

# Theoretical Study on the Topochemical Nature in the Initiation Process of the Solid-State Thermal Isomerization Reaction of Methyl 4-(Dimethylamino)benzenesulfonate

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The initiation process of the thermal isomerization reaction from methyl 4-(dimethylamino)benzenesulfonate (MDBS) to *N,N,N*-trimethylbenzenaminium-4-sulfonate (TBS) in the crystalline state has been studied by theoretical calculations: Structural optimization of possible ionic intermediates and the transition-state structure has been carried out by ab initio MO calculations. The comparison of the obtained transition-state structure with the molecular arrangement in the MDBS crystal indicates that cooperative rotation of molecules around their molecular long axes coupled with structural deformation of the methoxy group in an MDBS molecule is necessary for the topochemical initiation reaction for the thermal isomerization in the crystal.

## Introduction

Methyl 4-(dimethylamino)benzenesulfonate (MDBS) is known to be thermally isomerized to *N,N,N*-trimethylbenzenaminium-4-sulfonate (TBS) in the crystalline state,<sup>1</sup> as shown in Figure 1a. Sukenik et al. confirmed this reaction by field desorption mass spectrometry<sup>2</sup> and further showed, on the basis of the result from a single-crystal X-ray diffraction, that MDBS molecules are arranged to yield a "topochemical"<sup>3,4</sup> reaction in the crystal,<sup>2</sup> as shown in Figure 1b. That is, the molecular arrangement in the MDBS crystal is thought to be feasible for an S<sub>N</sub>2 type reaction,<sup>5</sup> since the methyl group of the methylsulfo group in an MDBS molecule is directed to the N atom of the adjacent molecule. Here, our recent work has shown that the conformation of the methylsulfo group in the crystal is realized only in the crystal but not in the free space.<sup>6</sup>

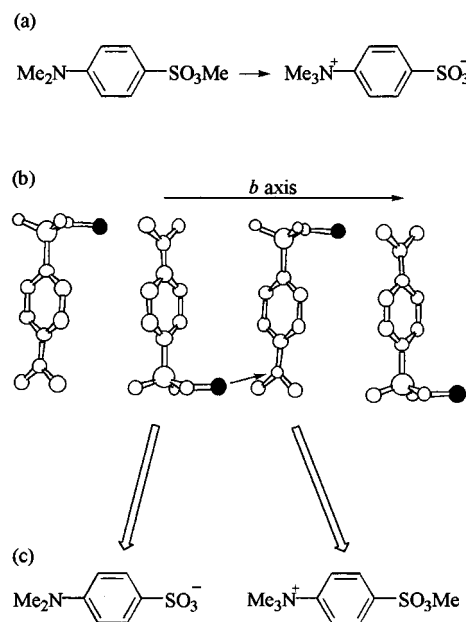
Although many studies on this solid-state reaction have been carried out so far,<sup>6–14</sup> the mechanism of this reaction still remains unsolved. Gavezzotti and Simonetta proposed possible ionic intermediates, shown in Figure 1c, in view of the unique crystal structure above.<sup>13</sup> However, molecular structures, total energies, and electronic properties of such intermediates have not yet been characterized.<sup>14</sup> On the other hand, the motional analysis for the MDBS crystal by Sarma and Dunitz,<sup>11</sup> with reference to collective rotation of MDBS molecules around the respective molecular long axes in the crystal,<sup>7</sup> has not clarified whether this reaction could be initiated by such a motion.

In this work the "topochemical" nature of the initiation reaction of this thermal isomerization will be discussed, with taking notice of the above-mentioned intermediates and the transition-state structure, both studied by ab initio MO calculations.

## Calculation

MO calculations were carried out using the Gaussian 94 program<sup>15</sup> on a CRAY T94/4128 at the Supercomputer Laboratory of the Institute for Chemical Research, Kyoto University.

Structural optimizations of both cation and anion intermediates were carried out by ab initio RHF calculation without any



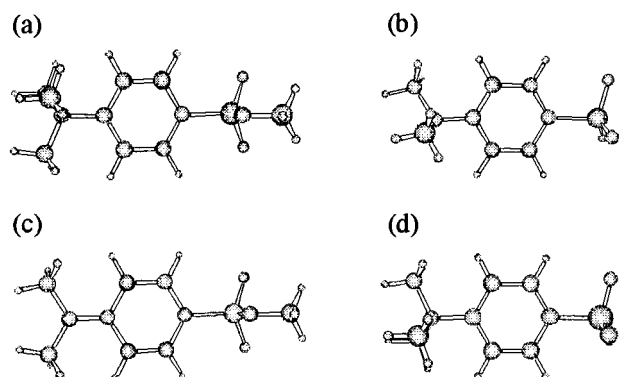
**Figure 1.** Schematics concerning solid-state thermal isomerization reaction from methyl 4-(dimethylamino)benzenesulfonate (MDBS) to *N,N,N*-trimethylbenzenaminium-4-sulfonate (TBS). (a) Chemical equation, (b) reaction process in the crystal, where filled circles indicate carbon atoms of the methyl groups to be transferred, and (c) possible anion and cation intermediates.

restriction to atomic freedom, using 6-31G\* basis sets for hydrogen, carbon, and sulfur atoms and 6-31G\* basis sets with diffuse functions for nitrogen and oxygen atoms.<sup>16</sup> Transition-state structure in the free space was optimized by use of TS and CalcFC options of the Gaussian 94 program,<sup>15</sup> using the same basis sets as above. The optimized structures of the intermediates and the transition state were examined by their normal vibration analyses.<sup>15</sup> Intrinsic reaction coordinate calculations around the optimized transition state were also carried out using the IRC option of the Gaussian 94 program.<sup>15</sup>

The total energies of MDBS, TBS, the ionic intermediates, and the transition state were calculated by the Møller–Plesset (MP2) method<sup>17</sup> with electron correlation, using the 6-31G\*

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**Figure 2.** Optimized geometries of (a) cation intermediate, (b) anion intermediate, (c) MDBS, and (d) TBS. The phenylene plane of each species is laid flat on the surface of the paper.

basis sets, but with diffuse functions added particularly for nitrogen, oxygen, and sulfur atoms.<sup>15</sup>

Intramolecular charge distributions were determined so that on the van der Waals surface of a molecule an electrostatic potential due to partial point charges distributed at all the atomic positions of the molecule, calculated by the CHelpG method,<sup>18</sup> could efficiently simulate the electrostatic potential obtained from the MP2 calculations. The Mulliken population analysis is also carried out.

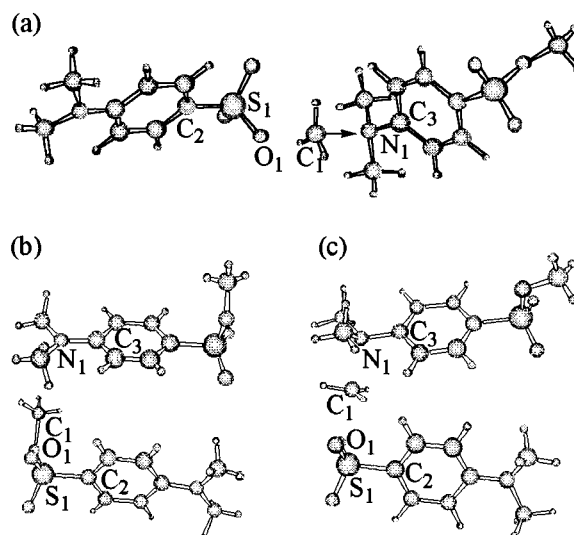
For all the calculations carried out above any effects by the crystal lattice were not taken into account.

## Results and Discussion

**Optimized Structures of MDBS, TBS, and Cation and Anion Intermediates.** As shown in Figure 1b,c, both anion and cation intermediates can be assumed to be generated at the initial stage of the MDBS thermal isomerization reaction.<sup>13</sup> Figure 2 shows optimized geometries of such (a) cation and (b) anion intermediates, together with those of (c) MDBS and (d) TBS. Total energies of these species calculated by the MP2 method are  $-2\,799\,684.467\text{ kJ mol}^{-1}$  ( $-1066.343\,351\text{ }E_h$ ),  $-2\,591\,791.656\text{ kJ mol}^{-1}$  ( $-987.161\,171\,6\text{ }E_h$ ),  $-2\,695\,923.939\text{ kJ mol}^{-1}$  ( $-1026.823\,058\text{ }E_h$ ), and  $-2\,695\,817.977\text{ kJ mol}^{-1}$  ( $-1026.782\,699\text{ }E_h$ ) for the cation intermediate, the anion one, MDBS, and TBS, respectively.

In the case of the anion intermediate, the conformation of the dimethylamino group against the phenylene plane is different from that of MDBS.<sup>6</sup> Here we notice the inversion angle, which is defined as the angle between the plane fixed by the two C atoms and the N atom of the dimethylamino group and the N—C bond connecting the group with the phenylene ring, and also the twist angle, which is defined as the angle of rotation of the dimethylamino group around the N—C bond axis. The inversion and twist angles for the anion intermediate obtained to be  $40.9^\circ$  and  $48.4^\circ$ , respectively, are certainly different from  $17.0^\circ$  and  $0.02^\circ$  for the optimized MDBS, respectively, or  $4.37^\circ$  and  $0.77^\circ$  for MDBS observed in the crystal,<sup>11</sup> respectively. Such structural characteristics of the anion intermediate could be connected with its charge distribution, with considering that inversion and twist of the dimethylamino group prevent a lone pair orbital of the N atom in the group from conjugating with  $\pi$  orbitals in the phenylene ring.

On the other hand, it is notable that the trimethylammonio group in the cation intermediate and the sulfonato group in the anion intermediate have rotational conformations around their group axes being common to those of the respective groups in TBS: that is, one of three N—Me bonds and also one of three



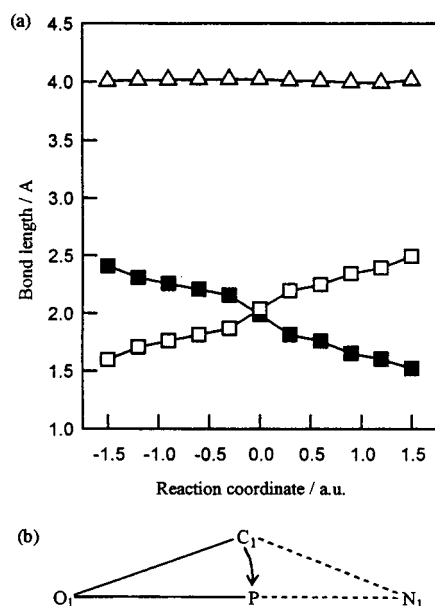
**Figure 3.** (a) Transition-state structure for the initial stage of MDBS thermal isomerization reaction, optimized in the free space. Molecular arrangements (b) in an MDBS crystal and (c) in a transition-state structure modified from the optimized one by adjusting only dihedral angles to those for a pair of MDBS molecules in the crystal.

S—O bonds lie in the same plane as the phenylene ring. In the case of the cation intermediate, the methylsulfo group is oriented nearly parallel to the molecular long axis, as can be seen in the optimized structure of MDBS. In contrast, the methylsulfo group of MDBS in the crystal stands nearly vertical to the molecular long axis, so that it is directed to the dimethylamino group of the adjacent molecule, parallel to a molecular stacking axis along the *b* axis of the crystal (see Figure 1b).<sup>6</sup> Accordingly, in the crystal, the methylsulfo group in the cation intermediate may have a similar orientation with that of MDBS above. These structural characteristics could be related to the topochemical reactivity of the cation intermediate in the crystal.

**Transition State for Methyl Cation Transfer.** Figure 3a shows the optimized structure of the transition state, with a coordination number of five for the carbon atom of the transferring methyl cation, calculated on the condition that these molecules are given in the free space, to consider the initial stage of the MDBS thermal isomerization reaction involving two MDBS molecules. Besides, any ab initio MO methods to calculate the transition-state structure with taking account of crystal field effects and the arrangement of a pair of molecules in the crystal as the initial structure have not yet been established.<sup>19</sup>

Normal vibration analysis for the structure above shows only one vibrational mode with an imaginary wavenumber at  $562.90i\text{ cm}^{-1}$ , indicated by an arrow in Figure 3a; this mode corresponds to intermolecular transfer of the methyl cation being detached from an O atom of the methylsulfo group in one MDBS molecule and connected with the N atom of the dimethylamino group in the other molecule, where O<sub>1</sub>, C<sub>1</sub>, and N<sub>1</sub> atoms are arranged almost linearly<sup>11</sup> with an angle of O<sub>1</sub>C<sub>1</sub>N<sub>1</sub> estimated to be  $178.4^\circ$ . This suggests that an MDBS dimer can yield a pair of ionic intermediates, by getting over the transition state above. In the calculated transition-state structure, O<sub>1</sub>—C<sub>1</sub> and C<sub>1</sub>—N<sub>1</sub> distances are 2.035 and 1.986 Å, respectively, while the O<sub>1</sub>—N<sub>1</sub> distance is 4.022 Å. Sarma and Dunitz have pointed out also the importance of the angle of O<sub>1</sub>C<sub>1</sub>N<sub>1</sub>, which must be close to  $180^\circ$ , to permit the S<sub>N</sub>2 type reaction.<sup>11</sup>

A large difference in the structure nearby the reaction center between the calculated transition state and the crystal is detected in the dihedral angles of C<sub>2</sub>S<sub>1</sub>O<sub>1</sub>N<sub>1</sub> and S<sub>1</sub>O<sub>1</sub>N<sub>1</sub>C<sub>3</sub>: that is,



**Figure 4.** (a) Calculated results of intrinsic reaction coordinate around the transition state of the methyl cation transfer reaction between two MDBS molecules. The origin of the abscissa (in atomic units) corresponds to the transition state. Open and filled squares and triangles denote  $O_1-C_1$ ,  $C_1-N_1$ , and  $O_1-N_1$  distances, respectively. (b) Schematic of the positional relation among the three atoms at the reaction center. The point  $P$  is placed at the same distance from the  $O_1$  atom as the  $O_1-C_1$  distance on the straight line running through the  $O_1$  and  $N_1$  atoms.

−175.10° and 118.48° in the transition state, with respect to −78.80° and 74.94° in the crystal (see Figure 3b), respectively. If the calculated transition state is deformed to allow the dihedral angles to coincide with the values of  $C_2S_1O_1N_1$  and  $S_1O_1N_1C_3$  in the crystal, we obtain the modified transition-state structure shown in Figure 3c, where no other structural parameters, such as  $O_1-C_1$ ,  $C_1-N_1$ , or  $O_1-N_1$  distances or the angle of  $O_1C_1N_1$ , have been deformed from those in the optimized transition state. Now, it is notable that this structure has several features in common with the molecular arrangement in the crystal.

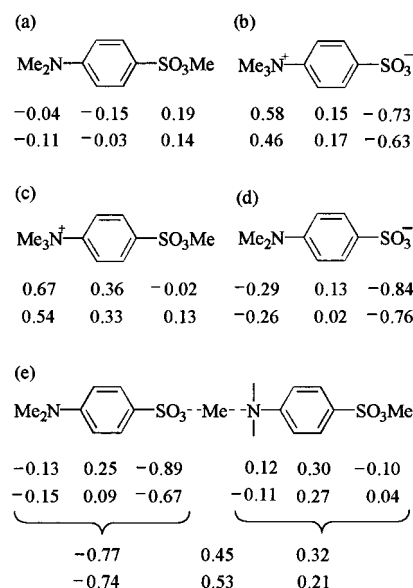
**Intrinsic Reaction Coordinate Calculation.** Figure 4a shows the results from the intrinsic reaction coordinate calculations around the transition-state structure. The  $O_1-N_1$  distance and the angle of  $O_1C_1N_1$  are obtained to be constant at about 4.02 Å and 178°, respectively, for all these calculations. On the other hand, the  $O_1-C_1$  and  $C_1-N_1$  distances vary monotonously with the reaction coordinate, which suggests these parameters could be the main components of the reaction coordinate. The smallest values of  $O_1-C_1$  and  $C_1-N_1$  distances in these calculations are obtained to be 1.52 and 1.44 Å, respectively, which are comparable to the  $O_1-C_1$  distance in the optimized MDBS and the  $N_1-C_1$  distance in the optimized cation intermediate, calculated to be 1.43 and 1.51 Å, respectively. This indicates that the range of the reaction coordinate calculated above is wide enough to further discuss the structural aspects of the initial stage of the reaction.

Figure 4b depicts a schematic of the positional relation among the three atoms to play the main role in the reaction, i.e.,  $O_1$ ,  $C_1$ , and  $N_1$  atoms, where the point  $P$  is placed at the same distance from the  $O_1$  atom as the  $O_1-C_1$  distance on the straight line running through the  $O_1$  and  $N_1$  atoms. In accordance with this figure, structural parameters representing such a reaction center in the three typical cases are summarized in Table 1, where the rotational angle  $\varphi$  indicates the angle of cooperative

**TABLE 1: Structural Parameters, Interatomic Distances, and an Angle, Concerning the Reaction Center (See Figure 4b) in Three Typical Cases**

$\varphi/\text{deg}^a$	$d(O_1-N_1)/\text{\AA}$	$d(C_1-N_1)/\text{\AA}$	$d(P-N_1)/\text{\AA}$	$O_1C_1N_1/\text{deg}$
0	4.80	3.49	3.35	150
9	4.38	2.96 <sup>b</sup>	2.94	169 <sup>b</sup>
19	4.02	2.78 <sup>b</sup>	2.58	142 <sup>b</sup>

<sup>a</sup>  $\varphi$ : angle of cooperative rotation of MDBS molecules around their long axes. <sup>b</sup> Values taken from ref 10.



**Figure 5.** Charge distributions on molecular segments (all values in elementary charge) obtained by ab initio MP2 calculations of (a) MDBS, (b) TBS, (c) cation intermediate, (d) anion intermediate, and (e) the transition state. For a pair of values shown below each segment, the upper and the lower values were calculated using the CHelpG method and the Mulliken population analysis, respectively.

rotation of MDBS molecules around their long axes from their original orientations realized in the crystal.

The original molecular arrangement in MDBS crystal, where  $\varphi = 0^\circ$ , shows much longer  $O_1-N_1$  and  $C_1-N_1$  distances and a still smaller angle of  $O_1C_1N_1$  than those in the optimized transition-state structure, respectively. Even if a molecular structural deformation permitting the  $C_1$  atom to move to the point  $P$  could be assumed, the  $P-N_1$  distance is still 1.38 Å longer than the  $C_1-N_1$  distance in the transition state. These values imply that the reaction could not be initiated under the original crystal structure if any other molecular motions may not be involved. Then, if only a cooperative rotation of molecules at  $\varphi = 9^\circ$  around their long axes is caused as examined by Sarma and Dunitz,<sup>11</sup> the  $O_1-N_1$  and  $C_1-N_1$  distances and the angle of  $O_1C_1N_1$  come fairly close to those in the transition state. However, the  $C_1-N_1$  distance is still 0.94 Å longer, even if the same kind of molecular structural deformation as above is assumed. In turn, if a further large angle of cooperative rotation at  $\varphi = 19^\circ$  (or higher angle)<sup>11</sup> could be applied as also tested by Sarma and Dunitz,<sup>11</sup> the  $O_1-N_1$  distance coincides with that in the transition state, whereas the angle of  $O_1C_1N_1$  and the  $C_1-N_1$  distance do not necessarily match with those in the transition-state structure. Judging from these results, it could be suggested that the cooperative rotation of molecules around their long axes coupled with the molecular structural deformation is at any rate an important factor for initiating the reaction in the crystal.

**Charge Distributions.** Figure 5 shows electric charge distributions on three molecular segments for each species

concerned in this work, which are derived from both the CHelpG method and the Mulliken population analysis. The notable differences between the calculated charges and formal charges on the respective molecular segments indicate charge polarization effects existing in these species.

At the bottom of Figure 5 charge distributions on molecular segments of two MDBS molecules in the transition state of the methyl cation transfer process are also shown. The positive total charge, 0.32 by the CHelpG method and 0.21 by the Mulliken population analysis, of MDBS accepting the methyl cation indicates that this molecule has already donated electrons in such a degree of charge to the methyl cation at the transition state.

### Concluding Remark

To study the topochemical nature of the initiation process of the thermal isomerization reaction from MDBS to TBS in the crystalline state, structural optimization calculations of not only possible ionic intermediates but also the transition state in the free space have been carried out using ab initio MO methods, bearing in mind that the method of such calculations with taking account of the crystal field effects has not yet been established. The optimized structures of the ionic intermediates are compared with those of MDBS and TBS as well as the structures observed for these molecules in the crystal, and their characteristics could be considered to assist the reaction in proceeding to the further steps.

It is notable that the optimized transition-state structure can be modified to have common features with the arrangement of a pair of molecules in the MDBS crystal by adjusting only two dihedral angles of  $C_2S_1O_1N_1$  and  $S_1O_1N_1C_3$ . By examining the crystal structure on the basis of such a transition-state structure, we conclude that the topochemical requirements for the initiation process of the reaction could be attainable by in-phase rotation

of MDBS molecules around their long axes coupled with structural deformation nearby the methoxy group in a molecule in the crystal.

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