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An MO Study of Organic Sulfur Compounds. Comparison with the Corresponding Oxygen Compounds

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The contribution of 3d orbitals of sulfur atom to the electronic structures of the sulfur compounds, H_2CS, CH_3SH, C_6H_5SH, and $C_6H_5SCH_3$ have been studied by means of *ab initio* MO method. The results have been compared with those of the corresponding oxygen compounds in order to clarify the peculiar properties of the sulfur compounds. The global molecular properties are scarcely affected by the 3d orbitals of sulfur atom since they are energetically highly located. However, the local characters such as charge distributions and LUMO are largely varied by the participation of 3d orbitals.

Sulfur forms not only organic sulfur compounds analogous to oxygen compounds but also various stable hypervalent compounds. It is well known that the nucleophilicity of the lone pair of sulfur atom is larger than that of oxygen. However, the basicity of sulfur atom is smaller than that of oxygen, reversely. In this manner, sulfur has some different chemical properties from those of oxygen. Thus it is of interest to investigate the electronic structures of sulfur compounds and consider the origin of peculiar properties theoretically.

We have investigated the effect of 3d orbitals of sulfur atom on the electronic structures of sulfur compounds. 3d orbitals of sulfur are thought to participate in the chemical bonding. The SCF calculation of α-thiocarbanion[1] and the GVB calculation of SF_6[2] showed that the effects of 3d orbitals on the stability and the reactivity are small. The contribution of vacant 3d orbitals to the global molecular properties may be small since they are energetically highly located.

However, in order to explain the NMR chemical shifts of substituted thiophenes in view of charge distribution, the contribution of 3d orbitals can not be neglected.[3] Furthermore, as Inagaki *et al.*[4] pointed out, vacant 3d orbital participation is important in determining the stereochemical courses of reactions where sulfur compounds undergo the attack of nucleophilic reagents.

In the present study, an *ab initio* MO calculation has been carried out for thioformaldehyde, methanthiol, thiophenol, thioanisole, phenol, and anisole in order to clarify the nature of electronic structures of organic sulfur compounds, especially the differences in the role of sulfur and oxygen atoms on the electronic structures of molecules. We have also calculated the rotational barriers of substituted benzenes and consider the steric effect. On the basis of the calculated results, the vacant 3d orbital participation to some molecular properties, such as reactivity, polarity, *etc.* is discussed.

Calculation

Ab initio MO calculation is carried out using a minimal STO-3G basis set with the POLYATOM version 2[5] and GAUSSIAN 70[6] program packages. For sulfur atom, the five 3d functions are added to the minimal basis set. The orbital exponent ζ of 3d functions is obtained by optimizing the total energy of H_2S. The optimized value is found to be 1.77. Boer and Lipscomb[7] reported $\zeta = 1.71$, obtained by means of the basis set of Slater type AO's. The orbital exponent of 3d functions optimized for CH_3SH also gives $\zeta = 1.77$. This value is used for all the other molecules in the present calculation.[8]

Figure 1 shows the geometric parameters of H_2S, H_2CS, CH_3OH, and CH_3SH used in the present MO calculation. These geometries are taken from experimental data.[9] We assume C_{3v} symmetry for a methyl group. C–S double bond length (1.61 Å) and C–S single one (1.82 Å) are about 0.4 Å longer than the corresponding C–O bond lengths.

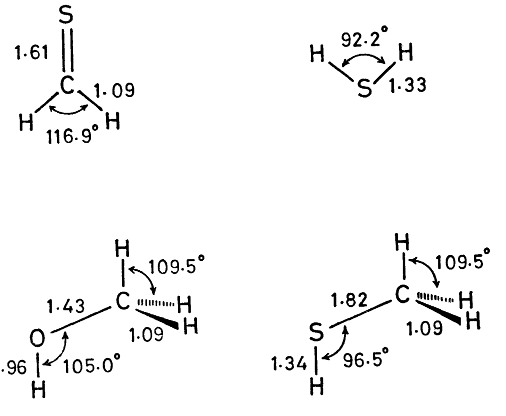

Fig. 1. Geometries of H_2S, H_2CS, CH_3OH, and CH_3SH used in this calculation. Units are shown in Å and degree.

The geometric parameters of C_6H_5OH, C_6H_5SH, $C_6H_5OCH_3$, and $C_6H_5SCH_3$ are given in Fig. 2(a). For phenyl and methyl groups, the geometries of benzene and methanol are used respectively, a staggered conformation being used for $C_6H_5OCH_3$ and $C_6H_5SCH_3$. The numbering of atoms of substituted benzenes is shown in Fig. 2(b).

Results and Discussion

Molecular Orbitals. In order to discuss the difference between the electronic structures of oxygen and

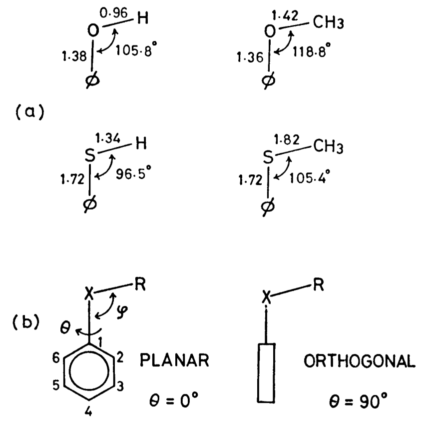

Fig. 2. (a) Geometries of benzene derivatives. Units are shown in Å and degree.
(b) The definition of angle θ and ϕ and the numbering of atoms.

sulfur compounds, we have used a composite molecular model in which the molecular orbitals of whole molecules are represented in terms of the molecular orbitals of the composite subsystems. Using this model, the effects of substituted groups and 3d orbitals on the parent molecules would be clarified in view of the orbital interaction.

The thiocarbonyl group undergoes nucleophilic attacks at the sulfur atom in contrast to the corresponding oxygen compounds.[10] Inagaki *et al.*[4] interpreted this in terms of the orbital interaction based on semi-empirical MO method. The vacant 3d orbitals of sulfur play a significant role in determining the stereochemical courses of the nucleophilic reactions of sulfur compounds. We have investigated the 3d participation by means of *ab initio* MO method.

The modes of orbital interaction between the π orbitals of benzene and π-type orbitals of OH, SH, and SCH_3 groups are shown in Figs. 3—5, the numbering of π orbitals of benzene being given in the left hand side of Fig. 3.

Since the energy of 2p-π of OH group lies lower than that of HOMO's (π_2 and π_3) of benzene, the main component of HOMO of phenol is the π_3 orbital

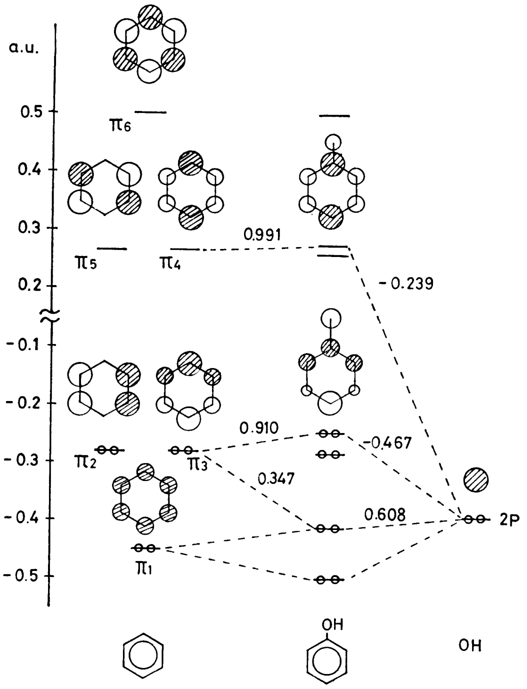

Fig. 3. The mode of the orbital interaction of phenol.

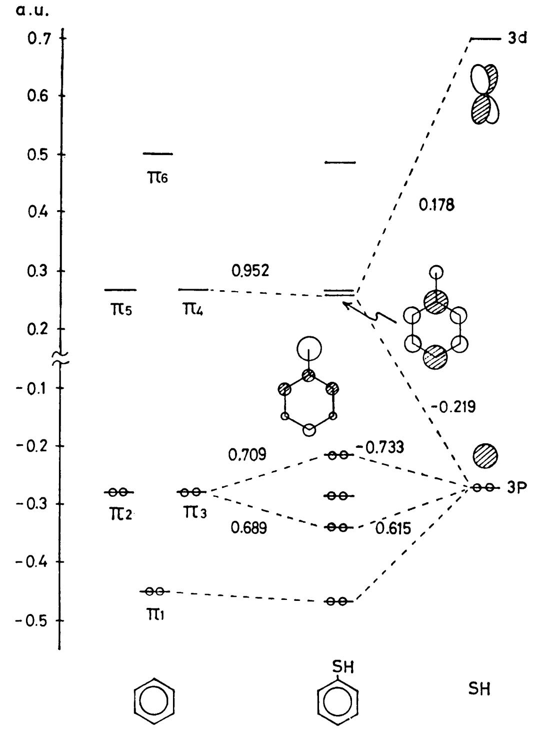

Fig. 4. The mode of the orbital interaction of thiophenol.

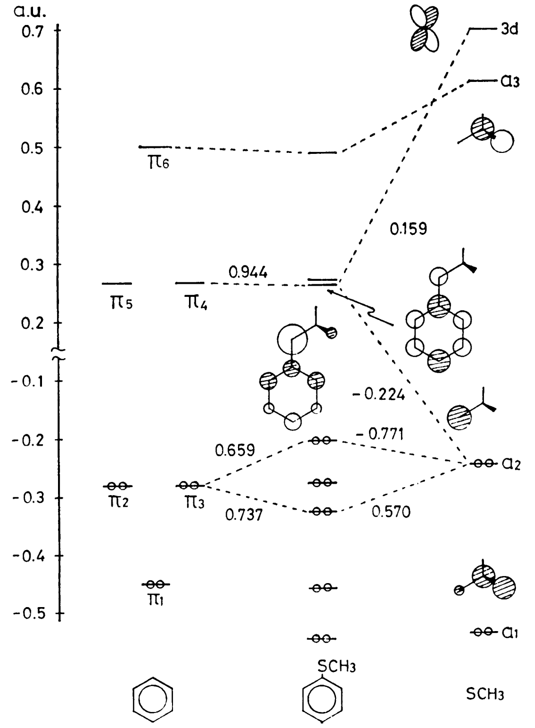

Fig. 5. The mode of the orbital interaction of thioanisole.

of benzene (Fig. 3). The interaction between the π-type orbital of a substituent and π_2 (or π_5) of benzene is symmetry forbidden. In C_6H_5SH (or $C_6H_5SCH_3$), 3p-π of SH group (or a_2 orbital of SCH_3 group) and π_3 orbital mix with each other in nearly equal weight, since the orbital energy of 3p-π of SH group (or a_2 orbital of SCH_3 group) is very close to the π_3 orbital of benzene (Fig. 4 or 5). Consequently the HOMO's of C_6H_5SH and $C_6H_5SCH_3$ have large amplitude at the sulfur atom in contrast to the cases of phenol and anisole. On the other hand, the contribution of the vacant 3d orbitals to *occupied* MO's is small and can be neglected.

The chemical reactivity of a given molecule can be explained qualitatively in terms of the frontier orbitals.$^{11)}$

HOMO plays the most important role for the electrophilic reaction. For thiophenol and thioanisole, 3p-π of the sulfur atom has the largest amplitude at HOMO. There are some experimental data showing that an electrophilic reagent attacks the sulfur atom first.$^{12)}$

Let us consider LUMO's of molecules, which are responsible for the nucleophilic reaction.

LUMO of C_6H_5SH (or $C_6H_5SCH_3$) has a π_4 character (Fig. 4 or 5) for the following reasons. π_4 is mixed by out of phase combination with 3p-π of the SH group (or a_2 orbital of the SCH_3 group), which gives rise to some increase in orbital energy. However, π_4 interacts strongly with the vacant 3d orbitals. As a result, the π_4 orbital energy is decreased. π_5 orbital also interacts with 3d orbital which is antisymmetric on the molecular axis, but this interaction is very small.

The orbital mixing of π_4 and 2p-π of OH group in phenol should be out of phase so that the orbital energy is increased, but π_5 orbital interacts hardly with oxygen 2p-π (Fig. 3). Thus, the main component of LUMO of phenol is π_5 orbital of benzene.

The LUMO's of benzene are scarcely influenced by the CH_3 group of OCH_3 and SCH_3, since the perturbation of their a_3 orbitals localized mainly in the CH_3 group is very small. It is concluded that the reversal of π_4 and π_5 in thiophenol and thioanisole is clearly due to the contribution of 3d orbitals.

Charge Distribution. Let us consider the effect of 3d orbitals on the charge distribution of the molecules.

Figure 6 shows the net charges of CH_3SH and H_2CS calculated without and with 3d orbitals. In the corresponding oxygen compounds, the electronegative oxygen atom pulls the bonding electrons, so that the neighboring atom has the positive net charge. It should be noted that when the heteroatom is sulfur, the neighboring carbon atom has negative charge (Fig. 6). This tendency is encountered also in other molecules (C_6H_5SH and $C_6H_5SCH_3$). In both cases, CH_3SH and H_2CS, the positive net charges on sulfur atoms are decreased by including the 3d orbitals. This effect is larger in the compound containing C–S double bond (H_2CS) than that with C–S single bond (CH_3SH).

The calculated total electron populations of substituted benzenes are summarized in Table 1. From a comparison of the charge distributions on the phenyl group, it is found that the polarization of the phenyl group in phenol or anisole is larger than that in the corresponding sulfur compounds. Thus, phenol and anisole should show stronger orth-, para-orientation than thiophenol and thioanisole.

The charge density has a linear relationship with NMR chemical shift.$^{13)}$ The ^{13}C NMR chemical shifts for these molecules are also given in Table 1.$^{14)}$ The NMR result shows that the polarization of the phenyl

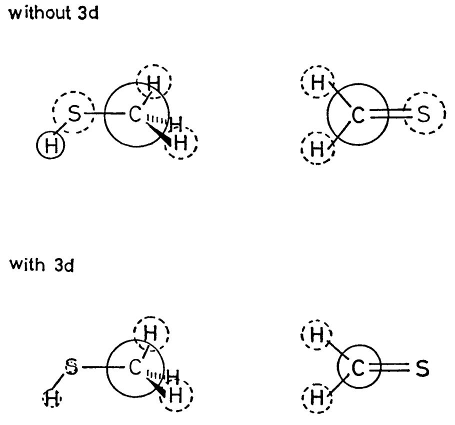

Fig. 6. The net charges of CH_3SH and H_2CS. The circle of the full lines means negative charge and the circle of the dotted lines means positive charge.

Table 1. Calculated total electron populations and carbon-13 NMR chemical shifts for thiophenol, thioanisole, phenol, and anisole

		C-1	C-2	C-3	C-4	C-5	C-6	X$^{d)}$
C_6H_5SH	a)	6.018	6.073	6.057	6.072	6.056	6.078	15.982
	b)	(6.098)	(6.075)	(6.055)	(6.073)	(6.055)	(6.074)	(15.841)
	c)	130.7	129.2	128.9	125.4			
$C_6H_5SCH_3$	a)	6.023	6.078	6.057	6.073	6.055	6.077	15.944
	b)	(6.101)	(6.083)	(6.056)	(6.074)	(6.055)	(6.074)	(15.815)
	c)	138.4	126.5	128.6	124.8			
C_6H_5OH		5.870	6.100	6.051	6.076	6.051	6.084	8.295
	c)	154.9	115.4	129.7	121.0			
$C_6H_5OCH_3$		5.862	6.101	6.053	6.078	6.052	6.084	8.255
	c)	160.2	114.1	129.5	120.7			

a) With 3d orbitals. b) Without 3d orbitals. c) ^{13}C NMR chemical shifts (in ppm), Ref. 14. d) X indicates a heteroatom.

group in phenol derivatives is very large and that in thiophenol derivatives is rather small. Thus the calculated electron populations are in good accord with experimental data.

It should be noted that the calculated charge densities of C-1 in C_6H_5SH and $C_6H_5SCH_3$ without 3d orbitals can not explain the ^{13}C NMR data. The calculation without 3d orbitals gives too large a negative charge on C-1, but chemical shifts shows that the charge of this carbon is less negative than that of other ones. On the other hand, the inclusion of 3d orbitals reduces the negative net charges on C-1 in C_6H_5SH (-0.018) and in $C_6H_5SCH_3$ (-0.023) which are smaller than those of all other positions. Therefore, these results show that the effect of 3d orbitals is important for the charge distribution of sulfur compounds.

It is interesting to analyze the electron distribution in a substituted benzene in terms of the intramolecular charge transfer between phenyl group (Ph) and the substituent {XR, (X=O, S and R=H, CH_3)}. This analysis clarifies the difference between oxygen and sulfur compounds for the π (or σ) type donor-acceptor interaction. Figure 7 shows the movements of π and σ electrons. The value of π electron movement gives a measure of the π donating ability of the substituent.

When the substituent has an oxygen atom, it acts as π-donor and σ-acceptor for the phenyl group {Fig. 7(a)}, whereas when the substituent has a sulfur atom, it acts as π-donor and σ-donor for the phenyl group {Fig. 7(c)}. In the cases of both phenol and anisole, the OH and OCH_3 groups always behave as a better π donor than the SH and SCH_3 groups, while the magnitude of charge transfer is almost the same.

The calculation of thioanisole without 3d orbitals shows larger π electron donating ability of the SCH_3 group than that of the OCH_3 group {Fig. 7(b)}. However, since the ^{13}C NMR chemical shift in para-position gives a measure of the π donating ability of the substituent, NMR data indicate that the OCH_3 group is a better π-donor than the SCH_3 group to the phenyl group. Thus the calculation of thioanisole without 3d orbitals is inconsistent with the ^{13}C NMR result. Whereas, the inclusion of 3d orbitals on sulfur atom reduces the magnitude of the charge transfer (0.05) Thus the effect of 3d orbitals seems to be important in view of the π electron donating ability of substituent to the phenyl group.

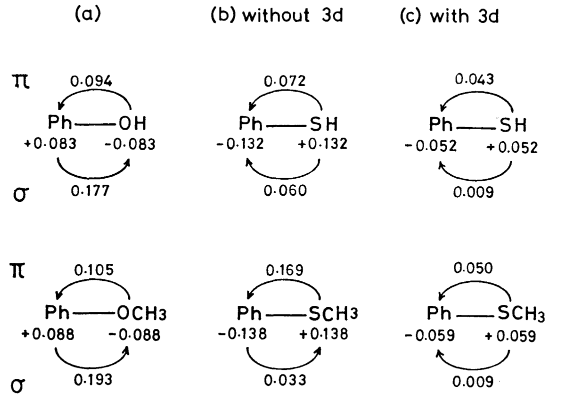

Fig. 7. The net charges and the charge movements of σ and π electrons due to the interaction between phenyl group and substituents.

Rotational Barrier. Let us consider not only the electronic effect but also the steric one. Both effects determine the most stable conformations of C_6H_5SH, $C_6H_5OCH_3$, and $C_6H_5SCH_3$ and the barriers of internal rotation. Our particular interest lies in the 3d orbital contribution of sulfur atom to the rotational barrier and conformation. As mentioned above, it is shown that the effect of 3d orbitals on the charge distribution is important. Let us see whether the participation of 3d orbitals to the rotational barrier is important or not.

Energy variation with the rotation of the SH group in C_6H_5SH is shown in Fig. 8. The bond angle <CSH, ϕ, {see Fig. 2(b)} is fixed at 96.5° for this molecule.[15] The planar structure is the most stable, and the calculated rotational barriers without and with 3d are 3.99 and 3.65 $kcal \cdot mol^{-1}$, respectively. There are no significant changes in both the rotational barrier and the shape of the energy curve caused by including 3d orbitals. The experimental value of rotational barrier of C_6H_5SH is smaller than 0.8 $kcal \cdot mol^{-1}$.[16] Since the present calculation uses the small basis set, the rotational barrier of C_6H_5SH may be overestimated. Rigorous calculation using a more extended basis set would give a lower rotational barrier.

The energy curve of $C_6H_5SCH_3$ calculated without 3d orbitals is shown in Fig. 9. The change of angle ϕ in $C_6H_5SCH_3$ is very important because of steric hindrance. Thus the rotational energy curve of this molecule is obtained by optimization with respect to angle ϕ. In this molecule, the planar conformations is probably most stable but the energy curve is very flat. (The energy difference between the planar and orthogonal conformations is to be 0.317 $kcal \cdot mol^{-1}$.) Thus, it seems that the SCH_3 group of $C_6H_5SCH_3$

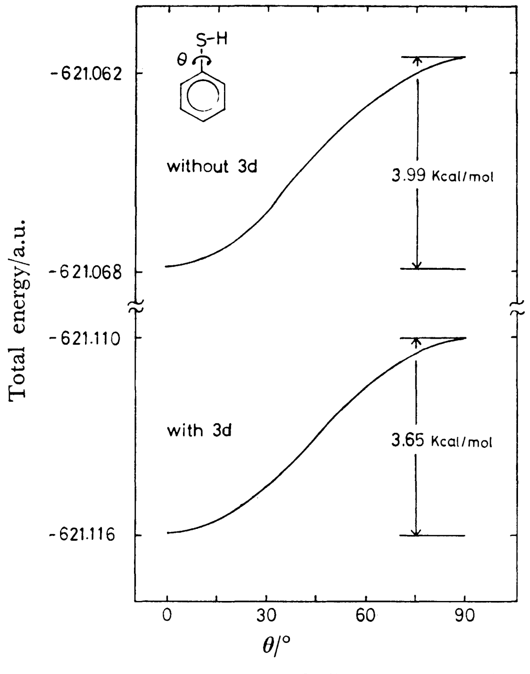

Fig. 8. The energy curve of C_6H_5SH as a function of rotation angle θ.

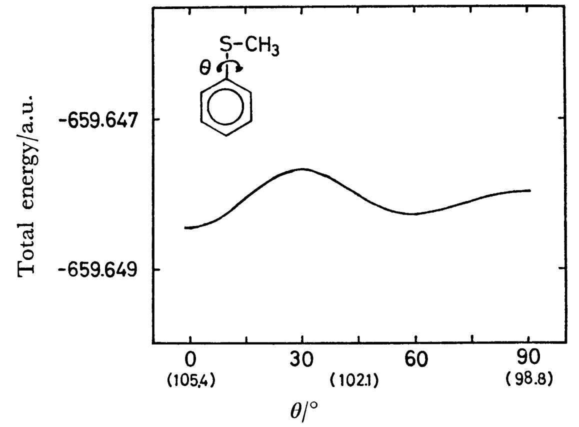

Fig. 9. The energy curve of $C_6H_5SCH_3$ as a function of rotation angle θ. The optimized angle ϕ at each angle θ (0°, 45°, and 90°) is also given in parentheses.

rotates almost freely.

It will be necessary to know the effect of 3d orbitals on the rotational barrier in $C_6H_5SCH_3$. So, we carried out MO calculation including 3d orbitals for planar and orthogonal conformations of this molecule. The geometry of $C_6H_5SCH_3$ optimized with respect to the angle ϕ by a basis set without 3d orbitals is used for the calculation with 3d orbitals. The energy difference is to be 0.237 kcal·mol^{-1}, which is almost the same as the result without 3d orbitals. Therefore, we might conclude that there is very small effect of 3d orbitals on the stable conformations and the rotational barriers in C_6H_5SH and $C_6H_5SCH_3$.

Let us compare oxygen (C_6H_5OH and $C_6H_5OCH_3$) and sulfur compounds (C_6H_5SH and $C_6H_5SCH_3$). The rotational barrier of C_6H_5SH is smaller than that of C_6H_5OH (5.2 kcal·mol^{-1}).[17] The energy curve of $C_6H_5OCH_3$ shown in Fig. 10 is somewhat complicated. The potential curve has two minima at $\theta=0°$ and $\theta=90°$, there are maximum at about $\theta=30°$—40° and $\theta=140°$—150°. The stabilization at $\theta=90°$ is probably caused by releasing the steric hindrance between the phenyl and OCH_3 groups, and that at $\theta=0°$ is brought forth by the strong conjugation between these groups. Whereas, $C_6H_5SCH_3$ gives a very flat energy curve because of the cancellation between the conjugation and steric hindrance between the phenyl and SCH_3 groups.

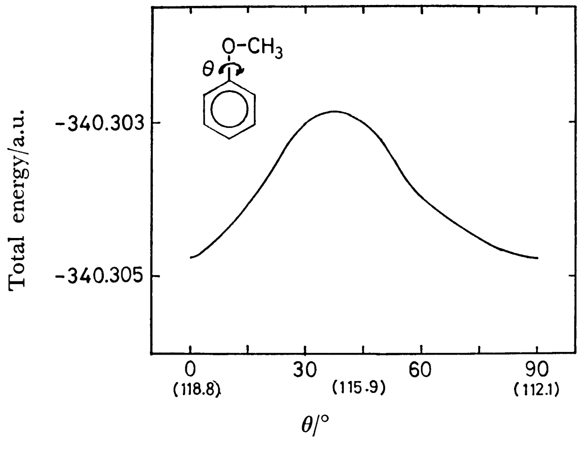

Fig. 10. The energy curve of $C_6H_5OCH_3$ as a function of rotation angle θ. The optimized angle ϕ at each angle θ (0°, 45°, and 90°) is also given in parentheses.

Conclusion

We have discussed the effect of 3d orbitals of sulfur on the electronic structures of molecules and the difference of the electronic structures between the oxygen and sulfur compounds. The calculated results suggest that the contribution of 3d orbitals to the charge distribution is important, but that to the stable conformation and rotational barrier is very small. Since the orbital energies of 3p AO of sulfur atom are almost the same as the 2p AO of carbon atom and the 3p orbitals of sulfur atom are rather diffuse, the molecular properties of sulfur compounds differ somewhat from the corresponding oxygen compounds. The shape and energy of LUMO are particularly sensitive to the participation of 3d orbitals.

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