Theoret. Chim. Acta (Berl.) 63, 55–68 (1983)

**THEORETICA CHIMICA ACTA**

# A Theoretical Study on the Photoisomerization of Thiophene

Toshio Matsushita, Hidetsugu Tanaka, and Kichisuke Nishimoto

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Yoshihiro Osamura

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

The photoisomerization of thiophene (3–5 and 2–4 transpositions of carbon atoms) has been studied with *ab initio* SCF and CI calculations. A possible reaction mechanism from the lowest excited singlet state $^1B_2$ of thiophene can be proposed from potential surface via Dewar thiophene. The $^1B_2$ state of thiophene would easily convert to the biradical intermediate by almost one step. The internal conversion of this species to the $S_0$ state would cause to the transposition of carbon atoms. The effect of phenyl substituent is also discussed.

**Key words:** Photoisomerization – Thiophene.

## 1. Introduction

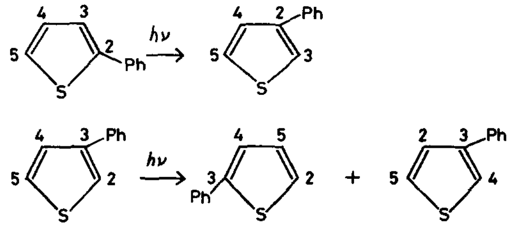
Many experimental studies have been carried out in the last decade on the photochemistry of five-membered heterocyclic ring systems. The greatest area of activity in this field has been the photoisomerization process which causes the changes of the heterocyclic nucleus (furans, isoxazoles, thiophenes and isothiazole) [1].

Wynberg and coworkers have studied the photoisomerization of thiophenes in great detail. They found that the irradiation of phenyl-thiophene derivatives

---

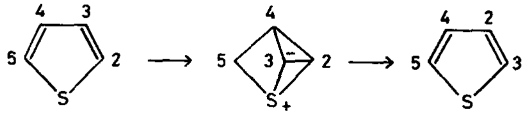
Offprint requests to: K. Nishimoto.

resulted in the interchanges of positions of carbon atoms [2];



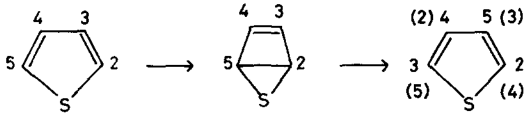
Major reaction of 2-phenyl-thiophene derivatives is the interchange of 2 and 3 carbon atoms, while the interchange of 3 and 5 (or 2 and 4) carbon atoms mainly occurs in 3-phenyl-thiophene derivatives. A number of speculative mechanism have been proposed to rationalize the rearrangement patterns.

Wynberg and coworkers [3] proposed Zwitterion–Tricyclic rout;

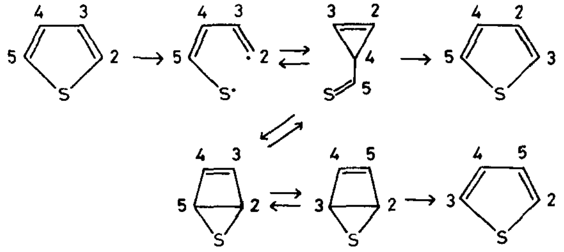


This mechanism can give account for the interchange between $\alpha$- and $\beta$-carbon atoms, but the major aspects of the rearrangement of 3-phenylthiophene is difficult to explain in terms of this pathway [3].

For the mechanism of 3–5 (2–4) transposition, internal cyclization-isomerization route was offered [1];



Van Tamelen and Whitesides [4] proposed the following pathway;



This scheme would explain the majority of results encountered with thiophene rearrangement, if Dewar structures and cyclopropenylthiocarbonyl are in equilibrium. It seems to be very difficult, however, to find the clear mechanism to explain the complex product distribution. There might be several competitive reaction mechanism. In order to attack the mechanism of the photoisomerization of thiophene from the theoretical point of view, we examine what is the structure of the lowest excited singlet states of thiophene and how proceeds the reaction.

## 2. Calculation

The potential curves and geometries in the excited states are calculated by the singly excited configuration interaction (SECI) method without inner shell excitation, in which the SCF MO's of the ground state calculated with the STO-3G minimal basis set are used [5].

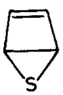
It has been suggested that the SECI or SCF procedure does not well describe a bond formation and break quantitatively. The potential curves of the ground and excited states are recalculated with an extensive CI calculation at the geometries optimized by the SCF and SECI calculations. The configurations which are used in the ground-state pathway include the all valence single excitations plus the double excitations within the six highest occupied MO's and five lowest unoccupied MO's (SDCI). The potential curve of the excited state is calculated with CI method including all valence singly excited configurations plus the doubly and triply excited configurations generated by using the five highest occupied MO's and four lowest unoccupied MO's (SDTCI), where the triply excited configurations related to the large coefficients in the SECI calculation are included.

Although the present limited CI wave function with STO-3G minimal basis set is still insufficient for describing the accurate potential curves, the calculations might be good enough to explore the qualitative feature of reaction pathway.

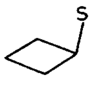
## 3. Results and Discussion

### *3.1. Structures of Several Intermediates in the Ground and Excited States*

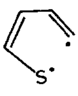
In this work, the reaction path of the interchange of carbon position is studied by the *ab initio* calculation in which thiophene is used as a model compound. Since the photorearrangement of phenyl substituted thiophene leads to the distinguishable product distribution, the effect of the substituent should be considered. First, we examine the essential feature of the rearrangement with thiophene itself, and then discuss the effect of phenyl substituent later on. For this reaction, the following intermediates (or transient species) could be postulated from many speculative reaction mechanism;



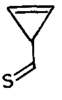
II



III



IV



V

The second species is the intermediate (or transition state) of the sulfur migration reaction of Dewar thiophene. Although cyclopropenylthiocarbonyl (the last species) is expected to be unstable [3], the possibility of the intermediacy of cyclopropenyl structure can not be ruled out, because the existence of three-membered intermediate is shown in photoisomerization of diaryisoxazole [6, 7].

It is of interest to examine the structures and energy relation of thiophene (I), Dewar thiophene (II), intermediate of sulfur migration of Dewar thiophene (III) and cyclopropenylthiocarbonyl (V) in the ground and excited states. The constraint geometry optimizations are carried out, for the $^1B_2$ and $^1A''$ states of I, the $^1A''$ state of II and the $S_1(^1A'')$ state of III, where all C—H bond distances

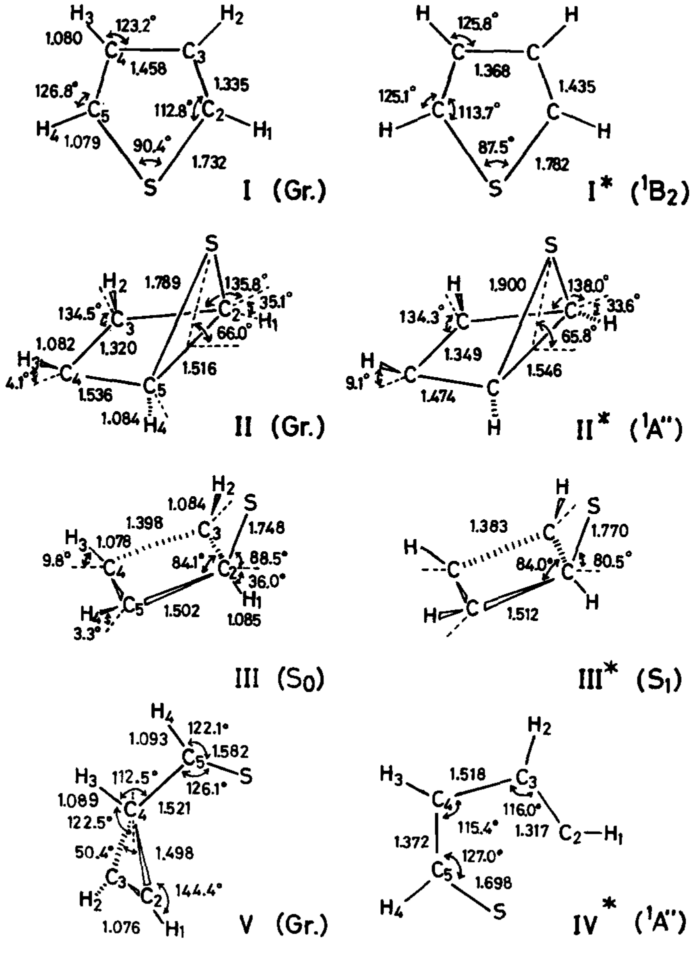


**Fig. 1.** Optimized geometries for the ground and excited states of thiophene I, II and III calculated with the SCF and SECI methods. Only the geometrical parameters specified in excited states are optimized and for the other parameters the ground-states values are used. Units are shown in Å and degree. The geometry of I(Gr.) is taken from Ref. [8]. A superscript asterisk in roman numerals I, II, III and IV means the geometry in the excited states. The numbering of atoms is also shown.

used are the optimized values in the ground states. The results are shown in Fig. 1 with their ground-state geometries. In Fig. 2, the vertical excitation levels of these states with other low lying excited states are shown. Note that the energy levels of the lowest excited singlet states of I, II, III and V are close.

In the $^1B_2$ state of thiophene, I*, which is one of the $\pi \rightarrow \pi^*$ state, one can see the enlargement of the $C_2$—$C_3$ bond and the shortening of the $C_3$—$C_4$ bond. The similar result can be seen for cyclopentadiene [9]. The electronic structure

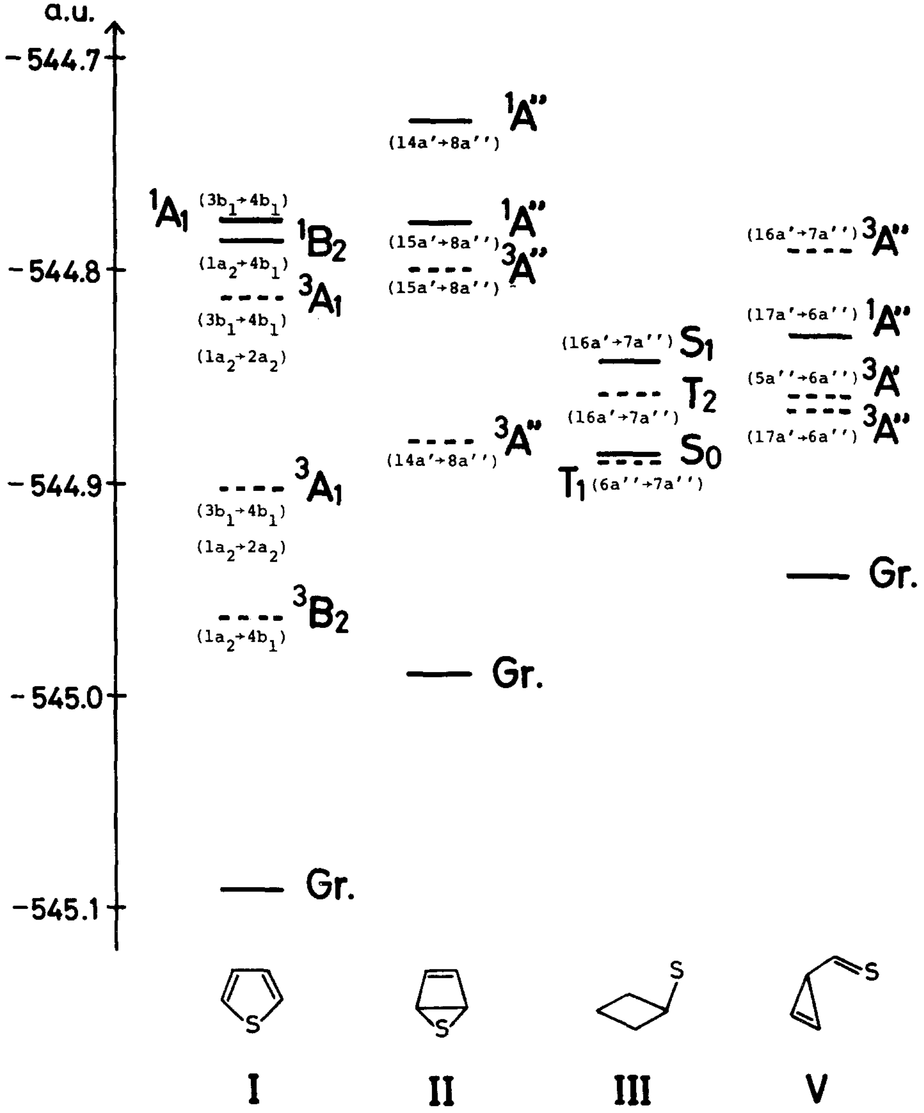


Fig. 2. The energies of the low-lying states of I, II and III calculated with the SECI method at the optimized geometries of their ground states. The major configurations contributing to each state are given above or under the line representing its energy level

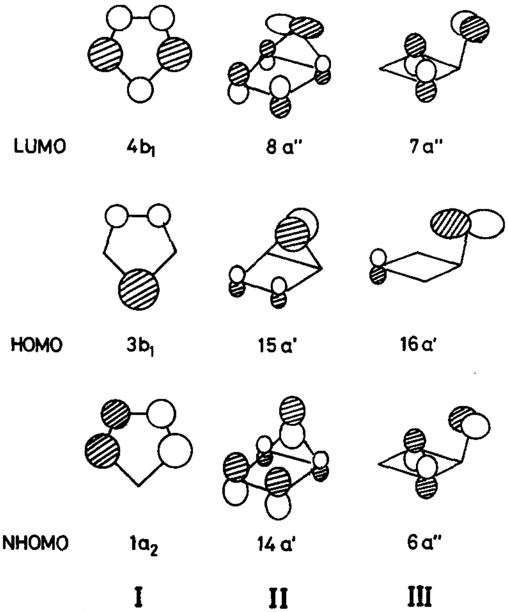
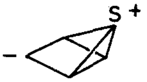


**Fig. 3.** Schematic description of some active MO's of I, II and III

of this state is mainly described by the excitation from the $1a_2$ to the $4b_1$ whose shapes are shown in Fig. 3.

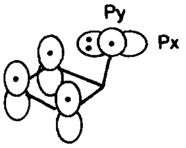
The geometries of Dewar thiophene, II and II* are shown in the second row of Fig. 1, where the $C_s$ symmetry is assumed for the optimization. One should notice that the $C_2$—S bond length of II is fairly larger than that of the ground state. This fact turns out to be that the geometry of II* collapses to the structure of the $S_1$ state of III (III*).

The optimized geometries of III and III* are shown in the third row of Fig. 1. Some constraint are imposed in the optimization III and III*. Four carbon atoms preserve a coplanarity and two hydrogen atoms $H_2$, $H_4$ and two carbon atoms $C_3$, $C_5$ are on a plane. Furthermore, $C_s$ symmetry is imposed, i.e. S, $C_2$, $C_4$, $H_1$ and $H_3$ atom are put on the symmetry plane. Since the removement of the $C_s$ symmetry restriction in the ground state III leads to the structure II, it is suggested that III is the transition state of the sulfur atom migration II↔II' in the ground state. It is interesting to see that the geometry of III* is similar to that of III except the $C_4$—$C_2$—S angle. Thus we fix the C—H flapping angles of the $S_1$ state to those of the $S_0$ state. Although the geometries are not fully optimized, the possibility of three cyclic structures

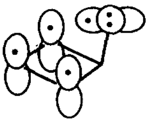


as a transition state or an intermediate in the sulfur migration reaction (II↔II') would be ruled out, because of the lengthening S—$C_3$ (or S—$C_5$) bond distance in the ground and $S_1$ state.

Let us consider the electronic structures of III and III*. The electron assignments of the ground ($S_0$) and $S_1$ states are illustrated as follows;



$S_0$



$S_1$

The weight of main configurations of III and III* are written as

$$\Psi_{S_0} \simeq 0.91\Phi_0 - 0.30\Phi_2$$

$$\Psi_{S_1} \simeq 0.85\Phi_1 - 0.42\Phi_3$$

where

$$\Phi_0 = |\cdots(15a')^2(6a'')^2(16a')^2|$$

$$\Phi_1 = |\cdots(15a')^2(6a'')^2(16a')^1(7a'')^1|$$

$$\Phi_2 = |\cdots(15a')^2(16a')^2(7a'')^2|$$

$$\Phi_3 = |\cdots(15a')^2(6a'')^1(16a'')^1(7a'')^2|.$$

The result suggests that III and III* have diradical character. In addition III* has ionic character partly due to the intramolecular charge migration. Three of six electrons are in the allylic carbon and the others in the sulfur atom. The $p_x$ orbital is occupied by two electrons and the $p_y$ by one electron in the ground state. One electron in the $p_x$ is transferred to the $p_y$ at the $S_1$ state. From these electron assignment, the $C_3$—S bond formation (the reaction III→II) would occur easily in the ground state, but not in the $S_1$ state.

Another possible intermediate IV*($^1A''$) in which one C—S bond is scissored is obtained with no activation energy from the vertical excited state $^1B_2$ of I by the torsional deformation of the $C_2$—$C_3$—$C_4$—$C_5$ initially. The electronic structure is mainly described by the excitation from the $4a''$ to the $19a'$, which are $\pi$ orbital of the $C_4$—$C_5$—S part and $\sigma^*$ orbital of the $C_2$—S part, respectively. The corresponding ground-state structure of IV* is not stable and the optimization leads to I. It should be noted that both the equilibrium structures of I* and IV* are derived from the same vertical excited state of I. The electronic structure of IV* is, however, different from that of I* because of the difference of the initial geometrical deformation.

### 3.2. *A Preliminary Consideration of the Reaction Schemes*

If the Dewar thiophene II is considered as one of the reaction intermediate, the first step should be ring closure (I↔II) and the second step is sulfur migration (II↔III↔I'). As the first step conserves the $C_s$ symmetry, the state correlation diagram is used in order to examine whether the reaction is favorable in the

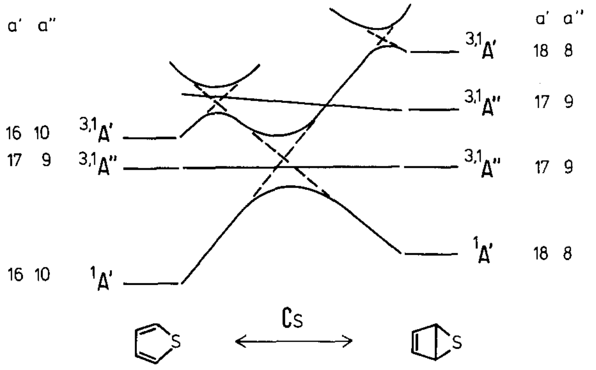


**Fig. 4.** The state correlation diagram for I↔II path conserving the $C_s$ symmetry

ground state or any low-lying excited states [10]. Fig. 4 shows the state correlation diagram of the isomerization I↔II conserving $C_s$ symmetry. The number of electrons belonging to each symmetry orbital ($a'$ and $a''$) is shown at both sides of this figure. The path I↔II is shown to be unfavorable in both the ground state ($^1A''$) and the excited state $^{3,1}A'$ which is originally $^{3,1}A_1$ state in thiophene, because of having a high energy barrier caused by the avoided crossing. Since the $^{3,1}A''$ state which comes from the $^{3,1}B_2$ states of thiophene can be connected smoothly with the $^{3,1}A''$ state of II, the reaction I↔II must be symmetry allowed in this state.

Fig. 5 shows the energy curves of the ground and several low-lying excited states for the angle variation ($\Delta\phi$) of $C_2$—$C_5$—S from the ground state's value 64.9° in II. The result would give the profile for the reaction scheme of II↔III. The

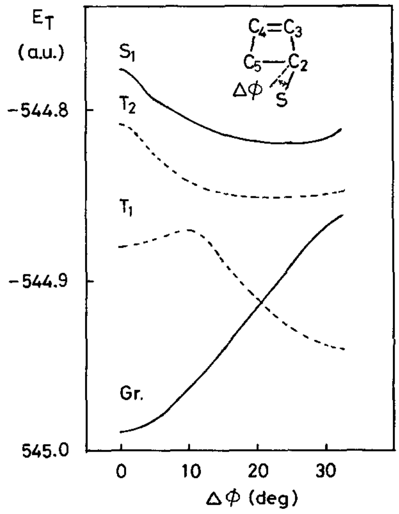


**Fig. 5.** Energy curves of the ground and some low-lying excited states of II for $\Delta\phi$ variation relative to the ground-state geometry

increase of $\Delta\phi$ unstabilizes the ground state significantly. The $T_1$ state becomes unstable in the region of $\Delta\phi < 10°$, but extremely stable in the region of $\Delta\phi > 10°$, since there is the avoided crossing of the $T_1$ and $T_2$ states at $\Delta\phi \simeq 10°$. The other two states, $T_2$ and $S_1$ are found to be stabilized by increase of $\Delta\phi$ and their energy minima are located at $\Delta\phi \simeq 20°$ and 25°, respectively. Such stabilizations can be reasonably explained by the antibonding character of $8a'$ of II shown in Fig. 3. The existence of the equilibrium structure III* can be proved by the result that the minimum point $\Delta\phi = 25°$ ($\phi = 90°$) in the $S_1$ state of II is the same as the $C_2$—$C_5$—S angle in III. While the Dewar thiophene II has the equilibrium structure in the ground state, II* in the lowest excited singlet state breaks C—S bond to form the biradical intermediate III* spontaneously. This result and the symmetry allowedness from I* to II* support that the reaction $I(^1B_2) \rightarrow II(^1A') \rightarrow III(S_1)$ proceeds with a low activation energy. Note also that the energy difference between the $^1B_2$ state of thiophene and the $^1A''$ state of Dewar thiophene is only ca. 5 kcal/mol, but in the triplet surface the $^3A''$ state locates ca. 52 kcal/mol above the $^3B_2$ state.

The other possibility remains on the reaction mechanism via the ring-opened intermediate IV*. In order to demonstrate the possibility of the reaction from IV* to III*, the energy variation is calculated for the rotation of the dihedral angle S—$C_5$—$C_4$—$C_3$ ($\Delta\theta$), which is shown in Fig. 6. Since the all low-lying states become unstable, the reaction from IV* to III* would be unfavorable.

In Fig. 7, the energy curves for the variation of the dihedral angle $C_2$—$C_3$—$C_4$—$C_5$ ($\Delta\gamma$) relative to the optimized geometry of IV*. The result would give the profile for the initial stage of the reaction $IV^* \leftrightarrow V(^1A')$. The $T_1$ state is stabilized by the increase of $\Delta\gamma$ and the energy minimum exists at $\Delta\gamma \simeq 30°$. The $S_1$ state becomes unstable, but the energy curve is very flat. Therefore, the reaction $IV^* \rightarrow V(^1A')$ would be more favorable than $IV^* \rightarrow III^*$.

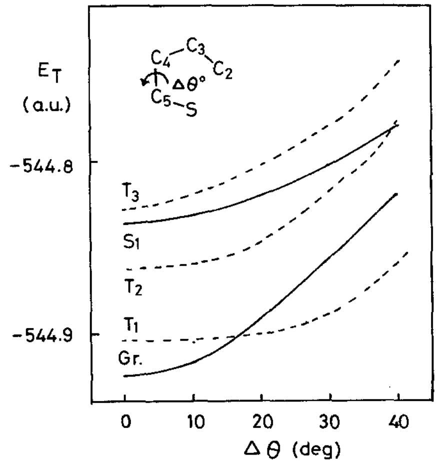


**Fig. 6.** Energy curves of the ground and some low-lying excited states for the variation of the deviation $\Delta\theta$ of the dihedral angle S—$C_5$—$C_4$—$C_3$ relative to the optimized geometry of IV*

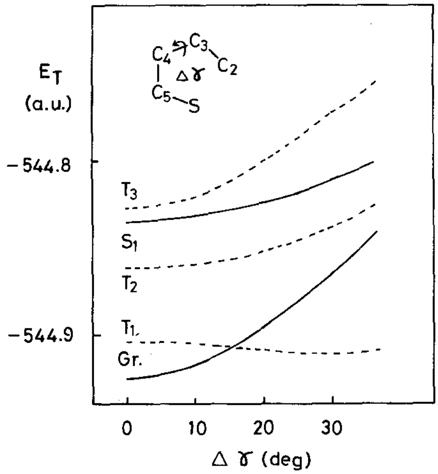
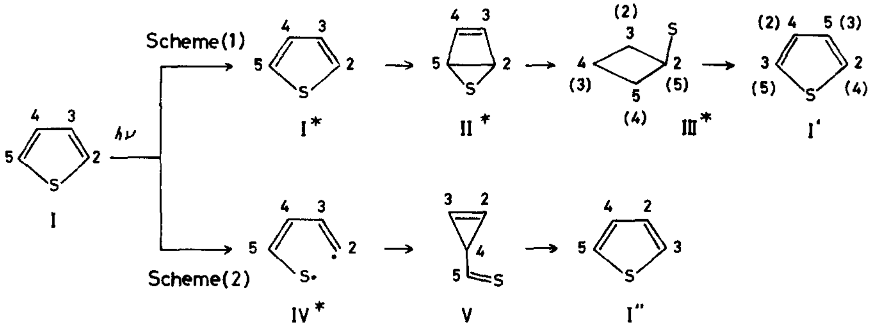


**Fig. 7.** Energy curves of the ground and some low-lying excited states for the variation of the deviation Δγ of the dihedral angle $C_2—C_3—C_4—C_5$ relative to the optimized geometry of IV*

From the above mentioned results on the excited state of thiophene, we may construct a reaction scheme of the photoisomerization process as follows.



If the molecule prefers scheme (1), the 3–5 or 2–4 transposition will occur. If the reaction path is favorable for scheme (2), the 2–3 or 4–5 transposition may occur.

### 3.3. Potential Energy Curve

In order to confirm the reaction scheme (1), I↔II↔III, the potential energy curves in both the ground and lowest excited singlet states are calculated with the SDCI and SDTCI methods in which the geometries are optimized with the SCF and SECI methods along the geometrical parameter $R$ and $\phi$, where $R$ is a half of the $C_2—C_5$ bond distance and $\phi$ is the $C_5—C_2—S$ angle. The choice of these parameters seems to be reasonable for describing the reaction paths I↔II and II↔III. In the calculation of the potential curve in the excited state, all C—H bond lengths used are the same values with those of optimized geometries in the ground state. Fig. 8 shows the summary of the potential curves. The values given in parentheses are obtained by the SCF and SECI methods.

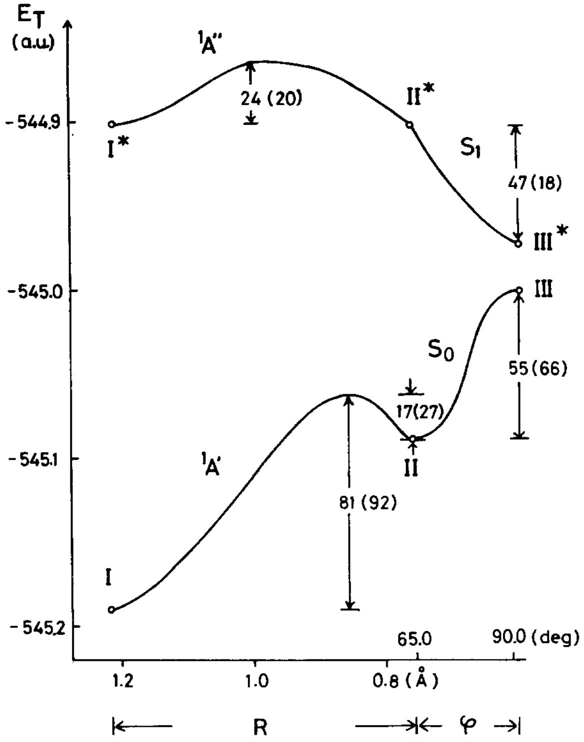


Fig. 8. Minimum energy path along the $R$ for I↔II and $\phi$ for II↔III by the SDCI and SDTCI calculations. The geometrical parameter $R$ is a half of the $C_2$—$C_5$ bond distance and $\phi$ is the $C_5$—$C_2$—S bond angle. Energy barriers are in kcal/mol. The values by the SCF and SECI calculations are shown in parentheses. Each circle corresponds to the optimized geometries shown in Fig. 1

The transition state for I*↔II* reaction is located at around $R \simeq 1.0$ Å with the activation energy ca. 24 kcal/mol. The fact that there is no activation energy for the II*→III* path may suggest the possibility of another direct path I*→III*. In order to examine this possibility, the $C_5$—$C_2$—S angle ($\Delta\phi$) is varied from the $C_s$ optimized geometry at $R = 0.9$ Å. The most stable structure, however, maintains the $C_s$ symmetry. This result suggested that the deformation from the $C_s$ symmetry would occur at the structure near II*. Therefore, the reaction profile I*↔II*↔III* seems to be reasonable for the potential curve of I*↔III*.

The activation energy of I→II for the ground-state path is found to be ≃81 kcal/mol and the transition state is located at around $R \simeq 0.85$ Å. This large activation energy of I→II is attributed to the avoided crossing and makes this reaction unfavorable. On the other hand, the activation energy of II→I is rather small (17 kcal/mol), although this reaction is assigned to be symmetry forbidden. This is due to the release of the strain energy which compensates for unfavorable electronic energy. III would be the transition state of II↔II′ path with the activation energy ≃55 kcal/mol.

If the internal conversion (IC) occurs from the $S_1$ to $S_0$ states at III, the reaction III → II → I easily proceeds to form the ground state thiophene since the intermediate II has enough energy to go over the barrier of II → I path (17 kcal/mol).

Let us point out the effect of doubly or triply excited configurations for the barrier height and stability. One important point is the stability of biradical species III*. Since the excitation is localized on the sulfur atom, the SECI method does not well describe the electronic structure of III*, quantitatively. For the ground state path, the lowering of the activation energies for II ↔ I and II ↔ III is about 10 kcal/mol by the calculation of the SDCI. The transition state for II ↔ I by the SCF method is located at around $R \simeq 0.85$ Å. The potential curve of I* ↔ II* given by the SECI method has the transition state near $R \simeq 0.9$ Å with the activation energy of about 20 kcal/mol which is less than that obtained by the SDTCI calculation. Since the configuration selection is done by the orbital energy in the present calculation, the correlation effect to be considered is unbalance on each point in the potential curve. Although there are some differences on the location of the transition state and the energy barrier by the inclusion of doubly and triply excited configurations, the important feature of the energy curves does not change.

### *3.4. The Effect of 3d Orbital*

In order to examine the effect of *d* orbital, the five 3*d* functions are added to the minimal basis set on sulfur atom (STO-3G*) [11]. By the inclusion of 3*d* orbitals, the $^1A_2$ state of thiophene becomes the lowest excited state and the enlargement of $C_4$—$C_5$—S angle from the ground-state value, $\Delta\chi$, makes this state stable. The energy variation for the angle $\theta$ (the dihedral angle S—$C_5$—$C_4$—$C_3$) at $\Delta\chi \simeq 8°$ in which the $^1A''$ state has minimum shows that the $S_1$ ($^1A''$) state and all other low-lying excited states become unstable. Therefore the path IV* → V* would be also unfavorable. For the reaction I ↔ II, there is the avoided crossing between the $^1A_2$ and $^1B_2$ states. The energy barrier caused by this avoided crossing would be very small because of the small energy difference between the $^1A_2$ and $^1B_2$ states (about 14 kcal/mol). Since the energy levels of the $^1A''$ state of II and the $S_1$ state of III are very close, there may be energy barrier for the reaction II* → III*. As shown in previous section, the inclusion of the doubly and triply excited configurations makes the $S_1$ state of III very stable. It is therefore expected that the energy barrier of II* ↔ III* calculated with the STO-3G* disappears by the SDTCI method. The feature of the potential curve of the scheme (1), therefore, do not change qualitatively by inclusion of the 3*d* orbitals.

### *3.5. The Effect of Phenyl Substitution*

Various photoisomerization of substituted thiophene may be discussed based on the present theoretically proposed scheme of thiophene itself. The major product distribution for 2-phenyl and 3-phenyl thiophene suggests that there are at least two distinguishable reaction mechanisms. The position of substituted phenyl group appears to control the reaction path. A preferable mechanism for each case can be speculated in terms of the electronic structure for phenyl substituted species. When the molecule has an aromatic ring on $C_2$, the $C_2$—S bond break is realized, because the $\sigma$-radical produced by $C_2$—S bond break can delocalize over the aromatic ring and stabilize the system greatly if the aromatic ring takes the perpendicular conformation to molecular plane. This stabilization, however, does not occur in the case of 3-phenylthiophene. On the other hand, when the molecule has an aromatic ring on $C_3$, $C_2$—$C_5$ ring-closure path becomes favorable because the amplitude of LUMO ($4b_1$ in thiophene) increases at $C_2$ position. Since the amplitude on $C_2$ position of 2-phenylthiophene is small, $C_2$ —$C_5$ bond formation is less favorable than in the case of 3-phenylthiophene. Those considerations would support that 3-phenylthiophene prefers scheme (2) to scheme (1) but 2-phenylthiophene does scheme (1).

## 4. Concluding Remarks

In this work, the mechanism of photoisomerization of thiophene is discussed based on the *ab initio* calculation. The energetics with the SCF and SECI methods are improved by adding the doubly and triply excited configurations. One possible reaction mechanism of photoisomerization (the 2–4 or 3–5 transposition of carbon atoms) of thiophene is proposed and is summarized schematically in Fig. 9. The $^1B_2$ state of thiophene converts easily to the biradical intermediate III* by one step reaction. This reaction may not experience II*, but the geometrical deformation from $C_s$ symmetry in I* ↔ III* path would occur near the $C_s$ structure of II*. Once the biradical intermediate III* is formed, the internal conversion to the ground state would lead to the isomerized products of thiophene.

Although Wynberg and coworkers ruled out the possibility of the three-membered intermediate in photoisomerization of thiophene, it is necessary to examine this problem theoretically. The detailed investigation of potential curve for scheme (2) will be waited.

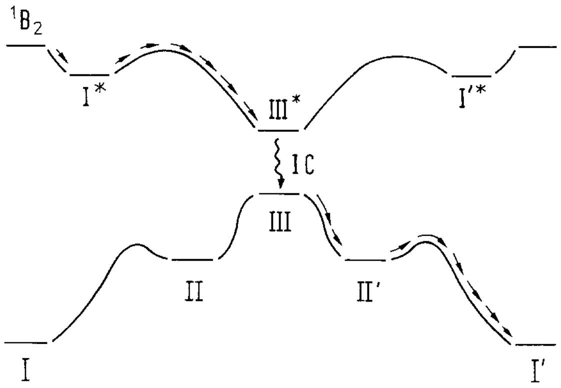


**Fig. 9.** Schematic description of a possible mechanism for the photoisomerization (the 2–4 or 3–5 transposition of carbon atoms) in low-lying excited state of thiophene

*Acknowledgments.* The authors thank the Computer Center, Institute for Molecular Science, for the use of HITAC M200H computer and the Library Program IMSPAC written by K. Morokuma and coworkers (IMS) and would like to express their gratitude to the Data Processing Center, Kyoto University, for its generous Permission to use the FACOM M200 computer.

## References

1. Padwa, A.: "Rearrangements in ground and excited states", De Mayo, P., Ed., Vol. 3, New York: Academic Press, 1980; Barltrop, J. A., Day, A. C., Irving, E.: J. Chem. Soc. Chem. Commun. 881, 1979; Barltrop, J. A., Day, A. C., Irving, E.: J. Chem. Soc. Commun. 966, 1979
2. Kellogg, R. M., Wynberg, H. J.: J. Am. Chem. Soc. **89**, 3495 (1967); Wynberg, H., Beekhuis, G. E., Van Driel, H., Kellogg, R. M.: J. Am. Chem. Soc. **89**, 3498 (1967)
3. Wynberg, H., Kellogg, R. M., Van Driel, H., Beekhuis, G. E.: J. Am. Chem. Soc. **89**, 3501 (1967)
4. Van Tamelen, E. E., Whitesides, T. H.: J. Am. Chem. Soc. **93**, 6129 (1971)
5. IMS library program IMSPAC is used for the SCF calculation
6. Ullman, E. F., Singh, B.: J. Am. Chem. Soc. **88**, 1844 (1966); Singh, B., Ullman, E. F.: J. Am. Chem. Soc. **89**, 6911 (1967); Singh, B., Zweig, A., Gallivan, J. B.: J. Am. Chem. Soc. **94**, 1199 (1972)
7. Tanaka, H., Matsushita, T., Osamura, Y., Nishimoto, K.: Int. J. Quantum Chem. **18**, 463 (1980); Tanaka, H., Osamura, Y., Matsushita, T., Nishimoto, K.: Bull. Chem. Soc. Jpn. **54**, 1293 (1981)
8. Kao, J., Random, L.: J. Am. Chem. Soc. **101**, 311 (1979)
9. Schweig, A., Thiel, W.: J. Comput. Chem. **1**, 129 (1980)
10. Yamabe, S., Morokuma, K.: J. Am. Chem. Soc. **100**, 7551 (1979); Yamabe, S., Minato, T., Osamura, Y.: J. Am. Chem. Soc. **101**, 4525 (1979); Minato, T., Osamura, Y., Yamabe, S., Fukui, K.: J. Am. Chem. Soc. **102**, 581 (1980); Yamabe, S., Minato, T., Osamura, Y.: Int. J. Quantum. Chem. **18**, 243 (1980)
11. Matsushita, T., Osamura, Y., Misawa, N., Nishomoto, K., Tsuno, Y.: Bull. Chem. Soc. Jpn. **52**, 2521 (1979)

Received August 30, 1982