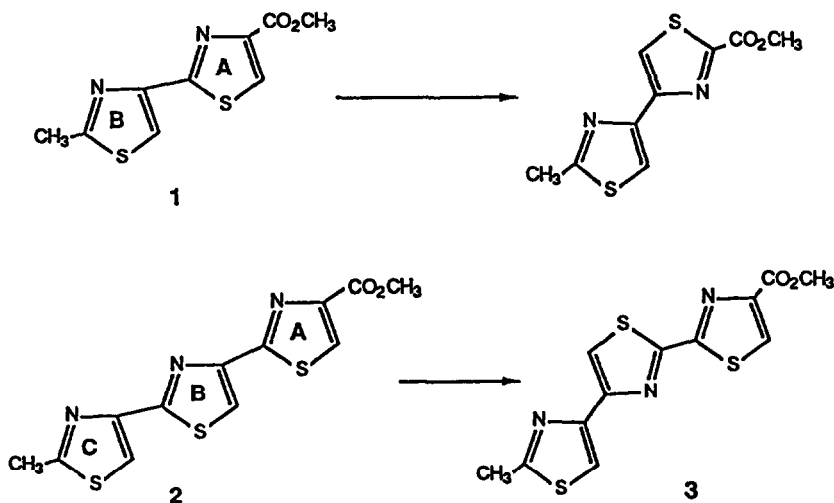


REMARKABLY HIGH SELECTIVITY IN PHOTOISOMERIZATION OF TRITHIAZOLES¹

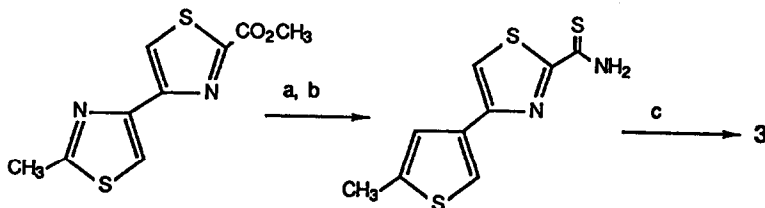
Isao Saito,* Takashi Morii, Satoru Mori, Kizashi Yamaguchi[§] and Teruo Matsuura
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University Kyoto 606, Japan
[§]Department of Engineering Science, Osaka University, Toyonaka, Osaka 450, Japan

Summary: Highly selective photorearrangement of trithiazole 2 is described and the selectivity is discussed in terms of LUMO bond index.

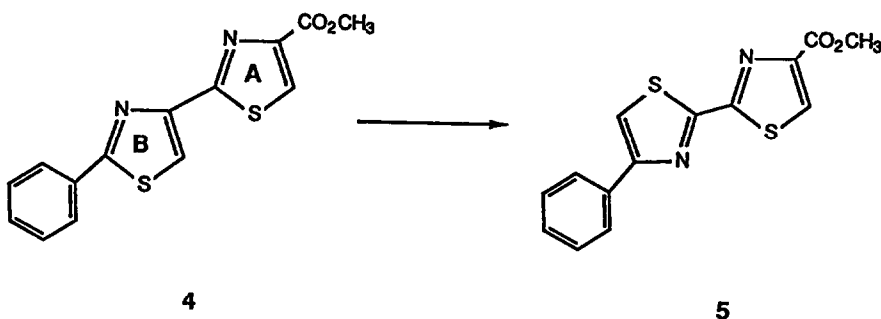
While a great deal of work has been done on the photorearrangement of a large variety of monomeric five-membered heterocycles, only little is known on the photorearrangement of dimeric, trimeric or polymeric five-membered heteroaromatic compounds such as polypyrroles and polythiazoles.² In our previous study on the photorearrangement of 2,4'-bithiazole 1, we observed that the thiazole ring attached to the electron-withdrawing carbomethoxy group (ring A) preferentially undergoes ring-atom transposition to give 4,4'-bithiazole via lowest π, π^* singlet state.³ Such a regiospecific phototransformation of conjugated polychromophores would provide particularly important information on the intramolecular excitation transfer within a complex polychromophoric molecule.⁴ The present paper discloses a highly selective photoreaction of trithiazole derivative 2 possessing three non-equivalent thiazole rings, each of which has the capability of undergoing photochemical ring-atom transposition reaction. Contrary to our earlier result, we found that the thiazole ring B rather than the expected ring A undergoes regiospecific photoisomerization. We also demonstrate that such an intriguing ring-selectivity is theoretically predicatable by calculated LUMO bond index.



Trithiazole **2⁵** was synthesized from methyl 2'-bromoacetyl-2,4'-bithiazole-4-carboxylate by condensation with thioacetamide according to the known procedure.⁶ External irradiation of **2** (0.34 mM) in dry acetonitrile with a 60 W transilluminator (~302 nm) under nitrogen atmosphere resulted in a clean transformation with an isosbestic point at 327 nm to give photoisomerized trithiazole **3** (94%) as a sole product. The structure of **3** was assigned on the basis of spectral data⁷ (HRMS, ¹H- and ¹³C NMR, ¹H-¹³C LR-HETCOSY) and confirmed by independent synthesis from methyl 2'-methyl-4,4'-bithiazole-2-carboxylate^{3b} as outlined below.



- (a) aq NH₃ (95%), (b) Lawesson's reagent / toluene/100 °C (93%)
 (c) BrCH₂COCOOCH₃/DMF/70 °C (35%)



A similar ring-selectivity was observed when the thiazole ring C of **2** was replaced by a phenyl group. Thus, irradiation of **4** (0.54 mM) under similar conditions gave 4'-phenyl-2,2'-bithiazole **5** in 50% isolated yield as a single product. The structure of **5** was again confirmed by spectral data⁷ and independent synthesis.⁸ Quantum yields for the formation of **3** and **5** at 302 nm are 0.0067 and 0.0016, respectively. In none of these cases has the other isomer been detected by HPLC analysis. The remarkably high ring-selectivity as well as the clean product formation are surprising, since irradiation of simple monothiazoles usually produce a mixture of all possible isomers.^{2,9} It should be reminded here that numerous isomers are possible for trithiazole **2**.

Of special interest is the fact that the observed ring-selectivity is quite different from that expected from the photorearrangement of bithiazole **1**. In the latter case, only the ring A photorearranges selectively to produce 4,4'-bithiazole as a result of preferential localization of the lowest π , π^* excitation at ring A.^{3a} In order to interpret the ring-selectivity, we calculated the LUMO bond indices by means of INDO SCF method.¹⁰ As shown in Fig. 1, the bond index between C2' and

C5' is extraordinary larger than those for C2-C5 and C2''-C5'' bondings in the lowest π, π^* singlet state of 2. Essentially the same result was obtained for 4.

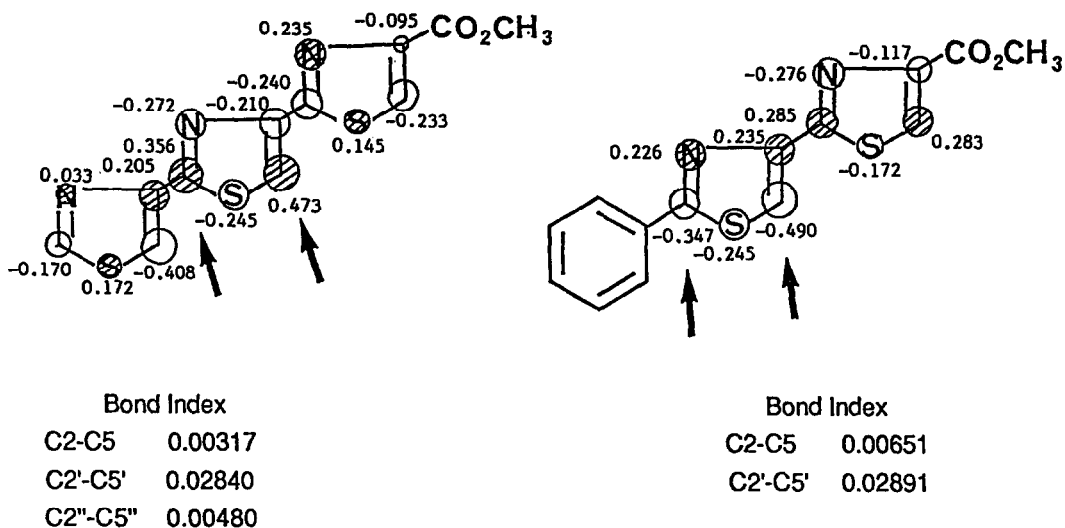
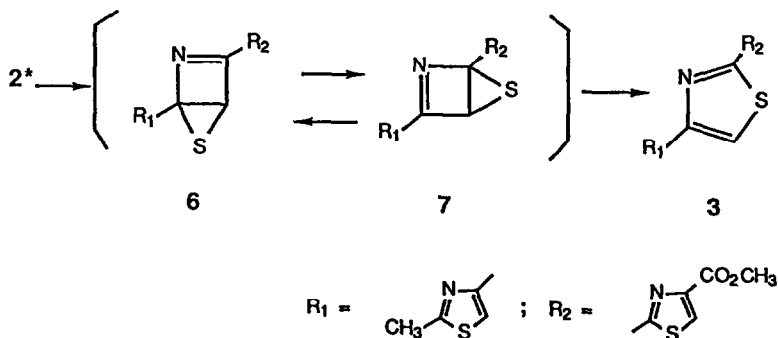


Fig. 1. LUMO coefficients calculated by INDO SCF method for 2 and 4

In the light of these calculations, we propose that lowest singlet state of 2 may result in a disrotatory closure preferentially at C2'-C5' to produce Dewar intermediate 6 which then undergoes 1,3-shift of the sulfur atom to give 7. Ring-opening of 7 would produce 3. Although other interpretations including ring contraction-ring expansion mechanism or tricyclic zwitterionic mechanism are possible for the formation of 3,^{2b,9} extremely high photoreactivity of the middle thiazole ring (ring B) in 2 would indicate a hint for the general rule for the ring-selectivity in photorearrangement of higher polythiazoles.



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References and Notes

- 1) Photoinduced reaction . 172
- 2) (a) A. Labiache-Combiere in "Photochemistry of Heterocyclic Compounds", O. Buchardt Ed., Wiley, New York, 1976, p 123. (b) A. Padwa, in "Rearrangements in Ground and Excited States", Vol 3, P. de Mayo Ed., Academic Press, New York, 1980, p 501.
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- 4) N. J. Turro "Modern Molecular Photochemistry", The Benjamin-Cummings Publishing Co. Inc., Menlo Park, California, 1978, p 340.
- 5) UV (CH₃CN) λ_{\max} 270 nm (ϵ 2.29 x 10⁴), 330 nm (ϵ 2.36 x 10⁴).
- 6) J. R. Riordan and T. T. Sakai, *J. Heterocyclic Chem.*, **18**, 1213 (1981).
- 7) Selected spectral data. **3**: mp 222-225 °C; ¹H NMR (CDCl₃) δ 2.75 (s, 3 H), 3.97 (s, 3 H), 7.72 (s, 1 H), 7.89 (s, 1 H), 8.26 (s, 1 H); ¹³C NMR (CDCl₃) δ 19.20 (q), 52.54 (q), 115.59 (d), 117.68 (d), 129.04 (d), 147.74 (s), 149.46 (s), 151.86 (s), 160.17 (s), 161.41 (s), 162.06 (s), 166.55 (s); MS, m/z (relative intensity) 323 (M⁺, 100), 292 (5), 282 (9), 265 (9), 250 (10), 99 (3), 155 (7), 114 (2). **5**: mp 173-174 °C; ¹H NMR (CDCl₃) δ 4.09 (s, 3 H), 7.61 (s, 1 H), 8.25 (s, 1 H), 7.30-7.55 (m, 3 H), 7.89-8.03 (m, 2 H); MS, m/z (relative intensity) 302 (M⁺, 100), 271 (16), 244 (19), 134 (44).
- 8) **5** was prepared from methyl 4-phenylthiazole-2-carboxylate^{3a} by the same route as for **3**.
- 9) For example, C. Riou, J. C. Poite, G. Vernin and J. Metzzer, *Tetrahedron*, **30**, 879 (1974).
- 10) Essentially the same result was obtained by ab-initio (STO-3G) calculation. The bond index for first LUMO is represented as follows: bond index (B_{r, s}) = (coefficient_r, LU)² (coefficient_s, LU)².

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