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Intramolecular O–H· ·N Hydrogen Bonds in 2-Hydroxybenzaldimine Compounds: Spectroscopic and Quantum Chemical Investigations

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Summary. Spectroscopic and quantum chemical data that characterize the intramolecular hydrogen bonds in a series of 2-hydroxybenzaldimine compounds (Ph(OH)(CH=N–*R*); *R* = –NH(Ph), –OH, $-OCH_3$, $-NH_2$, –Ph, –CHO, –H, $-CH_3$, $-(CO)(CH_3)$) are reported. Optimized geometries and vibrational spectra were calculated at HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels, NMR spectra at GIAO-BLYP/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory. The sequences of calculated frequencies (ν(OH) and ν(CN)) and chemical shifts (δ(OH)) agree reasonably well with the corresponding experimental data. The consistency of the calculated data is demonstrated by exploiting several correlations between bond distances, vibrational frequencies, chemical shifts, and hydrogen bond energies. In particular, there exists an almost perfect relation between the hydrogen bond strengths, as measured by *r*(O–H) distances, and the hydrogen bond distances *r*(H· ·N) and *r*(O· ·N). It is shown that electrostatic potentials and several kinds of partial charges (*Mulliken*, CHELPG, MK, and NPA) of the nitrogen atoms, to a first approximation, may serve as a means for characterizing the proton acceptor capabilities of the different imino groups.

Keywords. Hydrogen bonding; 2-Hydroxybenzaldimine compounds; Vibrational spectra; HF calculations; B3LYP calculations.

Intramolekulare O–H· ·N-Wasserstoffbrückenbindungen in 2-Hydroxybenzaldiminverbindungen: Spektroskopische und quantenchemische Untersuchungen

Zusammenfassung. Intramolekulare Wasserstoffbrückenbindungen in einer Reihe von 2-Hydroxybenzaldiminverbindungen (Ph(OH)(CH=N–*R*); *R* = –NH(Ph), –OH, $-OCH_3$, $-NH_2$, –Ph, –CHO, –H, $-CH_3$, $-(CO)CH_3$) werden mit Hilfe von spektroskopischen und quantenchemischen Daten charakterisiert und untersucht. Optimierte Geometrien und Schwingungsspektren wurden mittels *ab initio* (HF/6-31G(d,p)) und DFT Methoden (B3LYP/6-31G(d,p)) berechnet, NMR-Spektren mittels GIAO-BLYP/6-311++G(d,p)//B3LYP/6-31G(d,p). Die berechneten Frequenzen (ν(OH) und ν(CN)) sowie die chemischen Verschiebungen (δ(OH)) stimmen mit den entsprechenden experimentellen Daten gut überein. Die innere Konsistenz der Rechnungen wird durch verschiedene Korrelationen zwischen Bindungsabständen, Schwingungsfrequenzen, chemischen Verschiebungen und Wasserstoffbrückenbindungsenergien demonstriert. Insbesondere findet man eine nahezu perfekte Relation zwischen den Bindungsabständen *r*(O–H), die als Maß für die Stärken der Wasserstoffbrückenbindungen dienen, und den Wasserstoffbrückenbindungsabständen *r*(H· ·N) und *r*(O· ·N). Es wird gezeigt, daß die Protonenakzeptorfähigkeiten der unterschiedlichen Iminogruppen in erster Näherung durch elektrostatische Potentiale und verschiedene Partialladungen (*Mulliken*, CHELPG, MK und NPA) der Stickstoffatome charakterisiert werden können.

Introduction

Understanding the factors that govern the strengths of hydrogen bond (H-bond) interactions seems to be a rather simple and, at the same time, a very complicated task. Given a distinct proton donor group, X–H, and a series of similar proton acceptor groups, Y, from a simplified point of view the sequence of H-bond strengths should be directly determined by the proton acceptor capabilities of the acceptor groups, leading to the simple relationship: the larger the proton acceptor capabilities, the shorter the $r(\mathrm{H}\cdot\cdot Y)$ and $r(X\cdot\cdot Y)$ H-bond distances, and the stronger the H-bonds. As is evident, such a simple "proton acceptor capability – H-bond distance – H-bond strength" relationship can, if ever, only apply, if the actual H-bond geometries are exclusively determined by the H-bond interaction. More often, however, actual H-bond geometries and the resulting H-bond strengths are more or less strongly influenced by other energetic or geometric factors. Consequently, the H-bond strength sequence of a given series of compounds, as determined for instance from $\nu(X\mathrm{H})$ stretching frequencies or from $r(X\mathrm{H})$ bond distances, does not necessarily (and, indeed, in most instances does not) reflect the proton acceptor capabilities of the acceptor groups. Another, maybe even more pertinent question concerns the term "proton acceptor capability", which is rather an intuitive than a well-defined physical quantity. How could these "proton acceptor capabilities" be quantified without making direct reference to H-bonded species, or how could these "proton acceptor capabilities" be predicted from other properties of the acceptor groups that can independently be measured or calculated?

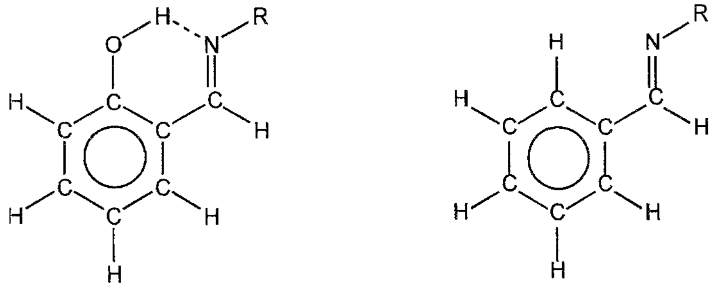
In a recent spectroscopic and quantum chemical study on intramolecular O–H··O type H-bonds in a series of 2-hydroxybenzoyl compounds [1] we have attempted to shed some new light on these issues. For these compounds, we experimentally observe largely differing H-bond strengths, but it has previously not been possible to give a consistent interpretation of the H-bond strength sequence based on purely experimental data [2]. Concerning geometric aspects of the H-bonds in these compounds, two points might be noted. First, the H-bond geometries are largely predetermined by the rigid framework of the heavy atoms, leaving only minor room for variations of the H-bond distances. Second, as a result of steric interferences, 2-hydroxybenzoyl compounds partially display more or less significant deviations from planarity, which affects the H-bond distances as well as the H-bond strengths. In Ref. [1] it has been shown that a reasonable and consistent understanding of the H-bond sequence can be obtained in terms of two quantities: (*i*) the H-bond distances ($r(\mathrm{H}\cdots\mathrm{O})$) and (*ii*) the partial charges of the oxygen acceptors $Q(\mathrm{O})$ which seem to be a proper vehicle to approximately account for the differences between the proton acceptor capabilities of the carbonyl groups.

The present paper deals with similar spectroscopic and quantum chemical investigations on intramolecular O–H··N type H-bonds in series of 2-hydroxybenzaldimine compounds. The main goal of this study was to examine whether the findings and conclusions of Ref. [1] are similarly valid for the compound family considered here. The paper is organized as follows: First, various IR and NMR spectroscopic data as well as calculated geometric, energetic, and spectroscopic data of 2-hydroxybenzaldimine compounds and of corresponding simple benzaldimine compounds are reported that are relevant for an experimental and a theoretical characterization of the H-bonds and the H-bond strengths. Second, in order to get evidence about the relevance and about the internal consistency of the computations, corresponding experimental and theoretical data are compared, and correlations between theoretical quantities are inspected that should be systematically related to each other. Subsequently, we focus on the correlation between r(OH), which serve as a measure of the H-bond strengths, and r(O··N) as well as on correlations between r(OH) and various kinds of Q(N) – *Mulliken* [3], CHELPG (charges from electrostatic potentials [4], as modified in Ref. [5]), MK (*Merz-Kollmann* [6, 7]), and NPA (Natural Population Analysis [8]) – which may be useful for a characterization of the proton acceptor capabilities. Throughout, the results obtained for the 2-hydroxybenzaldimine compound series are compared with those obtained for the 2-hydroxybenzoyl compound series.

Materials and Methods

The compounds included in this study are listed in Table 1, along with the subsequently used compound numbering. Short cut notations **HB*n*** and **B*n*** (n = compound number) will be used to designate 2-hydroxybenzaldimine and benzaldimine compounds, respectively.

Table 1. Compounds and their numbering



HB **B**

	R
1	H
2	CH_3^a
3	C_6H_5
4	CHO
5	(CO)CH_3
6	NH_2
7	NHC_6H_5
8	OH
9	OCH_3

[a] Experimental data from the symmetric ethylendiamine compounds (R = $-CH_2CH_2-$)

IR spectra of CCl_4 and $CDCl_3$ solutions were measured with a Perkin-Elmer 1740 FTIR spectrometer. The absence of intermolecular association effects was confirmed by appropriate dilution experiments. NMR spectra of $CDCl_3$ solutions were measured with a Bruker AM 400 WB NMR spectrometer. The quantum chemical calculations were performed with the Gaussian92 [9] and the Gaussian94 [10] programs. Optimized geometries, partial charges, and vibrational spectroscopic data were computed at the HF/6-31G(d,p) level and at the B3LYP/6-31G(d,p) level of theory.. GIAO [11–13] calculations of nuclear shieldings were performed at the BLYP/6-311++G(d,p) level of theory using the B3LYP/6-31G(d,p) optimized geometries. In some instances (one geometry optimization and three frequency calculations), the calculations failed due to the limitations of the available computer facilities.

Results and Discussion

Selected IR and NMR spectroscopic data of six 2-hydroxybenzaldimine and benzaldimine compounds are summarized in Table 2 (for three out of the nine compounds covered in Table 1, no experimental data are available). Correlations between ν(OD) and ν(OH) as well as between δ(OH) and ν(OH) are shown in Fig. 1. The linear correlation coefficients are $\bar{r} = 0.98$ for ν(OD) *vs.* ν(OH) and $\bar{r} = 0.99$ for δ(OH) *vs.* ν(OH). From both ν(OH) and δ(OH), the parameters which are most commonly used for a spectroscopic characterization of H-bond strengths, almost identical experimental H-bond strength sequences are obtained.

Selected calculated geometric, energetic, and vibrational spectroscopic data are compiled in Table 3. In order to inspect the internal consistency of the calculations, some correlations are shown in Fig. 2. Expectedly, the results are rather similar to those obtained recently for 2-hydroxybenzoyl and benzoyl compounds [1]. Because the ν(OH) frequencies of the 2-hydroxybenzaldimine compounds correspond to almost pure O–H stretching modes (>97% at the HF/6-31G(d,p) level and >85% at the B3LYP/6-31G(d,p) level), the correlation between r(OH) and ν(OH) (Fig. 2a) is almost perfect ($\bar{r} = 1.00$ at both the HF and the B3LYP level). Since ν(OH) are not available to us in all instances, r(OH) will subsequently be used for a theoretical characterization of the H-bond strengths. For r(OH) *vs.* δ(OH) (Fig. 2b), we also obtain a very satisfying correlation ($\bar{r} = 0.99$). Not unexpected, frequency *vs.* distance correlations involving the imino groups

Table 2. Experimental ν(OH), ν(OD), and ν(CN) stretching frequencies[a] (cm^{-1}), and δ(OH) proton chemical shifts[b] (ppm) of 2-hydroxybenzaldimine (**HB**) and benzaldimine (**B**) compounds

	HB				**B**
	ν(OH)	ν(OD)	ν(CN)	δ(OH)	ν(CN)
2	2900	2150	1635	13.25	1648
3	2909	2180	1620	13.30	1630
6	3100	2327	1625	11.10	1603
7	3100	2360	1602	10.90	1597
8	3220	2400	1620	10.15	1628
9	3200	2395	1615	9.85	1612

[a] From CCl_4 solutions; [b] from $CDCl_3$ solutions

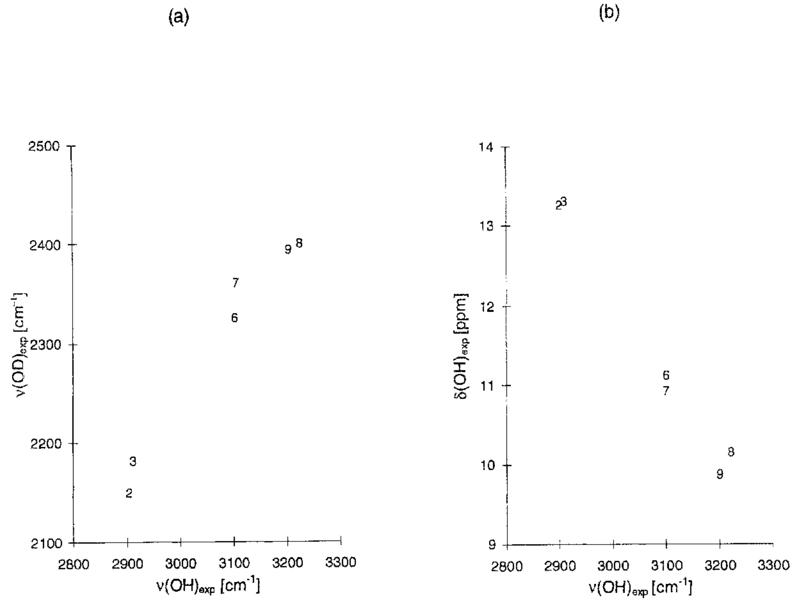


Fig. 1. Plots of experimental (a) ν(OD) *vs.* ν(OH) frequencies and of (b) δ(OH) proton shifts *vs.* ν(OH) frequencies

(Figs. 2c, d) are slightly worse, because the "ν(CN) frequencies" correspond to more or less strongly coupled vibrations with largely varying contributions from the C=N stretching mode (39–77% and 35–68% for the 2-hydroxybenzaldimine compounds, and 70–81% and 51–79% for the benzaldimine compounds, at the HF and the B3LYP level, respectively).

In Fig. 3a, the calculated r(OH) values are plotted against the experimental ν(OH) data, thus correlating theoretical with experimental H-bond strengths of the 2-hydroxybenzaldimine compounds. As far as the main trends are concerned, the experimentally observed H-bond strength sequence is fairly well reproduced at both computational levels. Linear correlation coefficients of $\bar{r} = 0.98$ and $\bar{r} = 0.97$ are obtained at the HF and the B3LYP level of theory, respectively. To a good approximation, the compounds may be divided into two subgroups: **HB1–HB5** (R = H or C≡), which display the stronger bonds, and **HB6–HB9** (R = N= or O–), which display the weaker H-bonds. Figure 3a also shows the well-known systematic underestimation of H-bond interactions at the HF level of theory which results in rather large OH frequencies (and, correspondingly, in rather small bond distances) and a rather small ν(OH) frequency range when compared with experimental data. In contrast, the B3LYP description of H-bond interactions yields frequencies and bond distances as well as corresponding frequency and distance ranges that are in reasonable good agreement with experiment. To date, B3LYP calculations seem to be the best choice for theoretical studies on H-bonds, not least because they represent a most reasonable trade-off between accuracy and cost.

In contrast to intermolecular H-bonds, for intramolecular H-bonds the definition and evaluation of H-bond energies is still a question of ongoing discussion. H-bond energies are usually calculated as differences between the

Table 3. Selected calculated data[a] of 2-hydroxybenzaldimine (**HB**) and benzaldimine (**B**) compounds

	HB										**B**	
	ν(OH)[b]	A(OH)[c]	ν(OD)[b]	ν(CN)[b]	δ(OH)[b]	r(OH)[e]	r(O··N)[e]	r(H··N)[e]	r(CN)[e]	ΔE[f]	ν(CN)[b]	r(CN)[e]
1	3914	278	2852	1883		0.9553	2.6980	1.8753	1.2605	60.65	1902	1.2541
	3133	335	2289	1696	13.23	0.9996	2.6018	1.7011	1.2884	74.56	1714	1.2776
2	3911	316	2849	1923		0.9553	2.7101	1.8828	1.2562	58.55	1941	1.2500
	3134	394	2286	1714	12.90	0.9994	2.6164	1.7124	1.2850	72.20	1739	1.2739
3	3927	379	2861	1887		0.9546	2.7122	1.8890	1.2620	56.19	1909	1.2551
					13.18	0.9980	2.6209	1.7205	1.2932	69.58	1705	1.2809
4	3924	275	2859	1849		0.9552	2.7059	1.8941	1.2710	58.55	1874	1.2618
	3138	309	2291	1657	13.33	0.9997	2.6109	1.7174	1.3024	72.73	1678	1.2871
5	3899	317	2840	1812		0.9559	2.6970	1.8709	1.2743	58.02	1851	1.2630
	3041	410	2224	1663	13.97	1.0043	2.5947	1.6924	1.2997	78.77	1681	1.2842
6	4001	233	2914	1924		0.9512	2.7300	1.9170	1.2566	48.83	1923	1.2533
	3370	271	2456	1697	10.77	0.9872	2.6532	1.7740	1.2892	63.54	1701	1.2837
7	4038	277	2941	1907		0.9495	2.7414	1.9336	1.2588	40.96	1905	1.2559
												1.2890
8	4026	219	2933	1918		0.9503	2.7309	1.9350	1.2560	49.10	1920	1.2530
	3427	242	2497	1682	10.03	0.9847	2.6553	1.7943	1.2870	54.09	1687	1.2819
9	4005	257	2917	1901		0.9512	2.7165	1.9161	1.2583	50.10	1902	1.2555
	3376	306	2460	1667	10.67	0.9871	2.6407	1.7723	1.2900	59.07	1673	1.2847

[a] First row, RHF/6-31G(d,p) data; second row, B3LYP/6-31G(d,p) data; [b] vibrational frequencies in cm^{-1}; [c] IR intensities in km/mol; [d] proton shifts in ppm from GIAO-BLYP/6-311++G(d,p)//B3LYP/6-31G(d,p) calculations; [e] bond distances in Å; [f] "H-bond energies" in kJ/mol (for definition, see text)

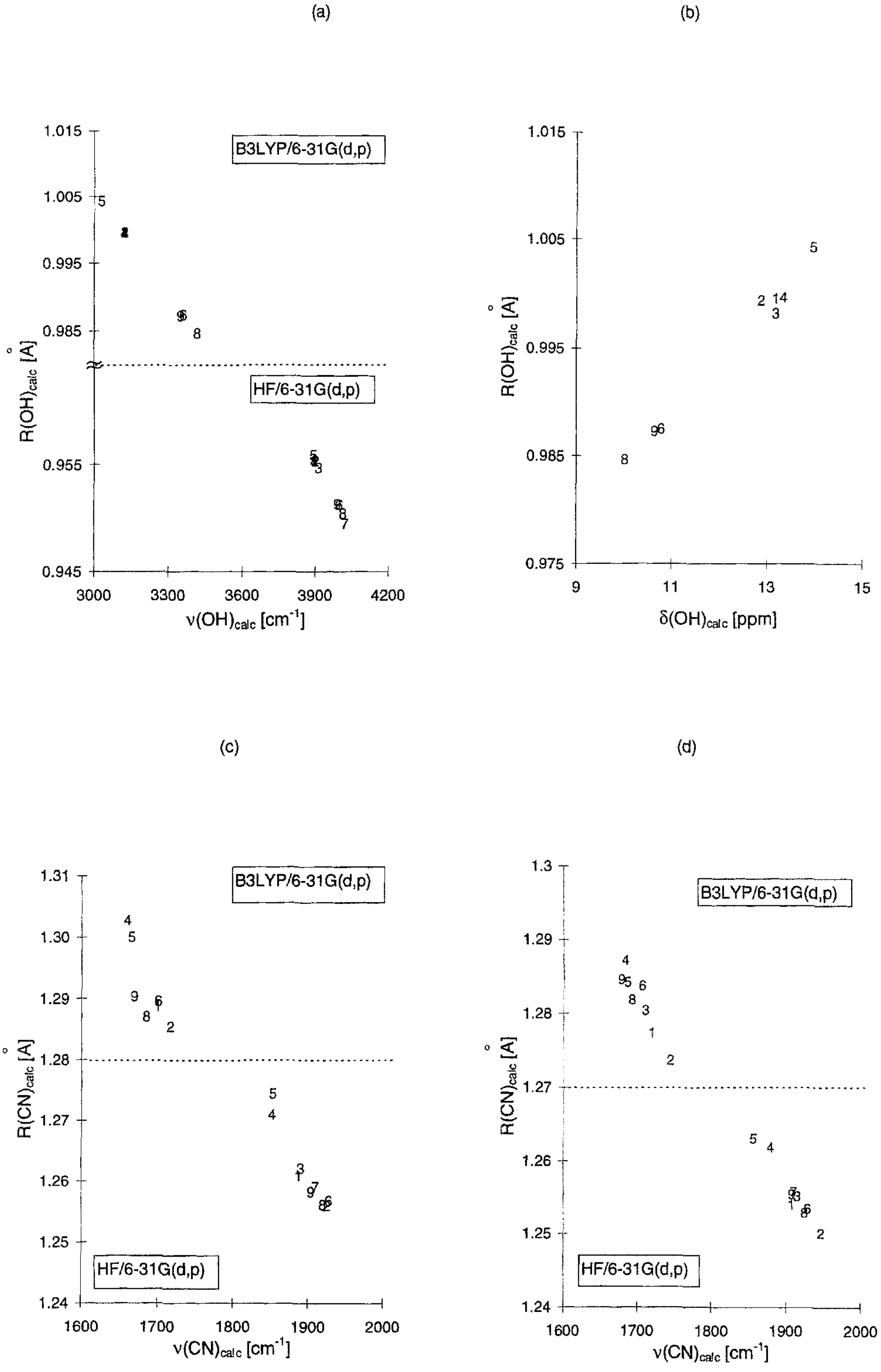


Fig. 2. Plots of calculated (a) r(OH) distances *vs.* ν(OH) frequencies, (b) r(OH) distances *vs.* δ(OH) chemical shifts, (c) r(CN) distances *vs.* ν(CN) frequencies of 2-hydroxybenzaldimine compounds, and (d) r(CN) distances *vs.* ν(CN) frequencies of benzaldimine compounds

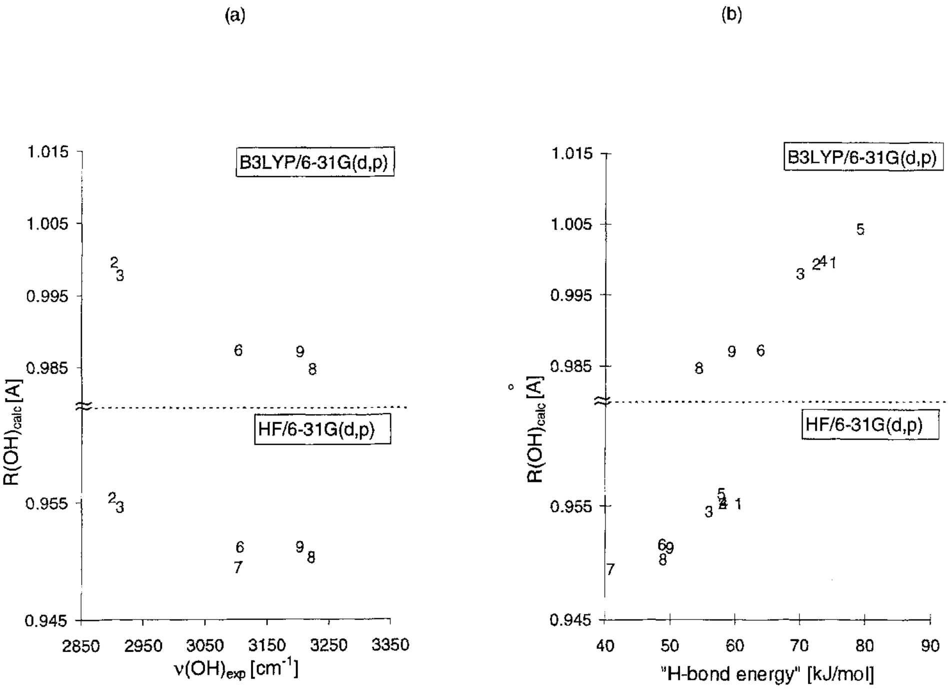


Fig. 3. Plots of (a) calculated r(OH) distances *vs.* experimental ν(OH) frequencies, and of (b) calculated r(OH) distances *vs.* "H-bond energies" (see text)

energies of a bonded and a non-bonded species, $\Delta E = E_{\text{ref}} - E_{\text{bonded}}$, and there exist several alternatives to define appropriate non-bonded reference states. As it has recently been shown [1], the rotameric species with the O–H group rotated by 180° around the C–O bond without subsequent geometry optimization seem to be the best choice. The sequences of the H-bond energies defined in this way agree well with other quantities that are usually used to assess something like H-bond strengths. In Fig. 3b this is shown for the 2-hydroxybenzaldimine compounds by a plot of r(OH) against these H-bond energies. The correlation is quite good; the linear correlation coefficients are $\bar{r} = 0.93$ and 0.99 at the HF and the B3LYP level of theory, respectively.

In Fig. 4, the bond distances of the 2-hydroxybenzaldimine compounds, again serving as a measure for the strengths of the H-bond interactions, are plotted against r(H··N) ($\bar{r} = 0.97$ and 0.99) and r(O··N) ($\bar{r} = 0.93$ and 0.97). In particular, the r(OH) *vs.* r(H··N) correlation is almost perfect and, compared to the corresponding correlations that have recently been obtained for the 2-hydroxybenzoyl compounds [1], we find a much more rigorous relationship between H-bond strengths and hydrogen bond distances. The differences between the two compound series are obviously due to geometric reasons. Whereas the 2-hydroxybenzaldimine compounds considered here are planar throughout, as a result of steric interferences the 2-hydroxybenzoyl compounds partly display significant deviations from planarity (*i.e.* large CCC=O torsion angles) which

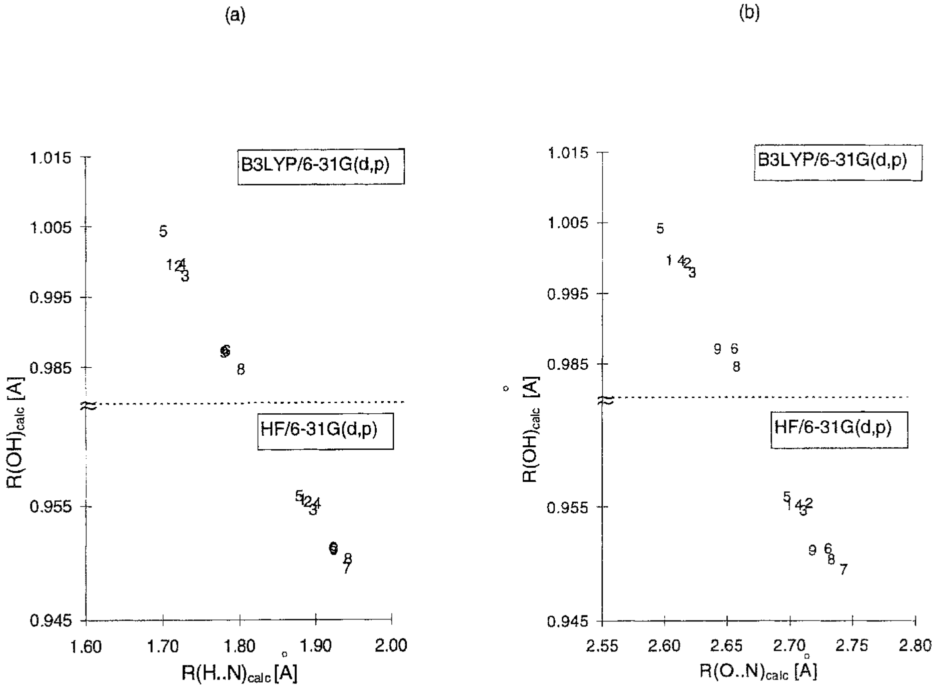


Fig. 4. Plots of calculated r(OH) distances *vs.* (a) r(H··N) and (a) r(O··N) H-bond distances

affect the H-bond distances and, hence, destroy the "natural" relationship between H-bond distances and H-bond strengths.

In Ref. [1], *Mulliken* partial charges of the carbonyl oxygen atoms have been used to characterize the proton acceptor capabilities of different carbonyl groups. In the present study, besides *Mulliken* partial charges we have also calculated several other quantities that might be useful for a characterization of the proton acceptor capabilities of different imino groups: CHELPG [4, 5] MK [6, 7], and NPA [8] partial charges as well as electrostatic potentials (Table 4). As shown in Fig. 5 by plots against r(OH) of the 2-hydroxybenzaldimine compounds and as is also indicated by the corresponding correlation coefficients given in Table 4, the results are qualitatively largely similar for all these quantities, and it is hardly possible to objectively give preference to one or the other of them. In all instances, the two subgroups **HB1**–**HB5** and **HB6**–**HB9** are safely distinguished and, moreover, the differences are quite reasonable in that the more electronegative N-substituents, nitrogen and oxygen, reduce the electron densities and weaken the H-bond strengths. On the other hand, the nitrogen partial charges and electrostatic potentials fail to reasonably reproduce the H-bond strengths within the two subgroups, which clearly shows the limitations of approximating proton acceptor capabilities by these simple quantities. This is, of course, not unexpected, since H-bond energies contain contributions from both coulomb interaction and electron delocalization [14, 15] and it is just the first term for which the partial charges could mainly account.

Table 4. Calculated[a] nitrogen partial charges (Q(N), e.u.) and electrostatic potentials (E_p(N), e.u.) of benzaldimine compounds

	Q(N)				E_p(N)
	Mulliken	CHELPG	MK	NPA	
1	−0.576	−0.724	−0.709	−0.691	−18.364
	−0.497	−0.637	−0.630	−0.641	−18.375
2	−0.498	−0.492	−0.411	−0.494	−18.358
	−0.393	−0.438	−0.369	−0.433	−18.368
3	−0.557	−0.582	−0.571	−0.508	−18.350
	−0.479	−0.500	−0.500	−0.440	−18.361
4	−0.551	−0.581	−0.571	−0.599	−18.341
	−0.419	−0.505	−0.498	−0.512	−18.353
5	−0.611	−0.722	−0.722	−0.651	−18.355
	−0.452	−0.579	−0.588	−0.533	−18.361
6	−0.329	−0.192	−0.155	−0.269	−18.317
	−0.288	−0.185	−0.160	−0.246	−18.314
7	−0.277	−0.166	−0.169	−0.258	−18.290
	−0.238	−0.216	−0.226	−0.242	−18.318
8	−0.126	−0.167	−0.139	−0.095	−18.283
	−0.142	−0.163	−0.153	−0.085	−18.303
9	−0.115	−0.278	−0.290	−0.105	−18.290
	−0.149	−0.257	−0.283	−0.100	−18.312
$\bar{r}^{b}$	0.913	0.952	0.915	0.916	0.962
	0.922	0.940	0.902	0.924	0.942

[a] First row, RHF/6-31G(d,p) data; second row, B3LYP/6-31G(d,p) data; [b] correlation coefficients for r(OH) *vs.* Q(N) or E_p

Conclusions

The results obtained for the O–H···N H-bonds in the 2-hydroxybenzaldimine compounds under investigation may be summarized as follows:

(*i*) The experimental H-bond strength sequences as observed by vibrational frequencies (ν(OH)) or chemical shifts (δ(OH)) are reasonably well reproduced by frequencies or bond distances at both the HF/6-31G(d,p) and the B3LYP/6-31G(d,p) level of theory.

(*ii*) To a good approximation, the compounds may be divided into two subgroups: **HB1–HB5** with hydrogen or carbon substituents at the imino nitrogens, which display the stronger bonds, and **HB6–HB9** with nitrogen or oxygen substituents at the imino nitrogens, which display the weaker H-bonds.

(*iii*) The r(OH) *vs.* r(H···N) and r(OH) *vs.* r(O···N) correlations are almost perfect. Obviously, the simple "H-bond distance – H-bond strength" relationship applies very well, despite the rigid heavy atom framework that largely predetermined the H-bond geometries.

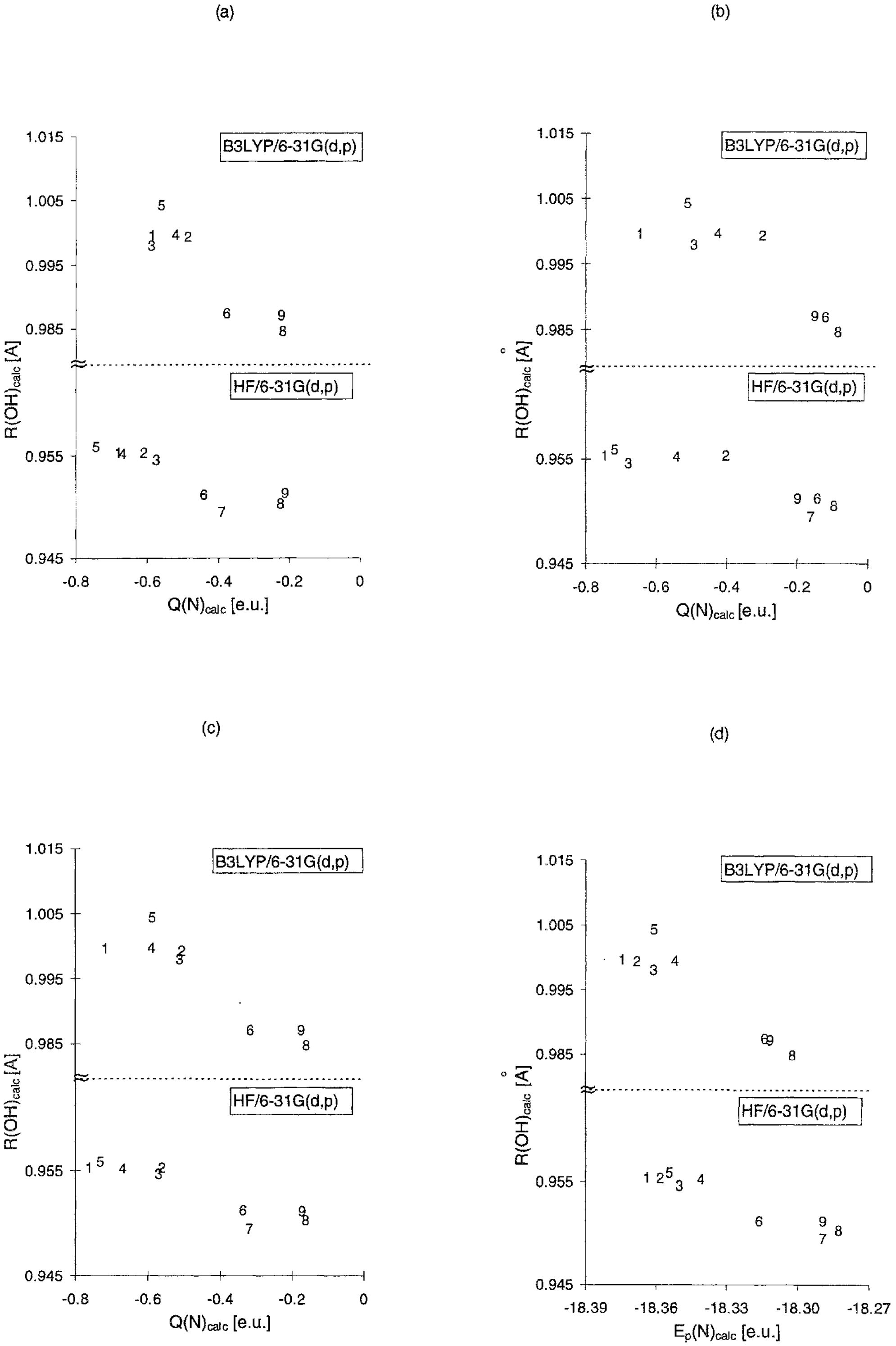


Fig. 5. Plots of calculated *r*(OH) bond distances of 2-hydroxybenzaldimine compounds *vs.* calculated (a) *Mulliken*, (b) CHELPG, and (c) NPA partial charges and (d) electrostatic potentials of benzaldimine compounds

(*iv*) The two subgroups, **HB1–HB5** and **HB5–HB9**, are safely distinguished by partial charges or electrostatic potentials of the imino nitrogens, and the differences are quite reasonable in that the more electronegative N-substituents, nitrogen and oxygen, weaken the electron densities as well as the H-bond strengths. On the other hand, partial charges and electrostatic potentials are not appropriate to reliably predict more details of the sequence of the H-bond strengths and of the proton acceptor capabilities.

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