Pergamon

Tetrahedron Letters 42 (2001) 6869–6872

TETRAHEDRON
LETTERS

[6.6](1,8)Naphthalenophane containing 2,2′-bithienyl-5,5′-ylene bridges[†]

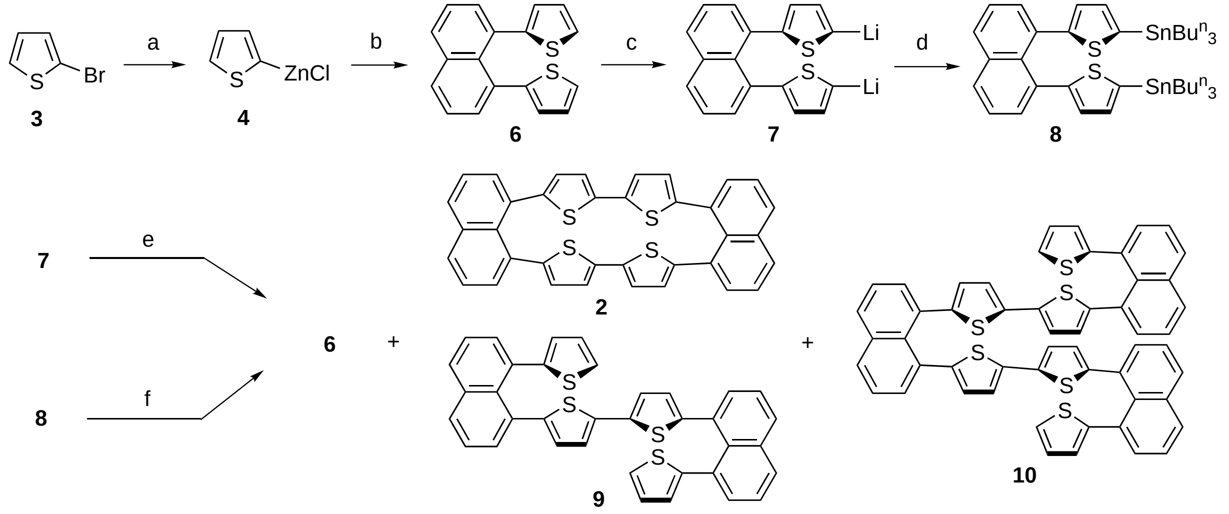
Masahiko Iyoda,* Kazumi Nakao, Terumasa Kondo, Yoshiyuki Kuwatani, Masato Yoshida, Haruo Matsuyama, Kentaro Fukami and Shigeru Nagase[‡]

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Received 17 May 2001; revised 2 July 2001; accepted 27 July 2001

Abstract—Two isomeric 1,8-[1,8-naphthylenebis(2,2′-bithienyl-5,5′-ylene)]naphthalenes (major and minor isomers) were synthesized using the coupling reaction of 1,8-di(5-lithio-2-thienyl)naphthalene with $CuCl_2$. The major isomer easily isomerized photochemically to yield the minor isomer. The redox and fluorescence behavior of the two isomers reflect both face-to-face interaction of the 2,2′-bithienyl-5,5′-ylene units and deformation of the naphthalene moieties. © 2001 Elsevier Science Ltd. All rights reserved.

Cyclophanes and cyclic oligophenylenes are the focus of attention of experimental and theoretical chemists,[1,2] because of their unique structures, π–π interaction, molecular strain, host–guest chemistry, aromaticity in some cases, and the synthetic challenges they present. Recently, we reported the synthesis and structure of the cyclic oligophenylene **1**, and disclosed an unusual strain and π–π interaction in this molecule.[3] The compound **1** is extremely stable in spite of its internal ring strain.[3] Our continuing interest in cyclic oligophenylenes led us to synthesize the thiophene analogue **2**, because of its face-to-face interaction and four possible isomeric



Scheme 1. Synthesis of **2** and related compounds (**9** and **10**). *Reagents and conditions*: (a) (i) Bu^nLi (1.1 equiv.), −78°C, THF, (ii) $ZnCl_2$ (1.25 equiv.), −78 to 0°C; (b) 1,8-diiodonaphthalene **5** (0.25 equiv.), $Pd(PPh_3)_4$ (cat.), 0°C–rt, THF; (c) Bu^nLi (3–3.4 equiv.); (d) Bu^n_3SnCl (3.6 equiv.); (e) $CuCl_2$ (3.4 equiv.); (f) $Cu(NO_3)_2{\cdot}3H_2O$ (2.7 equiv.).

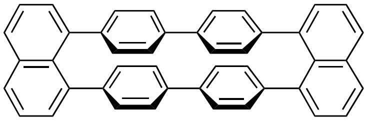
Keywords: coupling reactions; cyclizations; cyclophanes; macrocycles; naphthalenes; thiophenes.

* Corresponding author. Tel.: +81-426-77-2547; fax: +81-426-77-2525; e-mail: iyoda-masahiko@c.metro-u.ac.jp

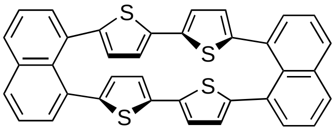
[†] Dedicated to Emeritus Professor Masazumi Nakagawa on the occasion of his 85th birthday.

[‡] Present address: Department of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan.

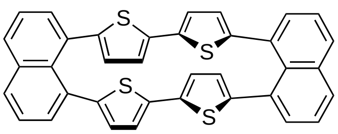
PII: S0040-4039(01)01396-X



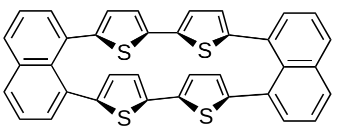
1



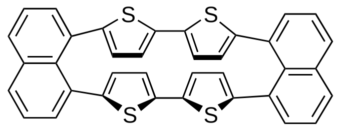
2a



2b



2c



2d

structures **2a**–**d**. In addition, the redox behavior of **2** is of interest, because bithiophene and its derivatives possess larger donor properties as compared to biphenyls.[4]

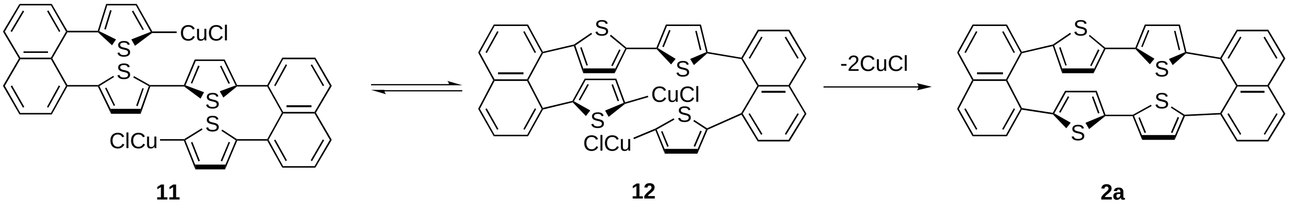
The synthesis of the title compound **2** was carried out using the sequence outlined in Scheme 1. Thus, the palladium-catalyzed reaction of 1,8-diiodonaphthalene (**5**) with 2-thienylzinc chloride (**4**) afforded **6** in 59% yield.[5] The reaction of **6** with Bu^{n}Li (3.4 equiv.) at 0°C in ether, followed by treatment with Bu$^n_3$SnCl (3.6 equiv.) from −50°C to room temperature formed **8** in 78% yield.[6] The copper-catalyzed coupling of **8** was first attempted in a similar manner for the synthesis of **1**.[3] However, the reaction of **8** with $Cu(NO_3)_2 \cdot 3H_2O$ (2.7 equiv.) in THF at room temperature for 1 h resulted in the formation of a complex mixture, from which **2** was isolated in 1% yield, together with **6** (52%), **9**[5c] (34%), and **10** (9%). This result shows that the C_{sp^2}–Sn bond in **8** is easily hydrolyzed to form the C_{sp^2}–H bond.[7] Therefore, we next employed the $CuCl_2$-mediated coupling of **7** for the synthesis of **2**.[8] The reaction of **6** with Bu^{n}Li (3 equiv.) at 0°C in ether, followed by treatment with $CuCl_2$ (3.4 equiv.) at 0°C to room temperature produced **2** (21%), **9** (7.2%), and **10** (2.5%), together with the starting **6** (22%). On the basis of the ^{1}H NMR spectrum, **2** was found to be a mixture of **2a** and **2b** (5:1). Pure **2a** was obtained by recrystallization of the reaction product from CS_2.

Interestingly, **2a** gradually isomerized to **2b** in refluxing toluene or chlorobenzene. Although the thermal isomerization of **2a** proceeds very slowly to afford **2b**, the photochemical transformation of **2a** into **2b** is an effective method. A solution of **2a** in chlorobenzene was irradiated using a metal halide lamp (National Skybeam MT-70) in a Pyrex tube at room temperature for 30 min to produce only the *syn-anti* isomer **2b** in 77% yield. This reaction requires diluted conditions (0.75 mmol/L) and short irradiation (30 min). A higher concentration and a longer reaction time decrease the yield of **2b**.

The assignment of **2a** and **2b** is based on the ^{1}H NMR data and MO calculations. The thiophene protons in the all-*anti* form **2a** appear at δ 6.42 (d, $J=3.4$ Hz) and 6.72 (d, $J=3.4$ Hz), whereas the corresponding thiophene protons in the *syn-anti* form **2b** show signals at δ 6.36 (d, $J=3.7$ Hz) and 6.66 (d, $J=3.7$ Hz). The *syn*-stacked thiophenophane is known to indicate an upper-field shift of thiophene protons as compared to the *anti*-stacked one, and the reported chemical shifts of the *syn*- and *anti*-isomers are similar to those of **2a** and **2b**.[9] The mechanistic consideration for the coupling of **7** can also suggest the preferential formation of **2a**. As shown in Scheme 2, the first coupling of **7** with $CuCl_2$ may form the all-*anti* **11**, the most stable conformer.[5c] The conformational change to **12**, followed by the coupling reaction, forms the all-*anti* isomer **2a**.

The HF/3-21G calculations of **2a** and **2b** revealed that the optimized structure of **2a** has two slipped thiophene rings as shown in Fig. 1.[10] In contrast, **2b** adopts a closely stacked structure of the two thiophene rings (Fig. 1). The face-to-face distances (3.00–3.87 Å) in **2b** are slightly longer than those (2.95–3.77 Å) in **2a**. In the four isomers of **2**, **2a** and **2b** are close in energy and are 5–9 kcal/mol more stable than **2c** and **2d** at the HF/3-21G level.

It has been reported that 1,8-di(2-thienyl)naphthalene **6** and its dimer **9** are oxidized to give stabilized radical-cations.[5] Therefore, **2a**, **2b** and **10** can be expected to produce more stabilized radical-cations **2a**$^{\bullet+}$, **2b**$^{\bullet+}$, and **10**$^{\bullet+}$ and to show lower oxidation potentials. As shown in Table 1, the oxidation potentials of **2a**, **2b**, **6**, **9**, and **10** measured by cyclic voltammetry revealed irreversible, fairly low values. Interestingly, **2b** and **10** show the second oxidations corresponding to the formation of the dications **2b**$^{2+}$ and **10**$^{2+}$. The dications **2b**$^{2+}$ and **10**$^{2+}$ may be stabilized by π-dimer formation or by separation of the two charges.



Scheme 2. Possible pathway for the formation of **2a**.

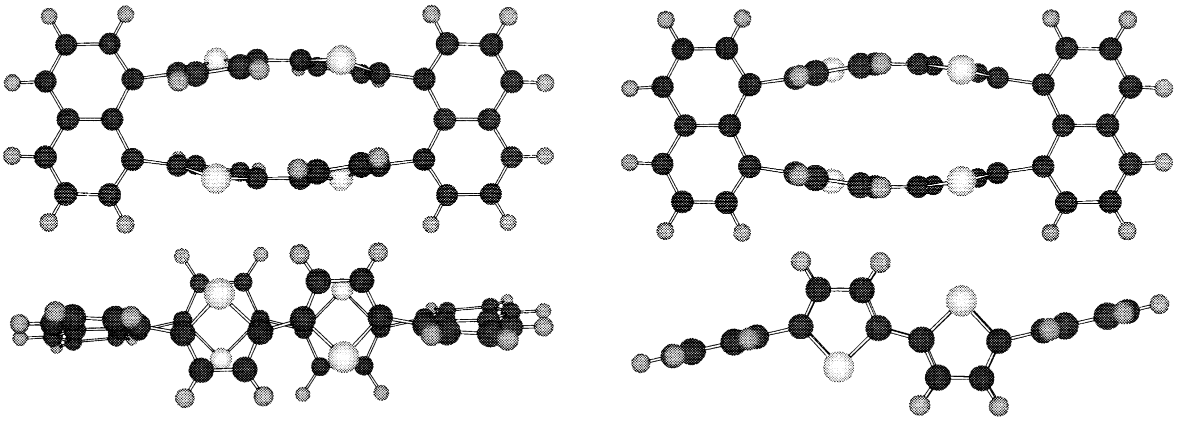


Figure 1. The HF/3-21G optimized structures of **2a** and **2b**.

Table 1. Oxidation potentials of **2a**, **2b**, **6**, **9**, and **10**[a]

Compound	$E^{ox}{}_1$ [V]	$E^{ox}{}_2$ [V]
2a	0.42	
2b	0.47	0.58
6	1.10	
9	0.70	
10	0.52	0.74

[a] V versus ferrocene/ferrocenium couple, 0.1 M $Bu^n_4ClO_4$, *o*-dichlorobenzene, glassy carbon-working and Pt-counter electrodes.

The title compounds **2a** and **2b** and related molecules (**6**, **9**, and **10**) show fluorescence in solution and in the solid state. UV and fluorescence spectra of **2a**, **2b**, **6**, **9**, and **10** in benzene are summarized in Table 2. The absorption maxima of **2a**, **2b**, **9**, and **10** are similar except for the shoulder absorption (428 nm) of **2a**, reflecting the 5,5′-di(1-naphthyl)-2,2′-bithiophene chromophor, whereas **6** shows an absorption at short wavelength (313 nm). In a similar manner, the emission of **2a**, **2b**, **9**, and **10** is also observed in the narrow region of 478–487 nm except for **6** (420 nm) (Fig. 2). The compounds **2a**, **2b**, and **10** show large Stokes shifts (139–141 nm), presumably due to the stacking structure of the two bithiophene moieties. Interestingly, **6** shows much lower fluorescence quantum yield as compared to **2a**, **2b**, **9**, and **10**, presumably due to mobility of the two thiophene rings. Although the conformational mobility of **2a** and **2b** seems to be smaller than that of **9**, their fluorescence quantum yields are lower than that of **9**. Since a ring strain decreases the fluorescence quantum yield,[11] the fairly large ring strain of **2a** and **2b** may cause a larger non-radiative process ($S_1 \rightarrow S_o$) or a larger contribution of the intersystem crossing ($S_1 \rightarrow T_1$) to decrease their fluorescence quantum yields.

Table 2. Fluorescence quantum yields and absorption coefficients of **2a**, **2b**, **6**, **9** and **10** in benzene

Compound	UV		Fluorescence	
	λ_{max}/nm	ε	λ_{max}/nm	$\Phi_f{}^a/10^{-2}$
2a	356	37,500	497	1.0
	428sh	2,790		
2b	347	21,700	486	5.4
6	313	12,800	420	0.5
9	327	23,600	478	15
	374	19,500		
10	346	41,000	486	6.6

[a] The quantum yield was calculated in benzene by using a 0.5 M solution of quinine sulfate as a standard ($\Phi_f = 0.546$).

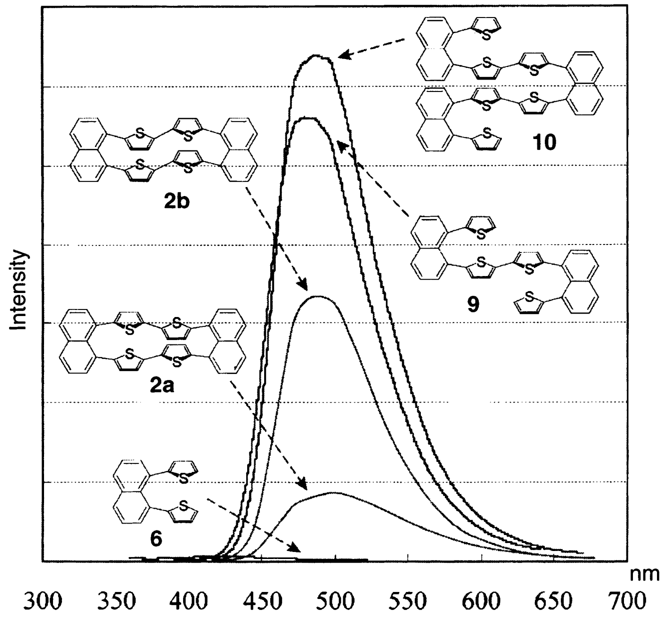


Figure 2. Fluorescence spectra of **2a**, **2b**, **6**, **9**, and **10** in benzene.

Acknowledgements

Financial support for this study was provided by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan (10440190). We also thank Professor Haruo Inoue and Dr. Masaki Sugita, Tokyo Metropolitan

University, for the measurement of fluorescence quantum yields.

References

1. For general reviews of cyclophanes, see: (a) *Cyclophanes*; Weber, E., Ed., *Top. Curr. Chem.* 1994, Vol. 172; (b) Vögtle, F. *Cyclophane Chemistry*, Wiley: New York, 1993; (c) Diederich, F. *Cyclophanes*; *Monographs in Supramolecular Chemistry*; the Royal Society of Chemistry: London, 1991.
2. For oligophenylenes, see: (a) Staab, H. A.; Binnig, F. *Chem. Ber.* **1967**, *100*, 293; (b) Irngartinger, H.; Leiserowitz, L.; Schmidt, G. M. J. *Chem. Ber.* **1970**, *103*, 1132; (c) Wittig, G.; Rümpler, K.-D. *Liebigs Ann.* **1971**, *751*, 1; (d) Fujioka, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3494; (e) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. B.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645; (f) Chan, C. W.; Wong, H. N. C. *J. Am. Chem. Soc.* **1985**, *107*, 4790; **1988**, *110*, 462; (g) König, B.; Heinze, J.; Meerholz, K.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1361; (h) Percec, V.; Okita, S. *J. Polym. Sci. Polym. Chem. Ed.* **1993**, *31*, 877; (i) Wong, T.; Yuen, M. S. M.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **1993**, *58*, 3118; (j) Rajca, A.; Safronov, A.; Rajca, S.; Shoemaker, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 488; (k) Hensel, V.; Lützow, K.; Jacob, J.; Gessler, K.; Saenger, W.; Schlüter, A.-D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2654; (l) Kelly, T. R.; Lee, Y.-J.; Mears, R. J. *J. Org. Chem.* **1997**, *62*, 2774; (m) Hensel, V.; Schlüter, A. D. *Chem. Eur. J.* **1999**, *5*, 421.
3. Iyoda, M.; Kondo, T.; Nakao, K.; Hara, K.; Kuwatani, Y.; Yoshida, M.; Matsuyama, H. *Org. Lett.* **2000**, *2*, 2081.
4. For recent examples, see: (a) Zhu, Y.; Wolf, M. O. *J. Am. Chem. Soc.* **2000**, *122*, 10121; (b) Frigoli, M.; Moustrou, C.; Samat, A.; Guglielmetti, R. *Helv. Chim. Acta* **2000**, *83*, 3043; (c) Lukevics, E.; Ryabova, V.; Arsenyan, P.; Belyakov, S.; Popelis, J.; Pudova, O. *J. Organomet. Chem.* **2000**, *610*, 8; (d) Cai, C.; Liakatas, I.; Wong, M.-S.; Bösch, M.; Bosshard, C.; Günter, P.; Concilio, S.; Tirelli, N.; Suter, U. W. *Org. Lett.* **1999**, *1*, 1847; (e) Ishikawa, M.; Lee, K. K.; Schneider, W.; Naka, A.; Yamabe, T.; Harima, Y.; Takeuchi, T. *Organometallics* **2000**, *19*, 2406; (f) Kaikawa, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Org. Lett.* **2000**, *2*, 4197; (g) Cherioux, F.; Guyard, L.; Audebert, P. *J. Chem. Soc., Chem. Commun.* **1998**, 2225.
5. For the nickel-catalyzed synthesis of **6**, see: (a) Kuroda, M.; Nakayama, J.; Hoshino, M.; Furusho, M. *Tetrahedron Lett.* **1992**, *33*, 7553; (b) Kuroda, M.; Nakayama, J.; Hoshino, M.; Furusho, M.; Kawata, T.; Ohba, S. *Tetrahedron* **1993**, *49*, 3735; (c) Kuroda, M.; Nakayama, J.; Hoshino, M.; Furusho, M.; Ohba, S. *Tetrahedron Lett.* **1994**, *35*, 3957.
6. All new compounds gave satisfactory spectral data. Compound **2a**: yellow cryst. mp 320–321°C (sublimed); MS: m/z 580 (M^+); ^{1}H NMR ($CDCl_3/CS_2$ 1:3): δ 6.42 (d, $J=3.4$ Hz, 4H), 6.72 (d, $J=3.4$ Hz, 4H), 7.49 (dd, $J=8.2$, 7.1 Hz, 4H), 7.57 (dd, $J=7.1$, 1.2 Hz, 4H), 7.89 (dd, $J=8.2$, 1.2 Hz, 4H); HRMS: calcd for $C_{36}H_{20}S_4$: 580.0448. Found: 580.0497. Compound **2b**: yellow cryst. mp 322–323°C (decomp.); MS: m/z 580 (M^+); ^{1}H NMR ($CDCl_3/CS_2$ 1:3): δ 6.36 (d, $J=3.7$ Hz, 4H), 6.66 (d, $J=3.7$ Hz, 4H), 7.50 (dd, $J=8.2$, 7.1 Hz, 4H), 7.57 (dd, $J=7.1$, 1.2 Hz, 4H), 7.87 (dd, $J=8.2$, 1.2 Hz, 4H); HRMS: calcd for $C_{36}H_{20}S_4$: 580.0448. Found: 580.0463. Compound **10**: yellow cryst. mp 198–200°C; FAB-MS: m/z 873 ($M^+ +1$); ^{1}H NMR ($CDCl_3$): δ 6.32 (d, $J=3.6$ Hz, 2H), 6.46 (d, $J=3.6$ Hz, 2H), 6.51 (dd, $J=3.4$, 1.2 Hz, 2H), 6.61 (d, $J=3.6$, 2H), 6.65 (dd, $J=5.0$, 3.4 Hz, 2H), 6.68 (d, $J=3.6$ Hz, 2H), 7.03 (dd, $J=5.0$, 1.2 Hz, 2H), 7.40 (dd, $J=8.2$, 7.1 Hz, 2H), 7.50–7.59 (m, 8H), 7.67 (dd, $J=7.1$, 1.2 Hz, 2H), 7.90 (m, 4H), 7.96 (dd, $J=8.2$, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 123.15, 123.39, 124.16, 125.11, 125.14, 125.22, 126.81, 127.87, 128.26, 128.50, 129.20, 129.27, 129.41, 130.57, 130.69, 132.01, 132.03, 132.11, 132.37, 132.38, 135.44, 135.54, 136.09, 136.51, 143.07, 143.20, 144.05.
7. (a) Ghosal, G.; Luke, G. P.; Kyler, K. S. *J. Org. Chem.* **1987**, *52*, 4296; (b) Harada, G.; Yoshida, M.; Iyoda, M. *Chem. Lett.* **2000**, 160.
8. Kabir, S. M. H.; Miura, M.; Sasaki, S.; Harada, G.; Kuwatani, Y.; Yoshida, M.; Iyoda, M. *Heterocycles* **2000**, *52*, 761 and references cited therein.
9. Nakamura, Y.; Kaneko, M.; Shinmyozu, T.; Nishimura, J. *Heterocycles* **1999**, *51*, 1059. The reported chemical shifts of the *syn*- and *anti*-isomers of [2.3](2,5)-thiophenophane are δ 5.81 and 6.16, and δ 6.66 and 6.78, respectively.
10. All calculations were carried out using the Gaussian 98 program.
11. (a) Elsaesser, T.; Lärmer, F.; Kaiser, W.; Dick, B.; Niemeyer, M.; Lüttke, W. *Chem. Phys.* **1988**, *126*, 405; (c) Hertzberg, J.; Nickel, B. *Chem. Phys.* **1989**, *132*, 235; (b) Castel, N.; Fisher, E.; Strauch, M.; Lüttke, W. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 301.