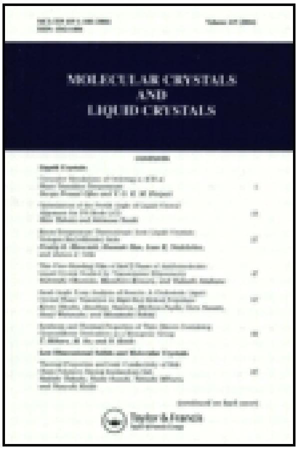

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MNDO-PM3 MO Studies on the Thermal Enantiomerization of 1′,3′,3′-Trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-Indoline]

Y. Abe [a], S. Okada [a], T. Horii [a], R. Nakao [a] & M. Irie [b]

[a] Research Institute for Advanced Science and Technology, Osaka Prefecture University, 1-2 Gakuen-cho, Sakai, 599-8570, Japan

[b] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581, Japan

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MNDO-PM3 MO Studies on the Thermal Enantiomerization of 1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-Indoline]

Y. ABE[a], S. OKADA[a], T. HORII[a], R. NAKAO[a] and M. IRIE.[b]

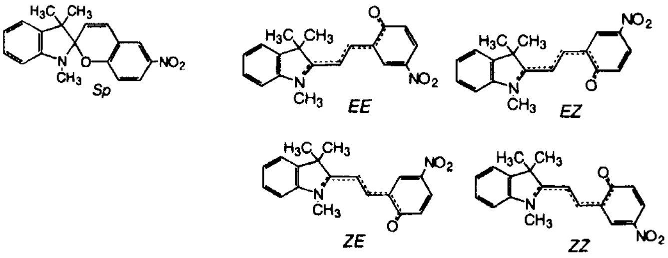
[a]*Research Institute for Advanced Science and Technology, Osaka Prefecture University, 1–2 Gakuen-cho, Sakai, 599–8570, Japan and* [b]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6–10–1, Higashi-ku, Fukuoka 812–8581, Japan*

Semiempirical MNDO-PM3 quantum chemical calculations were carried out for the isomers, stable and transition states, of the titled compound (Sp) to reveal the thermal enantiomerization of the photochromic spiropyran. To elucidate the mechanism in DMSO solution, COSMO calculations were carried out. Three possible conformations of photomerocyanines, EE, EZ, and ZE were optimized as planar, whereas ZZ isomer was not planar. Isomerization between EZ and ZZ and ring opening of Sp to ZZ were successfully calculated, while the other processes were prohibited. The mechanism for enantiomerization of (RS)-Sp was explained by a series of (R)-Sp to ZZ(R), ZZ(R) to ZZ(S), and ZZ(S) to (S)-Sp reactions.

Keywords: Molecular orbital calculation; Barriers to racemization; Spiro-2H- 1-benzopyran

INTRODUCTION

Sp is the most extensively studied photochromic compound[1]. UV irradiation of the colorless spiro-isomer leads to cleavage of the C(sp^3)-O bond to give a colored open-form isomer called photomerocyanine. The cyclization reaction of the photomerocyanine to the colorless spiro-isomer proceeds photochemically as well as thermally. To reduce the thermal cyclization reaction, 1'-methyl group was modified and chemically bonded to siloxane matrices[2-5]. The thermal cyclization mechanism was elucidated on the basis of the potential barrier heights during the conformational changes between the merocyanine-form isomers calculated by semiempirical MNDO-PM3 quantum chemical method[6]. Recently, it has been reported that the thermal ring-opening reaction causes enantiomerization of some benzospiropyrans[7-9]. Energy barriers for cyclization and ring-opening reactions of the titled compound were found as $\Delta G^{\neq}=92.0 \pm 0.7$ and 85.9 ± 0.3 kJ mol^{-1} at 22°C in DMSO-d_6, respectively[10]. In the present study, we have carried out semiempirical calculation on the reaction coordinate of the ring-opening and conformational changes between the merocyanine-form isomers to



confirm the mechanism of the ring-opening and cyclization reactions in DMSO solutions.

COMPUTATIONAL METHOD

The calculations were carried out at the restricted Hartree-Fock(RHF) level with the MNDO-PM3 semiempirical SCF-MO method, as reported in a previous report[6]. COSMO calculations were carried out using keywords of EPS=45.0 to reflect the reactions in DMSO solutions.

RESULTS AND DISCUSSION

From the data of our report[6], energy barrier for the thermal cyclization from merocyanine form EZ to Sp via ZZ was calculated to be $\Delta H^{\neq}$=90.79 kJ mol^{-1}. The experimental $\Delta G^{\neq}$ value was 92.0 kJ mol^{-1}. That of ring-opening, Sp → ZZ, was calculated to be $\Delta H^{\neq}$=120.93 kJ mol^{-1}, while the experimental $\Delta G^{\neq}$ value was 85.9 kJ mol^{-1}. The difference between the experimental and calculated data was ascribed to the neglect of the reaction conditions. Recalculation using COSMO method gave different potential energies and geometries from the reported ones.

Heat of formation for Sp was calculated to be -31.31 kJ mol^{-1}. Those of merocyanine forms ZZ , EZ, EE, and ZE were -28.97, -32.95, -47.58, and -42.68 kJ mol^{-1} respectively, and the conformations of the π-conjugated systems were planar and *C*s symmetry, except for ZZ . The geometries calculated without COSMO method gave *C*1 symmetry. The order of stability was the same as the data without COSMO calculation.

Mutual isomerization among the four merocyanine isomers were calculated by the same technique described in the former report by using COSMO method. Isomerization course between ZZ and EZ isomers could be calculated, while the other isomerizations were prohibited because of the geometrical discontinuity in the reaction pathway. The heat of formation at the transition state, TS(1), from ZZ to EZ isomer was -12.25 kJ mol^{-1}. The barrier heights to the TS(1) from ZZ and EZ were $\Delta H^{\neq}=16.72$ and 20.70 kJ mol^{-1} respectively. Those values without COSMO method were $\Delta H^{\neq}=85.11$ and 90.79 kJ mol^{-1}. The thermal isomerization between ZZ and EZ easily took place in a DMSO solution. The ZZ - EZ process was allowed from both directions based on the potential energy surface calculation. The reason why the EE and ZE isomers which are more stable than EZ isomer have not yet been observed experimeantally, whereas EZ conformer was observed by NMR

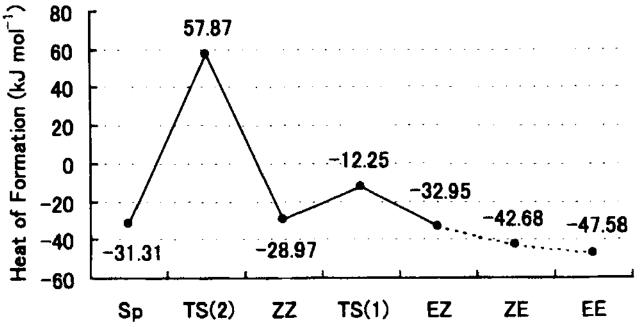


FIGURE 1. Energy diagrams of MNDO-PM3 calculation with COSMO method for DMSO solutions.

spectroscopy[10], is explained by the prohibition of thermal isomerization to EE or ZE from EZ or ZZ.

The geometries for the reaction coordinate for ring-opening of Sp to ZZ isomer were calculated. The energy maximum in the process was found at a bond length (C_2-O_{18}) of 1.995 Å which is shorter than the reported value of 2.116 Å[6]. The heat of formation at the TS(2) was 57.87 kJ mol^{-1}. Cyclization from ZZ to Sp also took place by the opposite route. The barrier heights to the TS(2) from ZZ and Sp were $\Delta H^{\neq}$=86.84 and 89.18 kJ mol^{-1} respectively. Those values without COSMO method were $\Delta H^{\neq}$=74.05 and 120.93 kJ mol^{-1}. From the above data we calculated the energy barriers from Sp to EZ and from EZ to Sp to be $\Delta H^{\neq}$=89.18 and 90.82 kJ mol^{-1} respectively. We also calculated thermodynamic parameters to obtain $\Delta G^{\neq}$ values for isomerizations. The energy barriers from Sp to TS(2), from EZ to TS(2) and from ZZ to TS(2) at 298 K were calculated $\Delta G^{\neq}$=86.2, 92.1 and 89.8 kJ mol^{-1}, respectively.

As the calculated values of the former two agreed very well with the experimental data[10], the last value may be reliable enough to discuss the mechanism. Enantiomerization from (R)-Sp to (S)-Sp or vice versa is reasonably explained by the energy barriers described in the previous section.

(1) An enantiomer of the spiropyran (R)-Sp changes to the merocyanine isomer ZZ(R) with an energy barrier of $\Delta G^{\neq}$=86.2 kJ mol^{-1}.

(2) As ZZ(R) has no *C*s symmetry, ZZ(R) enantiomerizes to ZZ(S) via a very small energy barrier which is not detected by a usual procedure to

calculate the TS. The heat of formation of the planar ZZ isomer was -27.53 kJ mol^{-1}, the difference with the optimized structure being only $\Delta H^{\neq} = 1.44$ kJ mol^{-1}.

(3) Finally, ZZ(S) cyclized to (S)-Sp with an energy barrier of $\Delta G^{\neq}=89.8$ kJ mol^{-1}.

As the energy barrier from ZZ to TS(2) was less than that from EZ to TS(2), enatiomerization occured faster than cyclization from EZ to Sp via ZZ.

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