Synthesis and photochromic properties of thiophenophan-1-enes containing a polyether bridge

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Received (in Montpellier, France) 5th January 2009, Accepted 8th April 2009
First published as an Advance Article on the web 22nd April 2009
DOI: 10.1039/b823492b

[2.*n*]Thiophenophan-1-ene derivatives containing a polyether bridge have been synthesized by the coupling reaction of bis(iodomethyl)dithienylethene with polyethylene glycols under high dilution conditions. All prepared [2.*n*]thiophenophan-1-enes were photochromic, as photocyclization of the open forms took place by UV irradiation to give a yellow solution of the closed form and their ring opening reactions occurred upon visible irradiation. There were significant differences in the quantum yields for the photocyclization reactions and the photo ring-opening reactions due to the difference in their structures since their electric properties are similar. The kinetic parameters of the thermal ring opening reaction of the closed forms of thiophenophan-1-enes were estimated and they were also dependent on their bridges.

Introduction

Photochromic compounds have been widely studied, since there have been possibilities for utilizing them as optical materials and materials for photomemory.[1] Among the photochromic compounds, dithienylethenes are the most promising compounds for several reasons; (1) both photoisomers are thermally stable and can be stored in the dark for extended times, (2) the fatigue resistance is quite high and the photochromic reaction can be repeated many times, (3) photoreaction is very rapid, the reaction takes place in several picoseconds *etc.*[2] Therefore, dithienylethenes have been studied vigorously as materials for organic molecular photomemory. On the other hand, there are two conformations in the open form of diarylethenes, the parallel and the anti-parallel.[2,3] In solution, these conformations exchange slowly and the photocyclization reaction proceeds only from the anti-parallel conformation.[3] Therefore, the quantum yield, namely the photon efficiency, for photocyclization reaction is dependent on the conformational ratio. Thus there are many efforts to overcome this problem, for example, to introduce bulky substituents at their inner positions to increase the ratio of the photoactive conformation,[3] utilizing host–guest chemistry[4] to carry out the photochromic reaction in the crystalline state,[5] and so on. Recently, we have reported that the photochromic reaction of [2.*n*]metacyclophan-1-enes takes place in high efficiency since there is no photoinactive conformation in [2.*n*]metacyclophan-1-enes.[6] The photochromic reaction proceeds not only in solution but also in a polymer matrix due to the conformational rigidity of the [2.*n*]metacyclophan-1-enes.[7] The conformation of the [2.*n*]metacyclophan-1-ene is "pre-structured" for the photocyclization reaction and this extends even to polymer matrices. The conformation is hardly effected by the medium since the conformational exchange is suppressed due to the steric hindrance between the inner substituents and the opposite aromatic rings. However, the reported closed forms of [2.*n*]metacyclophan-1-enes composed of benzene rings are not thermally stable.[6] This is due to the high aromatic stabilization energy of the benzene rings.[8] The difference in the energy of formation between the open form and the closed form of [2.*n*]metacyclophan-1-ene is large, since the former is aromatic (6π system) and the latter is anti-aromatic (12π system). These facts encouraged us to develop thermally stable photochromic cyclophan-1-enes for materials utilized in molecular photomemory. In this paper, we describe the syntheses and photochromic properties of [2.*n*]thiophenophan-1-enes containing flexible polyether bridges. The structure of the resulting thiophenophan-1-enes could be more flexible than [2.2]metacyclophan-1-enes and less flexible than diarylethenes. Moreover, since the aromatic rings of the cyclophan-1-enes are substituted by thiophene rings, which have a lower aromatic stabilization energy, one might expect a high thermal stability of both photoisomers, as for dithienylethenes.

Results and discussion

Syntheses of [2.*n*]thiophenophan-1-enes are shown in Scheme 1. Although the intramolecular cyclization reaction of bis(chloromethyl)dithienylethene **2a** was carried out, no desired thia[2.3]phane **3a** was obtained and a polymeric mixture was afforded instead. Thus the closed form **2b** was prepared by the irradiation of **2a** with UV light, then the coupling reaction with Na_2S was carried out under high dilution conditions. The two chloromethyl groups of **2b** are fixed and their separation is short relative to those of **2a**. Indeed, the intramolecular coupling reaction of **2b** afforded the closed form **3b**. The open form of thia[2.3]phane **3a** was obtained by the irradiation of **3b** with visible light.[9] The other thiophenophan-1-enes were prepared by the coupling reactions of bis(iodomethyl)dithienylethene **4** and the ethylene

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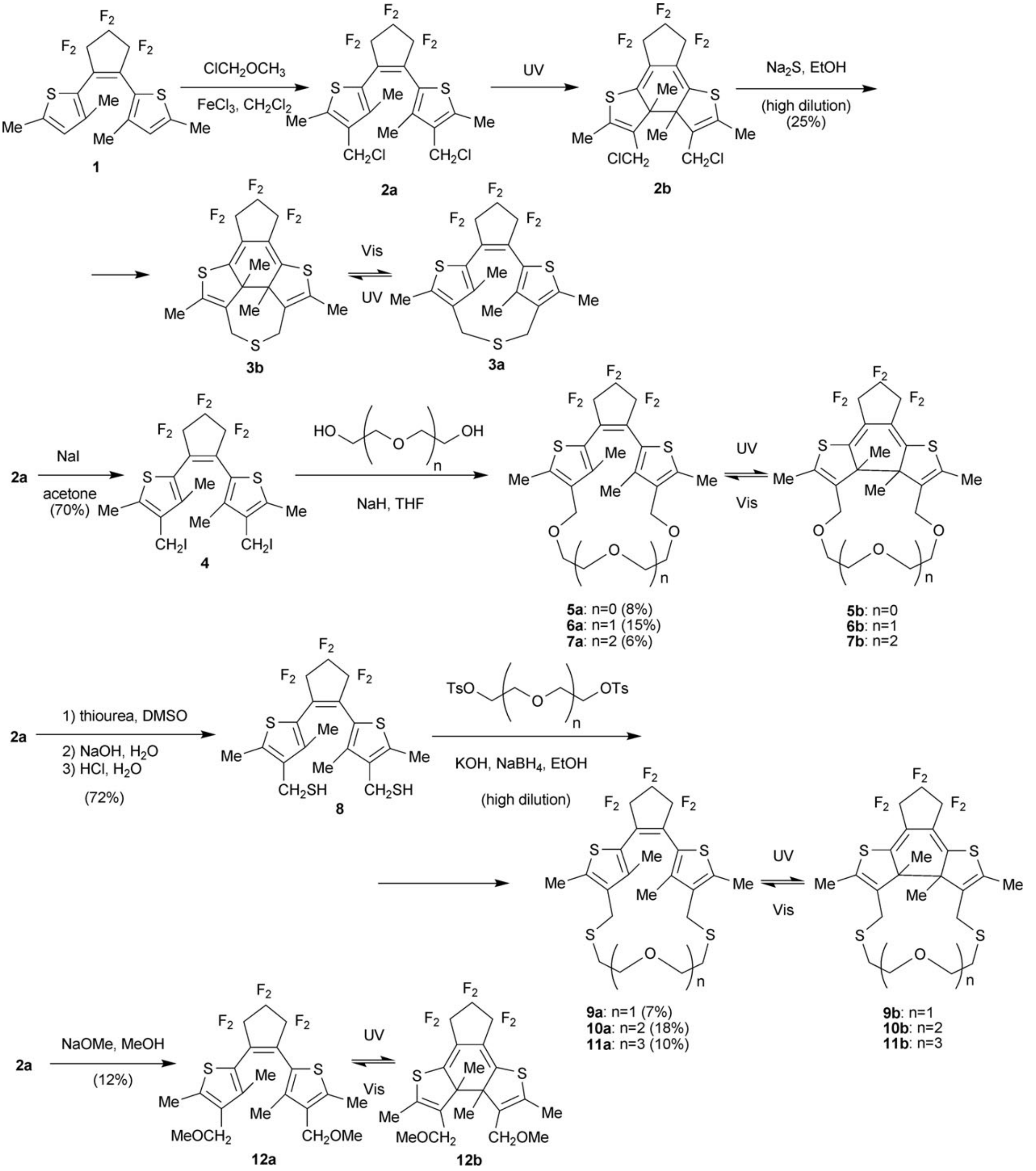

Scheme 1

glycols or bis(mercaptomethyl)dithienylethenes **8** and ethylene glycol ditosylates under high dilution conditions as shown in Scheme 1. The dithienylethene having two methoxymethyl groups **12** was also prepared as a reference for comparing photochromic properties with thiophenophan-1-enes.

The absorption spectral change of a solution of thiophenophan-1-ene **5** in CH_2Cl_2 upon irradiation with 330 nm light is shown in Fig. 1 as example. Upon UV irradiation, the colorless solution of **5a** turned yellow and the absorption maximum at 454 nm, which is attributed to the absorption of the closed form, gradually increased. The absorption spectrum and the color of the closed form returned to the initial state upon visible light ($>$420 nm) irradiation, indicating **5** is photochromic. All prepared thiophenophan-1-enes (**3**, **5–7** and **9–11**) and the dithienylethene **12** showed similar phenomena as described for **5**, and their photochromic reactions are shown in Scheme 1.

The absorption maxima and the molar extinction coefficients of the closed forms of thiophenophan-1-enes and the reference **12b** in CH_2Cl_2 in the visible region are summarized in Table 1. The absorption maxima of the closed form of the thiophenophan-1-enes were dependent on the chain length.

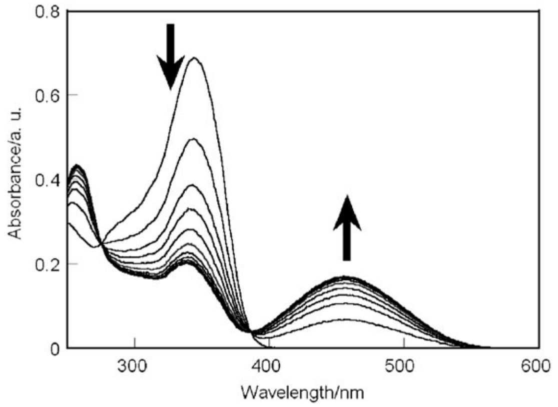

Fig. 1 Absorption spectral change of a solution of **3** in CH_2Cl_2 upon irradiation with 330 nm light.

Table 1 Absorption maxima (λ_{max}/nm) and molar extinction coefficients (ε_{max}/M^{-1} cm^{-1}) of the closed forms of thiophenophan-1-enes in CH_2Cl_2

	3b	5b	6b	7b	9b	10b	11b	12b
λ_{max}/nm	449	454	452	456	454	477	456	448
ε_{max}/M^{-1} cm^{-1}	5400	3300	5300	4900	7000	6400	4800	5700

Those of **7b** and **10b** were longest among their groups (without or with sulfur atoms on their bridges). Since there are four heteroatoms on the chains of **7b** and **10b** and the chains become more flexible and can avoid steric hindrance, these lengths could be suitable for good π conjugation in the closed forms. The molar extinction coefficients of the closed forms were estimated from the absorption spectra and HPLC analyses of the same solutions to obtain the concentrations of the closed forms. The molar extinction coefficient of **5b** was the smallest and that of **9b** was the largest.

Table 2 shows the quantum yields for the photocyclization reactions of the open forms of thiophenophan-1-enes in CH_2Cl_2 and those for the ring opening reactions of the closed forms in $CHCl_3$.[10] In contrast with dithienylethenes, the conformational exchange of thiophenophan-1-enes is suppressed by the steric hindrance between the inner substituents and the opposite thiophene rings. Hence the photoinactive parallel conformation can be excluded during purification. It is reported that the quantum yields for photocyclization reactions of the open forms of dithienylethenes in the crystalline state are dependent on the distance between the two reactive carbon atoms.[5] When the distance is longer than 4 Å, the photocyclization scarcely occurred.[5] Then the distances of the reactive carbon atoms of the most stable conformations of the open forms of thiophenophan-1-enes were estimated with AM1-MOPAC97[11] and the results are also summarized in Table 2. The energy minimized structures of **3a** and **7a** calculated on AM1 in MOPAC97 are shown in Fig. 2. The quantum yields of the small thiophenophan-1-enes such as **3a** (0.67) and **5a** (0.70) were higher than that of the reference **12a** (0.45). The distances between their reactive carbon atoms were estimated as 3.0 and 3.6 Å for **3a** and **5a**, respectively. Moreover, their conformations were fixed to anti-parallel, which is photoreactive. Then it seems that the quantum yields were dependent on their distances in such thiophenophan-1-enes with rigid structures. On the other hand, the quantum yields for photocyclization of thiophenophan-1-enes having flexible long chains such as **6a** and **9–11a** were similar to that of the reference **12a** and their values were below 0.50. The distances between the reactive carbon atoms of their most stable conformations were estimated as 4.3–5.0 Å which appears too long to undergo the photocyclization reaction efficiently.[5] However, since these large thiophenophan-1-enes are more flexible than small thiophenophan-1-enes such as **3a** and **5a**, it becomes easy for the reactive carbon atoms to access each other in solution. Moreover, the electronic circumstances of these thiophenophan-1-enes and the dithienylethene are similar. Thus their photocyclization reactions took place similarly to dithienylethene. In the case of **7a**, the distance is only 3.6 Å due to its structure and the reactive carbon atoms approach together. Thus, the quantum yield of **7a** is higher than those of the other flexible thiophenophan-1-enes. It seems that there are three groups in the quantum yields for the photo ring-opening (photobleaching, cycloreversion) reactions of the closed forms. Those of **3b**, **9b**, and **12b** were similar and the values were low at around 0.09. In contrast, the most reactive set contains **5b**, **7b** and **10b**, with values in the range 0.29–0.36. The observed differences are due to different potential energy surfaces,[12] however, we could not find any correlation between the quantum yields and the structures.

Table 2 Quantum yields for the photocyclization reactions of the open forms (at 313 nm, in CH_2Cl_2), the reactive C–C distances of the open forms, and quantum yields for photo ring-opening reactions of the closed forms (at 517 nm in $CHCl_3$)

Thiophenophan-1-ene	3	5	6	7	9	10	11	12
Photocyclization	0.67	0.70	0.42	0.66	0.49	0.47	0.42	0.45
C–C distance[a]/Å	3.0	3.6	4.3	3.6	4.7	4.5	5.0	—
Photo ring-opening	0.09	0.36	0.24	0.29	0.08	0.34	0.20	0.09

[a] Calculated on AM1-MOPAC97.

In the case of [2.*n*]metacyclophan-1-enes, the thermal stability of the closed forms were dependent on the chain length (*n*).[6] When the chain length of the metacyclophan-1-ene is small as in [2.2]metacyclophan-1-ene, the thermal ring opening reaction of the closed form is slower than for longer

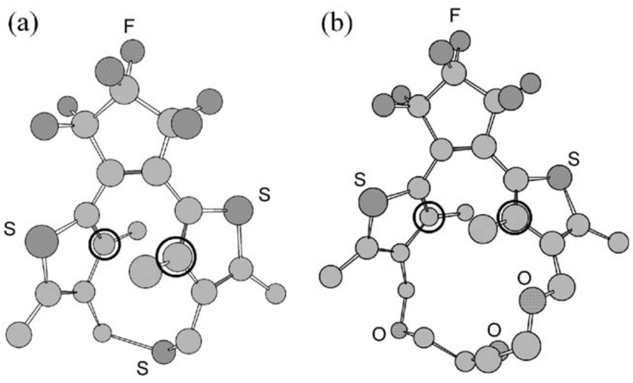

Fig. 2 Energy minimized structure of (a) **3a** and (b) **7a**. The reactive carbon atoms are circled.

Table 3 Kinetic parameters for the thermal ring opening reaction of the closed form of thiophenophan-1-enes

Closed form	**3b**	**5b**	**6b**	**7b**	**9b**	**10b**	**11b**	**12b**
A/s^{-1}	5.1×10^3	2.9×10^2	3.4×10^{14}	1.9×10^{10}	4.8×10^8	3.7×10^7	2.0×10^{10}	5.8×10^7
$E_a/\mathrm{kJ\ mol}^{-1}$	58	41	140	110	100	85	102	93
Half-life at 293 K/s	3.0×10^6	4.7×10^4	1.3×10^{10}	1.5×10^9	9.8×10^8	2.6×10^7	5.4×10^7	7.3×10^8

chains. This is due to the steric energies of the metacyclophan-1-enes. Since the small metacyclophan-1-enes, the open form, have large steric energy due to the steric repulsion of the inner substituents and the opposite benzene rings, the difference in the energy of formation between the aromatic open form and the non-aromatic closed form is small, and according to the Horiuti–Polanyi–Evans rule,[13] the activation energy becomes larger. The thermal stability of the closed forms of the synthesized thiophenophan-1-enes have been estimated, with results summarized in Table 3, while rates for the thermal ring-opening reaction were measured in toluene or decalin at various temperatures. It was found that the decay curves followed first-order kinetics. An Arrhenius plot of the thermal ring-opening reaction of **6b** is shown in Fig. 3 as example. Some dithienylethenes are known as thermally irreversible photochromic compounds.[2] In the thiophenophan-1-ene family, the thermal stability of compound **3b** having the shortest chain was quite low and the activation energy for the ring-opening reaction was only 58 kJ mol^{-1}. Also the closed form of the small thiophenophan-1-ene **5b** was thermally unstable with small activation energy. The pre-exponential factors of these thermal reactions were small and the temperature dependences for thermal reactions were low. The half-lives of these closed forms were 35 days and 13 h at 293 K, respectively. On the other hand, the closed form of thiophenophan-1-ene having three oxygen atoms on its bridge (**6b**) was extraordinarily stable and its activation energy was largest and the half-life was 422 years at 293 K. These values are better than those of the dithienylethene **12b**. Since the electronic circumstances of these closed forms are similar, these differences in thermal stabilities are owing to the difference in their steric circumstances. Different from the metacyclophan-1-enes composed of benzene rings, the closed forms of the small thiophenophan-1-enes were less thermally stable than those of the large thiophenophan-1-enes.

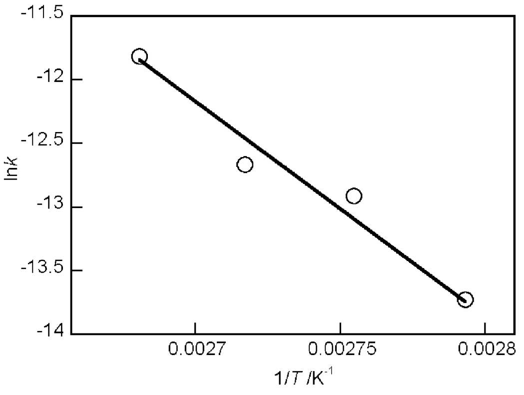

Fig. 3 Arrhenius plot for thermal ring opening reaction of **6b**.

Conclusion

Thiophenophan-1-enes having various chain lengths have been synthesized and their photochromic properties were investigated. The absorption maxima, the quantum yields for photocyclization reactions and photo ring-opening reactions, and the thermal stability of the closed forms were dependent on their chain length. These phenomena were due to the difference in their steric circumstances. Generally the smaller thiophenophan-1-enes such as **3** and **5** have different photochromic features from those of dithienylethenes, showing high quantum yields for photocyclization and low thermal stability of the closed forms, since they have rigid structures. In contrast, the larger thiophenophan-1-enes have similar features to those of dithienylethenes, with high thermal stability of the closed forms. The photochromic properties can thus be tuned by changing the bridge length of thiophenophan-1-enes. Among them, the closed form of a thiophenophan-1-ene having three oxygen atoms on its bridge **6b** was extraordinarily stable so as to allow us to utilize the material for photomemory applications.

Experimental

General remarks

All melting points were uncorrected. Absorption spectra were measured with an absorption spectrophotometer (Hitachi, U-3310). ^{1}H NMR spectra were recorded on a FT-NMR, JEOL-AL300, spectrometer at 300 MHz. All chemical shifts are given in ppm relative to TMS and coupling constants in Hz. Mass spectra were taken JEOL JMS-GCMATE II (EI, 70 eV). Photoirradiation was carried out by using a 500 W super high-pressure mercury lamp and monochromic light was obtained by passing it through a monochromator (JOBIN YVON). The quantum yields were determined by a similar manner to that described in the literature.[8] The samples were not degassed. Nomenclatures of thiophenophan-1-enes were referred to the IUPAC Phane Nomenclature.[14]

Syntheses

$2^3,2^3,2^4,2^4,2^5,2^5$-Hexafluoro-$1^3,1^5,3^3,3^5$-tetramethyl-5-thia-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclohexaphane (3a). A solution of 0.20 g of bis(chloromethyl)dithienylethene **2a**[6] (0.40 mmol) in 200 ml of ethanol was irradiated with UV light to afford a solution of the closed form **2b**. To a refluxing solution of 120 mg of $Na_2S{\cdot}9H_2O$ (0.50 mmol) in 1000 ml of EtOH, the solution of **2b** was added dropwise for 12 h. The solvent was evaporated *in vacuo* and CH_2Cl_2 and brine were added to the residue. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was subjected to silica-gel column chromatography. The hexane–chloroform (10 : 1) eluate was evaporated *in vacuo* and recrystallization of the residue from MeOH afforded 45 mg of **3a** in 25% yield; pale yellow plates; mp 163.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.36 (6H, s), 2.45 (6H, s), 3.50 (2H, d, J = 15 Hz), 3.98 (2H, d, J = 15 Hz). HRMS (EI): m/z = 454.0318 (M^+). Calc. for $C_{19}H_{16}F_6S_3$: 454.0316. Found: C, 50.00; H, 3.50. Calc. for $C_{19}H_{16}F_6S_3$: C, 50.21; H, 3.55%.

5-(3,3,4,4,5,5-Hexafluoro-2-(4-(iodomethyl)-3,5-dimethyl-(2-thienyl))cyclopent-1-enyl)-3-iodomethyl-2,4-dimethylthiophene (4). To a solution of 1.0 g of **2a**[6] (2.03 mmol) in 50 ml of acetone was added 1.52 g of NaI (10.2 mmol) and the solution was refluxed for 3 h. The solvent was evaporated *in vacuo* and 50 ml of chloroform was added to the residue. The precipitate was filtered off and the solvent was evaporated *in vacuo*. Recrystallization of the residue from hexane–chloroform afforded 1.0 g of **4** (1.14 mmol) in 70% yield; pale yellow plates; mp 168.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.69 (6H, s), 2.49 (6H, s), 4.19 (4H, s). HRMS (EI): m/z = 675.8717 (M^+). Calc. for $C_{19}H_{16}I_2F_6S_2$: 675.8688.

5,8-Dioxa-$2^3,2^3,2^4,2^4,2^5,2^5$-hexafluoro-$1^3,1^5,3^3,3^5$-tetramethyl-tetramethyl-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclononaphane (5a). To a refluxing mixture of 144 mg of NaH (6.0 mmol) in 40 ml of dried THF, a solution of 680 mg of **4** (1.0 mmol) and 62 mg of ethylene glycol (1.0 mmol) in 50 ml of THF was added dropwise for 5 h. The solution was refluxed overnight and the solvent was evaporated *in vacuo*. The residue was poured into brine and AcOEt was added. The organic phase was washed with brine and was dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was subjected to a silica-gel column chromatography. Recrystallization of the $CHCl_3$ eluate from MeOH afforded 40 mg of **5a** (0.084 mmol) in 8.4% yield; yellow prisms (MeOH); mp 135.1 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.54 (6H, s), 2.44 (6H, s), 3.13–3.20 (2H, m), 3.36–3.44 (2H, m), 4.28 (2H, d, J = 13 Hz), 4.44 (2H, d, J = 13 Hz), MS (EI): m/z = 482 (M^+). Found: C, 52.71; H, 4.36. Calc. for $C_{21}H_{20}F_6O_2S_2$: C, 52.27; H, 4.18%.

$2^3,2^3,2^4,2^4,2^5,2^5$-Hexafluoro-$1^3,1^5,3^3,3^5$-tetramethyl-5,8,11-trioxa-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclododecaphane (6a). Compound **6a** was obtained from **4** and diethylene glycol by a similar manner to that described for the synthesis of **5a**. The yield was 15%; pale yellow plates (MeOH–$CHCl_3$); mp 215.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.61 (6H, s), 2.47 (6H, s), 3.42 (4H, t, J = 8.4 Hz), 3.54 (4H, t, J = 8.4 Hz), 4.34 (4H, s). HRMS (EI): m/z = 526.1078 (M^+). Calc. for $C_{23}H_{24}F_6O_3S_2$: 526.1071. Found: C, 52.48; H, 4.58. Calc. for $C_{23}H_{24}F_6O_3S_2$: C, 52.46; H, 4.59%.

$2^3,2^3,2^4,2^4,2^5,2^5$-Hexafluoro-$1^3,1^5,3^3,3^5$-tetramethyl-5,8,11,14-tetraoxa-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclopentadecaphane (7a). Compound **7a** was obtained from **4** and triethylene glycol by a similar manner to that described for the synthesis of **5a**. The yield was 6.3%; pale orange needles (MeOH–$CHCl_3$); mp 168.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.67 (6H, s), 2.46 (6H, s), 3.50 (4H, t, J = 10.2 Hz), 3.62 (4H, s), 3.63 (4H, t, J = 10.2 Hz), 4.36 (4H, s). MS (EI): m/z = 570 (M^+). Found: C, 52.56; H, 4.92. Calc. for $C_{25}H_{28}F_6O_4S_2$: C, 52.61; H, 4.95%.

5,11-Dithia-$2^3,2^3,2^4,2^4,2^5,2^5$-hexafluoro-8-oxa-$1^3,1^5,3^3,3^5$-tetramethyl-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclododecaphane (9a). To a refluxing solution of 0.42 g of KOH (7.5 mmol) and 0.14 g of $NaBH_4$ in 250 ml of EtOH was added a solution of 0.73 g of **8**[6] (1.5 mmol) and 0.62 g of diethylene glycol ditosylate (1.5 mmol) in 50 ml of THF for 5 h and additionally the solution was refluxed for 24 h. The solvent was evaporated *in vacuo* and CH_2Cl_2 and brine were added to the residue. The organic phase was washed with brine and was dried over $MgSO_4$. The solvent was evaporated and the residue was subjected to the silica-gel column chromatography. Recrystallization of the $CHCl_3$–MeOH eluate from MeOH afforded 60 mg of **9a** in 7.1% yield; yellow prisms (MeOH); mp 126.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.86 (6H, s), 2.44 (6H, s), 2.56 (4H, t, J = 13.5 Hz), 3.40 (4H, t, J = 13.5 Hz), 3.60 (4H, s). MS (EI): m/z = 558 (M^+). Found: C, 49.15; H, 4.23. Calc. for $C_{23}H_{24}F_6OS_4$: C, 49.45; H, 4.33%.

8,11-Dioxa-5,14-dithia-$2^3,2^3,2^4,2^4,2^5,2^5$-hexafluoro-$1^3,1^5,3^3,3^5$-tetramethyl-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclopentadecaphane (10a). Compound **10a** was obtained from **8** and triethylene glycol ditosylate by a similar manner to that described for the synthesis of **9a**. The yield was 18%; yellow prisms (MeOH); mp 124.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.60 (6H, s), 2.45 (6H, s), 2.63 (4H, t, J = 12 Hz), 3.57 (4H, s), 3.69 (4H, t, J = 12 Hz), 3.70 (4H, s). MS (EI): m/z = 602 (M^+). Found: C, 49.83; H, 4.72. Calc. for $C_{25}H_{28}F_6O_2S_4$: C, 49.82; H, 4.68%.

5,17-Dithia-$2^3,2^3,2^4,2^4,2^5,2^5$-hexafluoro-$1^3,1^5,3^3,3^5$-tetramethyl-8,11,14-trioxa-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclooctadecaphane (11a). Compound **11a** was obtained from **8** and tetraethylene glycol ditosylate by a similar manner to that described for the synthesis of **9a**. The yield was 9.9%; yellow prisms (MeOH–H_2O); mp 106.0 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.65 (6H, s), 2.46 (6 H, s), 2.59 (4 H, t, J = 13 Hz), 3.57–3.70 (16 H, m). MS (EI): m/z = 646 (M^+). Found: C, 50.51; H, 4.95. Calc. for $C_{27}H_{32}F_6O_3S_4$: C, 50.14; H, 4.99%.

5-(3,3,4,4,5,5-Hexafluoro-2-(4-(methoxymethyl)-3,5-dimethyl-(2-thienyl))cyclopent-1-enyl)-2,4-dimethyl(3-thienyl))methoxymethane (12a). To a solution of sodium methoxide (8.8 mmol) in 30 ml of methanol, **2** (200 mg, 0.43 mmol) was added and the solution was stirred for 3 h at room temperature. The mixture was poured into brine and extracted with diethyl ether. The solution was dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was subjected silica gel column chromatography and recrystallization of the chloroform eluate from hexane afforded 26 mg of **12a** in 12% yield; brown prisms (hexane); mp 94.5 °C. δ_H(300 MHz; $CDCl_3$; TMS) 1.70 (6H, s), 2.46 (6H, s), 3.24 (6H, s), 4.23 (4H, s). MS (EI): m/z = 484 (M^+). Found: C, 52.23; H, 4.66. Calc. for $C_{21}H_{22}O_2F_6S_2$: C, 52.06; H, 4.58%.

Kinetic measurements. The activation energies and the pre-exponential factors for the thermal ring-opening reactions were estimated by the Arrhenius plots of the rate constants of the thermal ring-opening reactions of the closed form in the dark at several temperatures.

Acknowledgements

The authors thank the GDRI PHOENIX, CNRS for partial financial support and also are grateful to Zeon Co. Ltd. for providing perfluorocylopentene.

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