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Hydrogen Bonding: A Molecular Orbital Treatment by the EHT and the CNDO/2 Methods of Methanol and of Formic Acid

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By both the EHT and the CNDO/2 calculations, the linear dimer of methanol is found to be more stable than the cyclic dimer. The hydrogen bonds in the trimer are stronger than those in linear dimers. The proton potential function, charge densities, and overlap populations in the linear dimer of methanol have been obtained. The CNDO/2 calculations show that the *cis*-form of formic acid is more stable than the *trans*-form, in agreement with experimental data. The cyclic dimer of formic acid is more stable than the open dimer. The β-form of formic acid trimer is more stable than the α-form. The proton potential function and the charge densities in the cyclic dimer of formic acid have been obtained. The CNDO/2 method gives more realistic proton potential functions for the dimers of methanol and formic acid. The $O \cdots O$ stretching force constant in the dimers of methanol and formic acid have been estimated to be 0.13×10^5 dynes/cm and 0.27×10^5 dynes/cm, respectively, in agreement with experimental data.

Introduction

Considerable information is available in the literature [1, 2] on the spectroscopic and thermodynamic properties of hydrogen bonded systems. Since the early electrostatic model of the hydrogen bond, there have been several theoretical studies which have been reviewed by Coulson [3] and Bratoz [4]. Molecular orbital treatment of the hydrogen bond has received greater attention in recent years and the modified Pariser-Parr-Pople scheme, including σ-electrons [5, 6], Hoffmann's extended Hückel theory [7, 8], and the iterative extended Hückel theory [9] have been employed in these studies.

In view of the success of the semi-empirical molecular orbital studies on small organic molecules, we have investigated the hydrogen bonding in some simple systems by the extended Hückel (EHT) method [10] and the semi-empirical SCF all valence electron method with complete neglect of differential overlap (CNDO/2) [11]. Such a comparative study would be of value, since it has been suggested that the EHT approximation does not give correct proton potential functions in hydrogen bonded systems, possibly due to the absense of electron correlation [8]; probably for the same reason, the EHT method does not predict the relative stabilities of the keto and enol forms of acetylacetone [7]. The CNDO/2 approximation, on the other hand, takes into account all the important electron repulsions.

The hydrogen bond systems presently investigated are methanol and formic acid. In alcohols, both linear and cyclic structures for the dimer have been proposed [1, 12], although there is no conclusive experimental evidence in favor of either

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of the structures. Hydrogen bonds in linear trimers and polymers have been proposed to be stronger (per hydrogen bond) than those in dimers [13]. The relative stabilities of the (cyclic and linear) dimers and trimers of methanol as well as the proton potential function in the dimers have been examined. In the case of formic acid, the relative stabilities of the *cis* and *trans* isomers of the monomer and the open and cyclic structures of the dimer have been investigated. In addition, the proton potential function in the dimers has been obtained. In the light of the known structures of the two polymorphic forms of polymeric formic acid [14], the stabilities of two configurations of the formic acid trimer have been examined.

Methods of Calculation

EHT *method:* The EHT method [10] includes all the valence electrons. All overlap integrals, S_{ij}, are evaluated. The secular determinant is $|H_{ij} - ES_{ij}| = 0$. The diagonal element (coulomb integral), H_{ii} is equated to the negative value of the ionization potential of the corresponding valence state of the neutral atom. The off-diagonal element (resonance integral), H_{ij}, is evaluated by the method of Wolfsberg and Helmholtz [15] where $K = 1.75$.

$$H_{ij} = \tfrac{1}{2} K S_{ij} (H_{ii} + H_{jj}) .$$

The following H_{ii} values have been used in the calculations: $H_{ii}(\mathrm{C}, 2s) = -21.43$ eV, $H_{ii}(\mathrm{C}, 2p) = -11.42$ eV, $H_{ii}(\mathrm{O}, 2s) = -35.30$ eV, $H_{ii}(\mathrm{O}, 2p) = -17.76$ eV, and $H_{ii}(\mathrm{H}, 1s) = -13.60$ eV. The computer program described by Hoffmann [16] has been used in the present calculations.

CNDO/2 *method:* In this method, the product of two different atomic orbitals, $\phi_i(1)\phi_j(1)$, associated with electron 1 is neglected in electron interaction integrals. The LCAO-SCF Hartree-Fock matrix elements are approximated by

$$H_{ii} = -\tfrac{1}{2}(I_i + A_i) + [(P_{\mathrm{AA}} - Z_{\mathrm{A}}) - \tfrac{1}{2}(P_{ii} - 1)]\,\gamma_{\mathrm{AA}} + \sum_{\mathrm{B}(\neq \mathrm{A})} (P_{\mathrm{BB}} - Z_{\mathrm{B}})\,\gamma_{\mathrm{AB}} , \qquad (1)$$

$$H_{ij} = \beta_{\mathrm{AB}}\, S_{ij} - \tfrac{1}{2} P_{ij}\, \gamma_{\mathrm{AB}} . \qquad (2)$$

The first term in Eq. (1) represents the Mulliken electronegativity of the orbital. The middle term of Eq. (1) gives the destabilizing effect of a net excess electronic charge on Atom A (if $P_{\mathrm{AA}} > Z_{\mathrm{A}}$), and the final term gives the coulomb potential at ϕ_i due to net excess charges on other atoms in the molecule. The off-diagonal elements given in Eq. (2) use a semiempirical resonance integral proportional to overlap, the constant of proportionality β_{AB} depending only on the nature of atoms A and B. The final term in Eq. (2) is a correction to off-diagonal elements due to electron repulsion. The calculations have been carried out using the computer program described by Segal [17].

All the calculations were carried out with the IBM 7094 and the CDC 6500 computers at Purdue University.

Results and Discussion

Methanol

The total energy of methanol was calculated using the most stable configuration and conformation, I, (Fig. 1) obtained by Morokuma and Coworkers [7]. In this configuration, the O–H bond has the *trans* conformation to the C–H bond in the COH plane. The structural parameters for methanol were taken from Kimura and Kubo [18]. The conformations of the dimers (cyclic and linear) and trimers of methanol are shown in Fig. 1.

The energies of the cyclic and linear dimers of methanol were first calculated as a function of the O ··· O distance. The results (Fig. 2) of the calculations by both

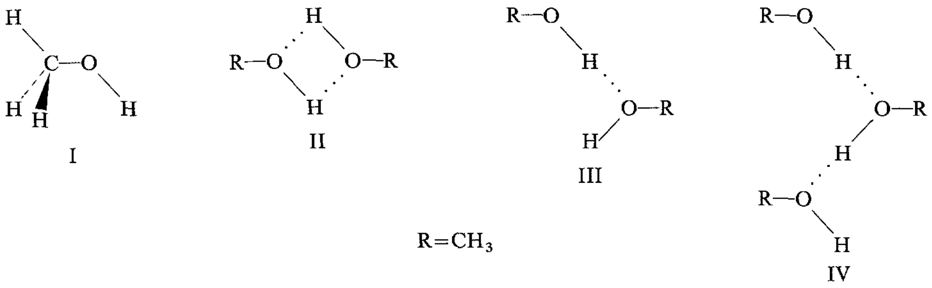


Fig. 1. Molecular arrangement of methanol monomer, dimer, and trimer

the EHT and the CNDO/2 methods show that the cyclic structure is much less stable than the linear dimer. No minimum energy configuration for the cyclic dimer is found by the EHT method even when the O ··· O distance is varied between 2.0 and 3.6 Å. The minimum around 2.1 Å obtained from the CNDO/2 calculations is shorter than the experimental value. The total energy at the minimum is considerably higher than that found for the linear dimer. The hydrogen bond energy calculated as the difference between the minimum energy of the

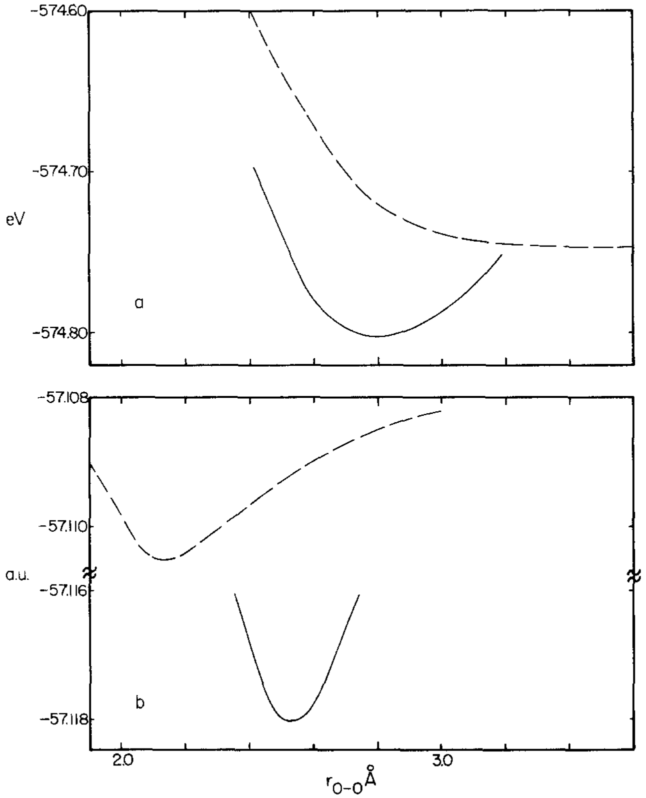


Fig. 2a and b. Total energy of the dimer of methanol as a function of the O ··· O distance: Cyclic dimer, dotted line; open dimer, full line. a) by the EHT method, b) by the CNDO/2 method dimer and the energy of two monomers for the cyclic dimer is found to be 1.7 kcal by the CNDO/2 method (Table 1). Remembering that this energy is for two bent hydrogen bonds in the cyclic dimer, the value is much too low compared with the experimental value of ~ 6 kcal [1]. The minima for the linear dimer are, however, seen distinctly at ~2.6 Å and 2.8 Å by the CNDO/2 and EHT methods, respectively; these values are close to the experimentally determined value of 2.66 Å [1]. The dissociation energy of the hydrogen bond in the linear dimer is 1.3 and 6.5 kcal, respectively, by the two methods (Table 1). The hydrogen bond energy by the CNDO/2 method is in good agreement with the experimental value [1].

Table 1. EHT *and* CNDO/2 *calculations on hydrogen bonding: methanol*

	EHT				CNDO/2	
	$r_{O\cdots O}$ [Å]	$D_{OH\cdots O}$ [kcals]	Overlap populations		$r_{O\cdots O}$ [Å]	$D_{OH\cdots O}$ [kcals]
			C–O	O–H		
Monomer, I[a]	–	–	0.429	0.499	–	–
Cyclic dimer, II	–	0.00[b]	–	–	2.1	1.70[d]
Linear dimer, III	2.8	1.30	0.427	0.478[c]	2.6	6.46[e]
Trimer, IV	–	–	–	–	2.6[f]	13.68[d]

[a] Energy of monomer was −287.373 eV and −28.5539 a.u. respectively by the EHT and CNDO methods.

[b] Value where the total energy levels off in Fig. 2.

[c] Overlap population of the H···O bond was 0.043.

[d] Energy of two hydrogen bonds.

[e] Experimental value is ~ 6 kcal.

[f] Assumed value; experimental value is ~2.66.

It was considered interesting to examine the effect of bending the hydrogen bond of the linear dimer of methanol on the dissociation energy. In-plane bending of the hydrogen bonded O–H bond (up to 20°) does not change the total energy of the linear dimer; out-of-plane bending, however, increases the energy of the dimer considerably, the out-of-plane bending energy being about 0.055 eV for 20°. The energy of the linear dimer also increases (0.025 eV by the EHT method and 0.0023 a.u. by the CNDO/2 method) if the conformation of the donor methanol molecule is such as to render the O–H bond (of the donor) out-of-plane with the hydrogen bond.

In order to examine the motion of the proton in the linear dimer (III) of methanol, the O–H distance was varied between 0.3 and 2.5 Å while keeping the O···O distance constant. The total energies of the linear dimer calculated by the EHT and the CNDO/2 methods has been plotted against the position of the proton in Fig. 3. The EHT method gives a distinct double minimum (Fig. 3a), but the minimum corresponding to the O–H equilibrium distance is at a higher energy than the minimum corresponding to the H···O distance. Varying the O···O distance only affects the position of the H···O minimum slightly, without changing the energy. Further, the position of the two energy minima are much too close (0.5 and 0.7 Å) to the two oxygen atoms of the dimer. This picture of the energy barrier for proton transfer obtained by the EHT method is not very acceptable. A similar behaviour has been found recently by Adam and coworkers [8] in their EHT calculations of the water-pyridine system.

The proton potential function by the CNDO/2 method (Fig. 3b) gives a well defined minimum at an O–H distance of 1.0 Å. The minimum corresponding to the H···O distance is not distinct; if the shoulder around 1.6 Å is taken to be due to the H···O minimum, both these distances seem to be reasonable. The second

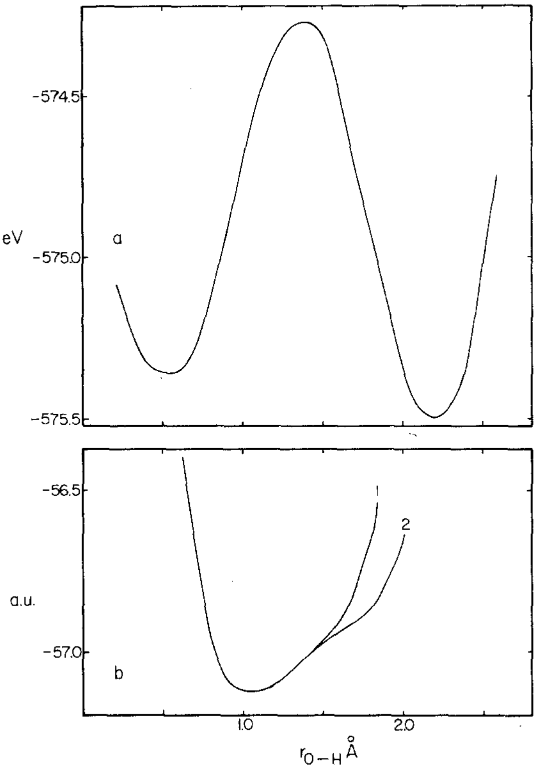
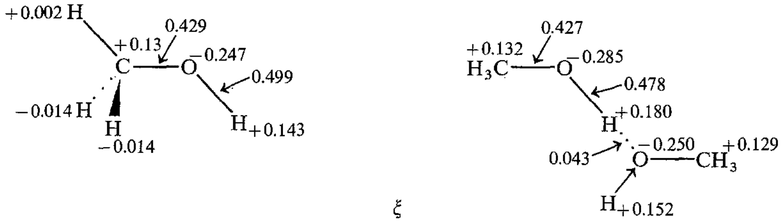


Fig. 3. a) Total orbital energy of (eV) of the linear methanol dimer by the EHT method as a function of the position of the hydrogen atom: the O···O distance is 2.8 Å. b) Total energy (a.u.) of linear dimer of methanol by the CNDO/2 method as a function of the position of the hydrogen atom. 1 and 2 correspond to O···O distance of 2.6 and 2.8 Å, respectively

energy minimum corresponding to the H···O distance is at a higher energy than the O–H minimum, as expected.

The O ··· O stretching force constant of the linear dimer was estimated by taking the second derivative of the energy curve around the equilibrium distance. The value of the force constant is 0.13×10^5 dynes/cm by the EHT method. The EHT method was preferred here since it gives a more realistic O···O distance. This is in good agreement with the range of values 0.06 to 0.24×10^5 dynes/cm suggested by Lake and Thompson [19] on the basis of spectroscopic data.

The molecular diagrams of methanol and methanol dimer ($r_{O \cdots O} \sim 2.6$ Å) by the CNDO/2 method are given in Fig. 4. By the CNDO/2 calculations, we find



	ξ	
	EHT	CNDO/2
H	1.0	1.2
C	1.625	1.625
O	2.275	2.275

Fig. 4. Molecular diagrams for methanol and methanol linear dimer. The numbers with signs are the charges on the atoms found by the CNDO/2 method. The numbers pointing towards bonds are the overlap populations by the EHT method. The orbital exponent values, ξ are also shown

that there is a definite overlap between the 1*s* orbital of hydrogen and the 2*s* orbital of the donor oxygen as well as between the hydrogen 1*s* orbital and the *p* orbital of the donor oxygen atom. The lower electron density at the donor oxygen site compared to acceptor oxygen site in the dimer may be taken as indicative of the donor-acceptor charge transfer.

Since the CNDO/2 calculations gave the hydrogen bond energy of the linear methanol dimer close to the experimental value, the total energy of methanol trimer, IV (Fig. 1 and Table 1), has also been calculated. The energy of two hydrogen bonds in methanol trimer is 13.7 kcal (6.8 kcal per hydrogen bond). The hydrogen bond in the trimer is a bit stronger than that in the dimer (6.46 kcal per hydrogen bond). This observation is in agreement with the proposal of Bellamy and Pace [13].

Formic Acid

Formic acid can exist in the *cis* (V) or *trans* (VI) form as shown in Fig. 5 and the *cis*-form of the carboxylic acid is known to be more stable than the *trans*-form [20]. The energies of the two forms were calculated by the CNDO/2 and the EHT methods by employing the following structural parameters of formic acid: C=O: 1.23 Å; C–O: 1.36 Å; C–H: 1.09 Å; O–H: 0.96 Å; ∢OCO: 120°, and ∢COH: 109°28′. The EHT method shows that the *trans*-form (−402.9139 eV) is more stable than the *cis*-form (−402.7835 eV), contrary to known facts. The CNDO/2 method, on the other hand, predicts the relative stabilities of the two forms correctly. The total energies of the *cis*- and *trans*-forms by this method are −45.3084 a.u. and −45.3073 a.u., respectively. It is heartening that the CNDO/2 method is generally more successful in predicting the relative stabilities of such structures[1].

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[1] It may be pertinent to mention here that a calculation on the keto and enol forms of acetylacetone by the EHT and CNDO/2 methods has shown that the latter method predicts the greater stability of the enol form. The total energies of the keto and enol forms are −78.3778 and −78.3815 a.u. respectively; the energy of stabilization of the enol form due to hydrogen bonding is about 2.3 kcal, a value in good agreement with the heat of tautomerization found experimentally by Powling and Bernstein [J. Amer. chem. Soc. 73, 4353 (1951)].

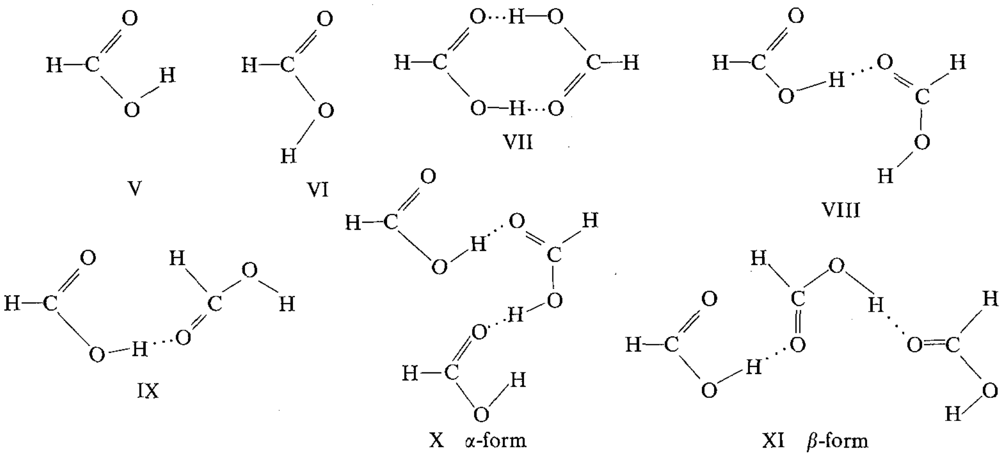

Fig. 5. Molecular arrangement of monomers, dimers, and trimers of formic acid

The energies of the cyclic dimer of formic acid, VII, were calculated as a function of the O ⋯ O distance by both the EHT and CNDO/2 methods (Fig. 6). The minimum energy is found at an O ⋯ O distance of 2.8 Å by the EHT method and at 2.45 Å by the CNDO/2 method. The experimental value [21] of the equi-

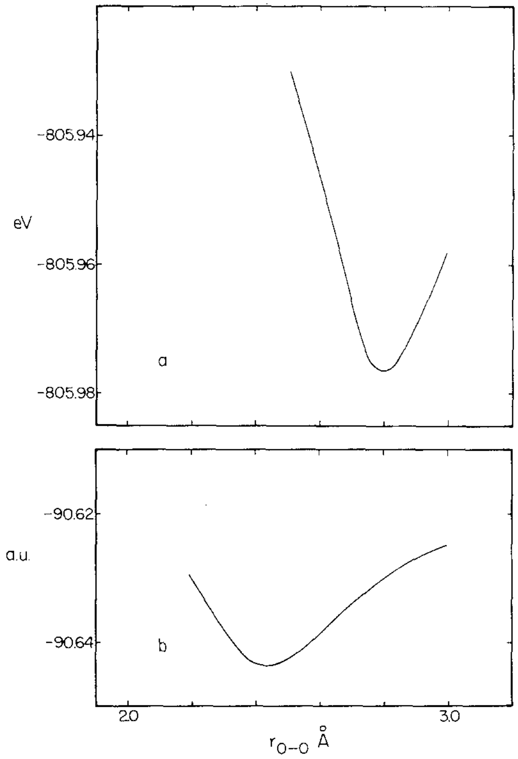

Fig. 6a and b. Total energy of the cyclic dimer of formic acid as a function of the O ⋯ O distance by a) the EHT method and b) the CNDO/2 method librium O ··· O distance is 2.73 Å, a value in between those predicted by the two methods. The minimum energies for the cyclic dimer obtained by the two methods are given in Table 2. The energy of the two hydrogen bonds is 16.8 kcal and 9.5 kcal by the CNDO/2 and EHT methods, respectively. The experimental value is about 14.0 kcal [1]. The value of 3.8 kcal reported by Morokuma and coworkers [7] based on EHT calculations is low.

There is some evidence to indicate that carboxylic acids can also exist in open dimeric structures [22]; these open dimers are likely to be the precursors of the polymeric carboxylic acids. Assuming the two configurations VIII and IX for the open dimer of formic acid, the energies were calculated (Table 2). While the two configurations of the open dimer are of comparable energies, they are both less stable than the cyclic dimer. The results are in agreement with the greater stability generally associated with the cyclic dimers.

The proton potential functions in the cyclic dimer of formic acid obtained by the two molecular orbital methods are shown in Fig. 7 where the total energy is plotted as a function of O–H distance. Here again, the EHT method gives unreasonable O–H and H ··· O distances (both as 0.5 Å), in addition to giving the H ··· O energy minimum at a lower energy than the O–H minimum. The O–H minimum by the CNDO/2 method is found arong 1.0 Å. A double minimum is distinctly seen when the O ··· O distance is 2.7 Å; at this O ··· O distance, the H ··· O energy minimum is higher than the O–H minimum as expected. The barrier height is also small as one would expect in such strong hydrogen bonds.

The O ··· O stretching force constant was estimated to be 0.27×10^5 dynes/cm by taking the second derivative of the energy around the equilibrium distance (by the EHT method). This value is in good agreement with that proposed by Stanevich [23] for carboxylic acids (0.35 to 0.50×10^5 dynes/cm).

The molecular diagram for the monomer and dimer of formic acid by the CNDO/2 method is shown in Fig. 8. The charge densities found presently are in disagreement with those recently reported by Ocvirk, Ažman and Hadži ([24], see however [26]). It can be seen that the charge densities at both the carbon and oxygen are greater in the dimer relative to the monomer.

Table 2. EHT *and* CNDO/2 *calculations on hydrogen bonding: formic acid*

	EHT		CNDO/2	
	$r_{O\cdots O}$ [Å]	$D_{OH\cdots O}$ [kcal] [a]	$r_{O\cdots O}$ [Å]	$D_{OH\cdots O}$ [kcal] [a]
Experimental	2.73	7.0		
Cyclic dimer, VII	2.8	4.73 [b]	2.45	8.4 [b]
Open dimer, VIII	2.70 [c]	8.26	2.70 [c]	4.95
Open dimer, IX	2.70 [c]	8.04	2.70 [c]	7.90
Open trimer, X	2.70 [c]	2.69	2.70 [c]	4.33
Open trimer, XI	2.70 [c]	6.99	2.70 [c]	7.03

[a] Per hydrogen bond; except in the open dimers in all the other cases there are two hydrogen bonds in the structure.

[b] At an OH ··· O distance of 2.7 Å, the value is 4.6 and 5.5 kcals respectively by the EHT and the CNDO methods. The value of D calculated from Fig. 6b is 5 · 3 kcals.

[c] Assumed value.

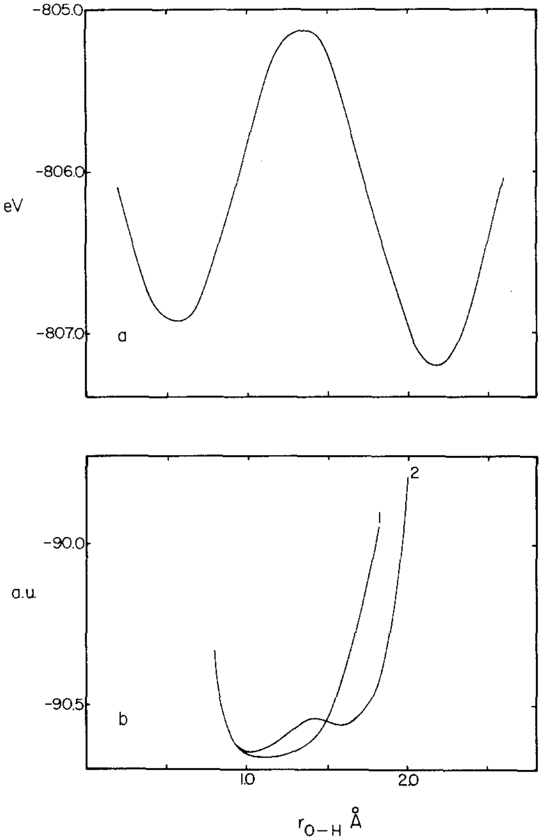

Fig. 7a and b. Total energy of the cyclic dimer of formic acid as a function of the position of the hydrogen atom: a) by the EHT method, O···O = 2.7 Å; b) by the CNDO/2 method; 1 and 2 refer to O···O distances of 2.45 and 2.7 Å, respectively

The energies of two forms of trimeric formic acid X and XI (Fig. 5) having the configurations similar to the α- and β-forms of formic acid polymer [14] were calculated by both the molecular orbital methods (Table 2). The results show that XI which is akin to the β-form is more stable. It should be noted that the β-form of the polymer has been isolated as a stable form and the crystal structure determined by X-ray crystallography [25].

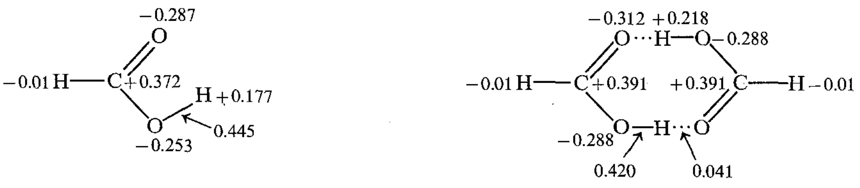

Fig. 8. Molecular diagrams of formic acid and formic acid dimer (see legend of Fig. 4 for other details)

Concluding Remarks

The CNDO/2 method appears to be more successful than the EHT method in giving reliable values of hydrogen bond energies as well as realistic proton potential functions. The CNDO/2 method also correctly predicts the stabilities of the *cis*-form of formic acid and the enol form of acetylacetone. A detailed investigation of the relative merits of the CNDO/2 and the EHT methods in the study of the hydrogen bond would be fruitful.

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