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A Non-Empirical Study of Hydrogen Bonding in the Dimer of Formamide*

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A non-empirical SCF calculation on the cyclic dimer of formamide in two different GTF basis sets has been performed and is compared to a similar calculation for the isolated monomer. The energy gain per H-bond is reasonable. Both the proton-donor and proton-acceptor show a global gain in electrons at the expense of the hydrogen of the bridge and of the C atoms. This gross changes in charge are reflected in the ε_{1s} values. They cover a σ gain for nitrogen and a σ loss for oxygen which are studied in detail on the difference density maps in the molecular plane. The covalent character of the H bond appears very small. Both basis sets yield similar conclusions.

Un calcul SCF non-empirique du dimère cyclique de la formamide a été fait dans deux bases de fonctions gaussiennes différentes et comparaison est faite avec le monomère isolé. Le gain d'énergie par liaison H est d'un ordre de grandeur raisonnable. Le donneur et l'accepteur de proton gagnent au total des électrons alors que l'hydrogène de la liaison H en perd ainsi que le carbone central; ces déplacements globaux se reflètent dans les valeurs des ε_{1s} correspondants. Ils couvrent un gain σ pour l'azote et une perte σ pour l'oxygène qui sont étudiés en détails sur les courbes d'isodensité différentielle dans le plan moléculaire. La liaison H apparait peu ou pas covalente. Les deux bases de gaussiennes choisies donnent les mêmes conclusions qualitatives.

Eine SCF-Rechnung mit nicht empirischen Parametern wurde mit zwei verschiedenen aus Gaußfunktionen aufgebauten Basissätzen für das zyklische Dimere und das Monomere des Formamid durchgeführt. Der Energiegewinn ist beträchtlich. Sowohl der Protonendonor als auch der -acceptor zeigen insgesamt einen Elektronengewinn auf Kosten des Brückenwasserstoffs und des Kohlenstoffatoms. Diese Änderung zeigt sich auch in den ε_{1s}-Werten. Der Gewinn und Verlust an σ-Elektronen für Stickstoff bzw. Sauerstoff wird an Hand von Elektronendichtekonturen untersucht. Der kovalente Charakter der Wasserstoffbrückenbindung ist sehr klein. Die beiden Basissätze führen zu ähnlichen Ergebnissen.

Introduction

Until very recently, the quantum-mechanical treatment of hydrogen-bonded molecules has been performed either on very truncated systems or by very approximate methods, or both, apart from the pioneer studies on the rather special entity FHF^- [1]. Clearly, the most satisfactory way to decide between conflicting concepts on the structure of the hydrogen bond would be to treat quantum-mechanically a hydrogen-bonded complex as a single large molecular entity with no truncation: a few steps towards this aim have already been attempted [2–4] by the use of procedures including all the valence electrons. A still better possibility is however to utilize the self-consistent LCAO MO procedure developed by Roothaan [5] which can now be applied on a rather large scale [6] owing

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to the use of Gaussian-type functions for the atomic orbital basis set [7]: one calculation of this kind has been performed very recently on the water dimer [8] and although the basis set utilized was only medium-sized, it seems that a number of interesting informations can be gained by this type of study, especially if more calculations are performed either on the same system with refined basis sets, or on other systems. The present paper reports on a nonempirical calculation of the cyclic dimer of formamide, and is part of a study of the structure of hydrogen-bonded peptides.

Standpoint and Method

One way to attack the problem of the hydrogen bond would be to start with the infinitely separated components and allow them to approach each other, investigating the potential energy surface and the variations of the electronic characteristics along the path of approach. This procedure would require a large number of calculations in different conformations so as to allow for all possible deformations of angles and bond lengths inside each constituent. Another possibility is to study the characteristics (structure and energy) of the hydrogenbonded complex and compare it to the non-bonded individual units. The first approach would seem ideally the best if all factors could be taken into account and if, among other things, no change of phase occured in the process. If, however, a comparison with experimentally existing compounds is desired, the less ambitious second approach is probably more realistic. Thus, in the case of formamide, the hydrogen-bonded entities are well-defined in the crystal where cyclic dimers occur in which two practically coplanar formamide units are linked by two hydrogen bonds, as revealed by the X-rays diffraction study [9]. We have adopted this geometry for the calculation of the dimer. On the other hand, we have made a calculation of the monomer, frozen in the geometry of the half-dimer. The differences observed between the dimer and the two isolated half-dimers can be considered as representing the intrinsic effect of "bonding" through the hydrogen bond, in particular any transfer of electrons observed under these conditions will result only from the establishment of the interactions between the monomeric units. The same point of view has been adopted in a previous calculation made in our laboratory by the CNDO/2 procedure [3].

The method adopted is a non-empirical self-consistent molecular orbital calculation including all electrons, using an atomic basis set of Gaussian-type functions (GTF). The calculations were performed with the CDC 3600 version [10] of the IBMOL program [6]. The input geometry used for the dimer is given in Fig. 1. Since only the coordinates of the heavy atoms are known by X-rays investigation, it was assumed that the hydrogen atom was colinear with the end atoms. Reasonable values of 1.0 Å for NH and 1.1 Å for CH bonds were adopted. The monomer was treated as a half-dimer as explained above.

The choice of the appropriate GTF basis set is not an entirely solved problem in a self-consistent calculation and its incidence on the final results may be quite important, particularly as far as structural features are concerned [11–14]. The optimization of the exponents of the individual AO's in the molecule seems to

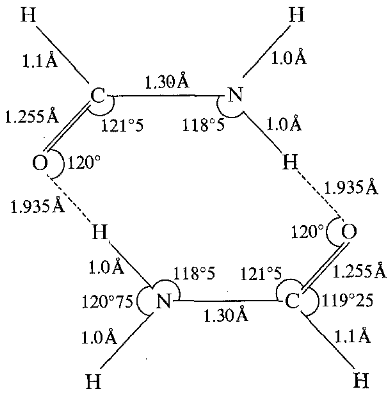

Fig. 1. Configuration of the dimer used as input geometry

be a good possibility as shown by Pitzer's calculation, with Slater AO's on methane [15], and some efforts have already been made in this direction [12, 14, 16]. For the present study, which involves a supplementary phenomenon with respect to the "usual" molecular binding, we have preferred to use GTF basis sets already extensively utilized for "normal" molecules so as to have a point of comparison. In order to avoid the inconvenience inherent to the use of a unique basis, we have performed our calculation in two rather different GTF sets:

Set A, which was initiated by Clementi and his group for calculations on large aromatics [17, 18], and is a ($7^s\,1^p/3^s$) atomic basis[1] contracted to ($2^s\,3^p/1^s$).

Set B, which was partially optimized on small molecules [11, 12] and is a ($4^s\,2^p/3^s$) basis, contracted into ($2^s\,1^p/2^s$). This second set is less rich in GTF than Set *A*, but it involves less contraction, in particular on the hydrogens, a feature which may have its importance in the problem investigated.

The exponents and coefficients corresponding to these two sets can be found in the original publications [17, 18, 11].

The IBMOL program contains an analysis of the wave function in terms of the usual Mulliken populations [19]. Although these populations do certainly express overall trends in the electronic structure of molecules, it is quite generally felt [20] that they must be used with caution in the interpretation of fine structural features. This is why we have supplemented our discussion by examining density contours calculated from the wave functions.

Results and Discussion

The energy results for the dimer and the monomer are given in Table 1 for the basis sets *A* and *B*. As expected [11], the total energies obtained with set *A* are much better on an absolute scale than those of set *B*, but we are essentially interested here in the comparison of the dimer with the monomer inside a given basis set. It is seen that both calculations indicate the dimer to be more stable

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[1] The notation ($7^s\,3^p/3^s$) stands for 7 GTF of *s*-type, 3 GTF for each *p*-type orbital on every "heavy" atom, and 3 GTF of *s*-type for every hydrogen atom.

Table 1. *Total and orbital energies (atomic units)*

	Set A		Set B	
	MONOMER	DIMER	MONOMER	DIMER
Total energy	−168.1848	−336.3931	−164.4493	−328.9292
Virial coefficient	1.9903	1.9899	2.0582	2.0579
Occupied orbital energies (reversed sign)	20.5142	20.5096 20.5096	20.7883	20.7921 20.7921
	15.6679	15.6519 15.6519	15.7991	15.7848 15.7848
	11.5449	11.5511 11.5511	11.5433	11.5482 11.5482
	1.4065	1.4133 1.4087	1.4323	1.4424 1.4376
	1.2481	1.2390 1.2464	1.2818	1,2741 1.2796
	0.8815	0.8887 0.8651	0.8878	0.8935 0.8726
	0.7912	0.7896 0.7821	0.8016	0.7995 0.7930
	0.7020	0.6759 0.7251	0.7079	0.6830 0.7299
	0.6336 π	0.6334 π 0.6285 π	0.6068 π	0.6092 π 0.6033 π
	0.5878	0.6068 0.5800	0.5823	0.6056 0.5781
	0.4529	0.4669 0.4483	0.4223	0.4424 0.4199
	0.4336 π	0.4304 π 0.4369 π	0.4097 π	0.4076 π 0.4150 π

Table 2. *Evolution of the orbital energies of the* 1 *s levels and of the gross charges in the corresponding atoms (set A)*

		Monomer	Dimer
ε	$1s_O$	20.51421	20.50956
	$1s_N$	15.66787	15.65194
	$1s_C$	11.54488	11.55110
q	O	8.3834	8.4206
	N	7.6388	7.6463
	C	5.8302	5.8186

than the isolated units, by 14 kcal/mol in set A and 19 kcal/mol in set B (for two hydrogen bonds). A comparison with the experimental value – 7 kcal per H bond in solids [21] – shows that the difference obtained is reasonable. However we do not think that too much significance must be attached to such a comparison on account of the hypothesis made in both experiment and theory.

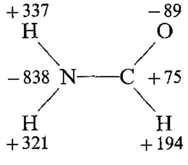
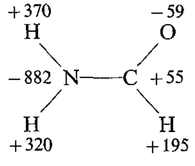
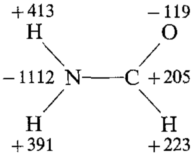
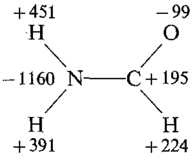
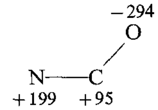
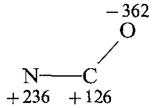
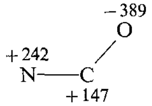
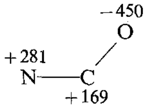
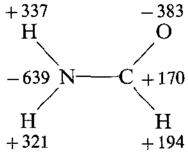
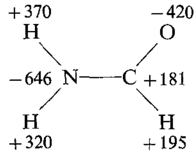
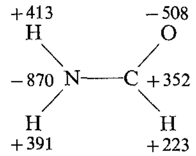
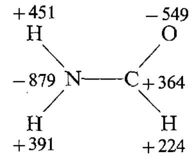
The splitting of the energy levels of the monomers by allowing for interaction shows the following features:

a) The general behavior is entirely the same in the two basis sets, in spite of the expected numerical differences (as usual [12], the deep MO's of set *B* are deeper than those of set *A*, the reverse being true for the higher orbitals). It can be observed that a general correlation exists between the changes in the gross atomic populations of the atoms and the orbital energy shifts. Those molecular orbitals which have large coefficients on atoms which loose electrons on dimer formation have their energy lowered and vice-versa. This is particularly visible on the deepest levels essentially made of the 1*s* atomic orbitals. These 1*s* molecular orbitals remain practically degenerate in the dimer. Their position and the corresponding gross charges on their atoms of localization in the monomer and dimer are given in Table 2 for set *A*. The loosening of the 1*s* electrons on O and N parallels the charge increase on these atoms upon dimerization whereas the tightening of the $1s_C$ level follows the corresponding decrease of global charge. This suggests that hydrogen-bonding could perhaps be detected by electron spectroscopy measurements of the ε_{1s} of the atoms involved, like other variations in chemical environments [22].

b) The π orbitals undergo very little splitting in the dimer, less than the σ levels in the same energy range.

c) The largest splitting occurs for the eighth occupied σ orbital of the monomer in both sets. In fact, the examination of the contour density map for this individual MO shows that although extending through the whole molecule, it is to a large extent essentially localized on the NH bond engaged in hydrogen bonding and this mainly on the hydrogen. The rather large intermolecular overlap between the 1*s* hydrogen atomic orbital and the opposite oxygen lone-pair gives rise to the energy splitting.

Table 3. *Mulliken population analysis*[a]

	Set *A*		Set *B*	
	Monomer	Dimer[b]	Monomer	Dimer[b]
σ net charges				
π net charges				
Total net charges				

[a] Unit of charge $= +10^{-3}e$.

[b] The oxygen and the upper hydrogen are the atoms engaged in hydrogen bonding.

Table 3 summarizes the values of the Mulliken populations in basis sets *A* and *B* respectively for the monomer and the dimer. The hydrogen atom engaged in the hydrogen bond, and the oxygen, lose σ electrons, while the nitrogen atom and, to a lesser extent, the carbon atom gain σ electrons. In turn the oxygen gains π electrons, whereas the nitrogen and carbon atoms lose them. Globally, the hydrogen of the bridge loses electrons for the benefit of both the proton-donor and the proton-acceptor. It is remarkable that these conclusions are qualitatively entirely similar to those obtained by an all-valence electrons semiempirical

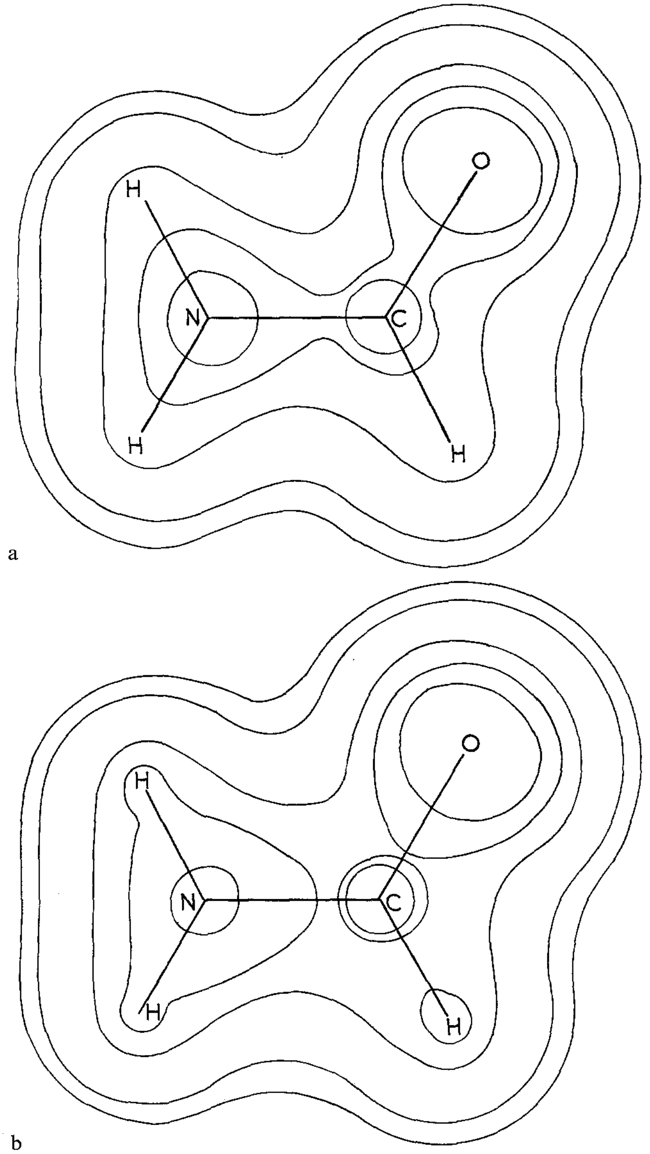


Fig. 2. Density contour maps in the monomer a) set *A*, b) set *B*. The values of the electron density are 0.01 (outer curve), 0.02, 0.10, 0.25 and 0.50 (inner curve)

method [3]. Moreover, the qualitative conclusions regarding the charge shifts do not depend on the GTF basis set. This seems to be also the case with the dimer of H_2O [8, 23].

The overlap populations are decreased in the dimer for NH and for CO, while they increase on CN. The overlap population on the H ··· O "bond" is 0.040 in Set *A* and 0.055 in Set *B*.

The density contours obtained from the wave functions in the two basis sets have been drawn for the dimer and the monomer. We reproduce here only the contours for the monomers (Fig. 2a and 2b) since at this scale the total density contours are not sensitive enough to display the minute differences of the dimer with respect to the monomers. These appear best on the difference density contours of Fig. 3 and 4, on which the following remarks can be made:

a) In basis set *A* (which is the most extended before contraction) no piling-up of electrons is observed between the hydrogen of the bridge and the oxygen.

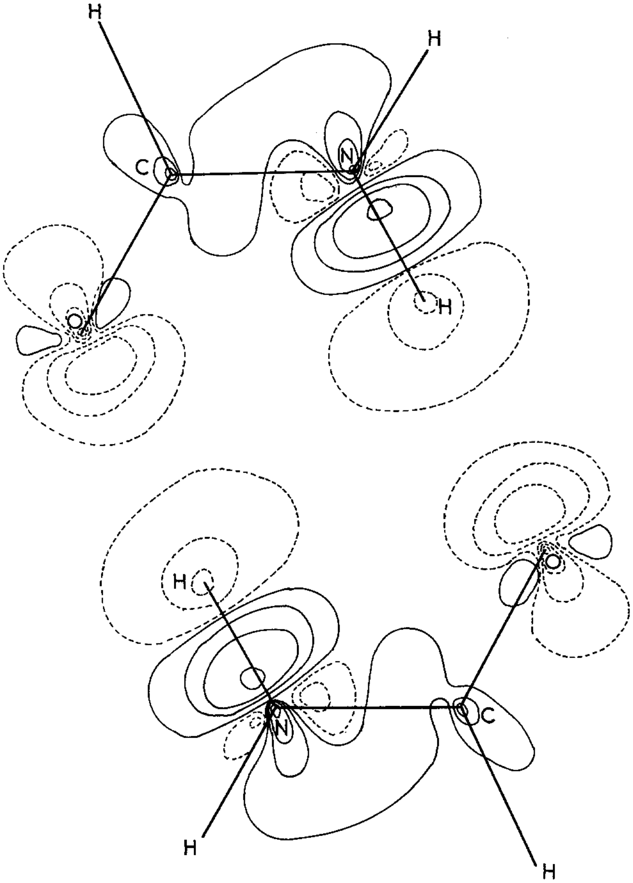


Fig. 3. This map represents the difference in electron density between the dimer and two monomers at the same distance, but supposed ideally not interacting, in set *A*. The dashed lines represent the contours inside which electron density is smaller in the dimer than in the monomer, and full lines represent the reverse situation. The values of this density difference are successively $\pm 10^{-3}$ (outer curves), $\pm 5 \times 10^{-3}$, $\pm 10^{-2}$ and $\pm 3 \times 10^{-2}$

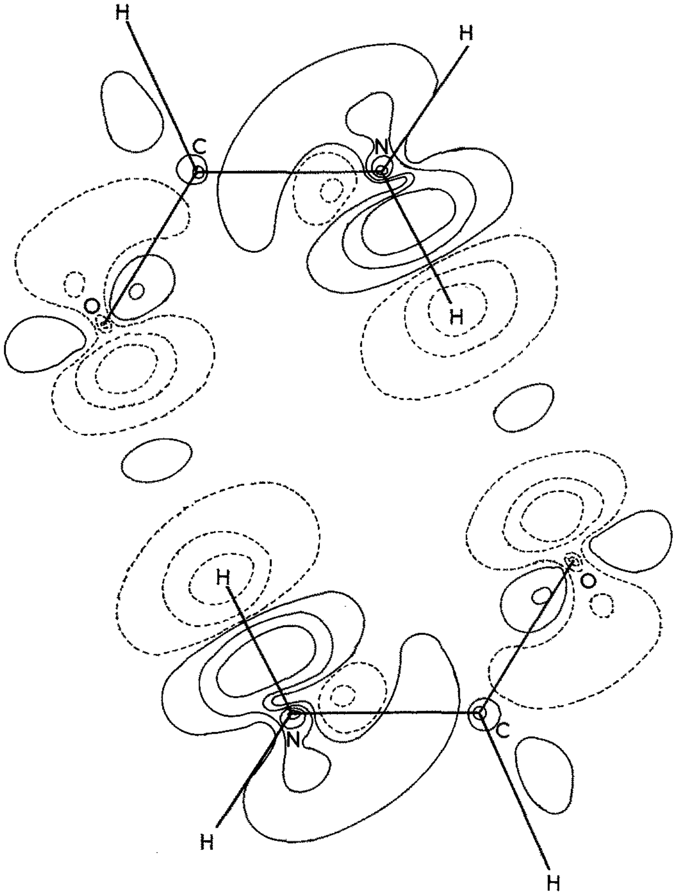


Fig. 4. Same as in Fig. 3, but for set *B*

In the other set *B* a very slight increase in density appears in this region: it must be remarked that the contraction of the GTF in this basis is less severe than in set *A* since every hydrogen is left with two functions instead of one, thus with a larger flexibility on this center for the variational process. The slight accumulation of electrons observed is probably only a reflection of this fact. At any rate, both density difference diagramms indicate that the "covalent" character of the hydrogen bond, if any, is very small. In fact, except perhaps a very narrow region around the proton, electrons seem rather to escape the zone of contact of the two monomers.

b) One observes an increase in the electron density on the NH bond of the dimer as compared to the same bond in the isolated monomer. At the same time the polarity of this bond increases. On the other hand, it is seen that the C–O σ bond does not loose electrons and that the loss observed around the oxygen atom concerns essentially the non-bonding electrons. One may wonder if the same situation would prevail in a linear C–O $\cdots$ H arrangement.

It is interesting to observe the close similarity in the density difference maps for the two basis sets A and B, although the two basis differ markedly as reflected in the isodensity curves for the monomer (Fig. 2a, 2b).

We have tried to analyze further the global effect observed on the differential density curves. For this purpose, the molecular orbitals of the dimer have been subjected to a unitary transformation so as to obtain two sets of molecular orbitals φ_i and $\varphi_{i'}$ each respectively localized on one monomer with a "tail" on the other, and subjected to the supplementary condition that the sum:

$$\sum_{i,i'} |\langle \varphi_{\substack{i \\ \text{or} \\ i'}} | \Phi_{\substack{i \\ \text{or} \\ i'}} \rangle|$$

of their overlaps with the corresponding molecular orbitals Φ of the isolated monomers be maximum.

The probability densities of the "monomer in the dimer" so obtained can then be compared to those of the real monomer and their difference can be considered as giving an image of the "charge transfer" from one unit to the other in the dimer. Fig. 5 shows the difference density maps so obtained (for set A)

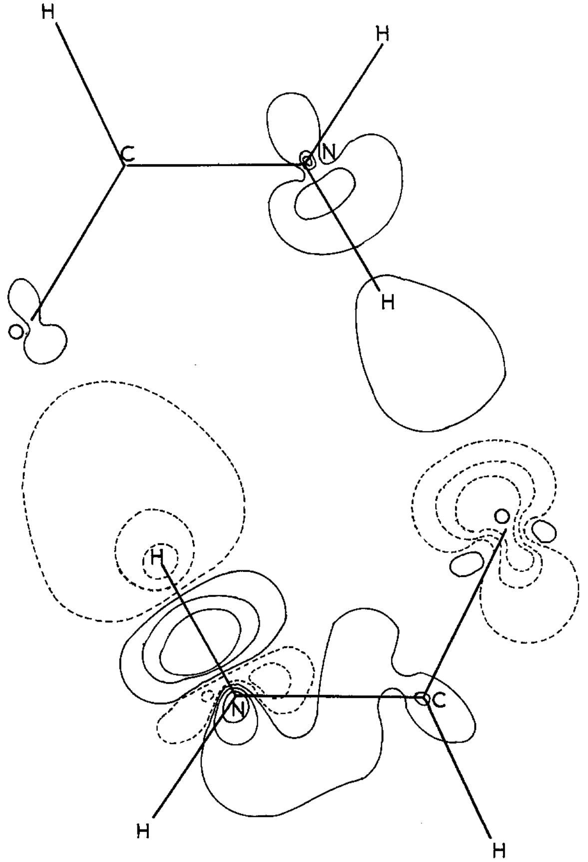


Fig. 5. Map of the "charge transfer" from one monomer to the other when engaged in hydrogen bonding (see text for explanations). The density difference values for the different curves are the same as in Fig. 3

between the "monomer in the dimer", and the real monomer both being located in the lower unit. It is seen that the charge transfer proper is small (it amounts to about 0.022e), and that the most important effect seems to be a rearrangement inside one unit under the polarizing field of the other. Of course two equivalent and opposing effects are superposed so as to result in the global effect observed in Fig. 3.

Conclusion

This exploratory study shows that a non-empirical SCF calculation can give a reasonable account of the energy gain due to hydrogen-bonding. We would like to stress once more, however, that no accurate energy value was expected in view of the approach choosen.

As to the modifications of the electronic structure of the dimer with respect to the isolated monomers, it has been seen that the results of the non-empirical calculations do not contradict those obtained previously with the CNDO/2 procedure: globally, nitrogen and oxygen gain electrons, while the carbon atom and the hydrogen of the bridge loose them, these variations resulting from a large σ gain and a smaller π loss on nitrogen, and from a smaller σ loss and larger π gain on the oxygen, whereas the overlap populations decrease on NH and CO while they increase on CN. The non-empirical calculation permits to go further by inspection of the density maps picturing the wave functions: this shows clearly the increased density in the neighbourhood of the nitrogen atom and in the region of the NC bond, whereas it appears that the electron loss on oxygen comes mainly from the non-bonding electrons, and that the electrons of the NH bond shift towards the nitrogen in the dimer. There is no doubt that the exploration of density contours are of prime importance in the interpretation of fine structural effects, together with the Mulliken populations.

As concerns the effect of the atomic basis set utilized, it is clear that it plays upon the numerical values, particularly of the energies, and also on the shape of the electron density curves without, however, changing the main qualitative conclusions. Nevertheless, the fact that one observes a slight increase in electron density in set *B* (and none in set *A*) on the hydrogen bond proper calls attention to the importance of the atomic representation in so far as one investigates minute structural differences: in the present case, the effect observed in set *B* might be more an artefact due to the "over-representation" of hydrogen than a reality.

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