A Molecular Orbital Treatment of Hydrogen Bonds.
I. Preliminary Results

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The hydrogen bond, a weak bonding between a hydrogen donor, such as hydroxyl and amino groups, and an acceptor, such as oxygen and nitrogen atoms, has long attracted the attention and interest of many researchers, in both the experimental and theoretical fields.[1,2]

As to the theoretical study, Coulson and Dannielsson[3] calculated semiempirically the delocalization energy of the hydrogen bond in a fictitious O—H···O fragment. Tsubomura's nonempirical study was carried out on water.[4] Arranging existing theoretical treatments, Coulson[5] tabulated the contribution of various kinds of energy to the hydrogen-bond stabilization of water, thus emphasizing that the delocalization energy plays an important role in the stabilization.

This series of papers will attempt to discuss the stabilization energy and other changes in electronic structures by the hydrogen-bond formation from the point of view not of the fictitious fragment but of the whole molecule.

In the present paper, as a preliminary discussion, we will calculate the changes in the electronic energy and the charge distribution upon the hydrogen-bond formation, by using the simple LCAO MO method extended by Hoffmann,[6] in which all valence atomic orbitals (AO) are taken into account. The Coulomb integral, H_{rr}, of an atomic orbital is the negative value of the ionization potential of the valence state of the neutral atom,[7] which is tabulated in Table I. The resonance integral, H_{rs}, between the rth and the sth AO's is given by the following equation:

TABLE I. COULOMB INTEGRAL OF VARIOUS ATOMIC ORBITALS (eV.)

Atom	Orbital		
	1s	2s	2p
Hydrogen	−13.60	—	—
Carbon	—	−21.43	−11.42
Oxygen	—	−35.30	−17.76

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[1] "Hydrogen Bonding," Ed. by D. Hadzi, Pergamon Press, London (1959).

[2] G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., San Francisco (1960).

[3] C. A. Coulson and V. Dannielsson, *Arkiv Fysik*, **8**, 239, 245 (1954).

[4] H. Tsubomura, This Bulletin, **21**, 415 (1954).

[5] C. A. Coulson, *Research*, **10**, 149 (1957).

[6] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[7] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

$$H_{rs}=\frac{1}{2}KS_{rs}(H_{rr}+H_{ss})$$

where $K=1.75$ and S_{rs} is the overlap integral between the AO's. Calculation is carried out on formic acid and its dimer, acetylacetone and salicylaldehyde (with a hydroxyl group as a proton donor and with a carbonyl group as an acceptor), and also on benzyl alcohol and allyl alcohol (with a hydroxyl group as a proton donor and a π electron system as an acceptor).

The program was coded so that, on giving tables of the Coulomb integrals of every kind of atom included, of the three-dimensional coordinates of atoms, and of the effective nuclear charges of atomic orbitals, the overlap integrals can be calculated with Slater AO's by means of the formulae of Mulliken et al.,[8] the resonance integrals can also be calculated, and the secular equation can be diagonalized to give the eigen-values and eigenvectors, the total energy, the atomic orbital populations, and the atomic populations. The effective nuclear charges employed were $Z_H=1.0$, $Z_C=3.25$ and $Z_O=4.55$.

In all compounds, except for those noted, the atomic distances were taken as follows:[9] C–H: 1.09Å, C–C: 1.54Å, C=C: 1.34Å, C–C (aromatic): 1.40Å, C–O: 1.23Å, C–O (alcohol): 1.43Å, C–O (carboxylic acid): 1.36Å, O–H: 0.96Å. The bond angles are assumed to be 120° for an unsaturated carbon atom, the tetrahedral angle for a saturated carbon atom.

The Electronic Structure of Non-Hydrogen-Bonded Molecules

Prior to discussing the hydrogen bond, a brief review of the calculated electronic structures of some carboxylic acid, of ketone, of aldehyde and of alcohol will be given in this section, since the extended LCAO MO method has not previously been applied to such polar compounds.

Figure 1 shows the net charge on each atom of formic acid and salicylaldehyde. One can see in the figure that, though the general tendency of the polarization is well visualized, the net negative charge on each oxygen atom seems to be too large, whereas the population on the hydroxyl hydrogen atom is unexpectedly small. In this approximation the polarity of a polar bond seems to be overestimated. This is because the Coulomb integral of an atomic orbital was kept constant although it might really be more positive when the population on the atom increases. It is indispensable for this extended LCAO MO method to decide the Coulomb integral of an atomic orbital in a polar group not merely by the ionization potential of the neutral atom but also by the population on the atom. On this point we will give a detailed discussion is a following paper.

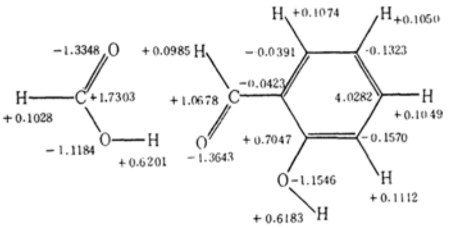


Fig. 1. Net charge of formic acid and salicylaldehyde.

The total energy of methyl alcohol is calculated for various configurations in Table II. As to the rotational isomers, the configuration I, in which the OH bond takes the trans conformation to the CH bond in the C–O–H plane*, is predicted to be a configuration of local minimum energy.

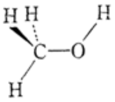
TABLE II. TOTAL ENERGY OF METHYL ALCOHOL AND ACETYLACETONE

A) Methyl alcohol

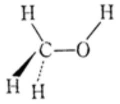
Configuration	∠COH	Total energy, eV.
III	110°	−287.4014
II	110°	−287.3941
I	110°	−287.4087
I	105°	−287.3293
I	100°	−287.2362

B) Acetylacetone

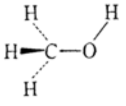
Configuration	Total energy, eV.
Keto	−789.4969
Enol	−788.3440



(I)



(II)



(III)

Keto and enol forms of acetylacetone are also compared in Table II. The keto form is more stable than the enol form, contrary to experience. This is either due to the inappropriate parametrization in this method, mentioned in the previous section, or to a substantial defect involved in the present method,

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[8] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[9] Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11, The Chemical Society, London (1958).

* In the figure, the bonds drawn with full lines denote those lying in the C-O-H plane, the atoms indicated by wadges being above the same plane and those by dotted lines, below that plane.

where electronic and nuclear repulsion energies are not explicitly taken into account.

Energy and Electron-distribution Changes Caused by Hydrogen-bond Formation

In this section will be calculated the energy and electron distribution changes caused by the hydrogen-bond formation. The configurations on which the calculations were carried out are shown in Fig. 2, as are the coordinates and the numbering of the atomic orbitals. They include some configurations in which the hydroxyl hydrogen is located near the carbonyl group (IV, V and VIII) or near the conjugated system (XI and XIII).

Overlap Integral.—Table III shows some values of the overlap integral between the hydroxyl hydrogen or the hydroxyl oxygen of a formic acid monomer and the carbonyl oxygen of the other monomer at various O_3-O_7 and O_7-H_6 distances. One can see from the table that a considerable amount of overlapping exists between the hydrogen, H_6 and the oxygen, O_3. (Compare the 1s—2s overlap integral in a normal O-H bond, 0.5076.) The overlap between O_3 and O_7 is very small.

Delocalization Energy.—Tables IV, V and VI give the total electronic energy of each configuration of the formic acid dimer, of salicylaldehyde and of acetylacetone respectively. In the tables "tetra" means the tetrahedral angle, 109°28′.

TABLE III. OVERLAP INTEGRALS BETWEEN PROTON ACCEPTORS AND DONORS IN FORMIC ACID DIMER

O_3-O_7	distance, Å	2.8	2.7	2.6	2.7	2.6
O_4-H_5	distance, Å	0.96	0.96	0.96	1.06	1.06
O_3-H_6	2s-1s	0.1365	0.1593	0.1853	0.1853	0.2148
	2px-1s	0.1151	0.1323	0.1513	0.1513	0.1719
	2py-1s	0.0258	0.0314	0.0381	0.0381	0.0461
	2pz-1s	0	0	0	0	0
O_3-O_7	2pz-2pz	0.0010	0.0014	0.0019	0.0014	0.0019

TABLE IV. DELOCALIZATION ENERGY OF HYDROGEN BOND IN FORMIC ACID DIMER[a)]

Model	$O_3\cdots O_7$ distance Å	$O_7\cdots H_6$ distance Å	$O_3\cdots H_6$ distance Å	Total energy eV.	Delocalization energy eV.
Monomer	—	0.96	—	−402.9270	—
1	2.8	0.96	1.89	−806.0106	+0.1566
2	2.7	0.96	1.79	−806.0181	+0.1641
3	2.6	0.96	1.69	−806.0031	+0.1491
4	2.7	1.06	1.69	−805.6966	−0.1574
5	2.6	1.06	1.60	−805.7198	−0.1342

a) ∠COH was assumed to be tetrahedral.

TABLE V. DELOCALIZATION ENERGY OF HYDROGEN BOND IN SALCYLALDEHYDE

Model	Configuration	$\angle C_5O_{11}H_{12}$	$O\cdots H$ distance, Å	Total energy, eV.	Delocalization energy, eV.
1	V	tetra	1.7	−895.9422	+0.0697
2	VI	tetra	—	−895.8623	−0.0102
3	VII	tetra	—	−895.8725	0
4	V	100°	1.63	−895.7905	+0.0918
5	VI	100°	—	−895.6987	0

TABLE VI. DELOCALIZATION ENERGY OF HYDROGEN BOND IN ACETYLACETONE

Model	Configuration	$\angle C_8O_{14}H_{15}$	$O\cdots H$ distance, Å	Total energy, eV.	Delocalization energy, eV.
1	VIII	tetra	1.64	−788.3440	+0.0813
2	IX	tetra	—	−788.2627	0
3	X	tetra	—	−787.9316	−0.3311
4	VIII	100°	1.57	−788.1908	+0.0901
5	IX	100°	—	−788.1007	0

TABLE VII. ORBITAL ENERGIES AND ATOMIC ORBITAL COEFFICIENTS

No.			1	2	3	4	5	6
Orbital energy			−37.6982	−35.4224	−21.5491	−18.6819	−18.5219	−18.3101
Orbital energy of dimer			−37.8687	−35.6519	−21.9509	−19.1322	−18.6206	−18.3317
			−37.5304	−35.2149	−21.1862	−18.2247	−18.4591	−18.2884
Atomic orbital coefficient	H_1	1s	−0.0172	0.0067	−0.2234	−0.0208	−0.1474	0.0
	C_2	2s	0.2744	0.0413	−0.4266	0.0428	−0.0289	0.0
		2px	0.0221	0.0331	0.1392	0.0385	0.1907	0.0
		2py	0.0107	0.0949	0.0812	0.1471	−0.1546	0·0
		2pz	0.0	0.0	0.0	0.0	0.0	0.2403
	O_3	2s	0.6186	0.6017	0.2515	−0.1266	0.0224	0.0
		2px	0.0090	0.0168	0.3015	−0.3297	0.5778	0.0
		2py	0.0097	0.0191	0.2871	−0.4246	−0.3640	0.0
		2pz	0.0	0.0	0.0	0.0	0.0	0.7348
	O_4	2s	0.5347	−0.6885	0.1373	−0.1023	−0.0532	0.0
		2px	−0.0066	0.0092	0.2658	0.6977	0.0434	0.0
		2py	−0.0034	0.0194	−0.3382	0.0669	0.5258	0.0
		2pz	0.0	0.0	0.0	0.0	0.0	0.5363
	H_5	1s	0.0496	−0.1031	0.1848	0.1747	−0.0374	0.0

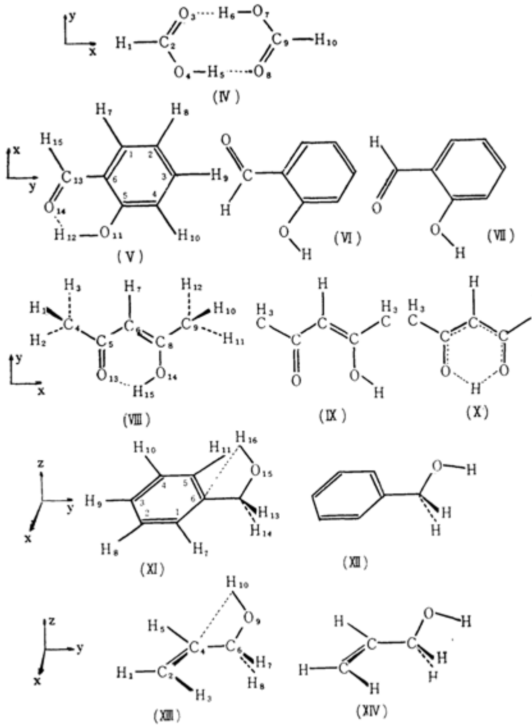

Fig. 2. Configurations compared.

In the present treatment, the delocalization energy due to hydrogen bonding, E_d, is given by the difference in the total electronic energies between a configuration with a hydrogen bond and a configuration without it.

For the formic acid dimer, the delocalization energy is calculated in Table IV as the difference between the total electronic energy of two monomers and that of a dimer. Model 2 (O···O distance 2.7Å and O-H distance 0.96Å) is the most stable from the viewpoint of the delocalization energy. It is interesting that the approach from 2.7Å to 2.6Å makes the dimer more unstable, though the O···H overlap gets larger. As was discussed in the preceding section, factors other than the delocalization will participate in deciding the most stable configuration of the hydrogen-bonded species. However, it is noteworthy that, in this example, the observed O···O distance in the gaseous dimer, 2.72—2.73Å,[10] corresponds well with the prediction. Model 3 shows that a also shortened O···O distance decreases the stabilization, though it also causes an increase of the oxygen-hydrogen overlap (Table III). The delocalization energy of model 2 is 0.164 eV., 3.77 kcal./mol., whereas the observed stabilization energy, ΔH, of two hydrogen bonds in the gaseous dimer is ca. 7.1 kcal./mol.[11] Coulson estimated the contribution of the delocalization energy to the stabilization energy of the hydrogen bond of water to be 8 ± 4 kcal./mol.[4,5] The value obtained in this approximation might be somewhat too small. There may be two reasons for this in addition to the one stated in the preceding chapter: 1) As was stated in the previous section, since in this approximation the polarity of a bond is emphasized too much, the delocalization of electrons on the proton acceptor to the proton donor seems to be hindered. 2) In this approximation the delocalization energy is exclusively attributed to the σ electrons (including so-called lone pairs), and not at all to the π electrons. Since a hydrogen atom has no

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[10] J. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944); O. Bastiansen, *Tids. Kjemi. Bergvesen Met.*, **4**, 81 (1944), cited in Ref. 2.

[11] Average value of data collected in Ref. 2.

OF FORMIC ACID AND ORBITAL ENERGIES OF ITS DIMER (MODEL 2)

7	8	9	10	11	12	13	14
−17.6885	−17.5253	−16.0660	−9.4663	0.9907	10.6161	15.1478	29.3562
−17.7038	−17.5484	−16.1880	−9.4673	1.7635	12.1657	15.2001	29.3304
−17.6733	−17.4925	−15.9437	−9.4654	2.0067	13.3014	15.8455	29.4173
0.0	−0.0700	0.4509	0.0	−0.1640	−0.1405	−1.1468	0.7473
0.0	−0.0232	0.1655	0.0	−0.3620	−0.2192	0.4499	−1.3246
0.0	0.1012	−0.3639	0.0	−0.4428	−0.3450	−1.1393	−0.2156
0.0	0.0808	0.0287	0.0	0.8258	0.5366	−0.4383	−0.6898
−0.0123	0.0	0.0	1.0048	0.0	0.0	0.0	0.0
0.0	−0.0190	−0.0438	0.0	−0.0455	0.0611	0.4732	0.8183
0.0	0.0899	0.6149	0.0	0.1285	0.1111	−0.1545	−0.4784
0.0	−0.6853	−0.0687	0.0	−0.1297	−0.1409	−0.3055	−0.5019
−0.5852	0.0	0.0	−0.4056	0.0	0.0	0.0	0.0
0.0	0.0548	−0.1053	0.0	0.0437	0.9007	−0.1422	0.0638
0.0	−0.3507	0.2913	0.0	−0.5895	0.3556	0.1301	−0.0062
0.0	−0.5977	−0.2301	0.0	0.5290	0.3020	−0.0599	0.1478
0.8140	0.0	0.0	−0.2649	0.0	0.0	0.0	0.0
0.0	−0.0596	0.0648	0.0	0.7980	−0.9594	0.0992	0.0754

π orbital, the direct overlap between oxygen atoms is very small, as is shown in Table III. This small overlap contributes almost nothing to the stabilization energy.

The contribution of the vacant 2pπ orbital on the intervening hydrogen atom, which might play the role of a stepping stone between two oxygen orbitals, will be discussed below.

There is another possibility of the π-electron stabilization. The transfer of the σ electron on the carbonyl oxygen to the O-H bond (see the next section) will actually change the Coulomb integral of their π orbitals. This effect may cause a variation in the total π electron energy of the system. As was shown in the previous section, this effect was not taken into account in the approximation employed here.

For salicylaldehyde the energy of the hydrogen-bonded configuration (V) is lower than those of other configurations (VI and VII). The delocalization energy is of the order of 0.07 eV. When the COH angle, i.e., the distance between the hydroxyl hydrogen and the carbonyl oxygen, is decreased, the delocalization energy seems to increase with the formation of a stronger hydrogen bond, though the total energy decreases. For the enol form of acetylacetone, the delocalization energy of model 1 referred to that of model 2 is 0.081 eV. Model 3 is the configuration in which the hydrogen atom, H_{15}, is situated between two oxygen atoms, with the COH angle tetrahedral, and in which the molecule has a normal plane of symmetry, with the C-O bond length of 1.33 Å and the C-C bond length of 1.44 Å. The calculation shows this configuration to be very unstable.

Orbital Energy.—Table VII shows the energy levels and their atomic orbital coefficients of the formic acid monomer, with the corresponding energy levels of its dimer. In the extended LCAO approximation every atomic orbital can conjugate with other atomic orbitals; therefore, no completely localized molecular orbital (lone-pair orbital) remains. In the present calculation, the highest occupied orbital is a sigma-type bond, and the next highest orbital seems to correspond to the lone-pair orbital. This point seems to be a difficulty which might be overcome by an SCF technique.

In the present calculation, each level of the monomer splits into two levels upon the dimer formation, one being higher and the other lower than the initial level, as may be seen in Table VII, which may cause a red shift for both π-π^* and n-π^* types of transitions in contradiction to the experimental finding by Barnes and Simpson (*J. Chem. Phys.*, **39**, 670 (1963)). They observed that the spectrum undergoes a blue shift upon dimerization. As to salicylaldehyde, the calculated sequence of the lone pair, the π and the σ orbitals does not agree with the order expected from the references.[12)] Hence, the present result is unsuccessful in predicting the shift of their transition.

This discrepancy probably stems from an inappropriate parametrization of the lone-pair atomic orbitals. The Coulomb integral of the 2p lone pair atomic orbital of oxygen remains at −17.76 eV., too low to be compared with the experimental results.

Population Analysis.—The atomic orbital population, N_r; the atomic population, M_X; the atomic orbital bond population, N_{rs}, and the

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[12)] E. g., J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).

bond population M_{XY}, are defined as follows :[13]

$$N_r = 2 \sum_i^{\text{occ}} \sum_s C_r^i C_s^i S_{rs}$$

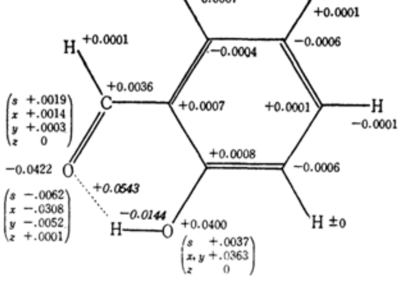
$$M_X = \sum_r^{\text{on}X} N_r$$

$$N_{rs} = 4 \sum_i^{\text{occ}} C_r^i C_s^i S_{rs}$$

$$M_{XY} = \sum_r^{\text{on}X} \sum_s^{\text{on}Y} N_{rs}$$

where C_r^i is the coefficient of the rth AO in the ith molecular orbital. Figure 3 shows the increase in the AO population and in the atomic population caused by the hydrogen bonding. The population on the carbonyl oxygen decreases, while, on the other hand, the population on the hydroxyl group increases. This is what one may expect. One can see in Fig. 3, in the case of formic acid, that the population on the 2px orbital, the orbital directing to the hydrogen atom of the partner molecule, plays a dominant role. An inspection of the orbital coefficients of the formic acid dimer makes it clear that the population transfers not within a monomer but from the carbonyl group of one monomer to the hydroxyl bond of the other. It is interesting that the increase in the population takes place at the oxygen atom, not at the hydrogen atom. The population on the hydrogen atom increases in some cases (e. g., formic acid) and decreases in other cases (e. g., salicylaldehyde).

a) Formic acid (difference between the model 2 and monomer)



b) Salicylaldehyde (difference between the models 1 and 3)

Fig. 3. Increase of population by hydrogen bond.

The bond populations of several interesting bonds are also given in Fig. 3 in italic letters. The bond population, $N_{O\cdots H}$, between the carbonyl oxygen and the hydroxyl hydrogen is positive, showing that there is a weak "bond" between them. The ratio of the AO population of the 2s atomic orbital of the oxygen to the sum of those of the 2px and 2py orbitals is approximately 1 to 2.2. On the other hand, the bond population, N_{OH}, of the hydroxyl group decreases. In the case of formic acid, for instance, the N_{OH} of the monomer, 0.458, decreases by (0.028) about 5% of the initial value.

These results qualitatively correspond to the lowering of the O-H stretching frequency in the infrared spectrum.[1]

The Contribution of the 2pπ Orbital on the Hydrogen Atom.—As has been stated previously, the vacant 2pπ orbital on the hydroxyl hydrogen was taken into consideration in order to see the effect of the direct conjugation of π electrons through the hydrogen atom.[14] The Coulomb integral of the orbital is taken to be −3.4 eV. on the basis of the spectroscopic date,[15] with the effective nuclear charge being $Z=1.0$. The energy levels thus calculated are shown in Table VIII. (The 2pπ orbital is considered only on the hydroxyl hydrogen.)

The π delocalization energy, which was −0.0002 eV. without the orbital, rises to 0.002 eV. when the 2pπ orbital is included ; the amount is still negligible, however. Thus, we can hardly expect the delocalization energy due to the 2pπ conjugation through the hydrogen atom.

Paoloni[16] discussed the contribution of the 2pσ orbital on the hydrogen atom to the delocalization energy. In this paper this effect is not considered.

The π Hydrogen Bond.—It has been recognized that π electron systems, such as the phenyl group or the olefinic group, can be proton acceptors when they interact with proton donors. Benzyl alcohol and allyl alcohol, for instance, are known to have a π hydrogen bond. The stabilization energy, ΔH, due to a π hydrogen bond has been estimated to be 1 to 2 kcal./mol.,[2] smaller than that of usual hydrogen bonds.

With respect to benzyl alcohol and allyl alcohol, we made the same calculation as was

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[13] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841, 2338, 2343 (1955). The notation is a little different from that of Mulliken's paper.

[14] D. N. Shigorin, Ref. 1, p. 191 (1959).

[15] L. C. Moore, "Atomic Energy Levels," National Bureau of Standards.

[16] L. Paoloni, *J. Chem. Phys.*, 30. 1045 (1959).

TABLE VIII. π ENERGY LEVELS OF FORMIC ACID AND ITS DIMER WITH 2p ORBITAL ON THE HYDROGEN ATOM

		Monomer	Dimer (model 2)
π Energy level	Occupied	−18.3131 eV.	−18.3365 eV.
			−18.2897
		−17.6894	−17.7060
			−17.6736
	Unoccupied	−9.4668	− 9.4696
			− 9.4686
		−2.5463	− 3.2799
			+ 0.7923
Total energy		−72.0049	−144.0117
Total energy (without hydrogen 2pπ orbital)		−71.9972	−143.9942

TABLE IX. ENERGY OF π HYDROGEN BOND IN BENZYL ALCOHOL AND ALLYL ALCOHOL

Benzyl alcohol

Model	Configuration	∠COH	$C_6 \cdots H_{16}$ distance, Å	Total energy, eV.	Delocalization energy, eV.
1	XI	tetra	2.33	−780.0563	−0.0129
2	XII	tetra	—	−780.0692	0
3	XI	90°	2.01	−779.6947	+0.0284
4	XII	90°	—	−779.6663	0

Allyl alcohol

Model	Configuration	∠CCO	∠COH	$C_4 \cdots H_{10}$ distance, Å	Total energy, eV.	Delocalization energy, eV.
1	XIII	110°	110°	2.35	−463.0088	−0.0141
2	XIV	110°	110°	—	−463.0229	0
3	XIII	110°	100°	2.18	−462.8460	+0.0005
4	XIV	110°	100°	—	−462.8455	0
5	XIII	105°	110°	2.24	−463.0052	+0.0078
6	XIV	105°	110°	—	−462.9974	0
7	XIII	105°	100°	2.07	−462.8414	+0.0200
8	XIV	105°	100°	—	−462.8214	0
9	XIII	100°	110°	2.12	−462.9125	+0.0271
10	XIV	100°	110°	—	−462.8854	0
11	XIII	100°	100°	1.95	−462.7471	+0.0365
12	XIV	100°	100°	—	−462.7106	0

carried out in the previous sections. The geometrical data of the molecules calculated are collected in Table IX. The overlap integrals between the hydroxyl hydrogen, H_{10}, and the nearest sp^2 carbon, C_4, for instance, in model 3 (with the hydrogen bond) and model 4 (without the hydrogen bond) of allyl alcohol are as follows:

	Model 3	Model 4
H1s-C2s	0.1519	0.0321
H1s-C2py	0.0898	0.0350
H1s-C2pz (π)	0.1368	0.0138

The magnitude of these overlap integrals for model 3 is of the same order as for the dimer of formic acid (Table III).

In spite of this large overlap, the delocalization energy calculated is extremely small. For the most stable CCO and COH angles (models 1 and 2) of allyl alcohol, the hydrogen-bonded configurations, XIII, is a little more unstable than the nonbonded configuration, XIV. There are two factors affecting the delocalization energy. One is the energetic contribution of the methylol group to the total electronic energy. Referring to Table II, in which the total energy of methyl alcohol is given with respect to three configurations, it may be considered that the methylol group in the configuration XIII of Fig. 2 makes a smaller contribution to the total energy than that in the configuration XIV of the same figure. The other factor is the stabilization due to the formation of a π hydrogen bond. On comparing models 1 and 2, since the $C_4 \cdots H_{10}$ distance is rather large and since, therefore, the delocalization energy is small, and is, furthermore, in this approximation estimated to be too small, the former factor overcomes the latter. If we shorten the $C_4 \cdots H_{10}$ distance by reducing the CCO or/and the COH angles, the energy of the configuration XIII referred to that of XIV becomes more stable, as is shown in Table IX.

Thus, the small stabilization energy of a π hydrogen bond seems partly due to the compensation with the energy difference between the configurations, such as I and II.

The change in atomic and bond population upon the hydrogen bonding, that is, the population difference between models 3 and 4 of allyl alcohol, is shown in Fig. 4. One can notice that the population transfers from the allyl group to the hydroxyl group. However, the change amounts to only 10% of that in a usual hydrogen bond (Fig. 3).

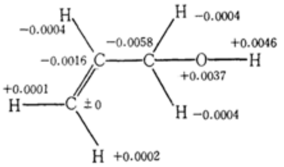

Fig. 4. Increase of population by π hydrogen bond (difference between the models 3 and 4).

Discussion

In discussing the changes in electronic structures by the hydrogen-bond formation, some defects of the extended LCAO MO method were revealed: 1) The absolute value of the Coulomb integral of the so-called lone-pair atomic orbital is too large. 2) A change in the population on a orbital does not affect the Coulomb integral of the orbital. Accordingly, the stabilization energy is very small.

These two defects may be overcome if the Coulomb integral is varied according to the AO population on the atomic orbital and according to those on the other atomic orbitals on the same atom. This correction may mean considering the electronic interaction implicitly.

Finally, a certain apparent parallelism between the delocalization energy and the experiments is observed; the electronic and nuclear repulsion energies are, however, not taken into account explicitly, as has been pointed out above, in the present treament. The agreement should be checked by further investigation. These improvements, together with the problems of the parametrization of the resonance integral, will be reported on in the near future.

Summary

1) The changes caused by hydrogen bonds in the electronic structure of several molecules have been discussed by the use of the extended LCAO MO method.

2) The delocalization energy have been calculated to be 3.8 kcal./mol.

3) The frequency shifts in the ultraviolet spectrum cannot be explained.

4) In the formic acid dimer it has clearly been shown that the population transfers from the carbonyl group to the hydroxyl group and that a small bond population arises between them.

5) The $2p\pi$ orbital on the hydrogen atom contributes almost nothing to the π delocalization energy.

6) The π hydrogen bond has also been discussed.

7) The defects in the extended LCAO MO method in treating molecules with polar groups or lone pairs have been pointed out, a method for improvement suggested, and some critical discussion of the present treatment added.

The calculation was carried out on the IBM 7090 at the Japan IBM Co., with the permission of the UNICON Committee, whose kindnees we hereby acknowledge.

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