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Molecular Orbital Theory of the Hydrogen Bond. VI. The Effect of Hydrogen Bonding on the n → π* Transition in Dimers ROH···OCH$_2$

Janet E. Del Bene

Contribution from the Department of Chemistry, Youngstown State University, Youngstown, Ohio 44503. Received December 11, 1972

Abstract: *Ab initio* SCF–CI calculations with a minimal STO-3G basis set have been performed to determine the excitation energies for the lowest excited singlet states in the hydrogen-bonded dimers ROH···OCH$_2$, where R is H, CH$_3$, NH$_2$, OH, or F. The vertical excitation energies in the dimers are greater than the vertical n → π* transition energy in H$_2$CO, and thus the experimentally observed blue shift of the n → π* band upon hydrogen-bond formation is reproduced by the theory. The blue shift is attributed to the additional energy required to break the hydrogen bond in the lowest excited singlet states of these dimers.

Ab initio molecular orbital calculations have recently been reported on various hydrogen-bonded systems.[1–16] In these studies, the structures and energies of hydrogen-bonded dimers have been determined, and various ground state dimer properties have been examined. There are many ground and excited state molecular properties which are affected by hydrogen-bond formation. One of these is the experimentally observed blue shift of the n → π* band of a molecule in a hydrogen-bonding solvent.[17] Early experimental studies of the effect of hydrogen-bonding solvents on such transitions were reported by McConnell,[18] by Brealey and Kasha,[19] and by Pimentel.[20] More recently, this same phenomenon has been investigated by Rao, Goldman, and Balasubramanian,[21] by Krishna and Goodman,[22] and by Baba, Goodman, and Valenti,[23] among others. It was observed that in many cases there was a correlation between the magnitude of the blue shift and the hydrogen-bond strength, as determined by some other experimental method. The blue shift was then qualitatively discussed in terms of the stabilization of the lone pair (n) orbital of the proton-acceptor molecule as a result of hydrogen-bond formation or the energy required to weaken or even break the hydrogen bond in the n → π* excited state. However, these discussions of the blue shift were based on qualitative considerations of the nature of the n → π* transition, rather than on any even semirigorous theoretical study of this phenomenon. It would therefore appear that the application of *ab initio* molecular orbital techniques to this problem could provide a more firm basis for an understanding of the blue shift.

In a recent work,[15] *ab initio* calculations were carried

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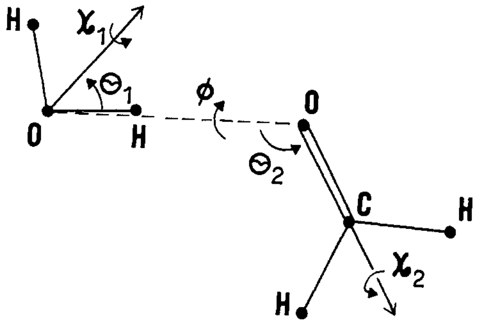

Figure 1. The intermolecular coordinate system illustrated in the equilibrium dimer H_2O–H_2CO. The intermolecular distance (R) is the oxygen–oxygen distance. The angle θ_1 is the angle between the intermolecular line and the principal axis of the proton-donor molecule, while χ_1 measures rotation of the proton-donor molecule about its own principal axis. The angles θ_2 and χ_2 are similarly defined for the proton-acceptor molecule. The angle ϕ describes rotation of the principal axis of the proton-acceptor molecule about the intermolecular line.

out to determine the structures and energies of a series of dimers $ROH\cdots OCH_2$, where R is H or one of the isoelectronic substituents CH_3, NH_2, OH, or F. Since the proton-acceptor H_2CO molecule in these dimers does exhibit an n → π* transition, this particular set of dimers provides an excellent opportunity to apply *ab initio* SCF–CI techniques to a study of the effect of hydrogen bonding on n → π* transition energies. It is the purpose of this paper to report and analyze the results of such a study and to discuss the origin of the blue shift in terms of these results.

Method of Calculation

A. Ground States. The ground state of a molecular system containing $2n$ electrons may be described by a single determinant wave function

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!}$$
$$\equiv |1\bar{1}\,2\bar{2}\ldots n\bar{n}|$$

in which each of n molecular orbitals (MO's) is occupied by two electrons. The MO's ψ_i are expressed as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation)

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu$$

where the expansion coefficients are determined by solving the Roothaan equations.[24] The basis set used in the study of the dimers ROH–H_2CO is a minimal basis consisting of least-squares Gaussian representations of Slater-type orbitals (STO-NG).[25] In particular, three Gaussians are used per Slater (STO-3G) and the standard scale factors proposed by Pople and coworkers for this basis have been employed.

B. Optimization of the Dimer Structures. In the study of the dimers ROH–H_2CO, optimized STO-3G geometries were used for water, the substituted water molecules, and formaldehyde.[12,14,26] These monomer geometries were held rigid for all dimer calculations. In order to describe the dimer structures, it is necessary to select in each monomer an intramolecular axis, called the principal axis. For H_2O and H_2CO, this axis is conveniently chosen as the C_2 symmetry axis. Since a substituted water molecule has no symmetry axis in the X–O–H plane (X is the nonhydrogen atom of the R group), the principal axis in such a molecule has been chosen as the bisector of the X–O–H angle. The relative orientation of the proton-donor and proton-acceptor molecules in the dimer may then be described with reference to the principal axes, in terms of an intermolecular distance (R) and five intermolecular angles. These are illustrated in Figure 1, which also shows the structure of H_2O–H_2CO. Optimization of each dimer structure was carried out to within ±0.01 Å in R, and ±1° in each intermolecular angle. The intermolecular energy of the dimer is obtained by subtracting the energies of ROH and H_2CO from the total energy computed for $ROH\cdots OCH_2$ at that point on the intermolecular surface at which the intermolecular coordinates have their optimum values.

The primary factor which determines the intermolecular energy ("hydrogen-bond energy") of a hydrogen-bonded dimer is the electrostatic interaction between the proton and a directed lone pair of electrons. However, it has been shown that the structures and energies of these dimers are also influenced by other factors, namely, the relative orientation of the permanent dipole moments of the proton-donor and proton-acceptor molecules and certain long range interactions.[14,15] All of these factors contribute to some extent to the hydrogen-bond energy of a dimer in the series $ROH\cdots OCH_2$. The optimized intermolecular coordinates and the hydrogen-bond energies for the dimers are summarized in Table I. A full discussion of these dimers can be found in ref 15.

Table I. Dimer Structures and Energies

$ROH\cdots OCH_2$ R =	R, Å	θ_1', deg[a]	χ_1, deg	θ_2, deg	χ_2, deg	ϕ, deg	ΔE, au[b]
H	2.88	1	0	119	0	180	−0.00530
CH_3	2.86	1	0	119	0	180	−0.00556
NH_2	2.80	−7	0	112	0	0	−0.00667
OH	2.78	−6	−5	114	0	39	−0.00700
F[c]	2.77	−4	0	120	0	0	−0.00798
F[c]	2.77	3	0	120	0	180	−0.00797

[a] $\theta_1' = \theta_1 - \angle X\text{–}O\text{–}H/2$, where X is the nonhydrogen atom of the R group. [b] ΔE is the intermolecular energy (hydrogen-bond energy). 1 au = 627.49 kcal. [c] Equilibrium "cis" (ϕ = 0°) and "trans" (ϕ = 180°) dimers exist.

C. Excited Singlet n → π* States. A first approximation to an excited electronic state may be made by promoting an electron from an orbital ψ_i, doubly occupied in the ground state, to a virtual orbital ψ_l. This virtual orbital approximation gives rise to both singlet and triplet configurations, the former described by the function

$${}^1\Psi_i{}^l = [|1\bar{1}\ldots i\bar{l}\ldots n\bar{n}| - |1\bar{1}\ldots \bar{i}l\ldots n\bar{n}|]/\sqrt{2}$$

While a single configuration may approximate an excited electronic state, it does not take into account electron reorganization in that state. An improved description of the excited state may be obtained by a

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configuration interaction (CI) calculation, which yields a state function $^1\Phi$ given as

$$^1\Phi = \sum_{i}^{\text{occ}} \sum_{l}^{\text{unocc}} A_{il}\Psi_i{}^l$$

with the coefficients A_{il} determined variationally. If the sums over i and l are taken over all occupied and virtual orbitals, respectively, a full first order CI wave function is obtained. However, because the number of such configurations may be quite large, it is generally not possible to obtain the full first order result. Therefore, in a previous work,[27] a well-defined method for selecting a subset of configurations to be included in the CI expansion of the wave function for a low-energy excited state was proposed. In this method, a parameter M is defined, and the M^2 singly excited configurations arising from electron excitation from the M highest occupied orbitals to the M lowest energy virtual orbitals are included in the CI calculation. However, in this study of dimers, it was necessary to slightly modify the configuration selection scheme. The reason for the modification, and the change made, will now be discussed.

It is advantageous to first examine the nature of the n → π* state of H_2CO. The H_2CO molecule, of C_{2v} symmetry in the ground state, has the configuration

$$1a_1{}^2 2a_1{}^2 3a_1{}^2 4a_1{}^2 1b_2{}^2 5a_1{}^2 1b_1{}^2 2b_2{}^2$$

The lowest energy vertical excited singlet state of this molecule has A_2 symmetry and arises primarily from the excitation $2b_2 \rightarrow b_1{}^*$ ($n \rightarrow \pi^*$). In the virtual orbital approximation, the energy of this excitation is 4.56 eV. For the CI calculation, M equals 4, the number of virtual orbitals resulting from the minimal basis SCF calculation. The virtual excitation energy is lowered to 4.21 eV by CI, when with $M = 4$ the configuration arising from the excitation $1b_2 \rightarrow b_1{}^*$ is included in the CI expansion. Thus, although the n → π* state of this molecule is fairly well represented by a single excited configuration, CI does lower the energy of this state by 0.35 eV, bringing the calculated (4.21 eV) and experimental (4.20 eV)[28] values into better agreement. It should be noted that the CI results at $M = 4$ are by symmetry full first order CI results.

As noted previously,[27] for minimal basis calculations on small molecules, the value of the parameter M is determined by the number of virtual orbitals obtained from the SCF calculation. Accordingly, in the dimer H_2O–H_2CO where there are six virtual orbitals, M has a value of 6 and 36 singly excited configurations have been included in the CI expansion of the wave function for the lowest excited singlet state. In the dimers ROH–H_2CO ($R \neq H$), M varies from six in HOF–H_2CO to nine in CH_3OH–H_2CO. In all dimers, the orbital corresponding to the $1b_2$ orbital in H_2CO is fairly well localized in the proton-acceptor H_2CO molecule and can be easily identified. However, in all dimers except CH_3OH–H_2CO (where M has its maximum value), the subset of M highest energy occupied orbitals does not include this orbital, which has a relatively low energy when compared with certain orbitals on the proton-donor molecules and others which are delocalized and span both donor and acceptor molecules. It is apparent from the H_2CO results that the excited configuration $1b_2 \rightarrow b_1{}^*$ is important in describing the H_2CO n → π* state. Therefore, the corresponding configuration should also be included in the description of the lowest excited singlet states of the dimers ROH–H_2CO. If the number of orbitals in the subset from which electron excitation is permitted remains equal to the number of virtual orbitals, then it is necessary to replace one of the M highest energy occupied orbitals in this subset by the orbital corresponding to $1b_2$. The replacement can be made quite systematically in dimers of C_s symmetry, where a high energy orbital of a′′ symmetry is localized on the proton-donor molecule. It was found that configurations arising from electron excitation from this orbital are not significant in the description of the lowest excited singlet states of the dimers. Hence, in this study of the dimer excited singlet states, an a′′ orbital has been replaced in the subset of M orbitals from which electron excitation occurs by the orbital corresponding to the $1b_2$ orbital of H_2CO. In H_2O_2–H_2CO, which has no symmetry plane, a similar substitution was made.

There are two important points which should now be noted.

(1) In CH_3OH–H_2CO, where M has its maximum value, the subset of nine high energy occupied orbitals has as its lowest energy member the orbital corresponding to $1b_2$. For this dimer, configurations arising from excitation from this orbital and from the a′′ orbital were simultaneously included in the CI calculation. The calculation was then repeated, setting $M = 8$ and omitting configurations involving excitation from a′′. It was found that the excitation energy and the electron distribution of the lowest excited singlet state of this dimer were independent of the presence or absence of configurations involving electron excitation from a′′.

(2) When the unmodified configuration selection scheme of ref 27 was employed and configurations involving electron excitation from the orbital related to $1b_2$ were not included in the CI calculation, the order of calculated excitation energies for the lowest excited singlet states of the dimers was exactly the same as the order reported below. However, without configurations arising from excitation from the orbital related to the H_2CO $1b_2$ orbital, the calculated dimer excitation energies were higher than those reported below by 0.33 to 0.35 eV. Such an energy difference is significant, since the inclusion of the $1b_2 \rightarrow b_1{}^*$ configuration was responsible for lowering the energy of the lowest excited singlet state of H_2CO by 0.35 eV. Hence, the inclusion of similar configurations in the dimers is necessary not for describing any electronic changes in the dimer excited states caused by hydrogen bond formation but for describing the change in the electron distribution in the proton-acceptor H_2CO molecule itself.

Results and Discussion

The energies of the lone pair orbitals, the virtual and CI excitation energies for the lowest vertical excited singlet states,[29] and the hydrogen-bond energies in the

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[29] The excitation energies are calculated at the optimized ground state geometries of the dimers. The transition energies are therefore vertical excitation energies.

Table II. Virtual, CI, and Lone Pair Orbital Energies of Importance in the Lowest Singlet Excited States of Dimers $ROH\cdots OCH_2$[a]

	ϵ_n[b]	Excitation energy		Hydrogen-bond energy in $ROH\cdots OCH_2$
		Virtual	CI	
H_2CO	−9.64	4.56	4.21	
$ROH\cdots OCH_2$				
R = H	−10.01	5.21	4.35	0.14
CH_3	−9.89	6.68	4.36	0.15
NH_2	−10.19	6.02	4.38	0.18
OH	−10.63	8.15	4.41	0.19
	−9.62	9.52		
F cis	−10.05	7.13	4.43	0.22
F trans	−10.05	7.38	4.43	0.22

[a] Energies in eV. [b] ϵ_n is the energy of the orbital related to $2b_2$ in the H_2CO monomer.

dimers $ROH\cdots OCH_2$ are given in Table II. For each dimer in the series, the calculated CI transition energy for the lowest excited singlet state is larger than the n → π^* transition energy of H_2CO, and hence the experimental blue shift of the n → π^* band associated with hydrogen-bond formation is reproduced by the theory. It is apparent from Table II that there is a close relationship between the strength of the hydrogen bond in the dimer and the magnitude of the blue shift. In fact, it can be seen that the energy of this shift is determined by the hydrogen-bond strength. That is, the vertical excitation energy in a dimer may be approximated to within 0.01 eV, as the sum of the vertical excitation energy in H_2CO and the energy of the hydrogen bond in the dimer $ROH-H_2CO$. Indeed, if the sum of the energies of the isolated ROH molecule and H_2CO in its vertical n → π^* state is compared with the energy of the lowest excited singlet state of the appropriate dimer $ROH\cdots OCH_2$, it is observed that these two energies differ by less than 400 cal. Hence, these results strongly suggest that the increase in the n → π^* transition energy upon dimer formation is essentially due to the additional energy required to break the hydrogen bond upon excitation to the lowest excited singlet state in the dimer. Moreover, in the excited state of H_2O-H_2CO, the potential curve as a function of the intermolecular distance (R) was examined and found to be repulsive, with the dimer correctly dissociating at large R to ground state H_2O and H_2CO in its n → π^* excited state. Thus, it appears that the interpretation that the blue shift of the n → π^* band upon dimer formation is determined at least in part by the energy required to break the hydrogen bond in the excited state is supported by both experimental and theoretical evidence.

An early interpretation of the blue shift was given in terms of the stabilization of the n orbital upon dimer formation. This rationalization of the origin of the blue shift should now be reexamined in light of the results presented in Table II. In dimers of C_s symmetry, it can be seen that the energy of the n orbital in the dimer is lower than it is in the monomer. However, within the series of dimers, there is no correlation between changes in the energy of this orbital and the n → π^* transition energies. Thus, it does not appear that a change in the energy of the n orbital of H_2CO upon dimer formation can quantitatively account for the shift of the n → π^* band in the dimers $ROH-H_2CO$.

It is also apparent that there is no correlation in the series of dimers between the single configuration n → π^* transition energies (the virtual energies of Table II) and the calculated CI energies. Considering the lack of correlation of both the orbital energies and the virtual excitation energies with the trend seen for the CI state energies, it is questionable whether the designation "n → π^*" should even be applied to the lowest excited singlet states of these dimers. On the other hand, it might be argued that this designation is a convenient one, since it does relate the n → π^* state in H_2CO to the corresponding state in the dimers. Moreover, the largest single contribution to the total wave function for the lowest energy excited singlet state in each dimer is made by the configuration in which an electron is excited from a somewhat delocalized n orbital to the π^* orbital of H_2CO.[30] If for these reasons the dimer excited states are still referred to as n → π^* states, it should be noted that such a description is a convenient but obviously oversimplified one.

Since the dimer $H_2O_2-H_2CO$ has no symmetry plane, a discussion of the nature of its lowest excited singlet state in relation to that of H_2CO is even more difficult. From an examination of the occupied molecular orbitals in $H_2O_2-H_2CO$, it can be determined that two of the high energy molecular orbitals in this dimer bear some resemblance to the n orbital of H_2CO. The energies of these are given in Table II along with the virtual excitation energies corresponding to electron excitation from these orbitals to the lowest virtual orbital (essentially the π^* orbital of H_2CO) in the dimer. The resulting configurations are the major contributors to the total CI wave function for the lowest excited singlet state of $H_2O_2-H_2CO$. Despite the difficulty of presenting a convenient qualitative description of this state, it is obvious from Table II that the CI description is quantitatively quite good in terms of the relationship between the excitation energy in this dimer and the calculated excitation energies of the other dimers in the series.

As noted previously, the n orbital, in particular, and a′ orbitals, in general, are delocalized to some extent on both proton-donor and proton-acceptor molecules in all dimers. In contrast, the a″ orbitals are not delocalized but are restricted to either the proton donor or the proton acceptor. In all dimers of C_s symmetry, the lowest virtual orbital is the localized π^* orbital of H_2CO. This should not imply that the π and π^* orbitals of H_2CO are unchanged in the dimers. However, although the energy of the π^* orbital (ϵ_{π^*}) of H_2CO decreases upon dimer formation, neither the change in ϵ_{π^*} nor the change in the quantity ($\epsilon_{\pi^*} - \epsilon_n$) correlates with the trend in calculated transition energies in this series of dimers.

It is now of interest to examine the electron population changes in the dimers in both the ground and the n → π^* excited states. Although Mulliken gross atomic populations[31] will be discussed for all dimers, the discussion of the orbital populations will be limited to dimers of C_s symmetry where orbitals may be classified as a′ or a″. Excitation from the ground to the

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(30) It is interesting to note that the configuration which makes the second largest contribution to the CI wave function arises when an electron is excited from an orbital located primarily on the proton-donor ROH molecule to the π^* orbital of H_2CO.

(31) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

Table III. Mulliken Gross Atomic Populations for Monomers and Dimers in Ground and Excited States[a]

	X	O	H	O	C	H_a[b]	H_b
H_2CO				8.188	5.925	0.943	0.943
				(7.795)	(6.460)	(0.872)	(0.872)
H_2O	0.835	8.330	0.835				
H_2O–H_2CO	0.850	8.363	0.814	8.197	5.911	0.934	0.931
	(0.850)	(8.351)	(0.813)	(7.811)	(6.458)	(0.860)	(0.857)
CH_3OH	6.071	8.280	0.826				
CH_3OH–H_2CO	6.072	8.313	0.802	8.197	5.910	0.933	0.931
	(6.072)	(8.300)	(0.802)	(7.812)	(6.457)	(0.859)	(0.857)
NH_2OH	7.279	8.223	0.805				
NH_2OH–H_2CO	7.292	8.255	0.778	8.200	5.911	0.936	0.919
	(7.290)	(8.238)	(0.778)	(7.820)	(6.460)	(0.861)	(0.845)
H_2O_2	8.189	8.189	0.811				
H_2O_2–H_2CO	8.208	8.226	0.783	8.199	5.907	0.931	0.924
	(8.206)	(8.209)	(0.782)	(7.819)	(6.457)	(0.856)	(0.850)
HOF	9.048	8.148	0.804				
HOF–H_2CO	9.076	8.191	0.777	8.199	5.905	0.927	0.927
(cis)	(9.074)	(8.175)	(0.775)	(7.824)	(6.454)	(0.846)	(0.853)
HOF–H_2CO	9.069	8.195	0.779	8.198	5.904	0.927	0.928
(trans)	(9.068)	(8.178)	(0.778)	(7.819)	(6.455)	(0.847)	(0.856)

[a] Populations in parentheses are for excited states. [b] H_a in a dimer is that H_2CO hydrogen having the larger z coordinate when the origin of the Cartesian coordinate system is placed at the oxygen atom of ROH and the hydrogen bond forms along the $+z$ axis. See Figure 1.

n → π^* states in the series of dimers ROH–H_2CO is accompanied by changes in the electron distribution in these dimers. It is important, in order to appreciate the changes which occur, to first note the changes in the atomic populations in H_2CO itself upon excitation to the n → π^* excited state and then to compare the monomer populations with those found in the dimers. It is also of interest to compare the ground and excited state electron densities of the proton-donor molecules to determine if there is any change in these populations when an excited state associated with the proton-acceptor molecule is formed.

From the data of Table III, it can be seen that there is a large change in the electron populations of the carbonyl atoms upon excitation to the H_2CO monomer excited n → π^* state. In particular, the oxygen atom which bears a negative charge of 0.188 electron in the ground state becomes positively charged in the excited state. In contrast, the carbon atom, which bears a small positive charge in the ground state, acquires a large negative charge of 0.460 electron in the excited state. The H_2CO hydrogens also become more positively charged in the excited state than they are in the ground state. This change in the electron distribution upon excitation is readily understood in terms of the nature of the $2b_2 \rightarrow b_1^*$ transition, in which an electron is excited from an orbital in the σ framework (primarily an oxygen lone pair orbital which is somewhat delocalized onto the hydrogen atoms) to a π^* orbital in the carbonyl group which is polarized toward carbon. Such a change in the electron distribution in the excited state may have important consequences with respect to the site of hydrogen-bond formation in this state. It has already been observed that the strength of a hydrogen bond formed between a proton and a directed lone pair of electrons may be related to the negative charge on the proton-acceptor atom.[14,15] Therefore, on the basis of the positive charge on the carbonyl oxygen, it would appear that hydrogen bonding at the oxygen atom through the σ framework would be unfavorable in the vertical n → π^* state of H_2CO. This observation is consistent with the calculated dimer excitation energies and with the repulsive potential curve with respect to R found for the excited H_2O–H_2CO dimer, which also suggest that the O–H···O bond formed in the ground state through the oxygen lone pair is essentially broken in the vertical excited n → π^* state of dimers ROH–H_2CO.

Table III also lists the gross atomic populations for the ground and excited states of dimers ROH–H_2CO. The electron distribution in the H_2CO molecule in the dimer excited states is similar to that found in the monomer. However, it should be noted that the carbonyl oxygen is slightly less positively charged in the dimer excited states than in the monomer, while the H_2CO hydrogens are more positively charged in the dimer excited states. In the proton-donor ROH molecules, it is interesting to note that the gross atomic populations of the hydrogen-bonded proton and the nonhydrogen atom of the R group (X) are essentially unchanged in going from the ground to the excited states of these dimers, but that the hydroxyl oxygen apparently loses electron density in the excited state. This loss results from electron transfer from ROH to H_2CO. Thus, in the ground states of the dimers, hydrogen bonding is accompanied by a small amount of charge transfer varying from 0.027 to 0.043 electron from H_2CO to ROH. In the n → π^* excited states, a still smaller amount of electron density (less than 0.022 electron) is transferred back from ROH to H_2CO. It was observed in paper IV[15] that upon hydrogen-bond formation in ROH–H_2CO the π orbital of H_2CO becomes more polarized toward oxygen in order to compensate for electron transfer from the oxygen of H_2CO through the σ electron system. In the excited states of dimers ROH–H_2CO, electron transfer also occurs in the σ framework, only from ROH to H_2CO. However, the σ electron system of H_2CO loses electron density due to the nature of the n → π^* transition. This loss appears as an increase in the excited state π electron density in the carbonyl group, especially at the carbon atom (see Table IV) toward which the π^* orbital is polarized.

Conclusions

The *ab initio* SCF–CI calculations which have been

Table IV. Mulliken Gross Carbonyl π Densities in the Ground and Excited States of the H_2CO Monomer and Dimers $ROH\cdots OCH_2$[a]

	O	C
H_2CO	1.085 (1.543)	0.915 (1.457)
$ROH\cdots OCH_2$		
R = H	1.115 (1.557)	0.885 (1.443)
CH_3	1.116 (1.558)	0.884 (1.442)
NH_2	1.123 (1.562)	0.877 (1.438)
F cis	1.128 (1.564)	0.872 (1.436)
F trans	1.128 (1.564)	0.872 (1.436)

[a] Densities in parentheses are for the excited states.

performed on the lowest excited singlet states of the dimers $ROH-H_2CO$ have produced vertical excitation energies which are greater than the vertical $n \rightarrow \pi^*$ transition energy obtained for H_2CO. Hence, the experimentally observed blue shift of the $n \rightarrow \pi^*$ band upon hydrogen-bond formation is reproduced by the theory. An analysis of the data shows that the magnitude of the blue shift is essentially equal to the strength of the hydrogen bond in the dimer. Such a relationship suggests that the blue shift reflects the additional energy required to break the hydrogen bond in the dimer lowest excited singlet states. This conclusion is also supported by the nature of the intermolecular potential curve as a function of R which was found to be repulsive in the dimer H_2O-H_2CO. No correlation in the series of dimers was found between the CI excitation energies and either the change in the energy of the H_2CO n orbital in the dimers or the virtual excitation energies. The general features of the electron distribution in H_2CO in the dimer excited states are similar to those observed in the excited state of H_2CO itself. Some of the electron density transfered in the dimer ground states from H_2CO to ROH is transfered back to H_2CO in the excited states.

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Comparative Study of Hybridization in Hydrocarbons[1a]

Zvonimir B. Maksić*[1b] **and Milan Randić**[1c]

Contribution from the Theoretical Chemistry Group, Institute "Rudjer Bošković," 41001 Zagreb, Croatia, Yugoslavia, and the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received February 25, 1972*

Abstract: A comparative study of the hybridization in some 30 hydrocarbons was made by using the EHT, IEHT, CNDO/2, and MOA methods. It was found that the hybridization in hydrocarbons is relatively insensitive to the method applied. The MOA method gives slightly better hybrids than other semiempirical methods, as judged from a comparison with available *ab initio* results and $J(^{13}C-H)$ coupling constants. The hybrids obtained by the MOA method might provide a good initial guess for wave functions for *ab initio* SCF calculations employing hybrid basis sets.

There are numerous methods and approaches available for a theoretical study of medium size molecules on the semiempirical level. These methods often differ in their intended or achieved accuracy. Some are designed for a description of a single molecular property; others are quite general in their applicability. Many of these approaches are unfortunately vague about the advantages or disadvantages of the individual approximations. It seems that the present trend is to produce more results for increasing numbers of molecules using the existing methods, rather than examining the underlying assumptions and evaluating the deficiencies. True, the semiempirical methods need to be applied to a large number of molecules in order to test their generality and to avoid a situation where the selected parameters suit only a small group of molecules. However, it also seems that the numerous applications of semiempirical methods have weakened the caution which the underlying assumptions suggest. Some attention has been given to the deficiencies of the diagonal elements,[2] but a particularly troublesome problem seems to be the choice of the off-diagonal elements.[3] It seems, therefore, that the comparative study of several semiempirical methods might be very illuminating, even if it is limited to a de-

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