}} \\ r^2 = 0.997, \quad SD = 0.00099, \quad n = 16 \tag{8}$$

ships (eqs 6 and 7) can be extended to the Laplacian.

The small interaction energies of the complexes studied imply small perturbations of the features of each monomer. For this reason, several characteristics of the hydrogen involved in the HB of the isolated monomers

have been calculated using the AIM methodology and compared with attributes such as interaction energy, HB distance, and electron density at the HB critical point. Because the last three properties of the HB are correlated (eqs 5−7), only the corresponding relationships with the HB distance are shown (the units of the atomic properties are au in all cases):

$$\text{HB distance} = (2.682 \pm 0.008) - \\ (2.96 \pm 0.11)(\text{atomic charge}) \tag{9} \\ r^2 = 0.98, \quad SD = 0.027, \quad n = 16$$

$$\text{HB distance} = -(1.17 \pm 0.21) - \\ (6.18 \pm 0.35)(\text{atomic energy}) \tag{10} \\ r^2 = 0.96, \quad SD = 0.040, \quad n = 16$$

$$\text{HB distance} = (0.30 \pm 0.11) + \\ (15.73 \pm 0.76)(\text{atomic dipolar magnetization}) \tag{11} \\ r^2 = 0.97, \quad SD = 0.04, \quad n = 16$$

$$\text{HB distance} = -(0.10 \pm 0.17) + \\ (0.055 \pm 0.003)(\text{atomic volume}) \tag{12} \\ r^2 = 0.95, \quad SD = 0.045, \quad n = 16$$

The good correlation coefficient of these four relationships, eqs 9−12, provides a basis for the prediction of the HB properties of other compounds with characteristics similar to those studied here.

Conclusion

The strain in compounds with three- and four-membered rings as well as in model systems has been shown to be the origin of an increase in the HB acidity. In particular, those C−H groups surrounded by three-membered rings are moderately strong HB donors. The characteristics of the HBs formed by the compounds studied here have been correlated with the geometrical and electronic properties of both the isolated monomers and the complexes. These relationships provide a basis for the prediction of the characteristics of new HBs in related systems.

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