The Resonance Energy and the Hindering Potential Barrier of the C-C axis of Glyoxal

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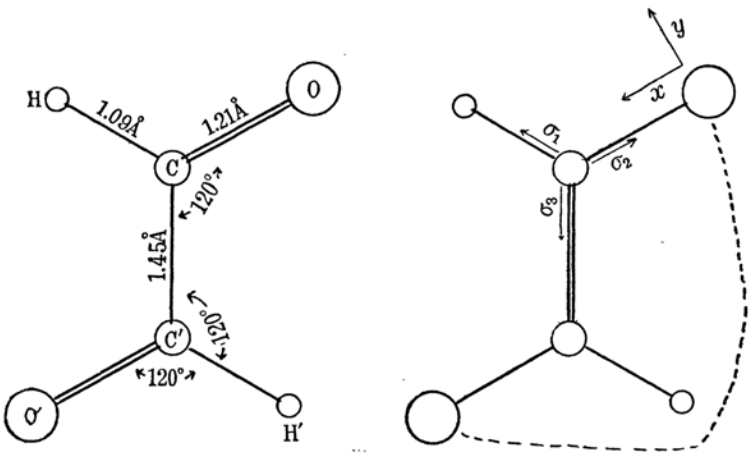
Introduction

There have been few investigations on the hindering potential about single bonds of aliphatic compounds which have conjugated double bonds. In these compounds the molecular structures are so remarkably influenced by quantum-mechanical resonance, that the potential barrier about the bond has to be calculated by taking into account the resonance energy. The hindering potential of butadiene[1] was discussed by calculating the energies of several structures of butadiene, by the method of Goeppert-Mayer and Sklar, but owing to the uncertainty of the correction of the energy zero of these structures, it was not possible to obtain a precise value of the hindering potential. On the other hand, Penny and Sutherland[2] calculated the hindering potential of O-O axis in H_2O_2 and of N-N in H_2N-NH_2 molecule by the use of Heitler-London's method. In this article the same method will be applied for the case of glyoxal having conjugated double bonds.

By electron diffraction investigation the stable structure of glyoxal molecule was determined to be planar and of the trans[3] form. Accordingly, in order to calculate the hindering potential barrier of glyoxal, it is sufficient to compute the difference between the energies of the perpendicular form and of the planar one. For the stable planar configuration the structure A and the structure B in Fig. 1 are considered as the possible non-polar resonance structures, while for the perpendicular configuration, the structure B is to be put aside from our consideration, since in this position the two double bonds do not resonate absolutely.



Structure A Structure B

Fig. 1.—The Configuration of Glyoxal molecule

§ 1. The case in which the structure a alone is considered

When we assume the molecule has only the form A, the wave function of this molecule in Heitler-London's approximation is expressed as follows:

$$\Psi_A = \{\phi^O{}_y(1)\phi^O{}_y(2)\}(\phi^H(3)\psi_{\sigma_1}(4))(\phi^O{}_x(5)\psi_{\sigma_2}(6))$$
$$(\phi^O{}_\pi(7)\phi^C{}_\pi(8))(\psi_{\sigma_3}(9)\phi'_{\sigma_3}(10))$$

(1) M. Katayama and Y. Morino; *Reports of the Institute of Science Technology, University of Tokyo*, **5**, 19, (1951).

(2) W. G. Penny and G. B. B. M. Sutherland: *J. Chem. Phys.*, **2**, 492 (1934).

(3) J. E. Lu Valle and V. Schomaker: *J. Am. Chem. Soc.*, **61**, 3520 (1939).

$$\{\psi^{O}_{y'}(11)\psi^{O}_{y'}(12)\}(\psi^{H'}(13)\psi_{\sigma_1'}(14))$$
$$(\psi^{O}_{x'}(15)\psi_{\sigma_2'}(16))(\psi^{C}_{\pi'}(17)\psi^{C}_{\pi'}(18)) \quad (1)$$

where bracket { } means a lone pair, and bracket ( ) a pair bond: for example,

$$(\psi^{H}(3)\psi_{\sigma_1}(4)) = \frac{1}{2}(\psi^{H}(3)\psi_{\sigma_1}(4)$$
$$+\psi^{H}(4)\psi_{\sigma_1}(3))(\alpha(3)\beta(4)-\alpha(4)\beta(3)) \quad (2)$$

and ψ^{H} denotes the wave function of hydrogen, and ψ_{σ_1}, ψ_{σ_2} and ψ_{σ_3} the hybridized wave functions of carbon atoms. The wave functions of π-electrons of oxygen and carbon atoms are designated by ψ^{O}_{π} and ψ^{C}_{π}, the directions of the coordinate axis being shown in Fig. 1. In this expression, 1s electrons of carbon atoms and 1s and 2s electrons of oxygen atoms are ignored. Thus in this approximation the energy of certain states of the molecule may be expressed by the following formula:

$$W = H(E) - 2\sum J_{pp'} - \sum J_{pt} + \sum J_{qr}$$
$$-\frac{1}{2}\sum J_{rs} - \sum u J_{tt'} \quad (3)$$

where $H(E)$ denotes the coulomb energy, $J_{pp'}$ the exchange energy between the wave functions of the electrons of different lone pairs, J_{pt} those between an electron of a lone pair and the other electron which does not belong to the lone pair, J_{qr} those between the electrons which make the same bond, J_{rs} those between the electrons which make different bonds, $J_{tt'}$ those between electrons which do not make a bond or a lone pair. u is the element of representation of symmetry group. The last term will be used in the calculation on § 2.

In order to calculate the energy difference due to the rotation about the C-C axis, it is sufficient to ignore from Eq. (2) the terms which do not vary with the rotating angle about the central C-C axis. Thus the remaining energy may be expressed as follows:

$$\begin{aligned} W(\varphi) = 4\{&U(yO:yO')+U(yO:H')+U(yO:xO') \\ &+U(yO:\sigma_2')+U(yO:O\pi') \\ &+U(yO:C\pi')+U(yO:\sigma_1')\} \\ +2\{&U(H:\sigma_1')+U(H:xO')+U(H:\sigma_2') \\ &+U(H:O\pi')+U(H:C\pi')+U(\sigma_1:xO') \\ &+U(\sigma_1:\sigma_2')+U(\sigma_1:O\pi')+U(\sigma_1:C\pi') \\ &+U(xO:\sigma_2')+U(xO:O\pi')+U(xO:C\pi') \\ &+U(\sigma_2:O\pi')+U(O\pi:C\pi')+U(\sigma_2:C\pi')\} \\ &+U(H:H')+U(\sigma_1:\sigma_1')+U(xO:xO') \\ &+U(\sigma_2:\sigma_2')+U(C\pi:C\pi')+U(O\pi:O\pi') \end{aligned} \quad (4)$$

where $U(a:b) = Q(a:b) - \frac{1}{2}J(a:b)$. The coulomb and the exchange energies, $Q(a:b)$ and $J(a:b)$, have respectively the following expression:

$$\left.\begin{aligned} Q(a:b) &= \int \psi_a(1)\psi_b(2)H\psi_a(1)\varphi_b(2)d\tau \\ J(a:b) &= \int \psi_a(1)\psi_b(2)H\psi_a(2)\psi_b(1)d\tau \end{aligned}\right\} \quad (5)$$

where H means Hamiltonian of $(a:b)$ system. It would be desirable to calculate the integrals, but unfortunately, the tables of these integrals given by Kotani[4] et al, are not available for this case, because the integrals to be used in the present calculation are those between the atoms farther apart than those given in their tables. Hence, for simplicity, the coulomb energy is assumed to be 20% of the Morse function and the exchange energy the remaining part of the Morse function. The dissociation energies,[5] the equiliblium distances and the vibrational frequencies are listed in Table 1, which are used to calculate the Morse functions. For the exchange integral between the π-electrons the value calculated by Penny[6] in ethylene molecule, 0.75 e. v., is used.

Table 1
Constants for Morse function

Bond	Dissociation Energy kcal.	Equilibrium Distance A.	Frequencies $cm.^{-1}$
H—H	102.4	0.74	4375
O—H	113.1	0.97	3660
O—O	34.3	1.32	1304
C—O	81.8	1.43	1030
C—C	83.0	1.54	990
C—H	92.3	1.10	2930

If the directions of the bondings of the two different atoms make the angles θ_1 and θ_2 with the line drawn through the nuclei of the two atoms, the exchange integral between these two electrons may be written in the following expression:

$$J(xO:xO') = J'(xO:xO')\cos^2\theta_1\cos^2\theta_2$$
$$+J_{\perp}(xO:xO')\cos\varphi\sin^2\theta_1\sin^2\theta_2 \quad (6)$$

where $J'(xO:xO')$ represents the exchange integral derived from Morse function, and $J_{\perp}(xO:xO')$ means the one between the perpendicular components of the wave functions to the O—O line. In order to estimate the value of $J_{\perp}(a:b)$, if both electrons, a and b, are referred to p-electrons, $J_{\perp}(a:b)$ has the same value as the exchange energy between π-electrons, and if a and b are referred to p-electron and hybridized sp^2-electron respectively, or both of them are referred to hybridized sp^2-electrons, the values of $J(a:b)$ are taken as 2/3 or 4/9 as those of π-electrons. φ represents the angle of rotation.

(4) M. Kotani et al: *Proc. Phys-Math. Soc.*, **20**, Extra No. (1938); **22**, Extra No. (1940).
(5) R. H. Gillette and A. Sherman: *J. Am. Chem. Soc.*, **58**, 1135 (1936).
(6) W.G. Penny: Proc. *Phys. Soc. London*, **46**, 333 (1934).

about the C—C axis, the zero of the angle being at the position where the molecule has the planar trans form. The calculated energies of the planar and perpendicular models of glyoxal by the method stated above are listed in Table 2. It is well established by this calculation that, if this molecule has the wave function Ψ_A only, i. e. if only the type A of molecule exists, the perpendicular form is more stable than the planar one.

§ 2. The case of the resonance between the structure A and B

It is evident that the molecule of the glyoxal has not only the contribution of the structure A, but also of other forms such as the structure B. In this paragraph the calculation is performed, considering the structure A and B as the resonance form. The structure B is represented by the following wave function:

$$\begin{aligned}\Psi_B = &\{\psi^{O}_{y}(1)\psi^{O}_{y}(2)\}(\psi_{\sigma_1}(3)\psi^{H}(4))(\psi_{\sigma_2}(5)\psi^{O}_{x}(6))\\ &(\psi_{\sigma_3}(7)\psi_{\sigma_3'}(8))(\psi^{C}_{\pi}(9)\psi^{C}_{\pi'}(10))\\ &\{\psi^{O}_{y'}(11)\psi^{O}_{y'}(12)\}(\psi_{\sigma_1'}(13)\psi^{H'}(14))\\ &(\psi_{\sigma_2'}(15)\psi^{O}_{x'}(16))(\psi^{O}(17)\psi^{O'}_{\pi}(18))\end{aligned} \tag{7}$$

As the result of the resonance between the structure A and B, the energy of the molecule is calculated from the following secular equation,

$$\begin{vmatrix} M_{11}-W & M_{12}-\frac{1}{2}W \\ M_{12}-\frac{1}{2}W & M_{22}-W \end{vmatrix} = 0 \tag{8}$$

$$M_{11} = Q+2J(O\pi : C\pi)-\frac{1}{2}\{J(O\pi : O\pi') + J(C\pi : C\pi')\}$$

$$M_{12} = \frac{1}{2}M_{11}+\frac{3}{4}\{J(C\pi : C\pi')+J(O\pi : O\pi')\} - \frac{3}{2}J(C\pi' : O\pi)$$

$$M_{22} = Q+J(C\pi : C\pi')+J(O\pi : O\pi')-J(C\pi : O\pi)$$

In this equation, M_{11} is the energy of the molecule when only the structure A is considered. The result of this calculation indicates that the energy of the ground state in the trans form is about 5.12 kcal. lower than the case of the structure A alone considered, if the resonance between two non-polar structures is considered. It will be evident that the cis-form is also stabilized by the resonance which has almost the same energy, so that the same amount of resonance energy is tentatively assumed for the cis-form. The calculated value of the energy of each form is shown in the lower part of Table 2. It can easily be seen that the planar form is more stable than the perpendicular one.

Table 2

Relative Energies of Several Configurations

	trans form	cis form	perpendicular form
Structure A only considered	33.72 kcal.	32.83 kcal.	30.13 kcal.
Resonance between the structures A and B being considered	28.60	27.71	30.13

Discussion and Acknowledgement

The calculation stated above indicates that the structure A gives the more stable perpendicular form than the planar ones, while the resonance between A and B makes the planar one more stable than the perpendicular one. Thus it may be concluded that the cons deration of the conjugation of double bonds contributes several kilocalories to the hindering potential about the central single bond, while the energy of the perpendicular form is the same as that in the case where only the form A is considered. The hindering potential of glyoxal has not been determined experimentally, but in the molecules of oxalyl-chloride it was confirmed by electron diffraction and dipole moment measurements[7] that the hindering potential is about 5 kcal., the trans-form being the most stable position. The value 1.5 kcal. ~2.4 kcal. obtained in this article is practically of the same order.

This calculation indicates that the cis-form is more stable than the trans-form, contrary to the observed result. This disagreement might be due to the approximate nature of the calculation; for instance, to the exclusion of the 1s and 2s electrons of O atoms. Moreover, it would be reasonable to take into account the polar structure as one of the canonical set. But, the higher order approximation as this ought not to be performed since the values J and Q used in this calculation are comparatively rough.

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(7) Y. Morino et al: unpublished.