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SINDO1 Study of the Photoisomerization Mechanisms of Thiophenes

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The mechanism of the photochemical isomerization of unsubstituted and 2-cyano- and 2-methyl-substituted thiophene was investigated with the semiempirical MO method SINDO1. Potential energy hypersurfaces of excited states and transition structures of the ground state were calculated with limited configuration interaction (CI) for a qualitative explanation of the reaction pathways. The internal cyclization–isomerization and the zwitterion–tricyclic route are compared. The influence of d orbitals on the latter reaction mechanism is discussed.

Introduction

Permutations of ring atoms are one of the best known features in the photochemical behavior of heterocyclic organic compounds.[1,2] Many experiments and theoretical investigations have been carried out in order to derive the mechanisms involved. Several schemes were developed for their classification. One of these is the so-called ring contraction–ring expansion mechanism (Figure 1a) which is the favored reaction pathway in photorearrangements of furans. Another scheme is the internal cyclization–isomerization mechanism of pyrroles (Figure 1b). The third scheme in the literature is the zwitterion–tricyclic route (Figure 1c) for the photoisomerization of thiophenes.[3] A major feature of this is the occurrence of an intermediate with an expanded valence due to d orbital participation. This valence expansion limits this mechanism to heterocyclic compounds with second-row atoms. It is comparable to mechanism 1a, but no double bond between carbon and the heteroatom can be formed here.

Wynberg et al. performed an extensive study of the photoisomerizations in aryl- and alkyl-substituted thiophenes.[4–6] The parent compound, however, could not be studied experimentally because the ring carbon atoms remain indistinguishable in reactant and products. By analysis of the interchange of labeled (^{2}D and substituent) ring carbon atoms they arrived at the proposition of mechanism 1c. Mechanism 1a, which should involve a triplet intermediate, was ruled out since no triplet sensitivity of the reaction could be found.

Couture and Lablache-Combier[7–9] performed an independent study of the 2-methylthiophene rearrangement. The products from quenching with methylamine were similar to those obtained in the quenching of the furan rearrangement. Thus the authors concluded that 2-methylthiophene undergoes photorearrangement in the same way as 2-methylfuran. This would mean a reaction according to reaction 1a. Considering the above mentioned relationship between pathways 1a and 1c, however, reaction 1c seems the more convincing alternative. This would be in agreement with the results of Wynberg et al. A possible triplet sensitivity was not investigated here.

A rather different result was obtained in a recent study of the photorearrangement of 2-cyanothiophene.[10] The authors analyzed the permutation pattern of the product carbon atoms and found that in the major product the sequence of carbon atoms was not changed, but the sulfur atom changed its position relative to the unchanged carbons. Also a back reaction from 3-cyanothiophene to 2-cyanothiophene could be found. This means that in this case the permutation is likely to go along the internal cyclization–isomerization pathway 1b. Reaction according pathway 1c is ruled out by these authors because none of the permutations found could be explained by this mechanism.

Finally, recent experiments show that an isomer of unsubstituted thiophene similar to the intermediate I_{0a} in reaction 1b can be isolated after irradiation.[11] A similar isomer is also obtained from other acceptor substituted thiophenes.[12] The fact that isolation is only possible at low temperatures (10 K) in an inert gas matrix indicates a very low thermal stability of these structures.

There were various explanations to resolve the controversial results of thiophene photorearrangement. One offered by Kellogg[13] is that a whole C=S fragment is removed from the molecule which turns over and recombines afterwards. This, however, does only show a bridging between reactions 1a and 1c. A bridge between 1a and 1b is established in a scheme by van Tamelen and Whitesides.[14] They state that a photoisomerization of any given heterocycle would end in an arbitrary product if a thermally allowed interchange between the intermediates in 1a and 1b is established. The products would then depend on the thermodynamically more stable intermediate in each special case. The major disadvantage of this proposition is that it cannot explain the fact that in the case of cyanothiophene back reaction from product to reactant is found while in the other cases it is not.

A first theoretical study of the thiophene photorearrangement has recently been published by Nishimoto et al.[15] These authors performed ab initio calculations using an STO-3G minimal basis set with inclusion of CI on the unsubstituted parent compounds. They try to explain possible mechanisms by examining state correlation diagrams for optimized ground-state structures of minima and

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Table I. Geometries (A, deg) of Ground-State Structures of Thiophene with Labeling from Figure 1

	r_{12}	r_{23}	r_{34}	r_{45}	r_{13}	r_{14}
R_0	1.770	1.375	1.487	1.375	2.580	2.580
I_{0a}	1.798	1.576	1.345	1.576	2.842	2.842
I_{0b}	2.842	1.345	1.576	1.521	2.842	1.798
I_{0c}	2.915	1.391	1.391	1.593	3.500	2.915
I'_0	1.896	1.397	1.541	1.505	1.902	2.170
I''_0	2.965	1.311	1.564	1.736	-	1.848

	α_{234}	α_{345}	α_{251}	α_{154}	α_{215}
R_0	113.5	113.5	43.1	109.6	93.7
I_{0a}	93.2	93.2	65.0	114.6	50.0
I_{0b}	93.2	86.8	114.6	65.0	-
I_{0c}	75.1	104.7	123.8	123.8	24.2
I'_0	64.8	108.3	48.0	79.2	84.9
I''_0	65.8	95.3	-	64.8	-

	ϕ_{2345}	ϕ_{3251}	ϕ_{4326}	ϕ_{3459}
R_0	0	180.0	-180.0	180.0
I_{0a}	0	119.1	-135.7	135.7
I_{0b}	0	60.6	-180.0	131.6
I_{0c}	-26.4	114.8	-129.8	127.7
I'_0	102.8	78.2	-150.3	139.6
I''_0	137.2	-	-184.6	-

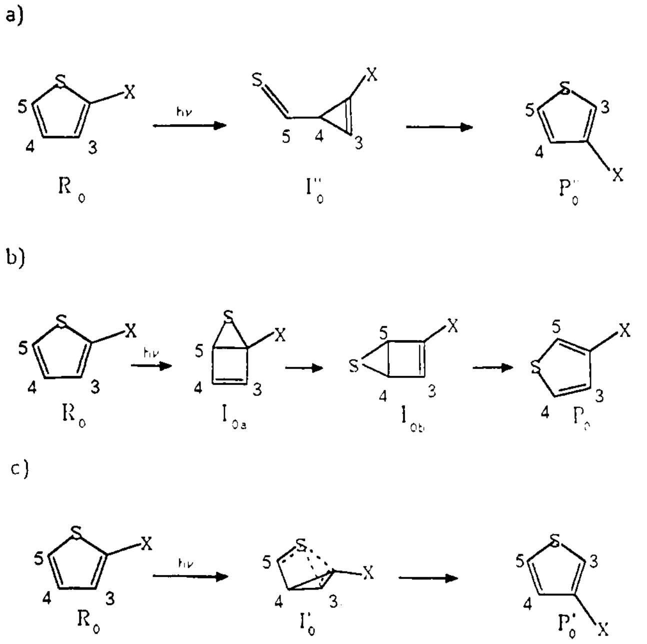

Figure 1. Various reaction mechanisms for thiophene photorearrangement: (a) ring contraction–ring expansion route, (b) internal cyclization–isomerization route, (c) zwitterion–tricyclic route.

postulated intermediates for pathways 1a and 1b. However, they do not consider a structure like I'_0 in Figure 1c, which is not stable without the inclusion of d orbitals on sulfur. They conclude that for the parent compound mechanism 1b is most favorable and try to estimate the effect of attaching an aromatic ring on either atom 2 or 3. The conclusion here is that mechanism 1a might be favored by attaching an aromatic system on atom 2.

In our present paper we give a deeper insight into the seemingly complex mechanism of thiophene photorearrangements. Especially, thermally unstable intermediates and transition structures of ground and excited states, whose properties may be calculated but not measured because of their short lifetimes, might serve in understanding this reaction and possibly substituent dependences. The thiophene photoreaction can obviously be placed between photorearrangements of compounds like furan which react according to mechanism 1a and compounds like pyrrole which react according to mechanism 1b. In thiophene, a change of mechanism might be induced by properly selected substituents.

Method of Calculation

The calculations were performed with the semiempirical MO method SINDO1[16] in its extension to second-row elements with d orbitals.[17] The reliability of the method for geometries and energies of sulfur compounds was documented in an extensive study[18] and compared with experimental and MNDO results. The suitability of SINDO1 for the study of photochemical reaction mechanisms was demonstrated for cyclopentanone,[19] diazirine,[20] di-π-methane,[21] 2-methylfuran,[22] and 2-cyanopyrrole.[23] The present study completes the sequence of the last two papers. As previously, we shall use the following notations. The minimum of the ground state of the reactant thiophene without and with substituents at the ring carbon 2 will be denoted by R_0. The vertical excitations at this geometry will be denoted by R_1, R_2, etc., the lowest triplet state by $^3R_1$, intermediates on the ground-state surface by I_{0a}, I_{0b}, etc., and transition structures by TS_{0a}, etc. A minimum on the first excited singlet surface is denoted by I_1. Minima are characterized by positive roots of the force constant matrix, whereas transition structures have one negative root.

Ground-state geometries for equilibrium (R_0, I_{0a}, etc.) and transition structures (TS_{0a}, etc.) were located by complete geometry optimization with a Newton–Raphson procedure.[24,25] Bond lengths were optimized within 1% and bond angles within 0.1°. Excited-state structures I_3, I_1, I'_1, and TS_1 were optimized on their respective CI surfaces with an accuracy slightly less than for ground-state

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Table II. Vertical Excitation Energies (eV) of Thiophene (a–c), 2-Cyanothiophene (d), and 2-Methylthiophene (e)

		energy[a]					
state	excitation	a	b	c	d	e	oscillator strength, a
$R_1(B_1)$	$\pi-\sigma^*$	5.00	4.98	4.53	4.29	4.53	10^{-2}
$R_2(A_2)$	$\pi-\sigma^*$	5.06	4.88	4.64	4.93	5.21	10^{-5}
$R_3(A_2)$	$\pi-\sigma^*$	6.14	6.11	5.10	5.39	5.64	10^{-6}
$R_4(B_2)$	$\pi-\pi^*$	6.71	6.13	5.23	6.89	6.29	5×10^{-2}
$R_5(B_1)$	$\pi-\sigma^*$	6.35	6.35	5.37	6.48	6.37	3×10^{-2}
$R_6(B_1)$	$\pi-\sigma^*$	6.62	6.58	5.46	6.67	6.66	10^{-2}

[a] (a) SINDO1 (17 × 17 CI), (b) SINDO1 (49 × 49 CI), (c) exp,[26] (d) SINDO1 (17 × 17 CI), (e) SINDO1 (17 × 17 CI).

structures. Further details of the optimization procedure can be found in the furan treatment.[22] The size of the configuration interaction was adjusted according to the need for an unambiguous qualitative explanation of the mechanisms.

Results and Discussion

1. Ground-State Geometries. The ground-state geometries of reactant thiophene (R_0), and intermediates I_{0a}, I'_0, and I''_0 (Figure 1) were located on the SCF hypersurface. The structure of I_{0b} is equal to that of I_{0a} and therefore not listed. Between I_{0a} and I_{0b} another intermediate I_{0c} was found similar to the situation in pyrrole.[23] It has C_s symmetry, and the sulfur atom is attached to only one carbon. The data are listed in Table I. The transition structures TS are labeled in the sequence of their occurrence between reactant and product: $R_0 - TS_{0a} - I_{0a} - TS_{0b} - I_{0c} - TS_{0c} - I_{0b} - TS_{0d} - P_0$ and $I'_0 - TS'_0 - P'_0$. Besides I_{0a} and I_{0b}, the structures of TS_{0a} and TS_{0d} as well as TS_{0b} and TS_{0c} are also equal for unsubstituted thiophene. One of each of the two equivalent transition structures will be listed in section 3 together with other intermediates important in the reaction. For substituted thiophenes the geometric and energetic equivalence of these pairs is, of course, removed.

2. Vertical Excitation of Thiophenes. Table II presents calculated and experimental data[26] on vertical excitation energies of thiophene, 2-methylthiophene, and 2-cyanothiophene. The 17 × 17 CI consisted of single excitations from the two highest occupied to the four lowest unoccupied MOs and the 49 × 49 CI by single excitation from the four highest occupied MOs to the six lowest unoccupied MOs. A comparison of calculated and experimental data for unsubstituted thiophene shows that the crucial excitation for the reaction can go to three close-lying states of π-π^* and π-σ^* type with appreciable oscillator strengths of magnitude 10^{-2}. With the 49 × 49 CI the π-π^* excitation is the lowest of the three. A fourth state of π-σ^* type has a negligible oscillator strength and can be disregarded in the following. For better agreement of absolute numbers of calculated excitation energies with experimental value the size of CI must be increased at least to 49 × 49. In order to detect further changes, we used also symmetry selected CIs for low-lying excited states of A_2, B_1, and B_2 symmetry. This procedure corresponds to the selection processes suggested by Klessinger[27] and Troe.[28] The situation is similar for 2-methylthiophene and 2-cyanothiophene. Here experimental data are not available. We felt, however, that the accuracy of the calculation was sufficient for the following investigations of the mechanisms of rearrangement.

3. Internal Cyclization–Isomerization Route. The following procedure was used to search for other intermediates I on the lowest excited surfaces and for transition structures TS relevant for the reaction mechanism which are located between R_0 and I_{0a}. We used an 18 × 18 CI for intermediates and transition structures on excited-state surfaces. It consisted of the above mentioned 17 × 17 CI plus a HOMO–LUMO double excitation. The double excitation is necessary for the detection of diradicals. For ground-state structures the number of configurations could be conveniently reduced. We removed all those singly excited configurations that did not contribute significantly to the ground state energy. This resulted in a 4 × 4 CI with HOMO–LUMO single and double excitation. This is sufficient for the detection of singlet–triplet degeneracies and diradicals.[29] The results for the geometries are given in Table III. Figure 3 contains the corresponding energies. The reaction pathway shown consists of a sequence of

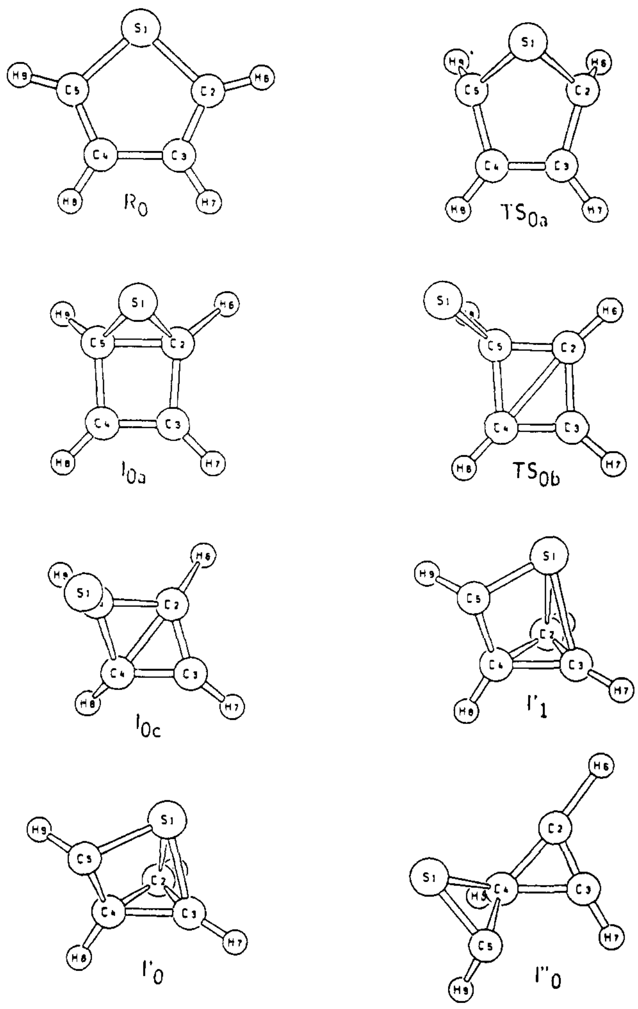

Figure 2. Geometrical structures of ground-state thiophene and intermediates.

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Table III. Geometries (Å, deg) of Other Intermediates and Transition Structures of Thiophene Relevant for Reaction Mechanisms

	r_{12}	r_{23}	r_{34}	r_{45}	r_{13}	r_{14}
I_3	1.793	1.403	1.459	1.436	2.690	2.580
I_{1a}	1.705	1.448	1.386	1.448	2.625	2.625
TS_1	1.786	1.442	1.416	1.442	2.881	2.881
I_{1b}	1.797	1.486	1.369	1.486	2.923	2.923
TS_{0a}	1.760	1.525	1.337	1.525	2.709	2.709
TS_{0b}	3.036	1.352	1.554	1.416	3.811	2.936
TS_{0c}	2.936	1.554	1.352	1.602	3.811	3.036
TS_{0d}	2.709	1.337	1.525	2.141	2.709	1.760
I'_1	2.264	1.325	1.564	1.445	2.264	2.380
TS'_0	2.373	1.445	2.550	1.368	1.807	2.461

	α_{234}	α_{345}	α_{251}	α_{154}	α_{215}
I_3	107.1	119.1	44.2	106.7	92.4
I_{1a}	111.5	111.5	44.1	112.5	91.7
TS_1	102.8	102.8	54.9	126.1	70.2
I_{1b}	96.2	96.2	62.0	125.6	56.1
TS_{0a}	105.3	105.3	52.5	110.9	75.0
TS_{0b}	87.1	94.6	125.5	130.6	25.4
TS_{0c}	87.1	95.0	130.6	125.5	25.4
TS_{0d}	105.3	75.0	110.9	52.5	56.6
I'_1	64.9	107.1	63.8	97.8	73.7
TS'_0	32.2	72.4	80.0	98.8	50.0

	ϕ_{2345}	ϕ_{3251}	ϕ_{4326}	ϕ_{3459}
I_3	0	172.5	-179.1	164.1
I_{1a}	0	175.1	-168.5	168.5
TS_1	0	153.7	-150.7	150.7
I_{1b}	0	136.2	-131.1	131.1
TS_{0a}	0	132.5	-99.5	99.5
TS_{0b}	0	136.0	-190.4	116.4
TS_{0c}	0	132.0	-187.0	116.4
TS_{0d}	0	38.8	-180.0	121.5
I'_1	80.8	82.0	-156.4	206.3
TS'_0	98.1	12.2	-167.2	174.6

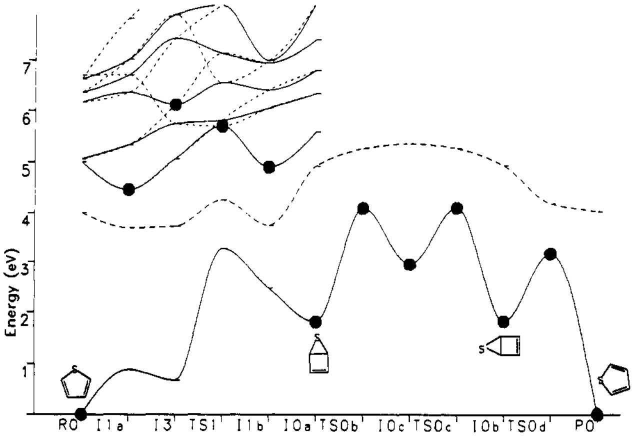

Figure 3. Internal cyclization–isomerization route for thiophene, adiabatic singlet curves (—), relevant diabatic (topological) singlet curves (- - -), lowest triplet curve (– –), points of optimized geometry (●).

optimized intermediates I and transition structures TS which are marked with a black dot on their respective potential energy surfaces. Between R_0 and I_{0a} we found an intermediate I_3 on the third excited singlet surface, which results from an avoided topological crossing of the second vertically excited singlet state (A_2) and the fourth vertically excited singlet state (B_2). Both belong to A″ in the lowered C_s symmetry of the system during the course of the reaction. The corresponding point on the ground-state surface does not designate a local minimum, but appears so only in between the structures of I_{1a} and TS_1. So it is the relaxation of the π-π^* excitation toward its topological minimum which initiates the reaction. From I_3, internal conversion to the second excited hypersurface occurs in a region which is energetically close to a transition structure TS_1 on the first excited singlet surface. Here a branching can occur with leads either to intermediate I_{1a} or I_{1b}. Whereas I_{1a} will lead back to the reactant R_0, I_{1b} can proceed to I_{0a}. Both processes are likely to occur by internal conversion. The efficiency of these internal conversion processes between first excited and ground state is much less than between excited states. This conclusion is well in agreement with the present standard assumption that a fast decay occurs between excited states until the first excited state is reached.

From I_{0a} the system can now proceed further on the ground-state surface via TS_{0b} to I_{0c} or return via TS_{0a} to R_0. Since the situation in the unsubstituted thiophene is symmetric with respect to I_{0c} the transition structures TS_{0a} and TS_{0d}, TS_{0b} and TS_{0c} have equal energies and geometries. The geometry of TS_{0a} is close to that of TS_1. The efficiency of the process depends on the relative height of the barriers TS_{0a} and TS_{0b}. From the pathway depicted in Figure 3 it is apparent that the rearrangement of the bicyclo[2.1.0] intermediate I_{0b} proceeds stepwise with a diradical intermediate I_{0c}. Similar to the case of pyrrole,[23] its diradical character shows up only in a UHF calculation.

4. Zwitterion-Tricyclic Route. Whereas the rearrangement via the internal cyclization–isomerization mechanism occurs in a sequence of small geometrical arrangements, the zwitterion–tricyclic route reaches an intermediate I'_1 only after a large change of geometry (Table III) from the vertical excitation of R_0. The geometry of I'_1 is characterized by a bonding of sulfur to three adjacent carbon atoms. This bonding can be achieved only by d orbital participation. Figure 4 shows the potential curves along the reaction pathway. Because of the large geometrical rearrangement between R_0 and I'_1, a linear interpolation between the two geometries was used to generate additional points for the energy calculation. Further stabilization is found when I'_1 relaxes via internal con-

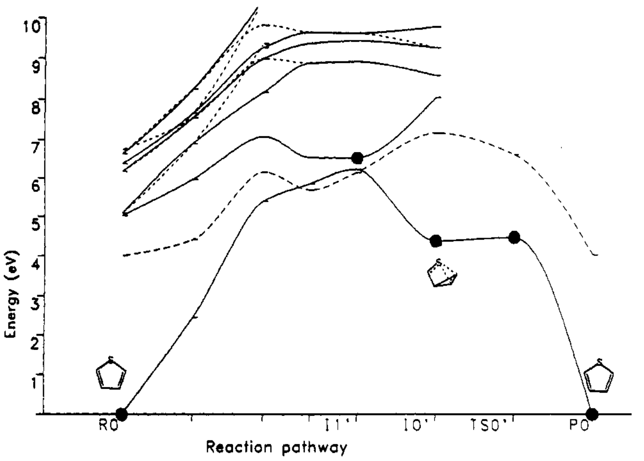

Figure 4. Zwitterion-tricyclic route for thiophene, adiabatic singlet curves (—), relevant diabatic (topological) singlet curves (- - -), lowest triplet curve (– –), points of optimized geometry (●).

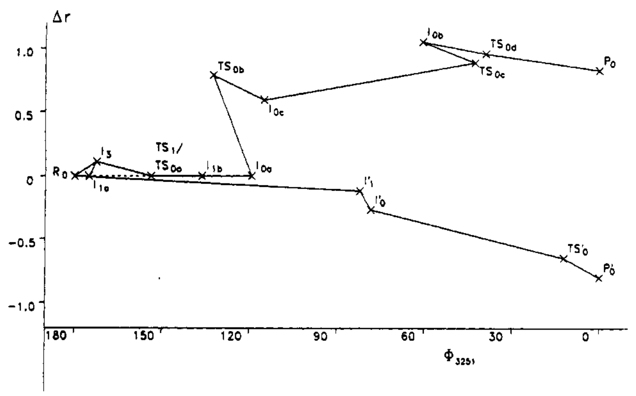

Figure 5. Reaction pathways in ϕ_{3251}, $\Delta r = r_{13} - r_{14}$ coordinate system (degrees, Å); forward reaction (—), back reaction (– –).

version to I'_0. Here the $S_{(1)}C_{(2)}$ and $S_{(1)}C_{(3)}$ bonds of equal length are formed. The final step of this mechanism leads over the small barrier of transition structure TS'_0 to product P'_0. In this process single bonds $S_{(1)}C_{(3)}$ and $C_{(2)}C_{(4)}$ are formed and the remaining bonds $S_{(1)}C_{(2)}$ and $C_{(3)}C_{(4)}$ finally broken. It must be pointed out here that intermediates I'_1 and I'_0 could be found only with inclusion of d orbitals on $S_{(1)}$. The participation of d orbitals is further indicated by the fact that in I'_0 three almost equally long CS bonds are formed.

For a relative assessment of the efficiency of the two reaction mechanisms we present both pathways in a coordinate system characterized by the dihedral angle ϕ_{3251} and bonding-nonbonding bond lengths differences $\Delta r = r_{13} - r_{14}$ (Figure 5). For both mechanisms ϕ_{3251} changes from 180° to 0°. The bond length difference Δr increases along the internal cyclization-isomerization route and decreases along the zwitterion-tricyclic route. From Figures 3-5 we conclude that the zwitterion-tricyclic route is less efficient because it involves larger geometric rearrangement steps and less efficient internal conversion in the initiation region.

5. Substituent Effects. In order to understand the effects of substitution and to search for a change of mechanisms we introduced two substituents at the $C_{(2)}$ atom which had been studied experimentally, the cyano group and the methyl group. In these cases the geometric and energetic symmetry with respect to I_{0c} is removed. Figure 6 shows the internal cyclization-isomerization route for 2-cyanothiophene. A comparison shows that the pattern of potential surfaces along the reaction pathway is very similar to that of the parent compound thiophene. We find several close-lying excited states until the occurrence of transition structure TS_1. The major difference is the closeness of first excited singlet and ground-state surface in this area and the increase of the barrier of TS_{0a} compared to TS_{0b}. The geometry of TS_{0a} is again very close to that of TS_1. So the barrier on the ground-state surface at geometry of TS_1 in Figure 6 gives a very good picture of TS_{0a}. This means the forward reaction is enhanced and the back reaction reduced. The pattern of the zwitterion-tricyclic route for this system in Figure 7 is also similar to that of the parent compound in Figure 4. The

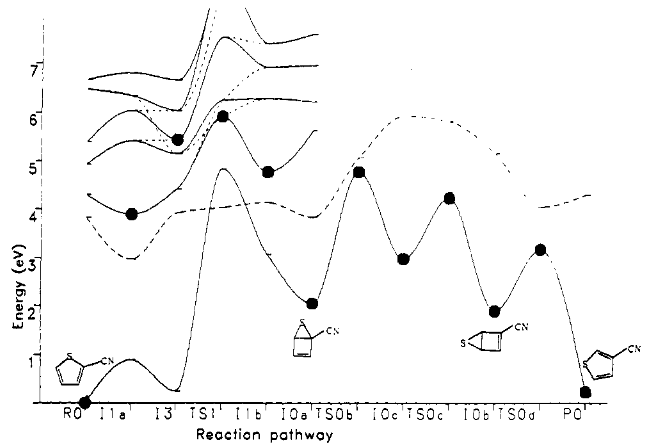

Figure 6. Internal cyclization-isomerization route for 2-cyanothiophene; labels as in Figure 3.

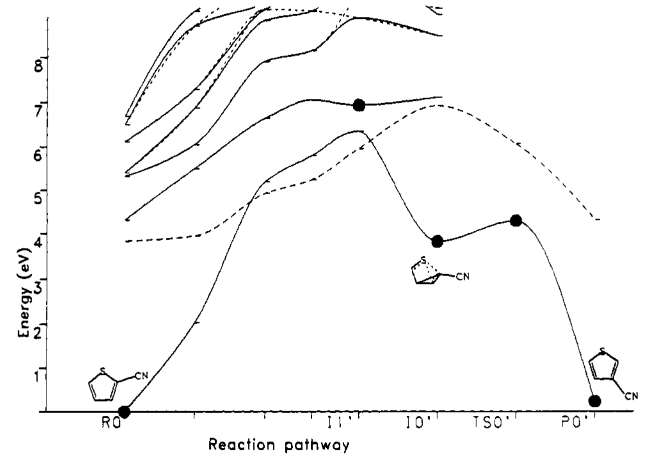

Figure 7. Zwitterion-tricyclic route for 2-cyanothiophene; labels as in Figure 3.

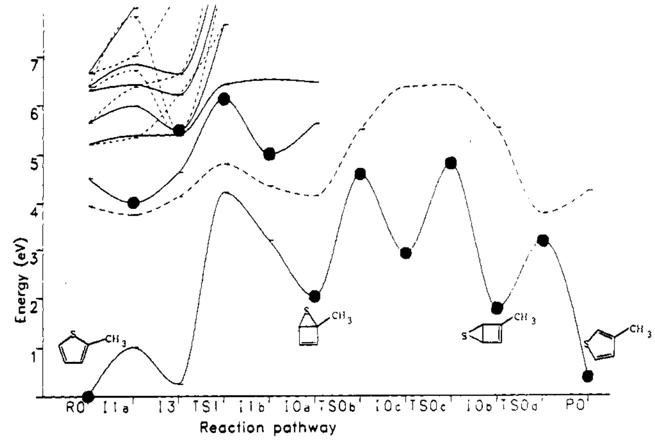

Figure 8. Internal cyclization-isomerization route for 2-methylthiophene; labels as in Figure 3.

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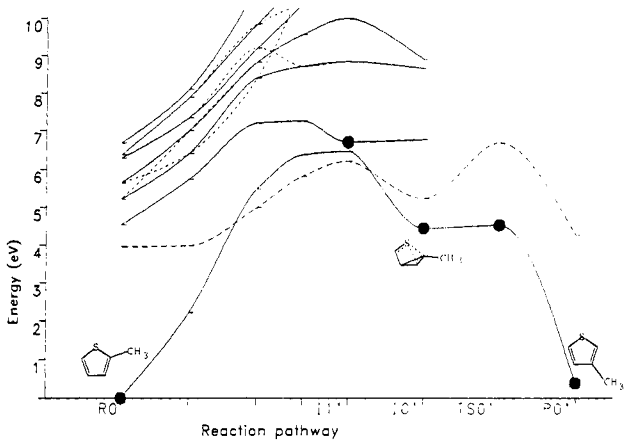

Figure 9. Zwitterion–tricyclic route for 2-methylthiophene; labels as in Figure 3.

major difference is the unfavorable upward shift of the energy minimum of intermediate I'_1 for the forward reaction and the steeper slope for the backward reaction. A comparison of both mechanisms clearly favors the internal cyclization–isomerization route. This is in agreement with conclusions from experiment.[10] For 2-methylthiophene the situation for the internal cyclization–isomerization mechanism (Figure 8) is closer to the one in parent thiophene than to the one in 2-cyanothiophene. This means it is less favorable than in 2-cyanothiophene. The barrier of TS_{0b} is slightly higher than for TS_{0a}, and the first singlet and the ground state are more separated in the region of TS_1. Also the energy of TS_1 is already substantially higher than the energy of I_3. For the zwitterion–tricyclic route of this compound (Figure 9) the curves are again similar to the one in Figures 4 and 7. The efficiency of this mechanism for this compound is enhanced compared to the one for 2-cyanothiophene due to the closeness of the first excited singlet and ground-state surfaces in the vicinity of I'_1. Also there is a rather flat profile of the barrier for backward and forward reaction which could mean an equalization in probability for the system to move either way. Altogether, however, we find that the forward reaction is also not very efficient in this case.

Conclusion

We have studied the reaction mechanism of thiophene and two substituted thiophenes, 2-cyanothiophene and 2-methylthiophene, with respect to permutation of the ring atoms. The two most important mechanisms are the internal cyclization–isomerization route and the zwitterion–tricyclic route. It is found that the internal cyclization–isomerization route consists of a sequence of small geometric rearrangements which can either lead to the product or return to the reactant in three regions close to intermediates I_3 and I_{0a} and transition structure TS_1. From the three systems 2-cyanothiophene is clearly favoring this route for formation of 3-cyanothiophene. But even in this case, the overall efficiency of product formation should be much less than for the internal cyclization–isomerization route of 2-cyanopyrrole to 3-cyanopyrrole,[23] due to the much larger energy gap between S_1 and S_0 in the vicinity of intermediate I_{1b}. The zwitterion–tricyclic route shows a rather large geometric rearrangement in the initiation step, but no branching. Altogether it seems less favorable than the other mechanism. It is conceivable, however, that this mechanism is dominant for 2-methylthiophene. From this investigation no clear decision in favor of the zwitterion–tricyclic mechanism can be made. The latter mechanism involves significant d orbital participation. Without d orbitals no intermediate of the type I'_0 could be found. It is conceivable that this mechanism will be favored in solution with polar solvents.

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AM1, PM3, and MNDO Calculations of Radical Formation Energies in the Gas Phase and in Solution

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The results of the quantum-chemical calculations of radical formation energies from simple organic molecules in gas phase and in dielectric polarizable medium using AM1 and MNDO Hamiltonians with original MNDO and recent MNDO-PM3 parametrizations in combination with self-consistent reaction field procedure are in satisfactory quantitative agreement with experimental data. A solvent-assisted merostabilization effect is observed only in the case of captodative radicals.

The formation of organic radicals is an essential part of many important reactions. The stabilization of radicals by substituents in the molecule, and by the solvent, has therefore been the focus of attention for many years. A specific merostabilization effect at a carbon radical center connected simultaneously with an electron-donor and an electron-acceptor substituent was defined by several authors some time ago.[1-4] However, quantum-chemical studies at different levels of sophistication did not indicate any substantial additional stabilization in these so-called

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