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Theoretical Study of Strong Hydrogen Bonds between Neutral Molecules: The Case of Amine Oxides and Phosphine Oxides as Hydrogen Bond Acceptors

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A theoretical study of the ability of amine oxides and phosphine oxides as hydrogen bond (HB) acceptors has been carried out using ammonium oxide, trimethylamine oxide, and phosphine oxide as model systems. The analysis of the energetic results indicate that only small spatial preferences are observed in the HB interaction. The value of the interaction energies are in several cases within the range of strong HB (>12 kcal/mol), and in complexes between amine oxides and strong acids in the gas phase, a spontaneous proton transfer is obtained. A logarithmic correlation between the electron density at the HB critical points and the HB distance that is able to fit not only calculated data but also experimental ones has been obtained. Finally, a linear relationship has been found between the number of HBs and the ^{31}P NMR shielding in the $H_3PO\cdots(HF)_n$ series, in good agreement with experimental reports.

Introduction

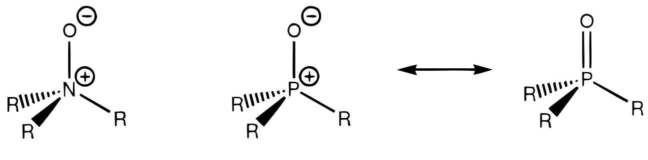
Hydrogen bonds (HBs) have been classified based on their interaction energies as weak (interaction energy between 2 and 12 kcal/mol), strong (12−24 kcal/mol), and very strong (>24 kcal/mol).[1] The importance of strong and very strong HB, also known as low-barrier hydrogen bonds, in enzymatic catalysis has been a subject of discussion over the past few years.[2]

Strong and very strong HBs are found in charged complexes, especially between bases and their conjugate acids or vice versa. Few strong HBs have been described between neutral systems as are the cases of β-diketones,[1] dimers of phosphinic acids,[3] and zwiterionic neutral proton sponges.[4]

One way to obtain a stronger neutral HB acceptor is to generate zwiterionic species with a formal negative charge in the acceptor atom. This approach has been used theoretically by Platts et al. to generate carbon atoms as strong HB acceptors.[5,6] If the atom with the formal negative charge is in general a good HB acceptor, such as nitrogen or oxygen, the zwiterionic compounds would be excellent candidates to generate strong HBs. This is the case for the amine oxides (**1** in Figure 1) where a formal negative charge is present on the oxygen and a positive charge occurs on the nitrogen. If the nitrogen is substituted by a phosphorus, the corresponding phosphine oxides (**2**) can be written as a zwiterionic form (**2a**) or a neutral one (**2b**) by formation of a pπ−dπ orbital.[7]

Derivatives of amine and phosphine oxides are important in the field of HBs. Thus, for example, pyridine *N*-oxide is one of the standard reference compounds for the study of HBs in solution[8−10] and triphenylphosphine oxide has been shown to be a very good proton acceptor in solution[11,12] and has also been proposed as a crystallization aid.[13−15]

In the present article, a series of HB complexes of model amine oxides (**1**, R = H and Me) and phosphine oxides (**2**, R = H) has been studied with several ab initio methods that include B3LYP/6-31G*, B3LYP/6-311++G**, and MP2/6-311++G** levels of theory. The calculated geometrical, energetic, and electronic characteristics of these complexes have been analyzed. Finally, the effect of the number of HB on the NMR shielding of these compounds has been calculated and compared to experimental data.



1 2a 2b

Figure 1. Schematic representation of the canonical form of amine oxides (**1**) and phosphine oxides (**2**).

a b

Figure 2. Schematic representation of the eclipsed (a) and staggered (b) HB interactions.

Methods

The geometries of the monomers and the complexes have been fully optimized with the program Gaussian 94[16] using the standard 6-31G*[17] and 6-311++G**[18] basis sets with the hybrid DFT-HF, B3LYP,[19,20] and second-order Moller−Plesset [21] (MP2) perturbation methods.

In all the cases, the steady-state nature (minimum or transition state) of the optimized complexes at the B3LYP/6-31G* level has been confirmed by calculating the corresponding frequencies at the same computational level. The interaction energies, E_I(AB), have been calculated as the difference between the

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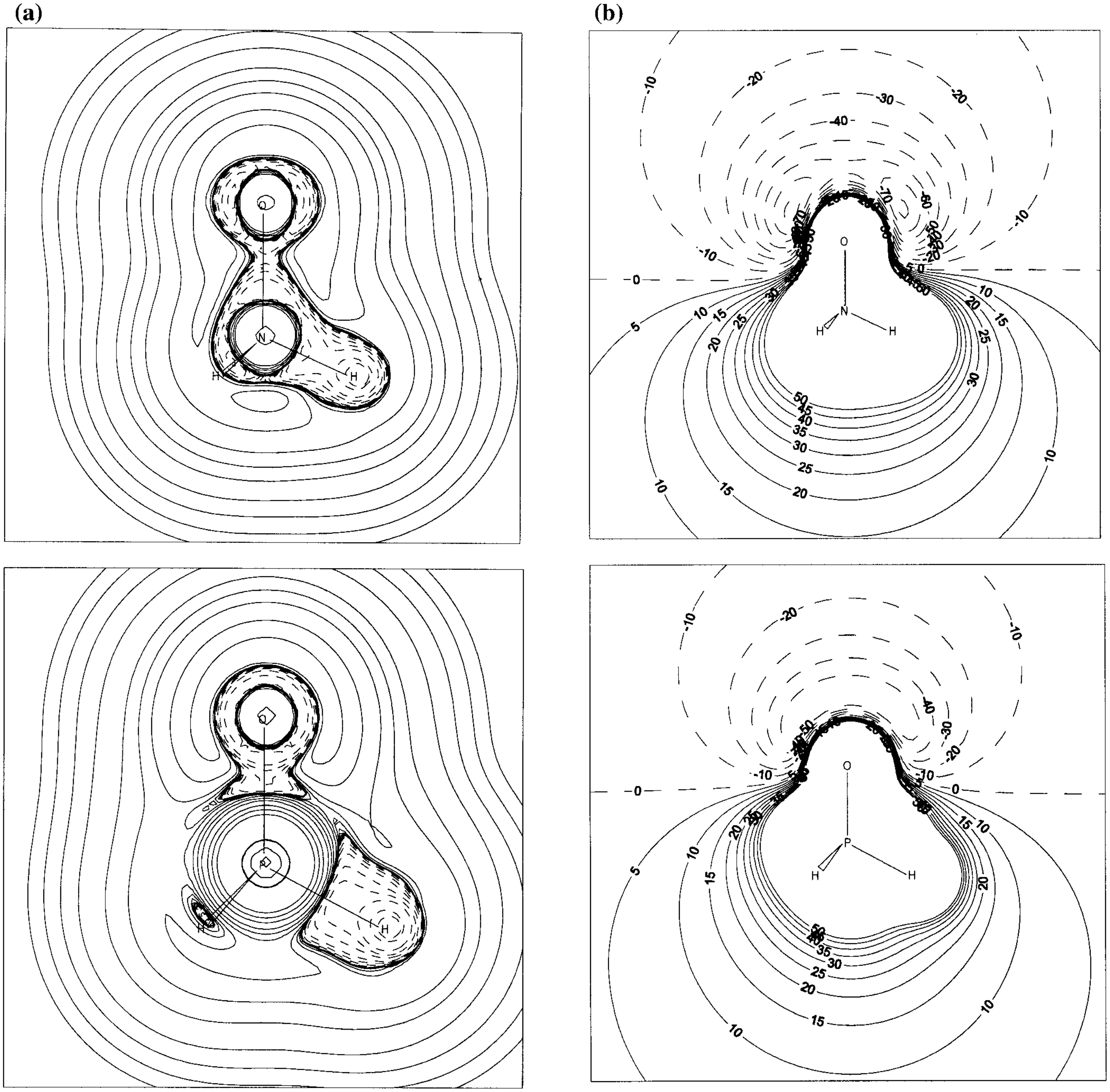

Figure 3. (a) Laplacian (e/au^5) and (b) molecular electrostatic maps (kcal/mol) of H_3NO and H_3PO. Solid lines indicate positive values, and dashed lines indicate negative ones.

energy of the complex and the sum of the energy of the monomers (eq 1).

$$E_I(AB) = E(AB)_{AB} - [E(A)_A + E(B)_B] \qquad (1)$$

where $E(AB)_{AB}$ represents the energy of the complex and $E(A)_A$ the energy of the isolated monomer A in its minimum configuration calculated with its corresponding basis set.

In addition, a corrected interaction energy, E_{CORR}, of the inherent basis set superposition error (BSSE) has been evaluated. The BSSE have been calculated using the Boys−Bernardi counterpoise technique[22] and eq 2.

$$E_{BSSE}(AB) = E(A)_A - E(A)_{AB} + E(B)_B - E(B)_{AB} \qquad (2)$$

where $E(A)_{AB}$ represents the energy calculated for monomer A using their geometry in the complex and the complete set of basis functions used to described the dimer.

The topological properties of the electronic charge density have been characterized using the atoms in molecules methodology[23] (AIM) with the AIMPAC program package.[24]

The nuclear magnetic resonance (NMR) spectroscopic properties of the isolated molecules and complexes have been calculated using the GIAO perturbation method[25] as implemented in the Gaussian-94 program.

Discussion

Geometry and Conformation. The selected HB acceptors (Figure 1) present the possibility of forming the HB in two extreme dispositions, eclipsed or staggered to one of the hydrogens of H_3NO and H_3PO or the methyl group in Me_3NO

TABLE 1: Relative Energy (kcal/mol) between the Eclipsed and Staggered Interactions[a]

	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**
$H_3PO\cdots HCl$	−0.01	−0.10	−0.09
$Me_3NO\cdots HCl$	5.78	4.86	
$H_3NO\cdots HF$	−2.78	−1.20	−0.99
$H_3PO\cdots HF$	1.19	−0.10	−0.14
$Me_3NO\cdots HF$	4.57	1.64	
$H_3NO\cdots HCN$	−1.61	−0.58	−0.92
$H_3PO\cdots HCN$	0.00	−0.06	−0.09
$Me_3NO\cdots HCN$	0.54	0.02	
$H_3NO\cdots HCCH$	−2.16	−1.40	−1.34
$H_3PO\cdots HCCH$	0.01	−0.08	−0.12
$Me_3NO\cdots HCCH$	0.94	0.05	
$H_3NO\cdots HCH_3$	−0.83	−0.62	−0.55
$H_3PO\cdots HCH_3$	0.00	−0.03	−0.04
$Me_3NO\cdots HCH_3$	0.39	0.02	

[a] Negative values indicate that the eclipsed configurations are more stable.

(Figure 2). To analyze, a priori, these two possibilities, a study of the electron density Laplacian and molecular electrostatic potentials (MEPs) of the isolated monomers has been carried out. The position of the lone pairs has been detected in the Laplacian maps by the presence of minimum values and the most favorable HB disposition has been associated with the negative regions of the MEP maps. The numerical analysis of the Laplacian indicate the presence of three minima around the oxygen and eclipsed to the hydrogen with values −5.16, −3.69, and −4.96 e/au^5 for H_3NO, H_3PO, and Me_3NO, respectively. In the same way, the MEP of these molecules present three minimum values of −83, −59, and −83 kcal/mol in a similar disposition around the oxygen atom. Similar conclusions have been described in the literature based on Boys' localized orbitals studies.[26]

However, a view of the corresponding maps (Figure 3) indicates that the minima, in both properties, are connected by a ring of similar values around the oxygen. Thus, small secondary interaction could favor the disposition of the interacting systems around the oxygen atoms in one position or another. For these reasons, the two possible dispositions (parts a and b in Figure 2) have been calculated for all the complexes and their relative energies are gathered in Table 1.

These results indicate the preference of the staggered interaction in the complexes of Me_3NO with HCl and HF, the absence of preference in the complexes with H_3PO, and a very small preference for the eclipsed disposition in the complexes with H_3NO. In any case, the relative energies are very small in almost all the cases, and the preferences in the Me_3NO complexes could be explained due to steric interactions with the methyl group and in the H_3NO complexes, with a possible secondary interaction between its eclipsed hydrogen atom and the negative part of the proton donor. The preference trends diminish as the HB acidity of the donor decreases (HF > HCN > HCCH > HCH_3).

The results obtained with the B3LYP/6-311++G** and MP2/6-311++G** methods are very similar, always predicting the same most favorable interaction. Although in some cases the B3LYP/6-31G* method gives a different preference interaction, the energy differences are very small. The analysis of the frequencies indicates that the most stable configuration of those two studied corresponds to a minimum, while the higher in energy is a transition state (one negative frequency with a small value) that connects two of the three symmetrical minima.

A selection of the geometrical parameters of the HB complexes are gathered in Table 2. A comparison of the three methods used indicates that the results are very similar, especially for the B3LYP/6-311++G** and MP2/6-311++G** ones. The results obtained at the B3LYP/6-31G* level can be considered as an adequate starting point to calculate higher computational levels or to obtain an initial estimation of the problem at not very high computational cost. Similar conclusions have been reported recently in a systematic study of the applicability of the B3LYP method in the research of HBs.[27]

It is worth mentioning the small values of the $N{-}O\cdots H$ angles in the complexes of H_3NO (in all the cases under 100°, except for the staggered $H_3NO\cdots HCN$) that together with the $O\cdots HX$ angles around 150° locate closer the eclipsed hydrogen of H_3NO and the negative part of the HB donor as an indication of a secondary stabilizing interaction. The same analysis for the rest of the complexes indicates that the $N{-}O\cdots H$ angles are larger in the complexes with Me_3NO and almost constant with a value around 140° in the ones with H_3PO. Regarding the $O\cdots HX$ angle, the observed values are very close to the linearity in the complexes of Me_3NO and H_3PO.

Regarding the bond distances, it is observed that the shorter $O\cdots H$ between the two possible interactions (eclipsed and staggered) corresponds to the most stable configuration for each case and level of calculation.

An interesting case corresponds to the complexes with HCl. While in $H_3PO\cdots HCl$ a standard HB is obtained, in $Me_3NO\cdots HCl$ the proton is transferred to the oxygen, being the system better described as $Me_3NOH^+\cdots Cl^-$. Finally, the $H_3NO\cdots HCl$ complex suffers a spontaneous double proton transfer producing $H_2(OH)N\cdots HCl$ as shown in Figure 4. Several factors are important to explain this difference. First, the oxides of amines (H_3NO and Me_3NO) are very strong bases (at the MP2/6-311++G** level the protonation energies are −230 and −244 kcal/mol while the calculated protonation of ammonia at the same level is −213 kcal/mol[28]), which explains the proton transfer from an acid as strong as HCl in gas phase. Second, the relative stability of the ammonium oxide versus its isomer hydroxyl amine must be considered. At the MP2/6-311++G** level, the hydroxylamine is 28 kcal/mol more stable than the ammonium oxide, in good agreement with the experimental evidence that only oxides of tertiary amines are stable since they are unable to evolve to hydroxylamines as in the case of Me_3NO. Thus, in the $H_3NO\cdots HCl$ system, a proton transfer from the HCl to H_3NO generates the charged H_3NOH^+ that transfers one of the N−H to the chloride ions and generates the more stable isomer, H_2NOH (Figure 4). Finally, H_3PO is 24 kcal/mol less basic than H_3NO, and at the same time it is only 3.7 kcal/mol less stable than the isomer H_2POH, which explains its regular behavior as a HB acceptor.

Other complexes such as the H_3NO dimer spontaneously evolve to the H_2NOH dimer following a similar mechanism to the one shown for $H_3NO\cdots HCl$ (Figure 4).

In general, very short distances are encountered in the HB systems studied here between amine oxides (H_3NO and Me_3NO) and strong HB donors (HF and HCN). Thus, the complexes with HF provide heavy−heavy atom ($O\cdots F$) distances of 2.38, 2.43, and 2.60 Å for the $H_3NO\cdots HF$, $Me_3NO\cdots HF$, and $H_3PO\cdots HF$ systems. The value of this parameter in other strong HB is typically under 2.5 and 2.6 Å for $O\cdots O$ and $N\cdots N$ pairs,[29] respectively. The distances in the complexes with HCCH can be considered as short (∼2.0 Å) taking into account the poor ability of this molecules as an HB donor. Finally, the complexes with HCH_3 are within the limit of HB and van der Waals complexes.

TABLE 2: Selected Geometrical Parameters of the HB Systems Studied[a]

	staggered			eclipsed		
system	O···H distance (Å)	N−O···H angle (°)	O···H−X angle (°)	O···H distance (Å)	N−O···H angle (°)	O···H−X angle (°)
$H_3PO\cdots HCl$	1.757	126.3	173.3	1.745	124.4	172.2
	1.750	*140.2*	*175.6*	*1.743*	*137.3*	*174.5*
	1.781	**142.0**	**175.1**	**1.774**	**139.7**	**174.3**
$Me_3NO\cdots HCl$	1.066	104.2	170.1	1.115	109.8	179.7
	1.065	*105.1*	*170.2*	*1.118*	*110.9*	*179.5*
	1.073	**104.2**	**171.4**			
$H_3NO\cdots HF$	1.491	89.7	151.3	1.440	91.0	150.7
	1.466	*96.9*	*160.3*	*1.436*	*95.1*	*156.2*
	1.457	**95.8**	**160.1**	**1.434**	**94.9**	**157.6**
$H_3PO\cdots HF$	1.701	100.7	148.9	1.698	106.8	152.5
	1.645	*138.3*	*174.5*	*1.643*	*138.2*	*174.3*
	1.665	**139.7**	**175.5**	**1.662**	**138.3**	**175.4**
$Me_3NO\cdots HF$	1.466	101.3	164.0	1.521	110.2	169.5
	1.441	*106.5*	*170.2*	*1.490*	*115.5*	*176.0*
	1.454	**106.5**	**171.0**			
$H_3NO\cdots HCN$	1.744	100.4	165.4	1.679	95.8	155.6
	1.831	*125.2*	*176.2*	*1.742*	*99.8*	*154.4*
	1.849	**130.6**	**179.9**	**1.701**	**97.3**	**153.8**
$H_3PO\cdots HCN$	1.937	176.0	179.5	1.937	169.9	178.6
	1.917	*154.9*	*177.7*	*1.914*	*152.5*	*177.3*
	1.939	**152.1**	**178.8**	**1.933**	**149.3**	**178.8**
$Me_3NO\cdots HCN$	1.781	116.0	175.9	1.791	124.0	178.8
	1.811	*131.2*	*179.3*	*1.810*	*133.0*	*179.9*
	1.798	**120.3**	**175.3**			
$H_3NO\cdots HCCH$	1.927	90.6	151.7	1.856	91.9	149.0
	1.997	*96.6*	*151.1*	*1.942*	*94.0*	*146.4*
	2.025	**92.5**	**144.2**	**1.938**	**92.9**	**144.5**
$H_3PO\cdots HCCH$	2.083	175.3	179.1	2.084	171.9	178.1
	2.071	*148.6*	*176.4*	*2.067*	*145.8*	*175.9*
	2.081	**146.9**	**178.2**	**2.071**	**143.5**	**177.8**
$Me_3NO\cdots HCCH$	1.958	109.8	166.9	1.906	121.3	175.6
	1.995	*124.2*	*174.4*	*1.993*	*130.3*	*177.6*
	2.006	**111.0**	**163.5**			
$H_3NO\cdots HCH_3$	2.351	87.6	164.4	2.221	87.2	163.6
	2.516	*89.9*	*156.2*	*2.387*	*86.6*	*154.3*
	2.524	**80.8**	**149.9**	**2.379**	**85.0**	**152.4**
$H_3PO\cdots HCH_3$	2.460	163.9	179.5	2.455	174.3	179.6
	2.466	*145.9*	*176.5*	*2.454*	*142.6*	*177.3*
	2.400	**143.4**	**176.9**	**2.379**	**141.8**	**176.4**
$Me_3NO\cdots HCH_3$	2.424	114.1	178.4	2.422	124.9	178.1
	2.472	*144.2*	*176.9*	*2.449*	*144.1*	*177.9*
	2.382	**144.0**	**177.0**			

[a] In regular letters the B3LYP/6-31G* results, in italics the B3LYP/6-311++G** ones, and in bold the ones obtained at the MP2/6-311++G** level.

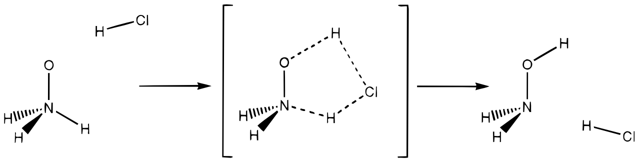

Figure 4. Schematic representation proposed for double proton transfer observed when the $H_3NO\cdots HCl$ complex is optimized.

Interaction Energies. The interaction energies, E_I and E_{I+BSSE}, of all the complexes in the different dispositions studied are gathered in Table 3. Since the BSSE correction is geometry dependent, the relative energies of the eclipsed versus the staggered disposition can change its sign, especially in those cases where the energy differences are small. However, since the complexes are not optimized on a BSSE corrected energy space, no conclusion can be drawn about the nature of each configuration when this correction is included.

The qualitative results obtained with the three methods studied here are similar. However, a quantitative analysis of the results shows some differences. One of the more striking cases corresponds to the staggered $Me_3NO\cdots HCl$ complex, which shows the largest BSSE (7.97 kcal/mol) at the MP2/6-311++G** level. This produces a reduction of its interaction enegies from $E_I = -22.35$ kcal/mol to $E_{I+BSSE} = -14.38$ kcal/mol. While the first value is similar to that obtained at the B3LYP/6-311++G** level, the second one is far different. This difference is probably due to the effect of the dissociation of the HCl molecule in the treatment of the BSSE.

Except in the case mentioned before, a general tendency is the largest values of the BSSE being at the B3LYP/6-31G*, followed by those obtained at the MP2/6-311++G** level, and the smallest corresponding to the B3LYP/6-311++G**. The inclusion of the BSSE correction diminish the error produce by the simpler method studied here (B3LYP/6-31G*) when compared to the MP2/6-311++G**.

For comparative purposes and in addition to the classification of the HB based on their interaction energy given in the Introduction, it is worth mentioning that the corresponding values of the water dimer calculated at the MP2/6-311++G** are $E_I = -6.08$ kcal/mol and $E_{I+BSSE} = -4.45$ kcal/mol (the experimental interaction energy is -5.4 ± 0.7 kcal/mol.)

TABLE 3: Calculated Interaction Energies, E_I and E_{I+BSSE} (in Italics), in kcal/mol

	B3LYP/ 6-31G*		B3LYP/ 6-311++G**		MP2/ 6-311++G**	
	eclip	stag	eclip	stag	eclip	stag
$H_3PO\cdots HCl$	−8.93	−8.92	−8.85	−8.75	−9.20	−9.11
	−7.48	*−7.39*	*−7.64*	*−7.64*	*−6.62*	*−6.63*
$Me_3NO\cdots HCl$	−20.89	−26.68	16.83	−21.69		−22.35
	−16.50	*−22.05*	*−15.62*	*−20.52*		*−14.38*
$H_3NO\cdots HF$	−28.11	−25.33	−20.89	−19.69	−20.78	−19.79
	−19.62	*−17.51*	*−19.77*	*−18.70*	*−16.97*	*−16.30*
$H_3PO\cdots HF$	−12.99	−14.18	−12.68	−12.58	−12.65	−12.51
	−9.12	*−9.02*	*−11.23*	*−11.25*	*−9.77*	*−9.79*
$Me_3NO\cdots HF$	−22.78	−27.35	−18.80	−20.44		−20.46
	−16.04	*−18.21*	*−17.83*	*−19.43*		*−16.92*
$H_3NO\cdots HCN$	−15.62	−14.01	−11.03	−10.45	−11.69	−10.77
	−11.66	*−10.48*	*−10.45*	*−9.86*	*−9.36*	*−9.18*
$H_3PO\cdots HCN$	−8.25	−8.26	−8.27	−8.21	−8.76	−8.66
	−6.61	*−6.62*	*−7.36*	*−7.39*	*−6.79*	*−6.85*
$Me_3NO\cdots HCN$	−12.88	−13.41	−10.77	−10.79		−11.60
	−10.22	*−11.72*	*−10.44*	*−10.45*		*−8.42*
$H_3NO\cdots HCCH$	−11.86	−9.70	−7.56	−6.16	−8.75	−7.41
	−7.84	*−6.04*	*−7.01*	*−5.77*	*−6.66*	*−5.73*
$H_3PO\cdots HCCH$	−4.60	−4.61	−4.55	−4.47	−5.44	−5.32
	−3.16	*−3.17*	*−3.63*	*−3.65*	*−3.54*	*−3.59*
$Me_3NO\cdots HCCH$	−7.69	−8.63	−5.74	−5.78		−7.49
	−5.16	*−5.33*	*−5.41*	*−5.61*		*−5.76*
$H_3NO\cdots HCH_3$	−4.54	−3.70	−1.61	−0.99	−2.63	−2.08
	−1.50	*−0.62*	*−1.35*	*−0.79*	*−1.52*	*−1.02*
$H_3PO\cdots HCH_3$	−1.34	−1.34	−0.76	−0.73	−1.57	−1.53
	−0.31	*−0.32*	*−0.39*	*−0.37*	*−0.53*	*−0.55*
$Me_3NO\cdots HCH_3$	−2.49	−2.88	−0.86	−0.89		−1.75
	−0.56	*−0.52*	*−0.75*	*−0.79*		*−1.09*

Thus, several of the complexes studied here are within the range of strong HB (>12 kcal/mol) (complexes of oxides of amines with HF and HCl) and others, such as $H_3PO\cdots HF$ and $H_3NO\cdots HCN$, are between medium and strong (∼10 kcal/mol). Except for the complexes where HCH_3 is involved, the rest are almost as strong as the water dimer. This is remarkable if one takes into account that an HB donor as weak as HCCH is considered.

An exponential relationship can be found between the interaction energies and the HB distances if the value corresponding to the $Me_3NO\cdots HCl$ complex is excluded.

$$E_I = -376.52 \exp(-2.02(\text{HB distance})) \qquad r = 0.98, \quad n = 22$$

A similar relationship has been recently described for the experimental kinetic and potential energy density as well as the calculated dissociation energy on HBs using the electron density on accurate X-ray diffraction experiments.[30]

Electron Density. The values of the electron density at the HB critical points, ρ_{bcp}, and the positive value of the Laplacian (Table 4) indicate that the present interactions correspond to strong HBs, except for the case of $Me_3NO\cdots HCl$ where, as previously indicated, the proton is transferred to the oxygen, which corresponds to a covalent bond. As expected, the values of ρ_{bcp} are larger than the ones observed in weak HB (for example, the value in the water dimer calculated at the MP2/6-311++G** level is 0.0231 e/au^3).

TABLE 4: Electron Density at the HB Critical Points, ρ_{bcp}, and its Corresponding Laplacian, $\nabla^2\rho_{bcp}$ Calculated at the MP2/6-311++G Level**

	staggered		eclipsed	
	ρ_{bcp}	$\nabla^2\rho_{bcp}$	ρ_{bcp}	$\nabla^2\rho_{bcp}$
$H_3PO\cdots HCl$	0.0336	0.1231	0.0343	0.1245
$Me_3NO\cdots HCl$	0.2525	−1.3950		
$H_3NO\cdots HF$	0.0857	0.1659	0.0912	0.1606
$H_3PO\cdots HF$	0.0412	0.1611	0.0412	0.1611
$Me_3NO\cdots HF$	0.0848	0.1611		
$H_3NO\cdots HCN$	0.0302	0.1083	0.0497	0.1329
$H_3PO\cdots HCN$	0.0224	0.0945	0.0228	0.0956
$Me_3NO\cdots HCN$	0.0366	0.1154		
$H_3NO\cdots HCCH$	0.0247	0.0804	0.0294	0.0964
$H_3PO\cdots HCCH$	0.0166	0.0686	0.0171	0.0704
$Me_3NO\cdots HCCH$	0.0241	0.0794		
$H_3NO\cdots HCH_3$	0.0099	0.0279	0.0125	0.0375
$H_3PO\cdots HCH_3$	0.0097	0.0330	0.0101	0.0347
$Me_3NO\cdots HCH_3$	0.0100	0.0331		

To confirm the possibility of a stabilizing secondary interaction in the eclipsed configurations, especially in those complexes with H_3NO, the corresponding electron density maps have been generated and explored. Only in the case of the $H_3NO\cdots HCCH$ (Figure 5a) a second bond critical point has been found that connects the eclipsed hydrogen of H_3NO with one of the carbons of HCCH. Even though in the $H_3NO\cdots HF$ (Figure 5b) and $H_3NO\cdots HCN$ complexes another bond path has not been found, it is clear that some kind of electrostatic interaction is established between these two opposite moieties, which contributes to the stability of the complexes.

The HB distance distribution of the cases studied here allows us to confirm the logarithmic correlation described by ourselves elsewhere[31] relating the logarithmic value of the electron density at the bond critical points with the interaction distance of a given pair of atoms simultaneously for HB and covalent bonds. Thus, long $O\cdots H$ distances are obtained in the HB complexes with HCH_3 and very short ones in the $Me_3NO\cdots HCl$, where the hydrogen is transferred to the oxygen. In order, to confirm the generality of the proposed equation, the corresponding values of the O−H covalent bonds of the hydroxylamine (H_2NOH) and hydroxylphospine (H_2POH) have been included. In addition, available experimental ρ_{bcp} values of $H\cdots O$ bonds from accurate diffraction experiments that range from 0.96 to 2.42 Å have been considered (Table 5).[32−34] The corresponding representation with all the mentioned data is in Figure 6.

The resulting equations are:

$$\ln \rho_{bcp} = (1.29 \pm 0.08) - (2.51 \pm 0.05)(\text{HB distance}) \qquad r^2 = 0.99, \quad n = 18 \text{ (only exptl data)}$$

$$\ln \rho_{bcp} = (1.04 \pm 0.16) - (2.394 \pm 0.08)(\text{HB distance}) \qquad r^2 = 0.97, \quad n = 25 \text{ (only calcd data)}$$

$$\ln \rho_{bcp} = (1.18 \pm 0.09) - (2.457 \pm 0.05)(\text{HB distance}) \qquad r^2 = 0.98, \quad n = 43 \text{ (exptl and calcd data)}$$

The nice fitting of all the data to the proposed relationship indicates their universality and their usefulness in the correlation of these two properties.

In addition, acceptable second-order relationships can be found between the interaction energies, E_I and E_{I+BSSE}, and the ρ_{bcp} values.

$$E_I = (1.55 \pm 0.76) - (412 \pm 41)\rho_{bcp} + (1869 \pm 407){\rho_{bcp}}^2 r^2 = 0.97, \quad n = 22$$

$$E_{I+BSSE} = (1.89 \pm 0.73) - (338 \pm 39)\rho_{bcp} + (1450 \pm 389){\rho_{bcp}}^2 \qquad r^2 = 0.96, \quad n = 22$$

The present correlations, which are similar to the ones proposed for other HB systems,[35−37] can be used to estimate

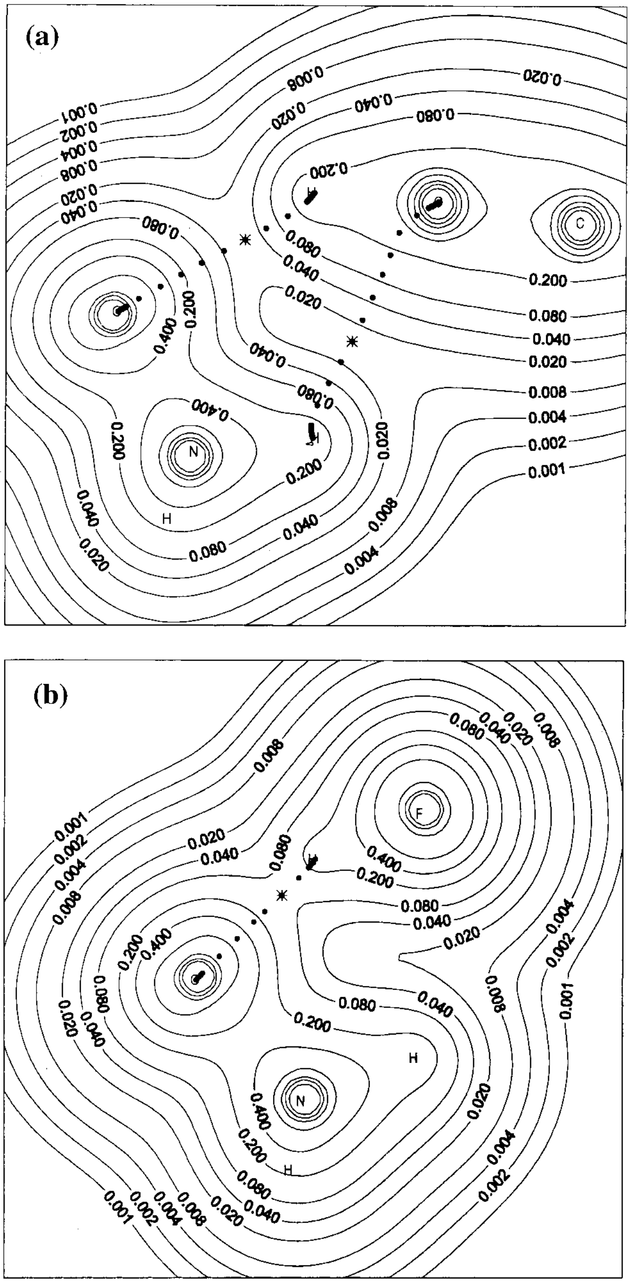

Figure 5. Electron density maps of (a) $H_3NO\cdots HCCH$ and (b) $H_3NO\cdots HF$. The positions of the HB critical points are indicated with a star and the bond paths with dots.

the interaction energies in those cases where this in not possible, as in intramolecular HB or in experimental solid-state HB determinations.

NMR. An experimental report has indicated the existence of a linear relationship between the chemical shielding of the phosphorus atom in phosphine oxides and the number of existing HB.[38] To study a similar model, we have optimized the complexes of H_3PO with one, two, and three molecules of HF at the B3LYP/6-311++G** level, both in eclipsed and staggered configurations. For the sake of comparison, the same study has been carried out with the $Me_3NO\cdots(HF)_n$ complexes in the staggered conformation.

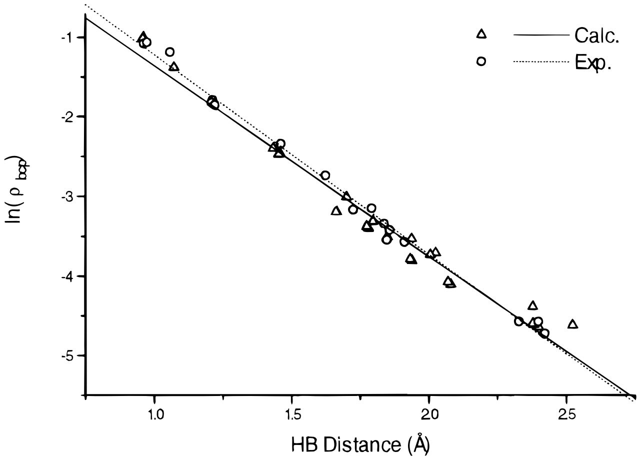

Figure 6. Logarithmic representation of ρ_{bcp} vs the HB distance. The fitted logarithmic relationships for the experimental (continuos line) and calculated data (dashed line) are displayed.

TABLE 5: Experimental Distance and ρ_{bcp} of H···O HBs and Covalent Bonds

distance (Å)	ρ_{bcp} (e/au^3)	source (ref)
1.213	0.1674	32
1.210	0.1615	32
1.838	0.0356	32
1.912	0.0282	32
1.792	0.0430	32
1.848	0.0290	33
1.858	0.0327	33
1.725	0.0422	33
1.221	0.1568	33
0.963	0.3390	33
2.329	0.0104	34
2.399	0.0104	34
2.421	0.0089	34
2.423	0.0089	34
1.058	0.3053	34
0.974	0.3453	34
1.625	0.0652	34
1.461	0.0963	34

TABLE 6: Interaction Energy (kcal/mol) in the $H_3PO\cdots(HF)_n$ and $Me_3NO\cdots(HF)_n$ Series where *n* is the Number of HF Molecules HB to the Oxygen Calculated at the B3LYP/6-311++G Level**

system	E_I (kcal/mol)
$H_3PO\cdots HF$ (stag)	−12.58
$H_3PO\cdots HF$ (eclip)	−12.68
$H_3PO\cdots(HF)_2$	−22.60
$H_3PO\cdots(HF)_3$ (stag)	−28.99
$H_3PO\cdots(HF)_3$ (eclip)	−29.04
$Me_3NO\cdots HF$	−20.44
$Me_3NO\cdots(HF)_2$	−36.05
$Me_3NO\cdots(HF)_3$	−48.00

In the case of the $H_3PO\cdots(HF)_2$ complex, the eclipsed and staggered configuration provide the same structure with a C_s symmetry and the HF molecules in an opposite disposition with respect to the P−O moiety. The corresponding interaction energies (Table 6) show a similar stability for both configurations in the $H_3PO\cdots(HF)_3$ complex (the eclipsed configuration is the most stable by 0.05 kcal/mol) as previously mentioned in the case of the $H_3PO\cdots HF$ complex (Table 1). The comparison of the E_I in these series shows that the new HB interaction stabilized less than the previous one. Thus, the contribution of the new HB are 12.7, 9.9, and 6.4 kcal in the $H_3PO\cdots(HF)_n$ and 20.4, 15.6, and 12.0 kcal/mol in the $Me_3NO\cdots(HF)_n$ series for $n = 1-3$. The total E_I of these series follows an exponential relationship with respect to the number of HB (Figure 7)

The corresponding NMR shieldings obtained at the same level of theory with the GIAO method are gathered in Table 7. The ^{31}P NMR shielding obtained for the two configurations studied indicates that this property does not significatively change with the disposition of the HB donor. In Figure 8a, the ^{31}P NMR

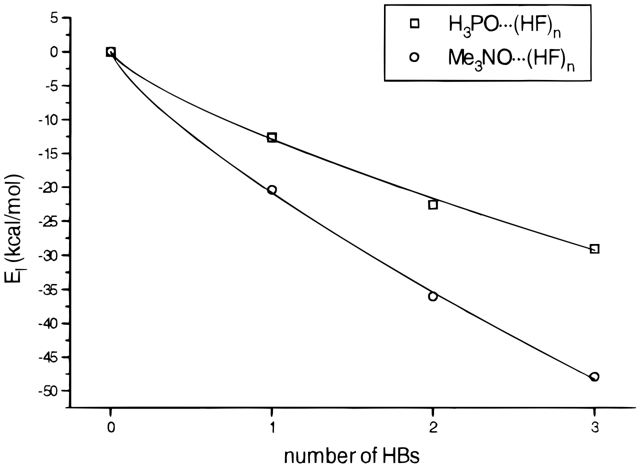

Figure 7. Exponential relationship between the E_I and the number of HBs. The fitted curves are: $E_I = -12.93n^{0.743}$, $r_2 = 0.998$, $n = 6$ for the $H_3PO\cdots{}_n(HF)$ complexes and $E_I = -20.84n^{0.765}$, $r^2 = 0.9995$, $n = 4$.

TABLE 7: NMR Shielding of the Complexes $H_3PO\cdots HF)_n$ and Me3NO···$(HF)_n$ where *n* Represents the Number of HF Molecules HB to the Oxygen Calculated with the GIAO Method at the B3LYP/6-311++G Level**

system	$^{31}P/^{15}N$	^{17}O	^{1}H
H_3PO	372.31	315.11	
$H_3PO\cdots HF$ (stagg.)	364.15	321.59	24.89
$H_3PO\cdots HF$ (eclip.)	364.48	319.31	24.79
$H_3PO\cdots(HF)_2$	351.09	316.30	25.66
$H_3PO\cdots(HF)_3$ (stagg.)	340.55	306.63	26.40
$H_3PO\cdots(HF)_3$ (eclip.)	337.08	309.67	26.65
Me_3NO	115.94	18.57	
$Me_3NO\cdots HF$	122.68	33.38	19.36
$Me_3NO\cdots(HF)_2$	122.95	46.44	21.95
$Me_3NO\cdots(HF)_3$	120.72	53.27	23.65

absolute shielding as a function of the number of HBs has been represented. Even though a polynomial relationship probably would provide a better correlation of the data, the small number of values and the discrete description of one of the variables recommends the establishment of a linear relationship.

$$^{31}\mathrm{P\ NMR} = (374 \pm 1) - (11.7 \pm 0.7)(\text{number of HBs}) \qquad r^2 = 0.98, \quad n = 6$$

The present relationship indicates that a NMR shielding variation of 11.7 ppm is produced by each additional HB. However, this value should vary depending on the strength of the HB donor, and thus the experimental data, which correspond to N−H as HB donors, provide a variation of only 4.7 ppm for each HB.

In the case of the complexes with Me_3NO, no relationship has been found in the ^{15}N NMR shielding with the number of HBs, but an acceptable linear relationship can be obtained in the case of the ^{17}O NMR shieldings (Figure 8b).

$$^{17}\mathrm{O\ NMR} = (20 \pm 2) + (12 \pm 1)(\text{number of HBs}) \qquad r^2 = 0.98, \quad n = 4$$

In both systems, a linear relationship can be obtained between the ^{1}H NMR shielding of the hydrogen involved in the HB and the number of HBs as shown in Figure 7c. For the $H_3PO\cdots(HF)_n$ complexes,

$$^{1}\mathrm{H\ NMR} = (24.0 \pm 0.1) + (0.84 \pm 0.06)(\text{number of HBs}) \qquad r^2 = 0.99, n = 5$$

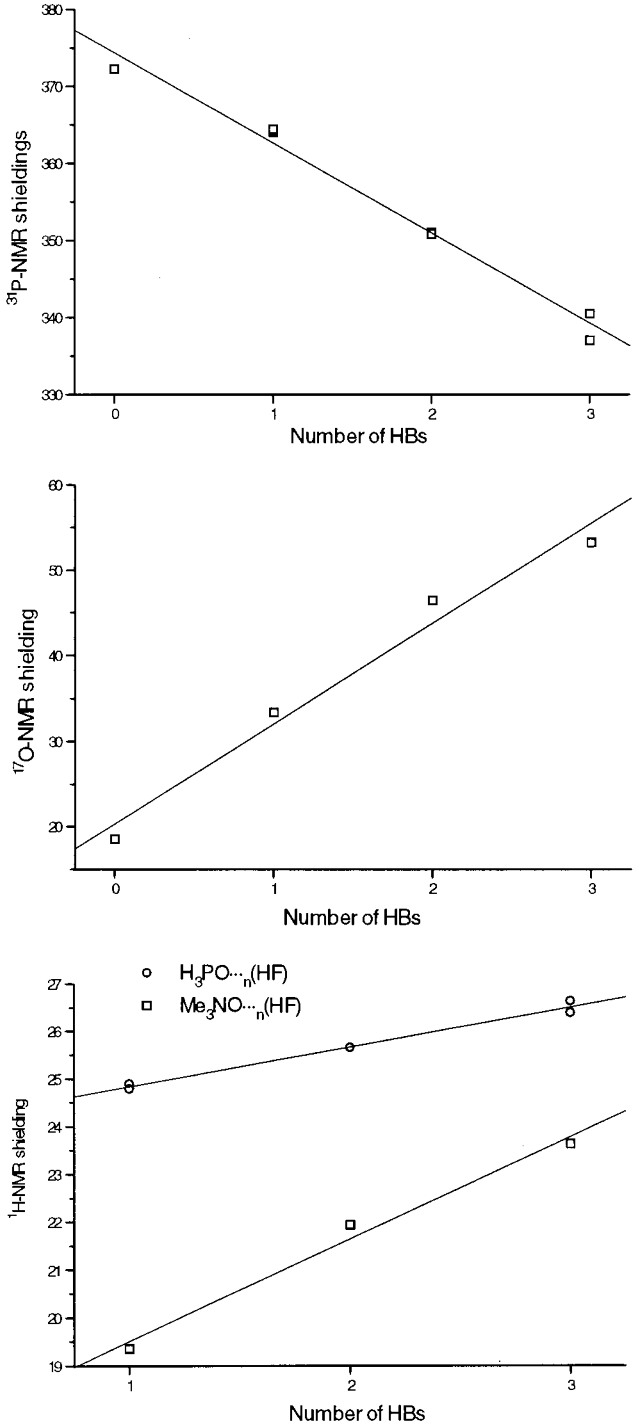

Figure 8. NMR shielding as a function of the number of HBs: (a) ^{31}P NMR shieldings in the $H_3PO\cdots n(HF)$ complexes; (b) ^{17}O NMR shieldings in the $Me_3NO\cdots(HF)_n$ complexes; (c) ^{1}H NMR shieldings in the $H_3PO\cdots(HF)_n$ and $Me_3NO\cdots(HF)_n$ complexes.

For the $Me_3NO\cdots(HF)_n$ complexes,

$$^{1}\mathrm{H\ NMR} = (17.4 \pm 0.5) + (2.1 \pm 0.3)(\text{number of HBs}) \qquad r^2 = 0.99, n = 3$$

The slopes of these two equations, 2.1 in the $Me_3NO\cdots(HF)_n$ complexes and 0.84 in the $H_3PO\cdots(HF)_n$ ones, are an indication of the relative strength of the HBs. In addition, the additive effect of the increasing charge on the oxygen atom due to HB is reflected in each individual interacting hydrogen atom.

Conclusion

A theoretical study of the ability of ammonium oxide, trimethylamine oxide, and phosphine oxide as HB acceptors has been carried out using B3LYP and MP2 ab initio methods. The interaction energies obtained for several of the complexes are within the range of strong HBs ($>$12 kcal/mol).

The electronic characteristics (Laplacian of the electron density and molecular electrostatic potential) of the isolated HB acceptors (H_3NO, H_3PO, and Me_3NO) have been used to predict a low spatial preference in the HB interaction. This fact has been confirmed by calculation of the eclipsed and staggered HB with respect to one of the hydrogens of H_3NO and H_3PO and one of the methyl groups of Me_3NO.

Some correlations have been obtained between the geometric, energetic, and electronic characteristics of these HBs. Thus, a logarithmic correlation between the electron density at the HB critical points and the H···O distance has been established for a range of HB (very large, medium, and short) and covalent bonds. The inclusion of experimental data of other O···H cases indicates that the present correlation can be considered universal. Additional correlations between the interaction energies and the electron density at the HB critical points and the HB distance have been established.

Finally, a correlation between the ^{31}P NMR shielding of the phosphine oxides and the number of HB has been obtained in agreement with previous experimental reports.

Note Added in Proof: Two related articles have been published while the present one was in the editorial process. The first one shows for the first time the existence of H_3NO in the gas phase,[39] and the second one reports the chemical bonding in hypervalent compounds including amine oxides and phosphine oxides within the AIM framework.[40]

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