Intramolecular Hydrogen Bond between Hydroxyl Group and π-Base in 2-Hydroxybiphenyl

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In order to clarify the nature of the intramolecular hydrogen bond between the hydroxyl group and the π-electron system in 2-hydroxybiphenyl, MO calculation based on the CNDO/2 MO method has been carried out. The total electronic energy of the molecule has been divided into one- and two-atomic terms. It was found that the resonance term mainly contributes to the intramolecular hydrogen bond formation. Contribution of other terms is discussed.

Since Wulf *et al.*1) reported the doublet of the first overtone of the O–H stretching vibration in 2-hydroxybiphenyl, many workers2—19) have studied the nature of the hydrogen bond with π-base, such as aromatic hydrocarbons and olefins. This type of hydrogen bond might play some role in the physico-chemical properties and chemical reactivity of the molecule. By adopting the theory of Mulliken's charge-transfer complex, some workers have concluded that charge-transfer interaction makes important contribution to this type of hydrogen bond formation.11,13,19) However, they did not make clear whether it is the main contribution, since no comparison of various terms in the interaction energies was made.

This paper describes an attempt to analyze the intramolecular hydrogen bond energy of 2-hydroxybiphenyl by the calculation based on the CNDO/2 method.20) 2-Hydroxybiphenyl, having antiseptic activity, is a typical molecule with intramolecular interaction of H$\cdots\pi$ type. The electron correlation is not taken into account in the CNDO/2 SCF method, and the calculated value of total electronic energy is not highly reliable. However, our object is to calculate the energy difference between the non-bonded and the hydrogen bonded systems. Since the effect of electron correlation might be mostly cancelled out we have used the simple semi-empirical MO method, CNDO/2. The total energy is divided into one- and two-atomic terms, the two-atomic term being further divided into resonance, exchange, and Coulomb terms. So far energy decomposition studies on intramolecular hydrogen bond with π-electron system do not seem to have been reported. Recently a study on the intermolecular hydrogen bonds of some small systems has been made by Kitaura and Morokuma,21) but their method can not be applied directly to the intramolecular hydrogen bond problem.

Procedure

Geometry. 2-Hydroxybiphenyl is assumed to be twisted around the central single bond (Fig. 1) because of the repulsions among non-bonded ring hydrogens. For biphenyl, the dihedral angle between phenyl planes was estimated to be *ca.* 40°.22) There is an additional steric hindrance between the hydroxyl group and phenyl ring in 2-hydroxybiphenyl. Ōki *et al.* assumed that the dihedral angle of the present molecule is 50°.13)

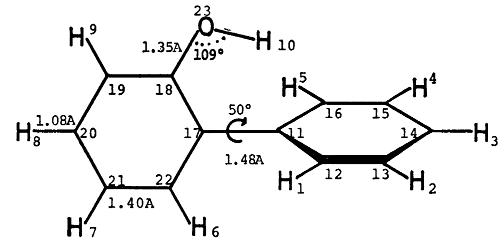

Fig. 1. Geometry and numbering adopted for the molecular orbital calculations.

In order to confirm the validity of the assumed conformation, we have carried out SCF-MO-CI calculation by the P-P-P method23) using variable β approximation and N-gamma for two-center electron repulsion integrals. This method provides satisfactory results for $\pi\rightarrow\pi^*$ transitions.24) The calculated results for 2-hydroxybiphenyl are summarized in Table 1 with experimental values. The calculated and experimental results agree satisfactorily.

Table 1. Calculated transition energies and oscillator strengths of 2-hydroxybiphenyl

Calcd		Obsd	
ΔE(eV)	f	ΔE(eV)	$\varepsilon\times10^{-3}$
4.38	0.11	4.36	6
5.26	0.51	5.06	12
5.70	0.31		
6.05	0.33	6.00$^{\text{sh}}$	23
6.15	0.81		
6.25	0.41		

Interaction Energies. The intramolecular hydrogen bond energy of 2-hydroxybiphenyl is given by the difference of total energies between hydrogen bonded structure **I** and non-bonded structure II shown in Fig. 2. The total energy can be expressed by the sum of one- and two-atomic terms:20)

$$E_{\text{total}} = \sum_{\text{A}} E_{\text{A}} + \sum_{\text{A}<\text{B}} E_{\text{AB}}, \tag{1}$$

where

$$E_{\text{A}} = \sum_{\mu}^{\text{A}} P_{\mu\mu}U_{\mu\mu} + \frac{1}{2}\sum_{\mu}^{\text{A}}\sum_{\nu}^{\text{A}}\left(P_{\mu\mu}P_{\nu\nu} - \frac{1}{2}P_{\mu\nu}^2\right)\gamma_{\text{AA}}, \tag{2}$$

$$E_{\text{AB}} = \sum_{\mu}^{\text{A}}\sum_{\nu}^{\text{B}} 2P_{\mu\nu}\beta_{\text{AB}}^{\circ}S_{\mu\nu} - \sum_{\mu}^{\text{A}}\sum_{\nu}^{\text{B}}\frac{1}{2}P_{\mu\nu}^2\gamma_{\text{AB}} + (Z_{\text{A}}-P_{\text{AA}})(Z_{\text{B}}-P_{\text{BB}})\gamma_{\text{AB}}. \tag{3}$$

We refer to the first, second, and third terms of two-atomic term (Eq. 3) as resonance, exchange, and Coulombic interaction energies, respectively. The difference in these energy terms between bonded and non-bonded structures, is used for discussing the nature of the hydrogen bond.

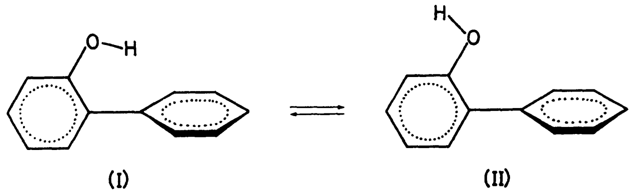

Fig. 2. Assumed geometry of 2-hydroxybiphenyl.

Results and Discussion

The calculated results for each term are summarized in Tables 2, 3, and 4. Intramolecular hydrogen bond energy ($\Delta E = E(\mathbf{I})_{\mathrm{total}} - E(\mathrm{II})_{\mathrm{total}}$) of the present molecule calculated by the CNDO/2 method is −0.193 eV, which is larger than the experimental value for

TABLE 3. CALCULATED TOTAL ENERGIES ASSOCIATED WITH TWO-ATOMIC TERMS (IN eV)

	Structure		
	I	II	$E(\mathbf{I})-E(\mathrm{II})$
$\sum_{A<B} E_{AB}$	−710.4209	−710.2212	−0.1997
$\sum_{A} E_{HA}$[a]	−20.4851	−20.0014	−0.4837
Resonance	−20.4196	−19.8876	−0.5320
Exchange	−6.1496	−6.2813	0.1317
Coulomb	6.0841	6.1675	−0.0834

[a] See Table 4.

TABLE 2. CALCULATED ONE-ATOMIC TERMS OF 2-HYDROXYBIPHENYL (IN eV)

Atom	Structure		Atom	Structure		Atom	Structure	
	I	II		I	II		I	II
1	−12.29295	−12.31117	9	−12.20039	−12.24681	17	−143.12038	−143.04830
2	−12.29397	−12.30978	10	−11.11982	−11.22776	18	−141.97950	−141.99221
3	−12.28841	−12.30532	11	−142.66898	−142.67655	19	−143.56136	−143.63519
4	−12.29552	−12.30903	12	−143.36160	−143.36896	20	−143.22607	−143.21155
5	−12.30162	−12.28555	13	−143.27698	−143.26206	21	−143.42328	−143.41195
6	−12.30627	−12.28959	14	−143.34993	−143.33280	22	−143.22066	−143.24660
7	−12.29422	−12.29170	15	−143.25843	−143.25778	23	−476.31951	−476.17039
8	−12.28768	−12.29543	16	−143.35772	−143.32587			

$\sum E_A(\mathbf{I}) - \sum E_A(\mathrm{II}) = 0.00709$ eV

TABLE 4. CALCULATED TWO-ATOMIC TERMS (E_{HA}) ASSOCIATED WITH THE HYDROXYL HYDROGEN AND OTHER ATOMS (IN eV)

Atom	Resonance		Exchange		Coulomb		
	I	II	I	II	I	II	$E_{HA}(\mathbf{I})-E_{HA}(\mathrm{II})$
1	0	0	0	0	−0.0011	−0.0017	0.0006
2	0	0	0	0	−0.0009	−0.0013	0.0004
3	0	0	0	0	−0.0006	−0.0011	0.0005
4	−0.0002	0	0	0	−0.0014	−0.0016	−0.0001
5	−0.0784	−0.0022	−0.0033	−0.0002	0.0371	−0.0005	−0.0416
6	0.0004	−0.0001	−0.0003	−0.0005	−0.0019	−0.0006	−0.0005
7	0	0	0	0	−0.0008	−0.0007	−0.0001
8	−0.0001	0.0004	−0.0005	−0.0003	−0.0005	−0.0010	−0.0003
9	−0.0002	−0.0627	0	−0.0040	0.0063	0.0190	0.0539
11	−0.3423	−0.0038	−0.0165	−0.0005	0.1186	0.0290	−0.2649
12	−0.0004	−0.0001	−0.0001	0	−0.0091	−0.0064	−0.0031
13	0.0001	0	−0.0001	−0.0001	0.0013	0.0012	0
14	0.0010	0	−0.0006	0	−0.0089	−0.0046	−0.0039
15	−0.0121	0	−0.0003	−0.0001	0.0048	0.0018	−0.0093
16	−0.7574	−0.0016	−0.0537	−0.0001	0.1131	−0.0050	−0.6913
17	0.1490	−0.0929	−0.0140	−0.0248	0.0210	−0.0011	0.2748
18	−0.1856	−0.2469	−0.0038	−0.0044	0.3917	0.3805	0.0732
19	−0.0939	0.0966	−0.0260	−0.0115	−0.0346	−0.0180	−0.2216
20	0.0017	−0.0025	−0.0007	−0.0002	0.0037	0.0049	0.0025
21	−0.0001	−0.0002	−0.0001	−0.0001	−0.0144	−0.0122	−0.0021
22	−0.0044	0.0016	−0.0004	−0.0005	0.0059	0.0028	−0.0028
23	−19.0967	−19.5732	−6.0292	−6.2340	5.4548	5.7841	0.3520
ΣE_{HA}	−20.4196	−19.8876	−6.1496	−6.2813	6.0841	6.1675	−0.4837

X-H···π type interaction (<3 kcal/mol).[25] Since the CNDO/2 method usually gives larger binding energies,[26] the present result seems to be reasonable. The change of one-atomic term ($\Delta\sum E_{\mathrm{A}}$) due to the formation of intramolecular hydrogen bond is quite small due to cancellation of one-atomic terms (ΔE_{A}) (Table 2). However, the two-atomic terms considerably stabilize the system, showing that energy of the hydrogen bond comes mostly from the two-atomic terms (Table 3). It should be noted that the interaction energy (ΔE_{HA}) between the hydrogen of hydroxyl group and the other atoms is remarkably large, more than double the value of $E(\mathbf{I})_{\mathrm{AB}}-E(\mathrm{II})_{\mathrm{AB}}$ (last column, Table 3). This shows that ΔE_{HA} greatly stabilizes the hydrogen bond, but some of the other two-atomic terms cause destabilization. The stabilization energy comes from the resonance (−0.532 eV) and Coulomb (−0.083 eV) terms. The exchange term (0.132 eV) plays the role of destabilization. The calculated result shows a decrease of O–H bond energy (atom 23 in Table 4), in line with the observed infrared spectral shift due to O–H vibrational lower frequency. Both the resonance and exchange terms of O–H bond energy decrease (−0.477 eV and −0.205 eV respectively), though the Coulomb term increases (0.329 eV).

It is evident that the hydrogen bond is formed mainly from resonance energy between the hydroxyl group and carbon atoms 11 (−0.339 eV) and 16 (−0.756 eV). For the sake of clarification, we have given the values of the term $P_{\mu\nu}S_{\mu\nu}$ between 1s orbital of the hydrogen of hydroxyl group and the valence orbitals of carbon atoms 11 and 16 as a measure of contribution to the resonance terms (Table 5). The amount associated with $2\mathrm{p}_z$ orbital of carbon atom 16 is the largest (0.014), those associated with other orbitals not being small.

Table 5. Overlap integral ($S_{\mu\nu}$), bond order ($P_{\mu\nu}$), and their product ($P_{\mu\nu}S_{\mu\nu}$) between 1s orbital of hydroxyl hydrogen and valence orbitals of atoms 11 and 16

Orbital		$S_{\mu\nu}$	$P_{\mu\nu}$	$P_{\mu\nu}S_{\mu\nu}$
C_{11}	2s	0.1043	0.0318	0.0033
	$2p_x$	−0.0277	−0.0142	0.0004
	$2p_y$	0.0804	0.0309	0.0025
	$2p_z$	0.0958	0.0545	0.0052
C_{16}	2s	0.1390	0.0474	0.0066
	$2p_x$	−0.0961	−0.0433	0.0042
	$2p_y$	0.0155	0.0071	0.0001
	$2p_z$	0.1357	0.1061	0.0144

It is of interest to investigate the potential energy of O–H···π bonded system. We have calculated the total energies as a function of O–H distance, where only the position of the hydrogen of hydroxyl group is varied, all the other atoms keeping their positions unchanged. The result is shown in Fig. 3. The potential curve has a minimum at 1.04 Å of O–H distance. In the case of the non-bonded one, the calculated equilibrium O–H distance is 1.03 Å. This lengthening of O–H distance due to hydrogen bond formation leads to a decrease in the force constant, reflecting the lower shift of O–H vibrational frequency as observed in the infrared spectra.[13] The charge density on oxygen atom is minimum at 1.2 Å, increasing considerably with the O–H distance (Table 6). The charge densities of carbon atoms 11 and 16 decrease monotonously with increase in distance. This suggests that the charge-transfer structure $(\mathrm{O{-}H})^{-}\cdots\mathrm{C}^{+}$ contributes to the intramolecular hydrogen bond formation to some extent. The present calculation shows that, when the O–H distance increases beyond 1.4 Å, the contribution of another type of charge-transfer structure $\mathrm{O}^{-}\cdots(\mathrm{H{-}C})^{+}$ increases (Table 6). Thus double minimums in line with the experiment of infrared spectroscopy might be expected, though the CNDO/2 calculation gives no confirmation.

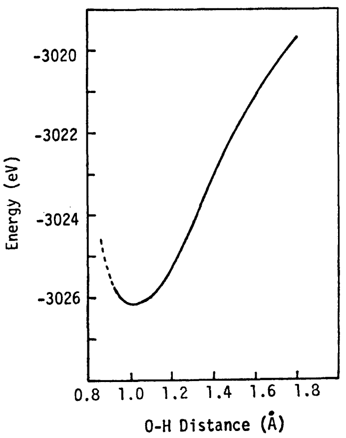

Fig. 3. Total energy of 2-hydroxybiphenyl in hydrogen bonded form as a function of O–H distance.

Table 6. Charge density on atoms in hydrogen bonded structure of 2-hydroxybiphenyl *vs.* O–H distance (Å)

O–H distance	Charge density				
	O_{23}	H_{10}	C_{16}	C_{11}	C_{12}
0.96	6.2594	0.8478	4.0215	3.9581	4.0160
0.98	6.2573	0.8502	4.0214	3.9579	4.0160
1.0	6.2554	0.8526	4.0213	3.9578	4.0161
1.2	6.2447	0.8726	4.0189	3.9547	4.0164
1.4	6.2525	0.8833	4.0141	3.9486	4.0176
1.6	6.2842	0.8796	4.0077	3.9387	4.0207
1.8	6.3669	0.8479	3.9962	3.9132	4.0254

Conclusion

Although hydrogen bonds of X–H···π type have been extensively studied, few investigations have been made on the changes of energy terms of all the atoms in the molecule due to the formation of the hydrogen bond. In the present work, we have tried to clarify the nature of X–H···π hydrogen bond and have obtained the following results. i) The contribution of one-atomic terms to the hydrogen bond in 2-hydroxybiphenyl is quite small. ii) The interaction between the hydrogen of hydroxyl group with the other atoms mainly contributes to stabilization of the hydrogen bonded conformation. However, considerable contribution to the instability comes from interactions among the other atoms. iii) Most of the stabilization energy comes from resonance terms of the interaction between 1s orbital of the hydrogen of hydroxyl group and orbitals of carbon atom 16, mainly of its $2p_z$ orbital. iv) Exchange interaction between the hydrogen of hydroxyl group and the other atoms destabilizes the hydrogen bond. It should be noted that if we consider only the interacting hydrogen moiety, we obtain more than double the hydrogen bond energy (Table 3). v) The calculated result of charge densities as a function of O–H distance indicates the involvement of charge-transfer structures in the hydrogen bonded formation.

The results verify at least qualitatively that the resonance term including charge-transfer is the main one to stabilize intramolecular hydrogen bond of O–H···π type. Although it was discussed that charge-transfer interaction made important contribution, this fact was not revealed concretely. The present result forms a contrast with the ordinary hydrogen bond of X–H···n type where Coulombic interaction also makes significant contribution to the stability. This characteristic of X–H···π type is considered to be due to the neutrality of the proton acceptor benzene-ring and delocalization of the electrons. The present treatment provides a method which is convenient for clarifying the nature of intramolecular hydrogen bonds of large molecles.

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