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Anomeric Effects in the Symmetrical and Asymmetrical Structures of Triethylamine. Blue-Shifts of the C−H Stretching Vibrations in Complexed and Protonated Triethylamine

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Quantum mechanical calculations using density functional theory with the hybrid B3LYP functional and the 6-31++G(d,p) basis set are performed on isolated triethylamine (TEA), its hydrogen-bond complex with phenol, and protonated TEA. The calculations include the optimized geometries and the results of a natural bond orbital (NBO) analysis (occupation of σ^* orbitals, hyperconjugative energies, and atomic charges). The harmonic frequencies of the C−H stretching vibrations of TEA are predicted at the same level of theory. Two stable structures are found for isolated TEA. In the most stable symmetrical structure (TEA-S), the three C−C bond lengths are equal and one of the C−H bond of each of the three CH_2 groups is more elongated than the three other ones. In the asymmetrical structure (TEA-AS), one of the C−C bonds and two C−H bonds of two different CH_2 groups are more elongated than the other ones. These structures result from the hyperconjugation of the N lone pair to the considered σ^*(C−H) orbitals (TEA-S) or to the σ^*(C−C) and σ^*(C−H) orbitals of the CH_2 groups (TEA-AS). The formation of a OH···N hydrogen bond with phenol results in a decrease of the hyperconjugation, a contraction of the C−H bonds, and blue-shifts of 28−33 cm^{-1} (TEA-S) or 40−48 cm^{-1} (TEA-AS) of the $\nu^s(CH_2)$ vibrations. The $\nu(CH_3)$ vibrations are found to shift to a lesser extent. Cancellation of the lone pair reorganization in protonated TEA-S and TEA-AS results in large blue-shifts of the $\nu(CH_2)$ vibrations, between 170 and 190 cm^{-1}. Most importantly, in contrast with the blue-shifting hydrogen bonds involving C−H groups, the blue-shifts occurring at C−H groups not participating in hydrogen bond formation is mainly due to a reduction of the hyperconjugation and the resulting decrease in the occupation of the corresponding σ^*(C−H) orbitals. A linear correlation is established between the C−H distances and the occupation of the corresponding σ^*(C−H) orbitals in the CH_2 groups.

1. Introduction

One of the characteristic features of hydrogen bond formation in a X−H···Y system is X−H bond lengthening accompanied by a red-shift and an infrared intensity increase of the X−H stretching vibration. These spectroscopic features are observed in the great majority of hydrogen bonds involving polar O−H or N−H groups. However, a number of theoretical[1] and experimental studies[2] have reported the existence of an unusual class of C−H···Y hydrogen bonds in which the interaction leads to X−H bond shortening along with a blue-shift and an infrared intensity decrease of the C−H stretching vibration. This effect has been observed experimentally for the last several decades, and the blue-shifted C−H bands are usually referred as "Bohlmann" bands.[3−4] The presence of Bohlmann bands has also been reported in methylamine, methanol, and methanethiol, where lowering of the stretching frequency of a C−H bond antiperiplanar to a lone pair was observed.[5−6] The contribution of Fermi resonance between the symmetric C−H stretch and CH bending overtones behind the red-shift has also been discussed.[6]

In the present work, we do not intend to dispute the nature of physical phenomena that lead to a X−H bond shortening but completely agree with those who conclude that there is no fundamental difference between both types of hydrogen bonds. The X−H bond length being controlled by a balance between two main factors acting in opposite directions, namely the X−H bond lengthening due to an increase of occupation of the σ^*(X−H) orbital and the X−H bond shortening due to an increase in the s-character of the X−H bond.[7] For complexes involving methyl halides and hydrogen peroxide, the contraction of the C−H bond has been shown to depend quantitatively on both parameters.[8]

However, blue-shifts can also occur at those C−H groups that do not themselves participate in a hydrogen bond. Several examples of this indirect perturbation are known. Complex formation between dimethyl ether and chloroform results in an increase of the CH_3 stretching frequencies.[9] Hydrogen bonds formed at the carbonyl group in *N*,*N*-dimethylformamide−water complexes are also found to play an important role in the blue-shift of the CH_3 stretching vibrations.[10] The same effect has also been predicted for simple carbonyl bases[11a] or esters interacting with water.[11b] It must be noticed that most of the recent studies have concentrated on the origin of the contraction (or blue-shift) of the CH bond participating in hydrogen bond formation, but less attention has been paid to the perturbation of the adjacent groups. However, recent experimental and theoretical investigations of the complex between triethylamine (TEA) and chloroform[12a] or water[12b,c] have shown that the C−H···N or OH···N hydrogen bonds formed at the nitrogen lone pair play an important role in the blue-shift of the CH_2

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stretching vibration. Phenol derivatives form strong hydrogen-bonded complexes with TEA,[13] and therefore stronger perturbations of the interatomic distances and the vibrational modes must be expected. Further it has been shown experimentally that complexation of TEA with phenol derivatives result in blue-shifts of the asymmetrical CH_2 and CH_3 stretching vibrations but only qualitative explanations such as an increase of the electronegativity of the C atom or an increase in s-character of the C bonded to the H could be provided at this time.[14] Still larger perturbations are expected for protonated TEA where the lone pair of the nitrogen atom is tied up in the NH^+ bond.

In this paper, our main focus is to discuss the origin of the blue-shift occurring at the groups not participating in a hydrogen bond. In the process, we also discuss the effect of hyperconjugation on the structure of TEA. Hyperconjugation and its effect on geometry have been studied for a long time and remain a matter of interest for the physical interpretation of several phenomena.[15,16] In fact, our results and subsequent analysis would reveal that the physical origin of the blue-shift in TEA on hydrogen bonding and protonation is the reduction of hyperconjugation and the resulting decrease in antibonding orbital occupation. The work is organized as follows. The first section deals with the optimized geometries of isolated TEA, its complex with phenol, and protonated TEA. The results of a natural bond orbital (NBO) analysis such as the occupation of relevant antibonding orbitals, charge-transfer energies, and NBO charges are discussed as well. The second section deals with the perturbation of the CH_2 and CH_3 stretching vibration resulting from the complexation or the protonation of TEA.

2. Computational Methodology

The geometries of isolated TEA, the phenol−TEA complex, and protonated TEA were fully optimized by the density functional three-parameter model (B3LYP)[17] using the 6-31++G(d,p) basis set. Frequency calculations were carried out at the same level to characterize the stationary points. The vibrational frequencies were retained unscaled. Charges on individual atoms, hybridization, orbital occupancies, and hyperconjugative energies were obtained by the natural bond orbital (NBO) population scheme.[18] Although the NBO data may be dependent on the basis set, comparison between different systems is meaningful as long as the same level of theory is used.[19]

The hydrogen-bonding energy of the TEA−phenol complex includes zero-point energy (ZPE) correction and the basis set superposition error (BSSE) computed by the counterpoise (CP) method.[20] The Gaussian 03 package was used for all the calculations analyzed in the present work.[21]

3. Results and Discussion

A. Optimized Geometries and NBO Results for Isolated TEA, TEA−Phenol Complex, and Protonated TEA. For a direct comparison, the optimized geometries of isolated TEA, TEA−phenol, and TEA−H$^+$ are gathered in Table 1. The same remark also holds for the NBO data presented in Tables 2 and 3.

We begin with considering the results for isolated TEA. Surprisingly, our calculations revealed the existence of two stable configurations for this molecule: the symmetric (henceforth referred as TEA-S) and the asymmetric (TEA-AS) one. The symmetric structure is 1 kcal/mol more stable than the asymmetric one. The optimized structures of these two configurations are illustrated in Figure 1. Our calculations show that the three C−N distances and the three CNC angles are almost equal in both TEA-S and TEA-AS. In TEA-AS, the C2−C11 distance, equal to 1.542 Å, is by 0.010−0.012 Å longer that the two other C−C distances. In TEA-S, all the three C−C distances are almost equal (1.531 Å). Further, our calculations clearly indicate that, in TEA-AS, the CH_2 groups are not equivalent. Indeed, the C3−H8 and C4−H9 distances, respectively equal to 1.1078 and 1.1073 Å, are longer than the other C−H distances ranging between 1.0941 and 1.0969 Å. In contrast, in TEA-S, the geometry of the three CH_2 groups is

TABLE 1: Relevant Distances (Å) and Angles (deg) in TEA, TEA−Phenol Complex, and Protonated TEA Calculated at the B3LYP/6-31++G(d,p) Level

bond length/ angle	TEA		TEA−phenol complex		TEA−H$^+$	
	TEA-S	TEA-AS	TEA-S	TEA-AS	TEA-S	TEA-AS
N1−C2	1.469	1.469	1.482	1.481	1.524	1.529
N1−C3	1.469	1.466	1.484	1.482	1.524	1.523
N1−C4	1.469	1.467	1.481	1.479	1.525	1.526
C2−C11	1.530	1.542	1.530	1.536	1.523	1.522
C3−C12	1.531	1.530	1.531	1.530	1.523	1.523
C4−C13	1.531	1.532	1.531	1.531	1.523	1.524
C2−H5	1.0940	1.0952	1.0917	1.0939	1.0906	1.0912
C2−H6	1.1089	1.0969	1.1061	1.0961	1.0931	1.0930
C3−H7	1.0939	1.0941	1.0921	1.0933	1.0908	1.0910
C3−H8	1.1086	1.1078	1.1063	1.1039	1.0931	1.0911
C4−H9	1.1085	1.1073	1.1061	1.1035	1.0930	1.0917
C4−H10	1.0939	1.0961	1.0929	1.0962	1.0908	1.0922
C11−H14	1.0948	1.0952	1.0940	1.0949	1.0933	1.0929
C11−H15	1.0960	1.0960	1.0952	1.0952	1.0934	1.0936
C11−H16	1.0945	1.0954	1.0940	1.0946	1.0953	1.0929
C12−H17	1.0959	1.0955	1.0953	1.0950	1.0934	1.0935
C12−H18	1.0948	1.0946	1.0938	1.0945	1.0930	1.0925
C12−H19	1.0945	1.0949	1.0934	1.0938	1.0954	1.0956
C13−H20	1.0947	1.0946	1.0934	1.0936	1.0931	1.0929
C13−H21	1.0944	1.0945	1.0942	1.0941	1.0953	1.0956
C13−H22	1.0959	1.0961	1.0953	1.0951	1.0935	1.0935
N1C2C11	113.5	117.3	114.8	117.2	112.6	114.3
N1C3C12	113.4	113.8	115.0	114.2	112.7	113.3
N1C4C13	113.3	113.2	114.8	114.5	112.7	112.5
H5C2N1	108.0	107.4	107.4	106.7	106.8	107.6
H6C2N1	110.8	108.4	109.7	107.6	106.0	106.3
H7C3N1	108.0	107.4	107.2	107.0	106.7	105.9
H8C3N1	110.8	112.1	109.6	110.5	105.9	106.4
H9C4N1	110.8	112.1	109.8	110.8	105.9	106.4
H10C4N1	108.0	107.7	107.4	106.9	106.6	106.3

TABLE 2: σ^* Occupation (e) in C−C and C−H Bonds of the CH_2 Groups

	TEA		TEA−phenol complex		TEA−H$^+$	
bond	TEA-S	TEA-AS	TEA-S	TEA-AS	TEA-S	TEA-AS
C2−C11	0.0112	0.0293	0.0091	0.0252	0.0051	0.0069
C3−C12	0.0113	0.0103	0.0087	0.0081	0.0052	0.0054
C4−C13	0.0112	0.0129	0.0090	0.0103	0.0051	0.0048
C2−H5	0.0123	0.0148	0.0124	0.0136	0.0112	0.0102
C2−H6	0.0316	0.0139	0.0273	0.0136	0.0112	0.0102
C3−H7	0.0122	0.0134	0.0125	0.0131	0.0111	0.0110
C3−H8	0.0313	0.0330	0.0270	0.0262	0.0112	0.0119
C4−H9	0.0312	0.0311	0.0278	0.0263	0.0112	0.0111
C4−H10	0.0123	0.0119	0.0132	0.0125	0.0111	0.0104

TABLE 3: $n_N \rightarrow \sigma^*$(C−C) or $n_N \rightarrow \sigma^*$(C−H) Hyperconjugation Energies (kcal mol^{-1}) in TEA and TEA−Phenol Complex

	TEA		TEA−phenol complex	
type	TEA-S	TEA-AS	TEA-S	TEA-AS
$n_N \rightarrow \sigma^*$(C2−C11)	2.2	9.4	1.1	7.2
$n_N \rightarrow \sigma^*$(C3−C12)	2.3	1.4	1.0	0.6
$n_N \rightarrow \sigma^*$(C2H6)	6.8	1.2	6.2	1.0
$n_N \rightarrow \sigma^*$(C2−H5)		1.2		1.4
$n_N \rightarrow \sigma^*$C3−H8)	6.7	8.5	6.1	6.2
$n_N \rightarrow \sigma^*$(C4−H9)	6.7	7.8	6.3	6.3

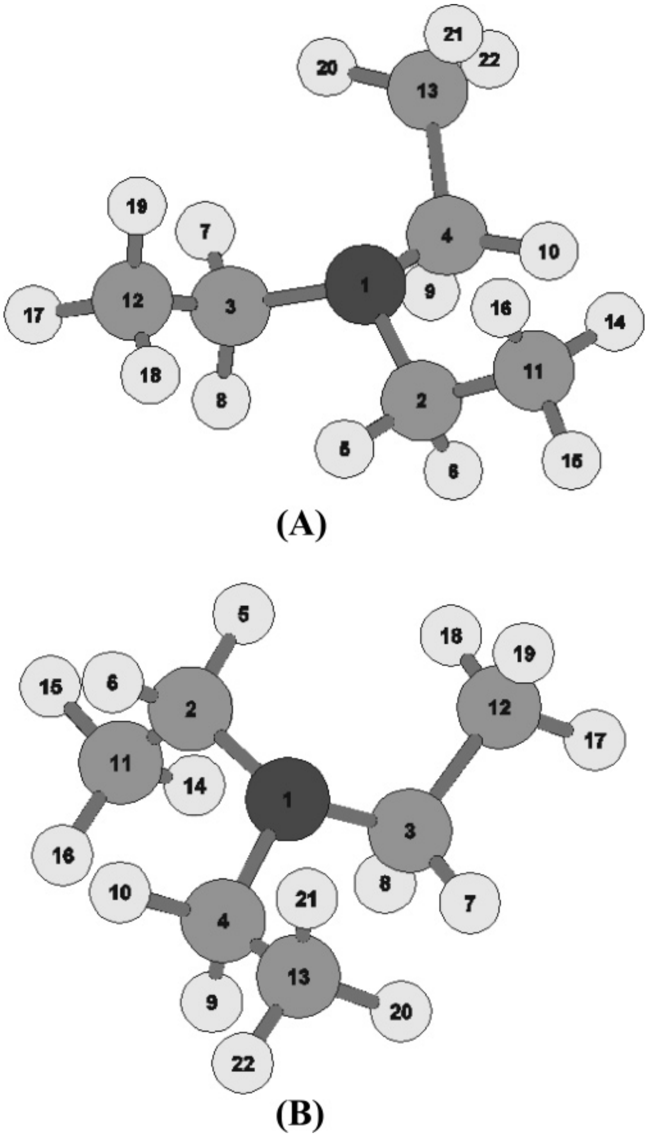

Figure 1. Stable structures of triethylamine. (A) Symmetrical TEA (TEA-S). (B) Asymmetrical TEA (TEA-AS).

nearly the same, but in each of the CH_2 groups, one of the C−H bonds is more elongated than the other one. Thus, the C2−H6, C3−H8, and C4−H9 distances are by ca. 0.0145 Å longer than the other C2−H5, C3−H7, and C4−H10 distances. Significant differences are also predicted for the angles involving the C11, H8, or H9 atoms. In TEA-AS, the H8C3N1 and H9C4N1 angles are indeed larger than the other HCN angles, and the N1C2C11 angle (117.3°) is found to be larger than the N1C3C12 (113.8°) or N1C4C13 (113.2°) angles. In TEA-S, the three NCC angles are found to be nearly equal (113. 3° and 113.5°). In contrast, the C−H distances in the three CH_3 groups are nearly the same in the two conformers. It must be mentioned that the structure of isolated TEA has not been discussed in ref 12a. However, it can be anticipated from the frequencies of the $\nu(CH_2)$ vibrations that the asymmetrical conformation was considered there. B3LYP/6-31G(d) calculations revealed two sets of C−H distances in each of the CH_2 groups, indicating a symmetrical-like conformation.[12c]

The NBO analysis reveals marked differences between the two conformers, namely different occupations of the σ* orbitals of the C−C and C−H bonds, reported in Table 2. In TEA-AS, the larger elongation of the C2−C11 bond parallels a much larger σ*(C2−C11) population as compared with the other σ*(C−C) occupations. The same remark also holds for the C3−H8 and C4−H9 bonds characterized by σ* populations equal to 0.033 and 0.31 e, respectively, substantially larger than those of the other C−H bonds ranging between 0.0012 and 0.015 e. Similarly, it can be seen from Table 2 that the population of the three antibonding σ*(C2−H6), σ*(C3−H8) and σ*(C4−H9) orbitals in TEA-S, ranging from 0.0312 to 0.0315 e, are markedly larger than in the other C−H bonds of the CH_2 groups that all take the value of 0.012 e.

The extent of coupling between N lone pair orbital and different σ* orbitals can be assessed from the hyperconjugative interaction energies estimated from the second-order perturbation theory:

$$E(2) = -n_{\sigma}\frac{|\langle \sigma_{\mathrm{LP}}|\hat{F}|\sigma^{*}\rangle|^{2}}{\epsilon_{\sigma}^{*} - \epsilon_{\sigma_{\mathrm{LP}}}} = -n_{\sigma}\frac{F^{2}_{\sigma_{\mathrm{LP}}\sigma^{*}}}{\Delta E} \qquad (1)$$

where σ_{LP} represents the N lone pair orbital and σ* is the antibonding orbital, whereas ϵ's represent orbital energies.

The hyperconjugation energies from the nitrogen lone pair to relevant σ* orbitals are reported in Table 3. In TEA-AS, the largest energy of 9.4 kcal mol^{-1} is obtained for the $n_N \rightarrow \sigma^*$(C2−C11) interaction, followed by the $n_N \rightarrow \sigma^*$(C3−H8) and $n_N \rightarrow \sigma^*$(C4−H9) interactions, equal to 8.4 and 7.8 kcal mol^{-1}, respectively. The hyperconjugative energies from the N lone pair to the other σ*(C−H) orbitals of the CH_2 groups are much smaller, ranging from 1.2 to 1.4 kcal mol^{-1}. In TEA-S, the second-order hyperconjugation energies for the $n_N \rightarrow \sigma^*$(C2−H6) and $n_N \rightarrow \sigma^*$(C3−H8) and $n_N \rightarrow \sigma^*$(C4−H9) interactions are very similar, taking values of 6.7 or 6.8 kcal mol^{-1}. The charge-transfer energies to the other σ*(C−H) bonds of the CH_2 group are negligible, being lower than 0.5 kcal mol^{-1}.

Thus our results clearly indicate the existence of an anomeric effect[16,22] taking place from the N lone pair to the three C−H bonds (C2−H6, C3−H8, and C4−H9) in TEA-S and to one of the C−C bonds (C2−C11) and to two C−H bonds belonging to two different CH_2 groups of TEA-AS. The three bonds participating in this hyperconjugation are in a "transoid" orientation with respect to the N lone pair in both TEA-S and TEA-AS.

It is worth mentioning that, in ethylamine, the "anti" conformation (with respect to the orientation of the lone pair) is 0.5 kcal mol^{-1} more stable than the "gauche" orientation due to the larger energy of the $n_N \rightarrow \sigma^*$(C−C) interaction compared with the energy of the $n_N \rightarrow \sigma^*$(C−H) interaction (8.3 vs 7.7 kcal mol^{-1}, B3LYP/6-31G(d,p)).[23] Our calculations show that the $n_N \rightarrow \sigma^*$(C2−C11) charge-transfer energy in TEA-AS is slightly larger that the $n_N \rightarrow \sigma^*$(C−H) transfer energies in both TEA-S and TEA-AS. The slightly larger stability of TEA-S may be due to a concerted charge transfer to the three equivalent σ*(C−H) orbitals.

A good way to examine the effect of the lone pair at the nitrogen atom on the structure of TEA is to introduce a reagent that will interact with the lone pair of this atom. Therefore, we have examined in a next step the hydrogen bond complex formed between TEA and phenol, where the N lone pair is partially involved in the OH···N interaction, and protonated TEA, where the proton is tied up in the formation of a N−H$^+$ valence bond.

Two TEA−phenol complexes are identified, resulting from the two stable structures of TEA. The structures of the complexes are shown in Figure 2. The calculated energies of complex formation are −7.9 and −9.0 kcal mol^{-1} for TEA-S and TEA-AS, respectively. The H-bonding energies, including

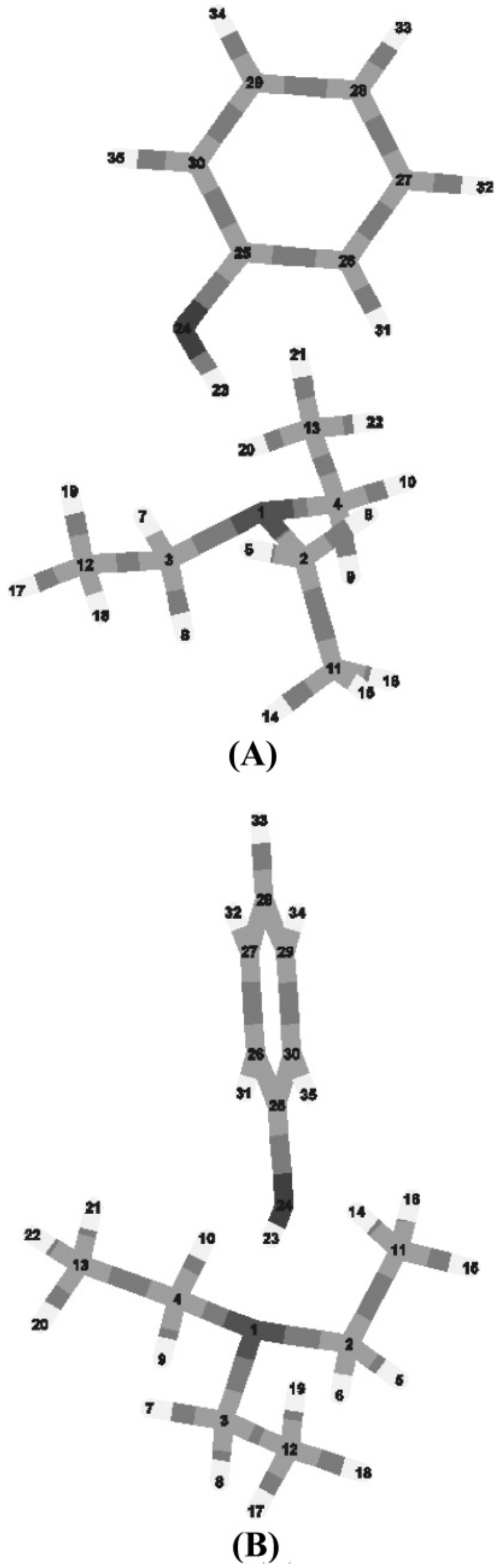

Figure 2. Optimized structures of the phenol−triethylamine complex. (A) phenol−TEA-S complex. (B) phenol−TEA-AS complex.

ZPE and BSSE correction, amount to −5.3 and −6.3 kcal mol^{-1}, respectively. These values are somewhat lower than the experimental data in solution, ranging from −7.3 to 9.2 kcal mol^{-1}.[24] The difference may be accounted for by the overestimation of the BSSE correction at the present level of theory.

The OH···N distance and OH···N angle are equal to 1.808 Å and 167.4°, respectively, for the phenol−TEA-S complex, whereas these parameters amount to 1.843 Å and 164.6° for phenol complexed with TEA-AS. The OH bond length in TEA-S and TEA-AS complexes equal to 0.9971 and 0.9997 Å, respectively, which are elongated by 0.0310 and 0.0336 Å from the isolated phenol molecule. This elongation primarily results from a larger occupation of the σ^*(O−H) orbital that increases from 0.007 to 0.075 e on going from isolated phenol to its complex with TEA. It must be mentioned here that, in the complex between TEA and chloroform, the distance between one of the Cl atom of chloroform and the H atom of one of the CH_3 groups is relatively short, suggesting a weak C−H···Cl interaction.[12a] In the present case, all the intermolecular distances are longer than 2.7 Å, ruling out any secondary interaction between the C−H bonds of TEA and the O atom of phenol. Complex formation also results in small variation of the C−C and C−H bond lengths in the phenolic ring, but it will not be discussed in the present work mainly intended to investigate the changes in the TEA moiety.[25]

Inspection of the data of Tables 1, 2, and 3 reveals that the perturbations resulting from the interaction with phenol are systematically larger for the C−C or C−H bonds involved in the hyperconjugative process that the other C−C or C−H bonds. Indeed, in the phenol−TEA-AS complex, the C2−C11 bond length decreases by 0.0016 Å, with the other C−C distances remaining unchanged. The C3−H8 and C4−H9 bonds are shortened by 0.0039 and 0.0038 Å, respectively. The other C−H bond lengths in the CH_2 groups are shortened by smaller amounts, ca. 0.0010 Å. In the phenol−TEA-S complex, the C2−H6, C3−H8, and C4−H9 bonds are shortened by ca. 0.0025 Å. In both complexes, an elongation of the three C−N bonds and very small variations of the C−H distances in the CH_3 groups are predicted.

Conventional Mulliken population analysis (charges on the N and H atoms) has been reported for the TEA−water complex (B3LYP/6-31G(d)).[12c] The NBO analysis carried out in the present work allow us to shed some light on the changes in bond lengths induced by the interaction with phenol. Marked contraction of the C2−C11, C3−H8, and C4−H9 bonds in phenol−TEA-AS complex can be related to the decrease in occupation of the corresponding σ^* orbitals in the complex. This occupation decreases by 0.0041 e for the C2−C11 bond and by 0.0068 and 0.0048 e for the C3−H8 and C4−H9 bonds. We also note a significant decrease of the hyperconjugation energies from the N lone pair to these bonds. The $n_N \rightarrow \sigma^*$(C2−C11) charge-transfer energy of 7.2 kcal mol^{-1} is found to be 2.2 kcal mol^{-1} lower than that in isolated TEA. The same remark also holds for the $n_N \rightarrow \sigma^*$(C3−H8) and $n_N \rightarrow \sigma^*$(C3−H8) charge-transfer energies, which are lower by 2.2 and 1.4 kcal mol^{-1} than that in free TEA-AS. The $n \rightarrow \sigma^*$(C2−H6), (C3−H8), and (C4−H9) hyperconjugation energies are smaller than in isolated TEA by ca. 0.5 kcal mol^{-1}. These results clearly indicate an *attenuation of the anomeric effect in complexed TEA, more pronounced for the asymmetrical structure than for the symmetrical one.*

The next step in our study is to discuss the same parameters for the protonated species where the N lone pair is tied up in the N−H$^+$ bond, the N−H$^+$ distance being 1.026 Å. The negative of the protonation enthalpy (proton affinity) is found to be 234.6 kcal mol^{-1} for both conformers, very close to the experimental value of 232.3 kcal mol^{-1}.[26]

In both conformers, protonation induces a significant increase of the C−N distances and an equalization of the C−C distances.

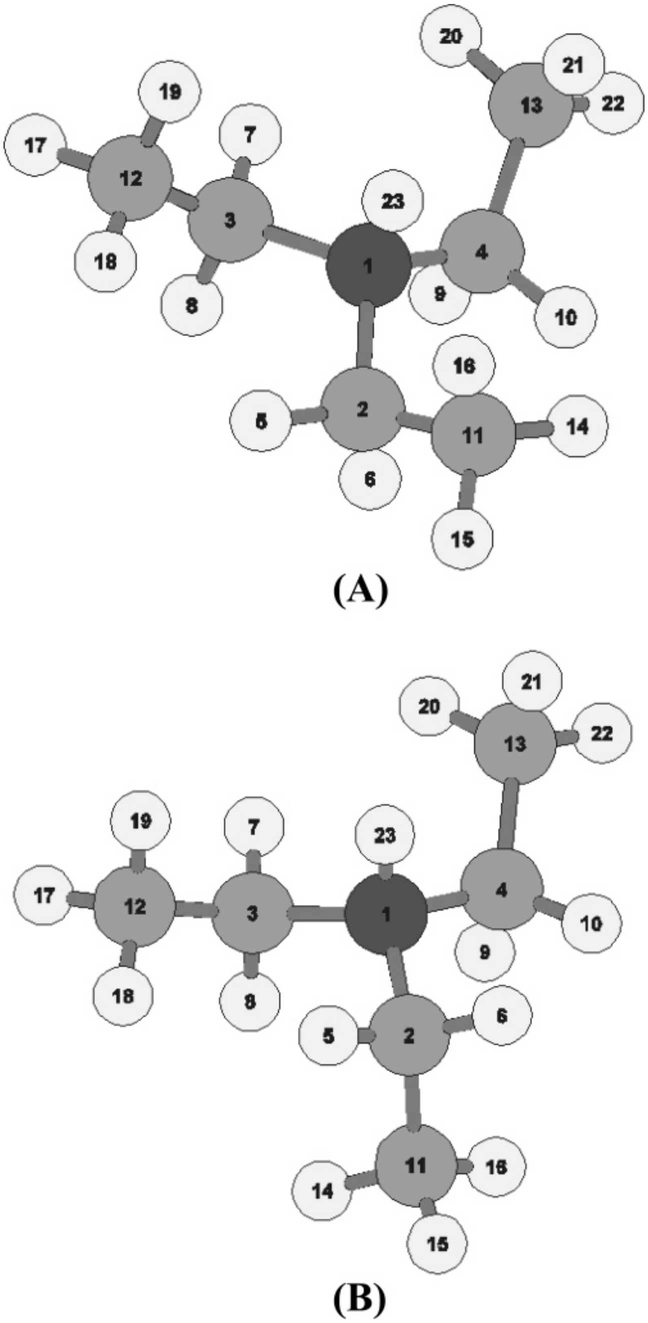

Figure 3. Optimized structures of protonated triethylamine. (A) TEA-S−H$^+$ (B) TEA-AS−H$^+$.

As a result of the cancellation of the delocalization effect, all the C−H distances are contracted. The largest contractions are predicted for the C2−H6, C3−H8, and C4−H9 bonds (0.0155−0.0156 Å) in TEA-S−H$^+$ and for the C3−H8 and C4−H9 bonds in TEA-AS−H$^+$ (0.0156−0.0167 Å) (Figure 3). Most of the C−H distances in the CH$_3$ groups are slightly decreasing upon protonation. Further, in TEA-AS, protonation results in a decrease of 4° of the N1C2C11 angle along with a decrease of the ca. 6° of the H8C3N1 and H9C4N1 angles, all the HCN angles being nearly equal to 106°. The dihedral angles do not change by more than 2°. The cancellation of the lone pair reorganization also results in marked changes of the occupation of the σ^* orbitals involved in the hyperconjugation effect. We note a marked decrease of the σ^*(C2−C11), σ^*(C3−H8), and σ^*(C4−H9) occupations by 0.0224, 0.0194, and 0.0201 e, respectively, in TEA-AS. Protonation of TEA-S results in a significant decrease of the σ^*(C2−H6), σ^*(C3−H8), and σ^*(C4−H9) occupations as well, by ca. 0.02 e.

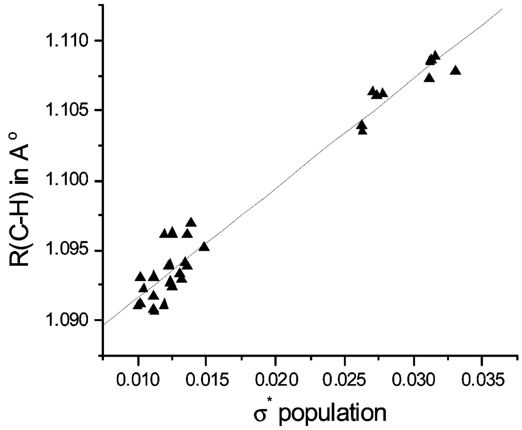

Figure 4. C−H distances in the CH$_2$ groups of as a function of the σ^* occupation of the corresponding C−H bonds (e).

Our results show that the C−H distances in the CH$_2$ groups and the corresponding occupations of the σ^*(C−H) orbitals are linearly correlated. This correlation illustrated in Figure 4 includes the data for the monomers, the phenol complexes, and the protonated species in both the symmetrical and asymmetrical structures:

$$r(\mathrm{C{-}H})\ (\text{Å}) = 1.0838 + 0.782\ \sigma^*(\mathrm{C{-}H})\ (\mathrm{e}) \qquad (R = 0.981) \tag{2}$$

No better correlation coefficient could be obtained when taking into account the change in hybridization of the C atoms. Indeed, complex formation with phenol and protonation of TEA does not induce a great change of the hybridization of the C bonded to the H atoms. The % s-character of the C atom of the CH$_2$ groups vary between 24 and 24.5% in isolated TEA and take values between 25.3 and 25.8% in the protonated species. Thus, *blue-shifts occurring at those C−H groups that do not participate in a hydrogen bond are mainly determined by a decrease of the n → σ*(C−H) hyperconjugative interaction.* It has been suggested that hyperconjugation does not need to be applied to obtain the observed shift in the TEA−water complex.[12b] However, in the present systems, the C−H distances vary within a broad range and the results indicate that these distances are mainly determined by hyperconjugation.

In contrast, blue-shifts of hydrogen-bonded C−H groups depends on two factors acting in opposite direction, generally the change in hybridization being the dominating one.[7,8] However, in the case of remote C−H bonds, hyperconjugative interaction is found to be the dominant factor to induce blue-shifts.

A last remark concerns the NBO charges. In isolated TEA-AS, the NBO charges on the H5, H6, H7, and H10 atoms of the CH$_2$ groups are all equal to 0.224 e, whereas the NBO charges on the H8 and H9 atoms are lower, taking values of 0.195 and 0.198 e, respectively. Meanwhile, in TEA-S, the NBO charges on H6, H8, and H9 are equal and amount to 0.198 e, which is lower than the NBO charges on H5, H7, and H10 atoms (0.224 e). However, in protonated TEA, there is an equalization of the charges that are nearly equal (between 0.257 and 0.259 e) for the six H atoms of the CH$_2$ groups. The same remark also holds for TEA-S, where the NBO charges on these atoms are equal to 0.258 e. This asymmetry in the charge distribution on H atoms of TEA results from the hyperconjugation.

B. Stretching Vibrations of the CH$_2$ and CH$_3$ Groups in TEA, TEA−Phenol Complex, and TEA−H$^+$. The unscaled

TABLE 4: Unscaled Vibrational Frequencies (cm^{-1}) and Infrared Intensities ((km mol^{-1}), in Parentheses) of the Stretching Vibrations of the CH$_2$ and CH$_3$ Groups in TEA-S, TEA-S−Phenol Complex, and Protonated TEA-S, Frequency Shifts, and Assignment of the Vibrational Modes

TEA-S	TEA-S−phenol	$\Delta\nu$	TEA-S−H$^+$	$\Delta\nu$	assignment[a]
2907(28)	2940(19)	33	3098(2)	191	νC2H6; (ν^{s}C2H$_2$, ν^{s} C4H$_2$)
2909(5)	2939(17)	30	3097(2)	188	νC3H8, νC4H9; (ν^{s}C3H$_2$)
2921(250)	2949(363)	28	3101(6)	180	νC4H9, νC3H8, νC2H6; (ν^{s}C2H$_2$, ν^{s}C4H$_2$)
3040(37)	3048(15)	8	3056(6)	16	ν^{s}C11H$_3$
3040(34)	3051(20)	11	3056(6)	16	ν^{s}C13H$_3$
3041(15)	3050(28)	9	3056(6)	15	ν^{s}C12H$_3$
3082(17)	3109(6)[b]	11	3159(6)	77	νC2H5, νC3H7
3083(15)	3094(9)	11	3164(8)	81	νC3H7, νC4H10
3086(1)	3101(9)	15	3164(8)	78	νC4H10, νC3H7
3106(9)	3114(9)[c]	8	3127(4)	21	ν^{as}C11H$_3$, ν^{as}C12H$_3$, ν^{as}C13H$_3$
3109(51)	3119(25)[c]	10	3127(10)	18	ν^{as}C11H$_3$, v^{as}C13H$_3$
3109(51)	3121(40)[c]	12	3129(10)	20	ν^{as}C12H$_3$
3118(54)	3130(48)	12	3140(2)	22	νC11H$_3$, νC12H$_3$, νC13H$_3$
3120(42)	3133(35)	13	3140(2)	20	νC11H$_3$
3121(41)	3139(44)	18	3141	20	νC12H$_3$, νC13H$_3$

[a] CnH$_2$ and CnH$_3$ indicate the vibrations of the CH$_2$ or CH$_3$ groups; the values in parentheses indicate the assignment in TEA-S−H$^+$. [b] Coupled with the ν^{as}C11H$_3$ mode. [c] Coupled with the νC2H5 and νC3H7 vibrations.

TABLE 5: Unscaled Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities ((km mol^{-1}, in Parentheses) of the Stretching Vibrations of the CH$_2$ and CH$_3$ Groups in TEA-AS, TEA-AS−Phenol Complex, and Protonated TEA-AS−H$^+$, Frequency Shifts (cm^{-1}), and Assignment of the Vibrational Modes

TEA-AS	TEA-AS−phenol	$\Delta\nu$	TEA-AS−H$^+$	$\Delta\nu$	assignment[a]
2916(37)	2964(12)	48	3110(2)	194	νC3H8, νC4H9; (ν^{s}C4H$_2$)
2926(143)	2966(261)	40	3098(4)	172	νC4H9, νC3H8; (ν^{s}C3H$_2$)
3037(33)	3045(46)	8	3066(2)	29	ν^{s}C11H$_3$
3039(26)	3052(11)	13	3094(7)	55	ν^{s}C2H$_2$, ν^{s}C12H$_3$
3040(29)	3050(16)	10	3126(2)	86	ν^{s}C13H$_3$
3043(29)	3047(26)	4	3055(4)	12	ν^{s}C12H$_3$
3061(21)	3063(18)	2	3159(7)	98	νC4H10; (ν^{as}C4H$_2$)
3079(8)	3094(6)	15	3157(9)	78	ν^{as}C2H$_2$
3081(8)	3090(9)	9	3168(5)	87	νC3H7; (ν^{as}C3H$_2$)
3102(39)	3110(29)	8	3137(1)	35	ν^{as}C11H$_3$
3106(17)	3117(38)	11	3142(2)	36	ν^{as}C13H$_3$
3109(65)	3113(27)	4	3128(6)	19	ν^{as}C12H$_3$
3112(43)	3121(42)	9	3145(5)	33	ν^{as}C11H$_3$
3117(50)	3131(13)	14	3128(6)	11	ν^{as}C12H$_3$
3120(41)	3130(54)	10	3141(2)	21	ν^{as}C13H$_3$

[a] CnH$_2$ and CnH$_3$ indicate the vibrations of the CH$_2$ and CH$_3$ groups. The values in parentheses refer to the assignment of the vibrations in TEA−H$^+$.

harmonic frequencies and infrared intensities of the CH$_2$ and CH$_3$ groups in the two monomers, their complexes with phenol, and the protonated species are reported in Tables 4 and 5. The approximate description of the vibrational modes and the frequency shifts ($\Delta\nu$) induced by complex formation or protonation are indicated in these tables as well.

Harmonic C−H stretching frequencies in the TEA monomer have been recently calculated at the B3LYP/6-31G(d,p) level, but the assignment of the vibrations for the different CH$_2$ and CH$_3$ groups have not been reported.[12a,27] Comparison of the stretching vibrations of the two conformers of TEA reveals interesting features. The frequencies of the ν^{as}CH$_3$ vibrations are very similar, being comprised between 3102 and 3121 cm^{-1}, but marked differences are predicted for the νCH$_2$ vibrations. Indeed, in free TEA-S, the ν^{s}CH$_2$ vibrations implying mainly a displacement of the most elongated C2H6, C3H8, and C4H9 bonds are calculated at 2907, 2909, and 2921 cm^{-1}. In contrast, the ν^{as}CH$_2$ vibrations in TEA-AS are predicted at 2916, 2926, and 3039 cm^{-1}. This last mode mainly corresponds to the stretching mode of the H atoms attached to the C2 atom. It should be mentioned that the effect of a lone pair to the anti C−H stretches, usually known as the “Bohlmann band”, has been observed for the last several decades.[3,4]

These theoretical data can be compared with the experimental ones. The experimental infrared spectrum of TEA recorded at room temperature in dilute carbon tetrachloride solution is characterized by absorptions at 2800 (doublet), 2870, 2895, 2931, and 2970 cm^{-1}.[14] This last absorption, characterized by a large infrared intensity, has been assigned to the ν^{as}(CH$_3$) vibration. The theory predicts a difference of only 20 cm^{-1} between the vibrations of the three CH$_3$ groups in both TEA-S and TEA-AS and the splitting of the degenerate vibrations (*E*) could not be observed experimentally in carbon tetrachloride solution. Taking an average calculated ν(CH$_3$) frequency of 3110 cm^{-1}, the scale factor is 0.955, generally applied at the present level of theory. The band at 2931 cm^{-1} can be assigned to the ν^{as}(CH$_2$) vibration of TEA-S; further, the weak absorption observed at 2895 cm^{-1} may originate from a small proportion of TEA-AS conformers that must be equal to ca. 20% according to our calculations. The experimental doublet centered at 2800 cm^{-1} characterized by a large infrared intensity has been empirically assigned to the ν^{s}(CH$_2$) modes enhanced by Fermi resonance with the in-plane deformation δ(CH$_2$) mode of both conformers. An interaction between these two levels is likely because, as calculated in the present work, the ν^{s}(CH$_2$) modes are predicted between 2907 and 2921 cm^{-1} and several vibrational modes involving a δ(CH$_2$) deformation are calculated between 1420 and 1490 cm^{-1}.

The interaction between phenol and TEA results in perturbations of the vibrational modes of phenol as well. The ν(OH) vibration, predicted at 3828 cm^{-1} in isolated phenol, is shifted to 3194 cm^{-1} in TEA-S complex and to 3141 cm^{-1} in the TEA-AS complex, giving harmonic frequency shifts of more than 600 cm^{-1}. Owing to the broadness of the ν(OH···N) absorption, the frequency shift is difficult to measure experimentally, and values between 380 and 560 cm^{-1} have been reported in the literature.[24,25] Our calculations also predict small perturbations of 2−10 cm^{-1} of the ν(C−H) vibrations of phenol predicted between 3165 and 3214 cm^{-1} in free phenol.[28] These perturbations will not be discussed in the present work mainly focused on the C−H stretching modes in TEA.

The calculated frequency shifts of the ν^{as}(CH$_3$) vibrations resulting from the interaction between TEA-S and phenol range between 8 and 18 cm^{-1}. This value is in relatively good agreement with experimental spectra, where the 2890 cm^{-1} band of TEA is blue-shifted by 5−12 cm^{-1} in the complexes with phenol derivatives.[14] The vibrations calculated between 3082 and 3086 cm^{-1} having a predominant ν^{as}(CH$_2$) character are predicted to be blue-shifted by 11−15 cm^{-1}. This agrees with the experimental shift of 10 cm^{-1}.[14] The large frequency shifts of 28−33 cm^{-1} of the C2H6, C3H8, and C4H9 stretching vibrations were not observed experimentally in the phenol complex. The infrared spectrum only shows an intensity decrease and a broadening of this absorption. It must be mentioned that a blue-shift of ca. 25 cm^{-1} has been observed in the TEA−water complex by using a nanosecond laser T-jump.[12b]

It must be also noticed that formation of blue-shifted hydrogen bonds results in a decrease of the infrared intensity of the stretching modes of the C−H bonds involved in the interaction. In contrast, there is no systematic variation of the infrared intensity in the present case that increases for some vibrational modes and increases for other ones.

Protonation of TEA results in a spectacular increase of the C−H stretching frequencies. In TEA-S−H$^+$, the ν^s(CH$_2$) vibrations are predicted in a very small frequency range, between 3097 and 3101 cm^{-1}. Protonation results in a blue-shift of the CH$_2$ vibrations by approximately the same amount, between 180 and 191 cm^{-1}. The vibrations imply a motion of both H atoms attached to the same C2, C3, or C4 atoms. In protonated TEA-AS, the C3−H8 and C4−H9 bond lengths become approximately equal. In agreement with these predictions, the modes calculated at 3110 and 3098 cm^{-1} can be now assigned to the symmetrical stretching vibrations of the C4H$_2$ and C3H$_2$ groups. On protonation, these two modes are blue-shifted by 194 and 172 cm^{-1}, respectively. The same remark also holds for the vibrations at 3157 and 3137 cm^{-1} assigned to the asymmetrical stretching vibrations of the C4H$_2$ and C3H$_2$ groups that are shifted by 98 and 87 cm^{-1} from neutral TEA. Except the mode at 3040 cm^{-1} involving predominantly the ν^s(C13H$_3$) vibration that is blue-shifted by 86 cm^{-1}, the shifts of the modes involving a stretching motion of the CH$_3$ groups are smaller, between 11 and 36 cm^{-1}. We also note a dramatic infrared intensity decrease of all the C−H stretching vibrations in both the symmetrical and asymmetrical structures.

It must be noticed that a recent theoretical study carried out on fluorinated dimethyl ethers lead to the same conclusions. In the isolated molecules, the C−H bonds in the trans position (C−H$_t$) to the O lone pair(s) are more elongated than the other ones as a result of the trans lone pair effect. Protonation results in a contraction of the C−H$_t$ bond in trans position, an elongation of the C−O bond, and a contraction of the C−F bonds. The blue-shifts of the ν(C−H$_t$) vibrations induced by protonation are between 80 and 180 cm^{-1}.[29]

4. Concluding Remarks

The first aim of the present study was to investigate the origin of the blue-shifts of the C−H stretching vibrations observed experimentally in the complexes between phenol derivatives and TEA.[10] Theoretical calculations carried out at the B3LYP/6-31++G(d,p) level revealed the existence of two stable conformations in isolated TEA. In the first structure that is by 1 kcal mol^{-1} more stable, the three C−C bonds are equivalent and one of the C−H bonds of each of the three CH2 groups is more elongated than the three other ones (TEA-S). In the second structure, one of the C−C bonds and two C−H bonds belonging to two different CH$_2$ groups are more elongated than the two other C−C or C−H bonds (TEA-AS). The differences are explained by hyperconjugation from the N lone pair to the corresponding σ*(C2−C11) or σ*(C−H) orbitals. It must be mentioned that, owing to the broadness of the bands observed at room temperature in carbon tetrachloride solution, the presence of these two structures can be hardly detected and measurements in argon matrixes or liquefied noble gases should give conclusive results.

The formation of the OH···N hydrogen bond with phenol results in a decrease of the anomeric effect in TEA-S and TEA-AS. Contraction of the C−C or C−H bonds involved in the hyperconjugation and blue-shifts of the ν(CH$_2$) stretching vibrations are predicted. It must be noticed that, in the complex between TEA and CHCl$_3$, short H···Cl contacts were found between the CH$_3$ groups and the Cl atoms.[12a] However, the ν(CH$_2$) vibrations of TEA were predicted to be more shifted than the ν(CH$_3$) ones, showing that the C−H···N hydrogen bond contributes significantly to the shift of the CH$_2$ stretching modes. The same conclusion also holds for the TEA−water complex, where there is no contact between the H atoms of TEA and the O atom of water.[12c] In the present complex, there is, at the exception of the OH···N bond, no contact between the nearby functional groups. It can thus be concluded that the blue-shifts of the C−H stretching vibrations only results from the formation of the strong OH···N hydrogen bond. It must also be noticed that an important property of the blue-shifted hydrogen bonds is a decrease of the infrared intensity of the C−H stretching frequency of the C−H bond involved in the interaction. Our calculations do not predict a definitive trend of the infrared intensities that decrease for some vibrational modes and increase for other ones.

Finally, protonation of TEA, where the proton is tied up in the N−H$^+$ bond, leads to an almost equalization of the three C−C bond lengths, the C−H bond lengths in the three CH$_2$ groups, and the HCN angles, owing to the cancellation of the lone pair reorganization. A spectacular increase of the ν(CH$_2$) frequencies and decrease of the infrared intensities are predicted by our calculations. *Our results clearly show that the blue-shift of the ν(CH$_2$) frequencies of TEA on protonation and hydrogen bonding is due to the lowering of the σ*(C−H) orbital occupation because of the reduction in the hyperconjugative interaction with the nitrogen lone pair orbital.* The fundamental difference between the blue-shifts in isolated C−H and hydrogen-bonded C−H groups is that, in the first case, the blue-shift is determined by a decrease in the occupation of the σ*(C−H) orbitals, while in the second case, the blue-shift is determined by two factors acting in opposite directions, namely the increase in the σ*(C−H), which elongates the C−H bond, and the increase in the s-character of the C, which shortens this bond.

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