Preparation of [2.2]-*para*-, *meta*-, and *ortho*-cyclophanes containing a 1,3-cyclohexano group

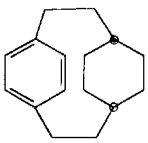
Shaw-Tao Lin,* Fu-May Yang and David W. Liang

Department of Applied Chemistry, Providence University, Sha-Lu, Taichung Hsien, Taiwan, 433, ROC

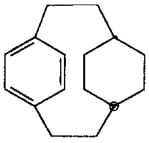
Received (in Cambridge) 21st January 1999, Accepted 20th April 1999

[2.2]-*para*-, *meta*-, and *ortho*-Cyclophanes containing a 1,3-cyclohexane ring bridged with two carbons were prepared through a coupling reaction to form dithiacyclophane, followed by oxidation to yield the sulfone and then pyrolysis.

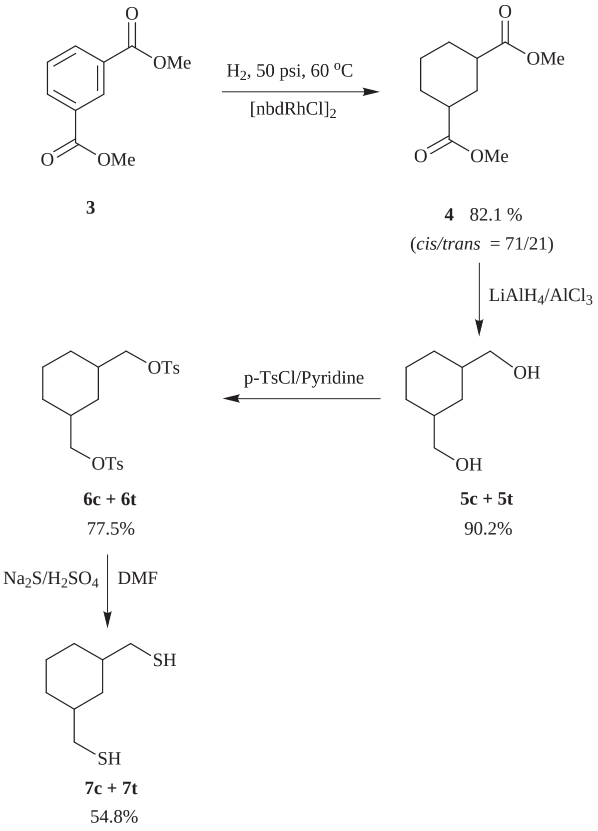
During the past three decades, cyclophanes have been studied extensively. Recent reviews have summarised the preparations, the properties, and the applications of various cyclophanes.[1] The majority of pure hydrocarbon cyclophanes that have been reported contain two arene rings.[1] It is interesting for comparison to obtain compounds which contain a cyclohexane ring. In previous studies, we have prepared the paracyclophanes bearing a benzene ring and a *cis-/trans*-cyclohexane ring bridged with two carbons, *i.e.*, 3*a*,4,5,6*e*,7,8-hexahydro[2.2]-paracyclophane (**1**, *cis*-1,4-1,4),[2] 3*e*,4,5,6*e*,7,8-hexahydro[2.2]-paracyclophane (**2**, *trans*-1,4-1,4).[3] Compound **1** was reduced using Li–NH_3 to form a diene, which is different from that obtained from the catalytic hydrogenation of [2.2]paracyclophane. On the other hand, the methine hydrogen in the rigid structure of compound **2** appears at high field (δ −2.36) in the NMR spectrum because of its placement over the π-cloud of the benzene ring. In this work, we report the synthesis of their analogues, prepared from coupling reactions of 1,3-bis(mercaptomethyl)cyclohexanes and α,α′-dichloroxylenes followed by oxidation and pyrolysis, for spectroscopic comparison and conformational analysis.



1



2

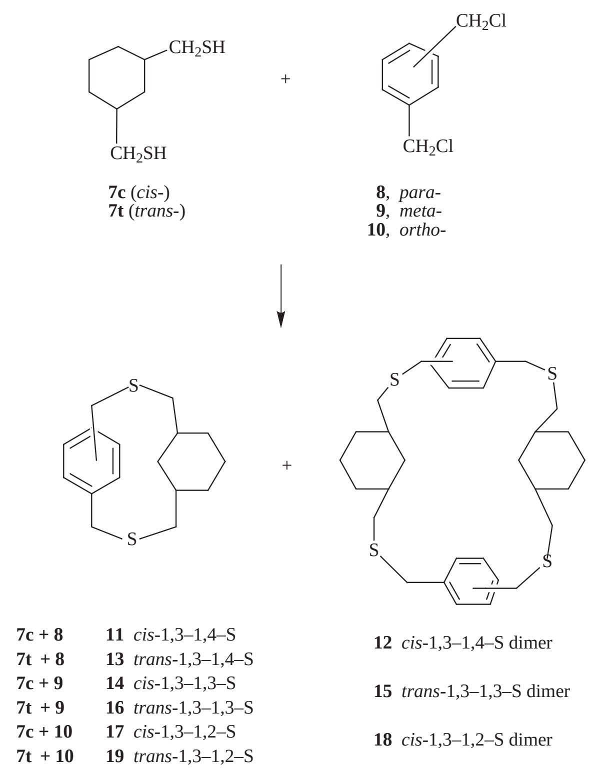


Scheme 1

Results and discussion

Hydrogenation of dimethyl isophthalate (**3**) using $(nbdRhCl)_2$, (nbd = norbornadiene) as a catalyst yields a mixture of *cis*- and *trans*-isomers of dimethyl cyclohexane-1,3-dicarboxylate (**4**) in a ratio of 71 : 29 (based on NMR analysis).[4] The mixture of isomers was reduced using $LiAlH_4$ in the presence of $AlCl_3$ to give the corresponding alcohols (**5**) in good yields.[5] Further reaction with toluene-*p*-sulfonyl chloride resulted in the ditosylates **6**, which were treated with NaSH and H_2SO_4 in DMF to give 1,3-bis(mercaptomethyl)cyclohexanes **7** as an inseparable mixture of *trans*- and *cis*-isomers.[3] The coupling reaction of α,α′-dichloroxylene **8**, **9**, **10** and dithiols **7** was carried out in an alcoholic NaOH solution, using the high dilution technique.[6] The resultant solution was concentrated and separated chromatographically to afford the corresponding dithiacyclophanes **11**, **13**, **14**, **16**, **17**, and **19** containing cyclohexane in either the *cis*- or *trans*-form, as well as the dimers **12**, **15**, and **18**.

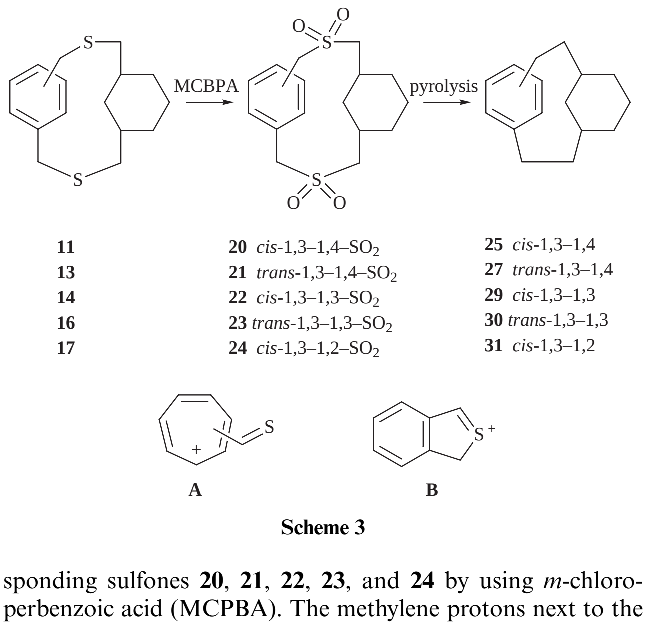
The coupling of α,α′-dichloro-*p*-xylene and *cis*-1,4-bis(mercaptomethyl)cyclohexane yielded only one compound containing one unit each of benzene and cyclohexane (called monomer in this work).[2] The *trans*-counterpart yielded monomer along with dimer and trimer due to the higher strain energy for the monomer.[3] In this series, the coupling reaction from *cis*-bis(sulfide) (**7c**) and α,α′-dichloroxylene (**8**, **9**, **10**) yielded a dimer, while the *trans*-bis(sulfide) (**7t**) resulted in the monomer only. One of the methylene protons between the bridgeheads in the *cis*-1,3-1,4-S **11** and *cis*-1,3-1,3-S **14** appears at relatively high-field ($\delta \sim -0.7$ ppm). It suggests that the *cis*-conformation of the cyclohexane ring forces the proton to face the benzene where it is shielded by the benzene ring current.[7] The fragmentations of the monomers **14**, **16**, **17**, and **19** in this series of compounds display a characteristic fragment of 135 amu which corresponds to C_8H_7S. This fragment ion is a base peak for the dithiacyclophanes, which resulted from the coupling reaction of *o*-dichloroxylene and 1,3-bis(mercaptomethyl)cyclohexane (*i.e.*, compounds **17**, **19**), and is a relatively small intensity peak



Scheme 2

from their *meta*-counterparts **14** and **16**. However, their *para*-counterparts **11** and **13** do not yield a fragment of 135 amu. The C_8H_7S fragment could be a ring structure with tropylium ion (**A**) or a five-membered ring (**B**) from the *ortho*-product, or ion **B** from the *meta*-product.

Compounds **11**, **13**, **14**, **16**, and **17** were oxidized to the corresponding sulfones **20**, **21**, **22**, **23**, and **24** by using *m*-chloroperbenzoic acid (MCPBA). The methylene protons next to the SO_2 group shift down-field by 0.4–0.8 ppm. The coupling constants are even larger than the corresponding values in their precursors and this suggests that a change in the H–C–H angle results from the formation of the sulfones.



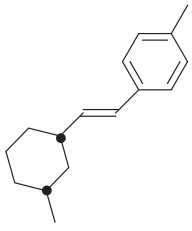
Scheme 3

Table 1 Yields of the cyclophanes from pyrolysis and their calculated strain energies (MM291)[14] and heat formations (PM3).[a,15]

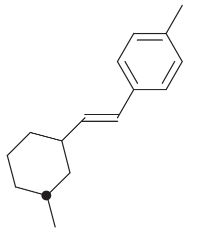
Product	Yield (%)	Strain energy/ kcal mol^{-1}	ΔH_f^o/kcal mol^{-1}
cis-1,4-1,4 **1**	14.2	52.42	22.29
trans-1,4-1,4 **2**	18.5	52.13	22.30
cis-1,3-1,4 **25**	34.5	45.15	20.54
trans-1,3-1,4 **27**	26.9	43.32	29.76
cis-1,3-1,3 **29**	52.0	28.46	0.67(a); 3.80(s)
trans-1,3-1,3 **30**	29.2	55.34	0.68(a); 3.25(s)
cis-1,3-1,2 **31**	62.0	23.81	−1.98(a); −0.60(s)
trans-1,3-1,2	—	73.65	−1.17(a); 6.10(s)

[a] Conformation of the cyclohexane in the cyclophanes was assumed to be a chair form; a and s represent *anti*- and *syn*-conformation.

A number of methods can be applied for the extrusion of SO_2 along with the formation of either C–C or C=C bonds. The Ramberg–Bäcklund reaction[8] and its modification methods[9] yielded products with the formation of double bonds from the extrusion of SO_2 from 2,11-dithia-4*a*,5,6,7*e*,8,9-hexahydro[3.3]-paracyclophane-2,2,11,11-tetraoxide.[2] This resultant compound was converted to a hyperstable monoene[10] under the catalytic hydrogen transfer reaction in a mixture of formic acid and triethylamine with 10% Pd/C as a catalyst. The combination of Stevens rearrangement and Hofmann elimination to transform sulfide linkages to carbon–carbon double bonds followed by catalytic hydrogenation is an alternative route.[11] The high strain characteristic of this series may result in a further hydrogenation as previously noted.[2] Pyrolysis is a direct process for the formation of C–C bonds from the sulfone series.[12] This process was employed for the preparation of compounds **25**, **27**, **29**, **30**, and **31**.[13] Hence, the corresponding sulfones **20**–**24** were pyrolyzed at 400 °C for 20 min, and then at 500 °C for 30 min at 0.3–0.4 Torr. During the process, the crude products were collected in a cold-trap at −196 °C. After column chromatography, a series of the cyclophanes were isolated with the accompanying ring-opened compound, *E*-1-(*cis*-3-methylcyclohexyl)-2-(4-tolyl)ethylene (**26**) and *E*-1-(*trans*-3-methylcyclohexyl)-2-(4-tolyl)ethylene (**28**) from compounds **20** and **21** which contained a *cis*-cyclohexane ring. The lower yields in the sulfur dioxide extrusion are not only due to the flexibility of the cyclohexane moiety, but more importantly, due to the high ring strain as shown in Table 1.

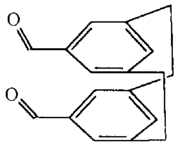


26

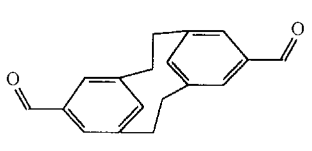


28

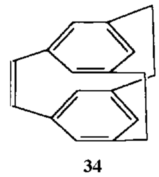
The [2.2]metacyclophanes have been reported as a *syn*-form.[16] Although *syn*-cyclophane **32** was prepared from the oxidation of 1,3,5-tris-bridged cyclophane **34** with OsO_4, it was readily isomerized to an *anti*-form **33** at room temperature.[17] In the same manner, our prepared compounds containing *meta*- or *ortho*-xylene with a cyclohexane ring would yield the *anti*-



32



33



34

forms. It is consistent with the calculated results which reveal that the *anti*-forms possess lower heats of formation. *anti*-Metacyclophanes are normally easily recognized by ^{1}H NMR, since the internal hydrogens of the cyclohexano group are strongly shielded because of their placement over the π-cloud of the opposite benzene ring.[18] The degree of the shielding depends on the distance between the hydrogens and the center of the benzene ring.

Conclusion

Hexahydroparacyclophane can be prepared through a coupling of α,α′-dichloroxylenes and *trans*-1,4-bis(mercaptomethyl)cyclohexane followed by oxidation and pyrolysis. The fact that hexahydro[2.2]paracyclophane was obtained in low yield is due to the high ring strain of the cyclohexane ring and the lability of the nonbenzylic radical intermediates. The high field-shifted resonance of one of the methylene protons between the bridgeheads in **11** and **14** results from the *cis*-conformation of cyclohexane. The higher ring strain of the *cis*-conformation leads to the formation of dimers **12**, **15**, and **18**.

Experimental

General

^{1}H NMR spectra were recorded at 250 MHz, and ^{13}C NMR at 62.86 MHz at ambient temperature. Chemical shifts for the samples in deuteriochloroform solution are reported in δ units relative to tetramethylsilane. EI mass spectra were obtained on a JEOL JMS DX-300 double-focusing mass spectrometer at the ionization potentials of 70 eV. Samples were introduced *via* a direct insertion probe.

IUPAC names for the cyclophanes used in this work (abbreviated names used in this paper are given in parentheses): **1** *cis*-tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),10,13-triene (*cis*-1,4-1,4); **2** *trans*-tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),10,13-triene (*trans*-1,4-1,4); **11** *cis*-3,11-dithiatricyclo[11.2.2.1^{5,9}]octadeca-1(15),13,16-triene (*cis*-1,3-1,4-S); **12** *cis*-3,11,18,26-tetrathiapentacyclo[26.2.2.2^{13,16}.1^{5,9}.1^{20,24}]hexatriacenta-1(30),13,15,28,31,33-hexaene (*cis*-1,3-1,4-S dimer); **13** *trans*-3,11-dithiatricyclo[11.2.2.1^{5,9}]octadeca-1(15),13,16-triene (*trans*-1,3-1,4-S); **14** *cis*-3,11-dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),13,15-triene (*cis*-1,3-1,3-S); **15** *cis*-3,11,19,27-tetrathiapentacyclo[27.3.1.1^{5,9}.1^{13,17}.1^{21,25}]hexatriaconta-1(33),13(35),14,16,29,31-hexaene (*cis*-1,3-1,3-S dimer); **16** *trans*-3,11-dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),13,15-triene (*trans*-1,3-1,3-S); **17** *cis*-3,12-dithiatricyclo[12.3.1.0^{5,10}]octadeca-5,7,9-triene (*cis*-1,3-1,2-S); **18** *cis*-3,12,20,29-tetrathiapentacyclo[29.3.1.1^{14,18}.0^{5,10}.0^{22,27}]hexatriacenta-5,7,9,22,24,26-hexaene (*cis*-1,3-1,2-S dimer); **19** *trans*-3,12-dithiatricyclo[12.3.1.0^{5,10}]octadeca-5,7,9-triene (*trans*-1,3-1,2-S); **20** *cis*-3λ^6,11λ^6-dithiatricyclo[11.2.2.1^{5,9}]octadeca-1(15),13,16-triene-3,3,11,11-tetrone (*cis*-1,3-1,4-SO$_2$); **21** *trans*-3λ^6,11λ^6-dithiatricyclo[11.2.2.1^{5,9}]octadeca-1(15),13,16-triene-3,3,11,11-tetrone (*trans*-1,3-1,4-SO$_2$); **22** *cis*-3λ^6,11λ^6-dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),13,15-triene-3,3,11,11-tetrone (*cis*-1,3-1,3-SO$_2$); **23** *trans*-3λ^6,11λ^6-dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),13,15-triene-3,3,11,11-tetrone (*trans*-1,3-1,3-SO$_2$); **24** *cis*-3λ^6,12λ^6-dithiatricyclo[12.3.1.0^{5,10}]octadeca-5,7,9-triene-3,3,12,12-tetrone (*cis*-1,3-1,2-SO$_2$); **25** *cis*-tricyclo[9.2.2.1^{4,8}]hexadeca-1(13),11,14-triene (*cis*-1,3-1,4); **27** *trans*-tricyclo[9.2.2.1^{4,8}]hexadeca-1(13),11,14-triene (*trans*-1,3-14); **29** *cis*-tricyclo[9.3.1.1^{4,8}]hexadeca-1(15),11,13-triene (*cis*-1,3-1,3); **30** *trans*-tricyclo[9.3.1.1^{4,8}]hexadeca-1(15),11,13-triene (*trans*-1,3-1,3); **31** *cis*-tricyclo[10.3.1.0^{4,9}]hexadeca-4,6,8-triene (*cis*-1,3-1,2).

Dimethyl cyclohexane-1,3-dicarboxylate (4c + 4t)

A mixture of *cis*- and *trans*-dimethyl cyclohexane-1,3-dicarboxylate was obtained from the hydrogenation of dimethyl isophthalate (12.24 g, 63 mmol) in a mixture of cyclohexane (150 mL) and buffer solution (50 mL, NaH_2PO_4–Na_2HPO_4; pH 7.4) using $(nbdRhCl)_2$ (0.29 g) as a catalyst and $(Bu)_4N\cdot HSO_4$ (1.69 g) at 60 °C and 50 psi of H_2 for 24 h. After extraction with ethyl acetate and drying over $MgSO_4$, vacuum distillation gave 10.05 g (82.1% yield), bp 129.0–131.5 °C/0.1 Torr (lit.,[4] 129.5–130.5 °C/0.1 Torr). The product contained the *cis*- : *trans*-forms in a ratio of about 71 : 29 based on ^{1}H NMR analysis.

cis-/*trans*-Cyclohexane-1,3-dimethanol (5c + 5t)

The above product (30.0 g, 0.15 mmol) in ether solution (500 mL) was treated with $LiAlH_4$ (7.2 g, 0.453 mol) and $AlCl_3$ (20.0 g, 0.176 mol) in 500 mL of dry ether in an ice-bath. After the mixture was stirred at ambient temperature for 2 h, NaOH (10%) was added slowly to decompose the excess of reducing agent. The resulting mixture was filtered through a layer of Celite. After the ether was removed, compounds (**5c** + **5t**) were spectroscopically pure and used for further preparation, 19.4 g (90.2%); mp 52.0–54.5 °C (lit.,[19] 54–55 °C).

cis-/*trans*-1,3-Bis(tosyloxymethyl)cyclohexane (6c + 6t)

Toluene-*p*-sulfonyl chloride (162 g, 0.84 mol) was added to 1,3-bis(hydroxymethyl)cyclohexane (*cis*/*trans* 71/29, 55.3 g, 0.38 mol) in 300 mL of pyridine at 0–5 °C. The mixture was refrigerated for 18 h and poured into 1000 mL of ice–water. The solution was neutralized with 1 M HCl solution to pH 7 and filtered to give compounds **6c** + **6t** as a white solid, 133.1 g (77.5%); mp 96.0–98.0 °C (lit.,[20] mp 99–100 °C). ^{1}H NMR δ 0.90 (m, 6H), 1.24 (m, 4H), 2.45 (s, 6H), 3.79 (m, 4H), 7.34 (d, 4H, *J* 8.0 Hz), 7.76 (d, 4H, *J* 7.9 Hz); IR (KBr) 1350, 1178 (ν_{SO_2}) cm^{-1}; EIMS *m*/*z* (rel. int.) 452 (M^+, 1.0), 109 (100).

cis-/*trans*-1,3-Bis(mercaptomethyl)cyclohexane (7c + 7t)

A solution of **6c** and **6t** (27.6 g, 0.061 mol) in 150 mL of DMF was added over 1 h to a mixture of 80.8 g (0.34 mol) of $Na_2S\cdot 9H_2O$, 9.2 mL of H_2SO_4, and 200 mL of DMF at 70 °C. After the mixture was stirred for 3 h at 70 °C, it was poured over 500 mL of ice, extracted with pentane (3 × 50 mL), dried over $MgSO_4$, filtered, and vacuum distilled (63.2–65.1 °C/0.3 Torr) to give 32.8 g (54.8%) of thiols (**7c** + **7t**); ^{1}H NMR δ 0.90 (m, 6H), 1.22 (m, 4H), 1.36 (t, 2H, *J* 10.0 Hz), 2.52 (br 4H); IR (KBr) 2550 (ν_{SH}), 1240 (ν_{CS}) cm^{-1}; EIMS *m*/*z* (rel. int.) 176 (M^+, 31), 95 (100); Anal. Calcd. for $C_8H_{16}S_2$: C, 54.49; H, 9.15. Found: C, 54.53; H, 9.02%.

cis-1,3-1,4-S 11, *trans*-1,3-1,4-S 13

A solution of compounds **7c** and **7t** (1.24 g, 7.0 mmol) and α,α′-dichloro-*p*-xylene **8** (1.21 g, 7.0 mmol) was added over a period of 70 h to a solution of NaOH (0.6 g, 1.5 mmol) in 95% ethanol (200 mL), using a high dilution technique. The solution was refluxed for an additional 2 h and then vacuum evaporated to give a viscous residue. The residue was extracted with CCl_4 (3 × 20 mL), dried over $MgSO_4$, filtered, and vacuum evaporated to give a waxy residue. The residue was separated chromatographically on silica gel with CH_2Cl_2–*n*-hexane (2 : 3 v/v) as an eluent to yield *cis*-1,3-1,4-S **11**, *cis*-1,3-1,4-S dimer **12** and *trans*-1,3-1,4-S **13**.

Compound **11**, white solid, mp 125.9–127.2 °C; yield 1.13 g (57.8%); ^{1}H NMR δ −0.63 (q, 1H, *J* 12.2 Hz), 0.23 (d, 1H, *J* 13.2 Hz), 0.69 (qd, 2H, *J* 3.6, 12.2 Hz), 0.91 (m, 3H), 1.29 (d, 2H, *J* 6.8 Hz), 1.57 (m, 1H), 2.26 (dd, 2H, *J* 7.6, 14.2 Hz), 2.50 (dd, 2H, *J* 2.7, 14.6 Hz), 3.61 (s, 4H), 7.09 (d, 2H, *J* 7.9 Hz), 7.23 (d, 2H, *J* 10.9); ^{13}C NMR δ 21.2, 32.3, 32.4, 34.2, 36.7, 129.5, 130.8, 137.1; EIMS *m*/*z* (rel. int.) 278 ($M^{\cdot+}$, 31), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2$: C, 69.01; H, 7.97. Found: C, 68.94; H, 7.99%.

Compound **12**, white solid, mp 132.5–133.5 °C; yield 0.13 g (3.4%); ^{1}H NMR δ 0.49–0.54 (m, 2H), 0.76–0.79 (m, 8H), 1.19–

1.41 (m, 16H), 3.60 (d, 4H, *J* 13.5 Hz), 3.68 (dd, 2H, *J* 4.1, 13.5 Hz), 71.14–7.24 (br, 8H); EIMS (rel. int.) 556 ($M^{\cdot +}$, 7), 104 (100); Anal. Calcd. for $C_{32}H_{44}S_4$: C, 69.01; H, 7.97. Found: C, 69.10; H, 7.99%.

Compound **13**, white solid, mp 119.5–121.2 °C, yield 0.44 g (22.8%); ^{1}H NMR δ 0.40–0.72 (br, 2H), 0.78–0.84 (m, 4H), 1.10–1.12 (m, 2H), 1.47–1.60 (m, 2H), 1.92 (dd, 2H, *J* 7.1, 13.5 Hz), 2.24 (dd, 2H, *J* 6.0, 13.5 Hz), 3.60 (d, 2H, *J* 12.7 Hz), 3.78 (d, 2H, *J* 12.7 Hz), 7.09 (d, 2H, *J* 7.9 Hz), 7.43 (d, 2H, *J* 7.9 Hz); ^{13}C NMR δ 21.2, 32.3, 32.4, 34.2, 36.7, 129.5, 130.8, 137.1; EIMS *m*/*z* (rel. int.) 278 ($M^{\cdot +}$, 39), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2$: C, 69.01; H, 7.97. Found: C, 68.94; H, 7.91%.

The same procedure was used to couple dithiols (**7c** and **7t**) and α,α′-dichloro-*m*-xylene (**9**) to yield *cis*-1,3-1,3-S **14**, *cis*-1,3-1,3-S dimer **15**, and *trans*-1,3-1,3-S **16**.

Compound **14**, white solid, mp 95.5–96.1 °C, yield 1.15 g (59.1%); ^{1}H NMR δ −0.7 to −0.65 (m, 1H), 0.59–0.65 (m, 4H), 0.88–0.92 (m, 1H), 1.35–1.39 (m, 2H), 1.55–1.79 (m, 2H), 2.20 (dd, 2H, *J* 9.5, 13.9 Hz), 2.86 (dd, 2H, *J* 2.3, 13.9 Hz), 3.70 (d, 2H, *J* 14.5 Hz), 3.79 (d, 2H, *J* 14.5 Hz), 6.93 (d, 2H, *J* 7.9 Hz), 7.08 (t, 1H, *J* 7.9 Hz), 7.88 (s, 1H); ^{13}C NMR δ 26.0, 32.2, 34.6, 37.4, 38.1, 38.7, 127.2, 127.8, 132.2, 139.5; EIMS *m*/*z* (rel. int.) 278 ($M^{\cdot +}$, 59), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2$: C, 69.01; H, 7.97. Found: C, 68.92; H, 7.93%.

Compound **15**, white solid, mp 102.5–104.3 °C; yield 40 mg (1.1%); ^{1}H NMR δ 0.35–0.60 (m, 7H), 0.71–0.88 (m, 4H), 1.12–1.28 (m, 3H), 1.72–1.82 (m, 6H), 2.14–2.33 (m, 8H), 3.68 (s, 8H), 7.16–7.28 (m, 8H); EIMS *m*/*z* (rel. int.) 556 ($M^{\cdot +}$, 2), 141 (100); Anal. Calcd. for $C_{32}H_{44}S_4$: C, 69.01; H, 7.97. Found: C, 68.91; H, 7.99%.

Compound **16**, white solid; mp 91.8–92.5 °C; yield 0.56 g (29.0%); ^{1}H NMR δ 0.80–1.20 (m, 4H), 1.40–1.46 (m, 4H), 2.05 (dd, 2H, *J* 10.9, 13.1 Hz), 2.46 (dd, 2H, *J* 3.8, 13.1 Hz), 3.74 (s, 4H), 7.02 (d, 2H, *J* 7.2 Hz), 7.14 (t, 1H, *J* 7.2 Hz), 7.98 (s, 1H); ^{13}C NMR δ 23.7, 30.7, 34.9, 37.8, 40.4, 127.2, 130.6, 136.5; EIMS *m*/*z* (rel. int.) 278 ($M^{\cdot +}$, 48), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2$: C, 69.01; H, 7.97. Found: C, 68.89; H, 7.86%.

The same procedure was used for the coupling of dithiols (**7c** + **7t**) and α,α′-dichloro-*o*-xylene (**10**) to yield *cis*-1,3-1,2-S **17**, *cis*-1,3-1,2-S dimer **18**, *trans*-1,3-1,2-S **19**.

Compound **17**, white solid, mp 137.2–138.0 °C, yield 0.80 g (41%); ^{1}H NMR δ 0.95–1.12 (m, 4H), 1.45–1.66 (m, 5H), 2.17 (m, 1H), 2.37 (dd, 2H, *J* 8.1, 14.4 Hz), 2.46 (dd, 2H, *J* 3.6, 14.4 Hz), 3.78 (d, 2H, *J* 13.2 Hz), 3.99 (d, 2H, *J* 13.2 Hz), 7.16–7.29 (m, 4H); ^{13}C NMR δ 23.7, 30.7, 34.9, 37.8, 40.4, 127.2, 130.6, 136.5; EIMS *m*/*z* (rel. int.) 278 ($M^{\cdot +}$, 17), 135 (100), 104 (17); Anal. Calcd. for $C_{16}H_{22}S_2$: C, 69.01; H, 7.97. Found: C, 69.11; H, 7.91%.

Compound **18**, white solid, mp 144.5–145.0 °C; yield 0.23 g (12.1%); ^{1}H NMR δ 0.95–1.12 (m, 4H), 1.45–1.66 (m, 5H), 2.17 (m, 1H), 2.37 (dd, 2H, *J* 8.1, 14.1 Hz), 2.46 (dd, 2H, *J* 3.6, 14.4 Hz), 3.78 (d, 2H, *J* 13.2 Hz), 3.99 (d, 2H, *J* 13.2 Hz), 7.16–7.29 (m, 4H); ^{13}C NMR δ 25.9, 32.3, 32.5, 32.8, 37.5, 37.6, 38.5, 39.8, 127.3, 130.3, 136.5; EIMS *m*/*z* (rel. int.) 556 ($M^{\cdot +}$, 1), 135 (100); Anal. Calcd. for $C_{32}H_{44}S_4$: C, 69.01; H, 7.97. Found: C, 68.92; H, 8.04%.

Compound **19**, white solid, mp 68.1–69.2 °C; yield 0.16 g (8.5%); ^{1}H NMR δ 0.84 (m, 1H), 1.07–1.15 (m, 2H), 1.25–1.34 (m, 3H), 1.50–1.61 (m, 4H), 2.38 (dd, 2H, *J* 8.4, 14.7 Hz), 2.48 (dd, 2H, *J* 5.5, 14.7 Hz), 3.68 (d, 2H, *J* 14.4 Hz), 4.18 (d, 2H, *J* 14.4 Hz), 7.12 (m, 2H), 7.42 (m, 2H); ^{13}C NMR δ 21.4, 31.8, 33.0, 33.8, 34.7, 34.9, 38.2, 127.1, 130.1, 136.1; EIMS *m*/*z* (rel. int.) 278 ($M^{\cdot +}$, 8), 135 (100), 104 (12); Anal. Calcd. for $C_{16}H_{22}S_2$: C, 69.01; H, 7.97. Found: C, 68.99; H, 8.15%.

cis-1,3-1,4-SO$_2$ 20

A mixture of **11** (1.0 g, 3.48 mmol), MCPBA (70% purity, 3.52 g, 14.3 mmol) and 20 mL of $CHCl_3$ was refluxed for 16 h. The solvent was removed by evaporation. The remaining solid was stirred with saturated $Na_2S_2O_3$ (50 mL) for 10 min to quench the excess of MCPBA. The solid was collected by filtration and washed with water (30 mL × 3) and ether (30 mL × 3) to give 1.13 g (95% yield) of compound **20** as a white powder; mp 315.7–317.0 °C (decomp.); IR 1335, 1120 (ν_{SO_2}) cm^{-1}; ^{1}H NMR δ −0.72 (dd, 1H), −0.60 (q, 1H, *J* 12.1 Hz), 0.85 (qd, 2H, *J* 3.5, 12.1), 1.19 (m, 1H), 1.38–1.69 (m, 5H), 2.80 (dd, 2H, *J* 6.8, 16.2 Hz), 2.89 (dd, 2H, *J* 2.5, 16.2 Hz), 4.24 (d, 2H, *J* 14.0 Hz), 4.40 (d, 2H, *J* 14.0 Hz), 7.43 (d, 2H, *J* 8.0 Hz), 7.67 (d, 2H, *J* 8.0 Hz); ^{13}C NMR δ 25.6, 32.3, 34.7, 35.1, 61.9, 63.5, 129.8, 131.7, 132.3; EIMS *m*/*z* (rel. int.) 342 ($M^{\cdot +}$, 2), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2O_4$: C, 56.11; H, 6.47. Found: C, 55.98; H, 6.55%.

trans-1,3-1,4-SO$_2$ 21

The same procedure was used to oxidize compound **13** to yield compound **20**, as a white powder, 1.01 g (85%); mp 343.5–345.8 °C (decomp.); IR 1332, 1123 (ν_{SO_2}) cm^{-1}; ^{1}H NMR δ 0.85–1.50 (m, 6H), 1.52–1.79 (br, 4H), 2.56 (dd, 2H, *J* 5.3, 15.3 Hz), 3.00 (dd, 2H, *J* 5.9, 15.3 Hz), 4.24 (d, 2H, *J* 13.6 Hz), 4.40 (d, 2H, *J* 13.6 Hz), 7.42 (d, 2H, *J* 7.9 Hz), 7.79 (d, 2H, *J* 7.9 Hz); ^{13}C NMR δ 21.0, 28.2, 31.7, 63.1, 130.3, 131.6, 131.9; EIMS *m*/*z* (rel. int.) 342 ($M^{\cdot +}$, 1), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2O_4$: C, 56.11; H, 6.47. Found: C, 56.01; H, 6.55%.

cis-1,3-1,3-SO$_2$ 22

The same procedure was used to oxidize compound **14** to yield compound **22**, as a white powder, 1.11 g (93%); mp 350.0–351.4 °C (decomp.); IR 1332, 1123 (ν_{SO_2}) cm^{-1}; ^{1}H NMR δ 0.13–1.66 (m, 9H), 2.10 (m, 1H), 2.94 (br, 4H), 4.31 (d, 2H, *J* 14.9 Hz), 4.41 (d, 2H, *J* 14.9 Hz), 7.49 (t, 1H, *J* 6.8 Hz), 7.64 (s, 1H), 7.66 (d, 2H, *J* 6.8 Hz); ^{13}C NMR δ 25.9, 32.5, 33.4, 39.6, 61.7, 62.3, 128.8, 130.0, 131.1, 131.7; EIMS *m*/*z* (rel. int.) 342 ($M^{\cdot +}$, 1), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2O_4$: C, 56.11; H, 6.47. Found: C, 55.98; H, 6.59%.

trans-1,3-1,3-SO$_2$ 23

The same procedure was used to oxidize compound **16** to yield compound **23**, white powder, 0.90 g (76%); mp 325.5–327.6 °C (decomp.); IR 1332, 1123 (ν_{SO_2}) cm^{-1}; ^{1}H NMR δ 1.20–1.23 (m, 6H), 1.51–1.63 (m, 4H), 2.65 (dd, 2H, *J* 4.8, 15.6 Hz), 3.05 (dd, 2H, *J* 6.6, 15.6 Hz), 4.26 (d, 2H, *J* 14.2 Hz), 4.44 (d, 2H, *J* 14.2 Hz), 7.31 (s, 1H), 7.56–7.61 (m, 3H); ^{13}C NMR δ 21.1, 29.1, 32.7, 33.0, 62.6, 129.6, 130.8, 131.2, 131.6; EIMS *m*/*z* (rel. int.) 342 ($M^{\cdot +}$, 1), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2O_4$: C, 56.11; H, 6.47. Found: C, 56.17; H, 6.59%.

cis-1,3-1,2-SO$_2$ 24

The same procedure was used to oxidize compound **17** to yield compound **24**, white powder, 0.96 g (81%); mp 204.8–206.2 °C (decomp.); IR 1332, 1123 (ν_{SO_2}) cm^{-1}; ^{1}H NMR δ 1.20–1.29 (m, 4H), 1.51–1.82 (m, 5H), 2.01–2.21 (br, 1H), 2.92 (m, 2H), 3.20 (m, 2H), 4.31 (d, 2H, *J* 16.0 Hz), 4.45 (d, 2H, *J* 16.0 Hz), 7.47 (m, 2H), 7.94 (s, 2H); ^{13}C NMR δ 20.3, 28.4, 31.3, 35.1, 59.0, 128.1, 129.5; EIMS *m*/*z* (rel. int.) 342 ($M^{\cdot +}$, 1), 104 (100); Anal. Calcd. for $C_{16}H_{22}S_2O_4$: C, 56.11; H, 6.47. Found: C, 56.23; H, 6.41%.

Pyrolysis of compound 20

Compound **20** (0.5 g, 1.5 mmol) was placed in a quartz tube (2.5 cm o.d. × 120 cm length) with a cold trap for pyrolysis. The pyrolysis system was pre-evacuated to a pressure of 0.3–0.4 Torr for 20 min and then the cold trap was cooled by means of liquid nitrogen. During pyrolysis, the temperature was held at 400 °C for 20 min, and then at 500 °C for 30 min. After the trap was warmed to room temperature, the residue in the trap was dissolved in CH_2Cl_2 (30 mL × 3). A waxy material obtained from the CH_2Cl_2 solution was subjected to chromatographic separation on 20% $AgNO_3$ on Al_2O_3 (1.5 cm o.d. × 30 cm length) with hexane as an eluent to give *cis*-1,3-1,4 **25** and *E*-1-(*cis*-3-methylcyclohexyl)-2-(4-tolyl)ethylene **26**.

Compound **25**, white solid, mp 48.3–49.0 °C, 111 mg (34.5%); ^{1}H NMR δ −1.82 (d, 1H, *J* 14.1 Hz), −1.05 (dt, 1H, *J* 9.9, 14.1 Hz), 0.46 (m, 2H), 0.61–0.81 (m, 4H), 1.21–1.37 (m, 5H), 1.63 (m, 1H), 2.58 (dd, 1H, *J* 7.7, 12.8 Hz), 2.63 (dd, 1H, *J* 7.6, 12.8 Hz), 2.90 (dd, 2H, *J* 7.1, 12.8 Hz), 7.09 (d, 2H, *J* 8.2 Hz), 7.64 (d, 2H, 8.2 Hz); ^{13}C NMR δ 27.0, 33.6, 34.6, 34.7, 40.1, 41.5, 130.0, 131.0, 141.6; EIMS *m*/*z* (rel. int.) 214 ($M^{\cdot+}$, 1), 104 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.70; H, 10.42%.

Compound **26**, viscous liquid; 25 mg (7.9%); ^{1}H NMR δ 0.84 (d, 3H, *J* 6.7 Hz), 1.76–1.80 (m, 10H), 2.91 (s, 3H), 6.11 (dd, 1H, *J* 6.7, 16.0 Hz), 6.31 (d, 1H, *J* 16.0 Hz), 7.09 (d, 2H, *J* 7.5 Hz), 7.25 (d, 2H, *J* 7.5 Hz; EIMS *m*/*z* (rel. int.) *m*/*z* 214 ($M^{\cdot+}$, 8), 118 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.51; H, 10.31%.

Pyrolysis of compound **21** gave *trans*-1,3-1,4 **27** and *E*-1-(*trans*-3-methylcyclohexyl)-2-(4-tolyl)ethylene **28**.

Compound **27**, viscous liquid, 86 mg (26.9%); ^{1}H NMR δ 0.05 (m, 1H), 0.32 (m, 1H), 0.60 (m, 1H), 0.76–1.01 (m, 2H), 1.16–1.80 (m, 9H), 2.24 (m, 1H), 2.42 (m, 1H), 2.90 (dd, 1H, *J* 8.2, 13.2 Hz), 3.11 (d, 1H, *J* 13.2 Hz), 7.08–7.30 (m, 3H), 7.37 (d, 1H, *J* 8.1 Hz); ^{13}C NMR δ 23.4, 30.8, 31.7, 33.0, 33.1, 34.6, 35.3, 37.5, 40.3, 129.2, 130.1, 132.1, 133.1, 142.3, 144.5; EIMS *m*/*z* (rel. int.) 214 ($M^{\cdot+}$, 12), 104 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.70; H, 10.33%.

Compound **28**, viscous liquid, 34 mg (10.5%); ^{1}H NMR δ 0.92 (d, 3H, *J* 6.7 Hz), 1.76–1.80 (m, 10H), 2.59 (s, 3H), 6.10 (dd, 1H, *J* 6.7, 16.0 Hz), 6.31 (d, 1H, *J* 16.0 Hz), 7.09–7.25 (m, 4H); EIMS *m*/*z* (rel. int.) 214 ($M^{\cdot+}$, 5), 118 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.49; H, 10.22%.

Pyrolysis of compound **22** gave *cis*-1,3-1,3 **29**: viscous liquid, 167 mg (52%); ^{1}H NMR δ −1.62 (d, 1H, *J* 13.3 Hz), −0.65 (br, 1H), −0.24 (m, 1H), 0.88 (m, 1H), 1.08–1.36 (m, 4H), 1.48–1.85 (m, 6H), 2.46–2.57 (m, 2H), 2.86–3.06 (m, 2H), 6.90 (d, 1H, *J* 7.5 Hz), 6.97 (t, 1H, *J* 7.5 Hz), 7.19 (t, 1H, *J* 7.5 Hz), 7.51 (s, 1H); ^{13}C NMR δ 26.9, 28.2, 28.6, 30.9, 31.3, 33.1, 35.0, 37.0, 37.2, 36.6, 43.9, 45.6, 124.9, 126.2, 129.5, 129.7, 133.2, 135.9, 143.0, 144.2; EIMS *m*/*z* (rel. int.) 214 ($M^{\cdot+}$, 30), 104 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.71; H, 10.32%.

Pyrolysis of compound **23** gave *trans*-1,3-1,3 **30**: viscous liquid, bp 142–145 °C/0.8 Torr; 98 mg (29.2%); ^{1}H NMR δ −1.68 (d, 1H, *J* 13.4 Hz), 0.24 (t, 1H, *J* 13.4 Hz), 0.70 (m, 1H), 0.98–1.55 (m, 7H), 2.21–2.59 (m, 4H), 2.80 (ddd, 2H, *J* 2.0, 2.7, 13.4 Hz), 3.28 (dd, 2H, *J* 4.1, 13.4 Hz), 6.90 (d, 1H, *J* 7.4 Hz), 6.91 (d, 1H, *J* 7.4 Hz), 7.11 (t, 1H, *J* 7.4 Hz), 7.44 (s, 1H); ^{13}C NMR δ 24.4, 30.5, 32.4, 33.9, 34.5, 34.9, 35.3, 36.3, 36.9, 37.0, 124.9, 126.5, 128.6, 131.8, 142.0, 142.7; EIMS *m*/*z* (rel. int.) 214 ($M^{\cdot+}$, 85), 104 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.71; H, 10.44%.

Pyrolysis of compound **24** gave *cis*-1,3-1,2 **31**: viscous liquid, freezing point 19.5–21.0 °C; 199 mg (62% yield); ^{1}H NMR δ 0.90 (m, 1H), 1.26–1.68 (m, 8H), 1.86–1.99 (m, 4H), 2.54–2.67 (m, 3H), 2.90–2.98 (m, 2H), 7.01–7.16 (m, 4H); ^{13}C NMR δ 15.9, 26.9, 29.0, 31.7, 32.1, 33.6, 125.9, 129.8, 143.0; EIMS *m*/*z* (rel. int.) 214 ($M^{\cdot+}$, 75), 104 (100); Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.66; H, 10.29%.

Acknowledgement

Financial support by the National Science Council of the Republic of China (NSC-86-2113-M-126-002) is gratefully acknowledged.

References

1 (*a*) F. N. Diederich, *Cyclophanes*, Royal Society of Chemistry, Cambridge, 1991; (*b*) F. Vogtle, *Cyclophane Chemistry: Synthesis, Structures and Reactions*, John Wiley & Sons, Chichester, 1993; (*c*) V. V. Kane, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron*, 1994, **50**, 4575; (*d*) R. Gleiter and M. Merger, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2427.

2 (*a*) F. M. Yang and S. T. Lin, *J. Org. Chem.*, 1997, **62**, 2727; (*b*) H. Hopf, R. Savinsky, B. Diesselkamper, R. G. Daniels and A. de Meijere, *J. Org. Chem.*, 1997, **62**, 8941.

3 S. T. Lin, F. M. Yang and L. H. Lin, *Tetrahedron*, 1997, **53**, 16133.

4 T. Inukai and T. Kojima, *J. Org. Chem.*, 1971, **36**, 924.

5 N. G. Gaylord, *Reduction with Complex Metal Hydrides*, John Wiley & Sons, New York, 1956, pp. 391–531.

6 (*a*) A. C. Davies, *Chem. Ind.*, 1977, 203, (*b*) T. Yamato, K. Noda, K. Tokuhisa and M. Tashiro, *J. Chem. Res.* (*S*), 1994, 210; P. N. Swepston, S. T. Lin, A. Hawkins, S. Humphrey, S. Siegel and A. W. Cordes, *J. Org. Chem.*, 1981, **46**, 3754.

7 (*a*) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; (*b*) Johnson and Bovey's 'Table of Predicted Values of Shielding Contributions from Ring Currents in Aromatic Hydrocarbons' is contained in Appendix B of J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, New York, 1965.

8 (*a*) L. A. Paquette, *Org. React.*, 1977, **25**, 1; (*b*) J. M. Clough, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 3, p. 861.

9 (*a*) T. L. Chan, S. Fong, Y. Li, T. O. Man and C. D. Poon, *J. Chem. Soc., Chem. Commun.*, 1994, 1771; (*b*) C. Y. Meyers, A. M. Malte and W. S. Matthews, *J. Am. Chem. Soc.*, 1969, **91**, 7510.

10 (*a*) W. F. Maier and P. v. R. Schleyer, *J. Org. Chem.*, 1981, **103**, 1891; (*b*) A. B. McEwen and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1986, **108**, 3951.

11 V. Boekelheide and T. A. Hylton, *J. Org. Chem.*, 1973, **38**, 3928.

12 (*a*) G. Bordwell, E. Ludger and R. Ludovica, *Angew. Chem.*, *Int. Ed. Engl.*, 1979, **18**, 515; (*b*) S. A. Sherrod, R. L. D. Costa, R. A. Barnes and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1565.

13 (*a*) I. Tabushi, H. Yamada, K. Matsushita, Z. Yoshida, H. Kuroda and R. Oda, *Tetrahedron*, 1972, **28**, 3381; (*b*) I. Tabushi and K. Yamamura, *Top. Curr. Chem.*, 1983, **113**, 145.

14 (*a*) N. L. Allinger, Y. H. Yuh and J. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8551; (*b*) N. L. Allinger, K. Chen, M. Rahamn and A. Pathiaseril, *J. Am. Chem. Soc.*, 1991, **113**, 4105.

15 J. J. P. Stewart, *Reviews in Computational Chemistry*, eds. K. B. Lipkowitz and D. B. Boyd, VCH, New York, 1990, p. 45.

16 (*a*) R. H. Mitchell, T. K. Vinod and G. W. Bushnell, *J. Am. Chem. Soc.*, 1990, **110**, 3487; (*b*) R. H. Mitchell, T. K. Vinod and G. W. Bushnell, *J. Am. Chem. Soc.*, 1985, **107**, 3340; (*c*) V. Boekelheide, *Top. Curr. Chem.*, 1983, **113**, 87; (*d*) F. Vogtle, *Top. Curr. Chem.*, 1983, **115**, 1; *ibid.*, 1983, **113**, 1.

17 (*a*) V. Boekelheide and R. A. Hollins, *J. Am. Chem. Soc.*, 1973, **95**, 3201; (*b*) R. H. Mitchell, *Org. Chem.* (*N.Y.*), 1983, **45**, 239; (*c*) D. Kamp and V. Boekelheide, *J. Org. Chem.*, 1978, **43**, 3470.

18 (*a*) Y. Fukazawa, H. Kitayama, K. Yasuhara, K. Yohimuar and S. Usui, *J. Org. Chem.*, 1995, **60**, 1696; (*b*) Y. H. Lai and T. H. Lim, *J. Org. Chem.*, 1994, **59**, 3381; (*c*) H. F. Grutzmacher and E. Neumann, *Chem. Ber.*, 1993, **126**, 1495; (*d*) Y. H. Lai and H. T. Yap, *J. Chem. Soc., Perkin Trans. 2*, 1993, **703**, 1373; (*e*) T. Wong, M. S. Yuen, T. C. Mark and H. N. Wong, *J. Org. Chem.*, 1993, **58**, 3118; (*f*) Y. H. Lai and T. H. Lim, *J. Org. Chem.*, 1989, **54**, 642; (*g*) Y. H. Lai, *J. Org. Chem.*, 1988, **53**, 2360.

19 G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 1953,404.

Paper 9/00583H