Synthesis and Properties of a Bis(2-buteno)-Bridged Bis(adamantane): X-ray and Molecular Dynamic Studies of the *trans,trans* Isomer

Kata Mlinarić-Majerski*, Dražen Pavlović, Vjekoslav Milinković, and Biserka Kojić-Prodić

Rudjer Bošković Institute, Department of Chemistry,
P. O. Box 1016, 10000 Zagreb, Croatia
E-mail: majerski@rudjer.irb.hr

Received January 20, 1998

Keywords: Bis(adamantane), bis(2-buteno)-bridged / Synthesis / Molecular dynamic studies

The synthesis of the *trans,trans* isomer of the bis(2-buteno)-bridged bis(adamantane) **3** has been developed, and its structure was established by spectral and X-ray structure analysis. Since the results of dynamic NMR studies indicate that **3** is conformationally mobile and the transition-state free energy ($\Delta G_c^{\neq}$) required to interconvert two equivalent conformers was estimated to be ca. 60 kJ mol^{-1}, the lowest energy conformer was subjected to a molecular dynamic simulation at 323 K in the gas phase. Three conformations **3a**, **3b** and **3c** were found. The conformations **3a** and **3c** have *anti*-oriented adamantane units, while in **3b** the adamantane molecules occupy the *syn* conformation. By analysing the conformational processes in macrocyclic diene **3**, it was found that the calculated conformation **3a** with molecular symmetry of C_{2h} is very close to that found in solution at –50 °C, but differs from that which was observed in the solid state by X-ray-crystallographic analysis.

There is considerable current interest in macrocyclic compounds and their potential applications. The rapidly expanding field of supramolecular chemistry has revealed a number of useful building blocks for the synthesis of artificial receptor molecules. The synthesis of receptor molecules with large cavities generally meets with the problem that such cavities collapse because of the inherent flexibility of large organic molecules. The first macrocyclic compounds that contain a polycyclic cage system as a building block have been reported recently.[1][2][3][4] It has been found that a polycyclic group, such as the cubyl group, may be viewed as a low-molecular weight concentrated lipophilic center which fixes the ionophore in the membrane.[3] Also, several unusual crown ethers[5] and molecular clefts[6] that incorporate polycyclic systems into the molecule have been synthesized. Manifold bridging seems to us to be increasingly important, not only because the esthetically appealing structures that can be obtained, but also because manifold bridging is a prerequisite for the construction of host molecules and the formation of molecular cavities. It was shown that it is possible to replace benzene rings by adamantane units that can serve as "rigid" building blocks, even in strained ring compounds like cyclophanes.[1][2] The synthesis and chemistry of cyclophanes has attracted considerable attention in recent years because of their unusual structures, conformational properties, and ability to act as host to both neutral molecules and ionic species.[7]

As a part of an extensive program that involves the synthesis of macrocyclic molecules which contain adamantane as an essential building block,[4][5a][8] we recently prepared a series of novel macrocyclic thioethers that contain a 1,3-bridged adamantyl system.[4] The macrocyclic thioether **1** served as a starting material for the preparation of the *trans,trans* isomer of the bis(2-buteno)-bridged bis(adamantane) **3**.

Results and Discussion

In order to find an effective methodology for the synthesis of various types of aliphatic "cyclophanes", we have investigated the potential application of various rearrangement reactions to prepare macrocyclic hydrocarbons (Scheme 1). Ring-contraction experiments on the thioether **1** by methylation/Stevens rearrangement sequence resulted instead in ring opening of **6**. The products, i. e. **7** and **8**, were obtained in a 1.3:1 ratio (GLC, DB−210, 220°C) and subsequently were isolated by column chromatography in 51% of overall yield.[9] Although the Ramberg−Bäcklund rearrangement of α-halo sulfones has proven to be an exceptionally efficient and versatile method for the preparation of olefins,[10] attempts to synthesize macrocyclic dienes **3** and **4** by using this method failed. Reaction of macrocyclic thioether **1** with *N*-chlorosuccinimide, followed by oxidation of the intermediate α-chloro sulfide with *m*-chloroperbenzoic acid afforded the *S,S,S′,S′*-tetroxide **9**. Attempts were made to prepare α-chloro sulfones by direct halogenation of **2** with NCS or with hexachloroethane in the presence of *n*BuLi. However, in both cases, only starting material was isolated. On the other hand, application of Meyer's modification[11] of the standard Ramberg−Bäcklund procedure (in which the α-halo sulfone is formed in situ by treatment of the sulfone with KOH, *t*BuOH, and CCl_4) proved to be successful. Intermolecular cyclization of 1,3-bis(2-bromoethyl)adamantane with thioacetamide under previously developed conditions[4] gave macrocyclic thioether **1**, which subsequently was oxidized by using 2.5 equiv. of *m*-CPBA, thereby affording disulfone **2** in 95%

  1434−193X/98/0606−1231 $ 17.50+.50/0

yield. Ramberg−Bäcklund rearrangement of disulfone **2** afforded a mixture of ring-contracted products, two dienes **3** and **4** (product ratio 3:1), and a small amount of **5**. Dienes **3** and **4** were separated from **5** by column chromatography on silica gel by using a 0 → 40% CH_2Cl_2/pentane gradient-elution scheme. The resulting mixture of dienes **3** and **4** then were separated by column chromatography on Al_2O_3 (activity I) that had been impregnated with 10% $AgNO_3$.

Scheme 1

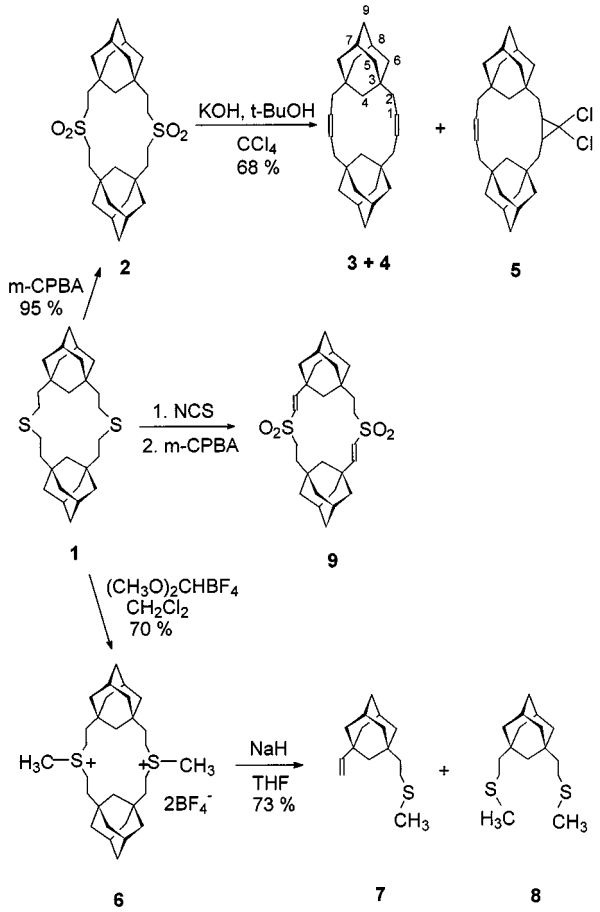
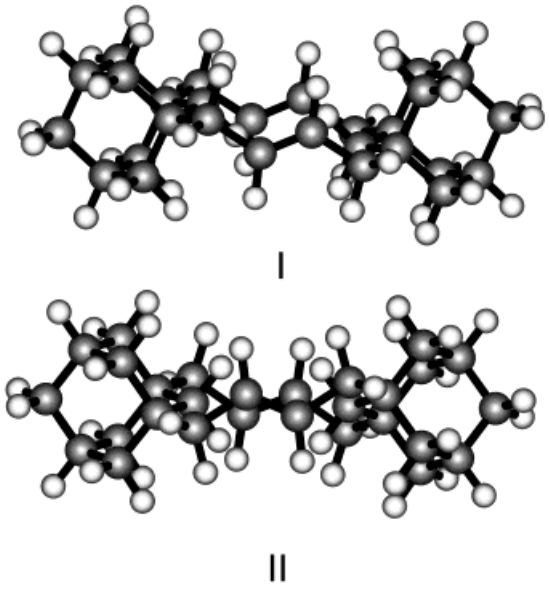
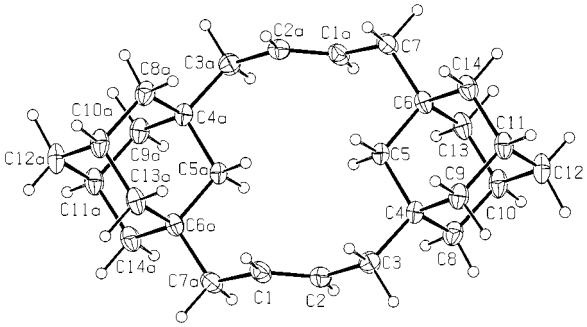


Figure 1. **I**: MMX-optimized geometry of the lowest energy conformation of **3**; **II**: MMX-optimized geometry of the *trans,trans*-diene with crossed arrangement of the double bonds



Based on analytical and spectroscopic data, the structures of **4** and **5** were assigned. However, from analysis of the ^{13}C- and ^1H-NMR spectra of the major product, taken at room temperature, we were not able to define the structure of diene **3**, since two *trans,trans* isomers could possibly be obtained, i. e. **I** and **II** (see Figure 1). Final unambiguous identification of **3** was achieved by X-ray-structural analysis (Figure 2). The bond lengths, bond angles, and torsional angles derived from this analysis are summarized in Table 1.

Figure 2. Molecular conformation of **3** in the crystal; inversion-symmetry-related atoms are labelled with "a"



In the solid state, **3** displays approximately rectangular shape with antiplanar torsions along its sides and with synclinal and anticlinal torsions at each corner. The structure of **3** in the crystal possesses a center of symmetry (C_i symmetry); as a consequence, **3** displays a slightly distorted chair conformation. The two opposite adamantane moietes are tilted up and down with respect to the mean plane of the macrocyclic ring and also are twisted around their median lines. Also, the chair conformation is calculated, by means of molecular mechanics MMX force fields, to be the lowest energy conformation (Table 1). Comparison of the molecular structure derived from X-ray results with that of the chair conformation obtained from molecular mechanics calculations (MMX force field) shows good agreement for the C−C bond lengths. The values of the bond and torsion angles of the macrocyclic ring are also well reproduced by the calculations (Table 1). However, the MMX-derived molecular symmetry (C_{2h}) differs from that which was observed in the solid state (C_i).

The results of dynamic NMR studies indicate that **3** is conformationally mobile.[8] At low temperatures, ring inversion in **3** becomes slow on the NMR time scale, whereas at room temperature the molecule rapidly interconverts from one conformation to the other. In order to determine the Gibbs energy of activation ($\Delta G_c^{\neq}$) and the coalescence temperature (T_c) of this conformational process, a series of variable-temperature ^{13}C- and ^1H-NMR measurements were performed over the temperature range −50 to +55°C (Figure 3).

The assignment of the carbon signals is based on the analysis of signal intensities and coupling modes in proton-

Figure 3. Aliphatic region of ^{13}C-NMR spectra of diene **3** in $CDCl_3$ recorded at various temperatures; numbering as shown in Scheme 1

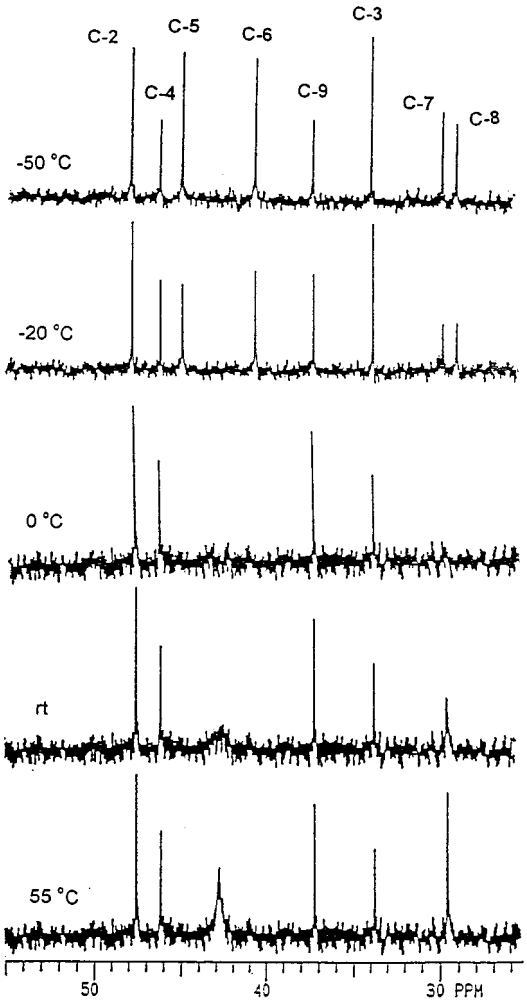
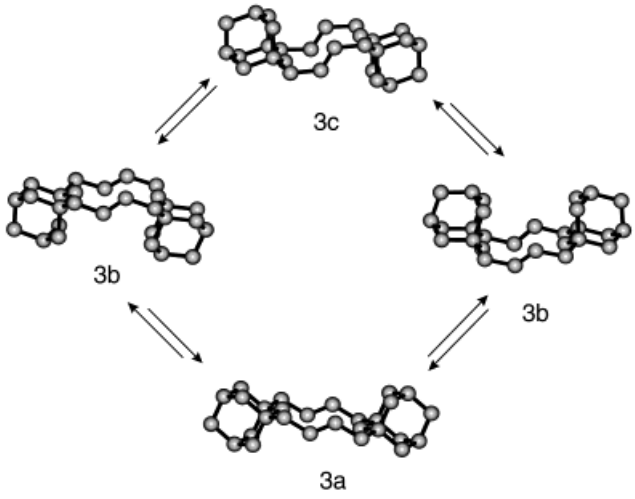


Figure 4. Illustration of the ring-inversion cycle for chair-like *trans,trans*-diene **3; f**or greater clarity hydrogen atoms are not shown



and 29.59). Substantial line broadening of the C-7/8 and C-5/6 signals was observable at room temperature (Figure 3). Significant changes appeared primarily in the aliphatic region of the ^{13}C-NMR spectrum of **3**. The olefinic resonance signals remained practically unchanged with only little broadening observed over the temperature range 0 to −35°C. This could be due to a decrease in spectral resolution, since gradual precipitation of **3** was observed to occur at the low-temperature limit. The processes detected in the dynamic ^{13}C-NMR spectra also cause concomitant lineshape changes in the ^{1}H-NMR spectra.[8] At room temperature, the spectrum is consistent with time-averaged C_{2h} symmetry.

In the ^{13}C-NMR studies, the exchange rate constant (k_c) of the observed conformational interconversion at T_c was calculated from the approximate Gutowsky−Holm equation[12] by taking the coalescence temperature (T_c) to be that at which no observable valley exists between the spectral peaks. The maximum chemical-shift difference of the two carbon peaks at the low-temperature limit, where the rate of exchange is negligible, was taken as Δν. The Gibbs energy of activation ($\Delta G_c^{\neq}$) at coalescence was estimated by using the Eyring equation.[13]

Table 1. Selected bond angles, torsional angles, and bond lengths of **3** as obtained by X-ray structure analysis and by MM+ force-field calculations[a]

Atoms[b]	Bond angles [°] X-ray	MM+	Atoms[b]	Torsional angles [°] X-ray	MM+	Atoms[b]	Bond lengths [Å] X-ray	MM+
C1−C2−C3	125.1(2)	124.0	C1−C2−C3−C4	−120.8(2)	−116.7	C1−C2	1.323(3)	1.342
C2−C3−C4	114.5(2)	113.9	C2−C3−C4−C5	54.4(2)	52.0	C2−C3	1.502(3)	1.509
C3−C4−C5	110.4(1)	110.9	C3−C4−C5−C6	179.3(1)	178.8	C3−C4	1.545(3)	1.547
C4−C5−C6	112.0(1)	111.9	C4−C5−C6−C7	−178.6(2)	−178.8	C4−C5	1.538(2)	1.542
C5−C6−C7	110.0(2)	110.9	C5−C6−C7−C1a	−54.9(2)	−52.0	C5−C6	1.535(2)	1.542
C1−C7a−C6a	114.3(2)	113.9	C7a−C1−C2−C3	175.3(2)	177.6	C6−C7	1.542(3)	1.547
			C2−C1−C7a−C6a	−114.3(2)	−116.7	C7−C1a	1.503(3)	1.509

[a] MM+ calculation were performed using the computer program HYPERCHEM 4.5. − [b] Numbering as in Figure 2.

coupled ^{13}C-NMR spectra at −50°C. Four different carbon atoms corresponding to the adamantane segment (methylene carbon atoms C-5 and C-6 and methyne carbon atoms C-7 and C-8) give rise to signals at δ = 44.26, 40.01, 29.26 and 28.49, respectively. Coalescence among these resonances occurs as the temperature is increased. At +55°C, two signals are observed in this spectral region (δ = 42.82

Analyses of the temperature-dependent ^{13}C-NMR spectra afforded the kinetic and thermodynamic data listed in Table 2. Here, $\Delta G_c^{\neq}$ was estimated to be ca. 60 kJ mol^{-1}.

Table 2. Temperature-dependent ^{13}C-NMR-spectroscopic data, kinetic and thermodynamic parameters for **3**

Carbon atoms	T_c [°C][a]	$\Delta\nu$ [Hz][b]	k_c [s^{-1}]	$\Delta G_c^{\neq}$ [kJ mol^{-1}]
C-5/6	35	320.6	712.2	58.7
C-7/8	22	58	128.8	60.3

[a] Temperatures are accurate within 1°C (Varian Gemini 300). – [b] Chemical shift difference between magnetically unequivalent carbon atoms was determined at −50°C.

Although NMR experiments provide quantitative data for the equilibrium between two conformers with effective C_{2h} symmetry, the possible conformational pathways for ring inversion are unknown. It might be anticipated that this process involves a complex sequence of several conformations. Therefore, the computer-generated lowest energy 3-D structure **I** of C_{2h} symmetry (Figure 1) was subjected to a molecular dynamic simulation (MD) at 323 K in the gas phase. Three different conformations were found, two of which (**3a** and **3c**) possess C_{2h} symmetry and *anti* orientation of the adamantane moieties and one of which (**3b**) possesses C_s symmetry and *syn* orientation of the adamantane units, as shown in Figure 4. The lowest local minima detected over molecular dynamic simulations were minimized separately by using semi-empirical (AM1[14] and PM3[15]) and force-field (MMX)[16] methods (Table 3). Since the calculated conformation of **3a** is the lowest energy conformer of **3**, the observed activation energy of 60 kJ mol^{-1} (obtained by NMR) could be interpreted as being the barrier to ring inversion between two equivalent conformers **3a**.

Table 3. Calculated relative conformational energies in kJ mol^{-1}

Conformation	MM+	AM1	PM3
3a	0	0	0
3b	10.71	11.42	3.22
3c	54.81	37.11	22.84

In conclusion, the new bis(2-buteno)-bridged bis(adamantane) **3** was synthesized, and its structure was established by X-ray analysis. The results of dynamic NMR studies clearly demonstrate that macrocyclic diene **3** (with a 14-membered ring) exists as a mobile molecule in solution, and the energy barrier required for the conformational changes shown in Figure 4 is ca. 60 kJ mol^{-1}. The ^{13}C-NMR spectrum of **3** at −50°C is in accord with the C_{2h} symmetry of conformation **3a**. Molecular mechanics calculations, performed by using Allinger′s MMX force field, also showed that the lowest energy chair conformer of **3** possesses C_{2h} symmetry.

We gratefully acknowledge the support of the project by the *Ministry of Science and Technology of the Republic of Croatia* and, in part, by the *U.S.−Croatia Joint Fund,* No. JF 141, in cooperation with the *National Science Foundation* and the *Ministry of Science and Technology*. We thank Professor *A. P. Marchand* for the critical reading of the manuscript

Experimental Section

General Methods: Thin-layer chromatography was performed on Merck silica gel 60 F-254 TLC plates, and column chromatography was carried out by using Merck silica gel 60. IR spectra were recorded with a Perkin Elmer model 297 spectrometer. NMR spectra were recorded in $CDCl_3$ solvent with a Varian Gemini 300 spectrometer by using internal TMS as reference.

Dynamic NMR Measurements: Variable-temperature ^{13}C-NMR spectra were obtained at 75 MHz. Low-temperature NMR spectra were obtained by cooling the sample with dry nitrogen, which was passing through variable-temperature coils immersed in liquid nitrogen. The corresponding high-temperature NMR spectra were obtaind by direct heating of the air flow used to spin the sample.

Calculations: Molecular mechanics calculations were performed by using the computer programs PC MODEL (version 4.0)[17] or HYPERCHEM (version 4.5).[18] Molecular dynamics simulations were performed by using AMBER parameters implemented in the PC program HYPERCHEM. Simulations were performed at 323 K; constant bath temperature, simulation time 20 ps and time step 1 fs. The lowest local minima detected by molecular dynamics simulations were minimized. For each conformer, both force-field (MMX)[16] and semi-empirical (AM1[14] and PM3[15]) minimizations were performed. Force-field calculations were carried out by using the Newton−Raphson algorithm up to a gradient of 10^{-3} kcal mol^{-1} A^{-1}. AM1 and PM3 calculations were performed by using the restricted Hartree−Fock method (RHF) and convergence limit of 10^{-4} kcal mol^{-1} A^{-1} with full optimization of all geometrical variables (bond lengths, bond angles and torsional angles).

X-ray Crystallography: Suitable single crystals of **3** were grown by slow crystallization in CH_3Cl. X-ray intensity data were collected with an Enraf-Nonius CAD4 diffractometer by using graphite-monochromatized Cu-K_α radiation (λ = 1.5418 A). Crystals of diene **3** are monoclinic and belong to the space group *C*2/*c*: a = 14.119(3) A, b = 12.022(1) A, c = 12.826(1) A, β = 92.721(1)°, Z = 4, d_c = 1.150 gcm^{-3}; reflections collected 4952, observed reflections 2030 [$I > 2\sigma(I)$], 1869 reflections used in the refinement, R = 0.058, wR = 0.074, S = 0.085. The data were corrected for Lorentz and polarization effects by the Enraf−Nonius SDP/VAX package.[19] The structure was solved by SHELX86.[20] Hydrogen-atom coordinates were determined from successive difference Fourier syntheses. Refinement was obtained by full-matrix least-squares minimization [$\Sigma w(F_o - F_c)^2$] with the SHELX77[21] system of programs that employs F values. Atomic scattering factors were those included in SHELX77.[21] The molecular geometry was calculated by using the program EUCLID.[22] The four symmetry-related molecules in the unit cell possess chair conformations with crystallographic inversion symmetry.The molecular structure was drawn by ORTEP.[23] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, supplementary publication no. CSD-101001. Copies of the data may be obtained free of charge on application to CSD, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44(0)1223/336033, e-mail: deposit@ccdc.cam.ac.uk].

S,S,S′,S′-Tetroxide **2**: Disulfide **1** (0.222 g, 0.5 mmol) was dissolved in 5 ml of $CHCl_3$, cooled to 0°C, and 0.43 g (2.5 mmol) of 85% *m*-chloroperbenzoic acid was added with stirring. The external cold bath was removed, and the reaction mixture was stirred at

room temperature for 12 h. The reaction mixture was then poured into 20 ml of saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted twice with 20-ml portions of $CHCl_3$. The combined organic layers were washed with saturated aqueous NaCl solution and dried ($MgSO_4$). After filtration, the solvent was removed to give 0.24 g (95%) of **2** as a white solid, m.p. > 350°C. − IR (KBr): ν = 2895 (s), 2840 (m), 1295 (s), 1160 (m), 1115 (s) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.04−2.68 (m, 8 H), 2.14−1.89 (m, 4 H), 1.66−1.17 (m, 28 H), 0.97 (s, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 44.60 (t, 4 C), 44.38 (t, 2 C), 41.47 (t, 8 C), 37.59 (t, 4 C), 35.73 (t, 2 C), 32.51 (s, 4 C) 28.26 (d, 4 C). − $C_{28}H_{44}S_2O_4$ (508.77): calcd. C 66.09, H 8.72; found C 66.16, H 8.75.

Dienes **3** *and* **4** *and Ene* **5**: To disulfone **2** (0.508 g, 1 mmol), dissolved in 10 ml of a mixture of CCl_4 and *t*BuOH (ratio 2.5:1), was added 0.80 g (14.3 mmol) of KOH. The resulting mixture was refluxed with stirring for 12 h under nitrogen, and then allowed to cool to room temperature. The reaction mixture was poured into 20 ml of water, and the resulting aqueous suspension extracted with Et_2O (3 × 20 ml). The combined ethereal extracts were washed twice with water and then with saturated NaCl solution. The ethereal solution was dried ($MgSO_4$) and filtered. Concentration of the filtrate in vacuo gave 0.26 g (68%) of crude product, which consisted of a mixture of dienes **3** and **4** and ene **5**. The mixture of products was column-chromatographed on silica gel by using a 0 → 40% CH_2Cl_2/pentane gradient-elution scheme, thereby affording 0.145 g of dienes **3** and **4** (product ratio 3:1) and 0.05 g (12%) of ene **5**.

5: IR (KBr): $\tilde{\nu}$ = 3020 (w), 2890 (s), 2850 (s), 1625 (w), 1445 (m), 970 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 5.50−5.35 (m, 2 H), 2.66 (d, 2 H), 2.21−1.20 (m, 32 H), 0.98−0.80 (m, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 128.72 (d), 58.12 (d), 47.43 (t), 46.79 (t), 46.23 (t), 44.63 (t), 44.54 (t), 40.61 (t), 40.51 (t), 36.79 (t), 33.52 (s), 32.61 (s), 29.59 (s), 29.28 (d), 28.74 (d).

Dienes **3** *and* **4** were separated by column chromatography on Al_2O_3 (activity I that had been inpregnated with 10% $AgNO_3$) by elution with pentane, thereby affording 0.110 g (30%) of *trans*,*trans* isomer **3** and 0.032 g (8%) of *cis*,*trans* isomer **4**.

4: IR (KBr): $\tilde{\nu}$ = 3010 (w), 2890 (s), 2840 (m), 1630 (w), 1450 (m), 970 (m), 735 (w) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 5.60−5.47 (m, 2 H), 5.40−5.25 (m, 2 H), 2.12−1.16 (m, 34 H), 1.07−0.94 (m, 1 H), 0.70−0.60 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 129.19, 129.05, 127.48, 127.12, 48.05, 47.97, 47.50, 47.19, 45.21, 45.13, 45.02, 44.97, 44.62, 44.46, 41.58, 41.21 (2 C), 40.08, 39.61, 37.27, 34.85, 34.51, 33.95, 33.70, 30.03, 29.91, 29.79, 29.29.

An analytical sample of **3**, m.p. 212−214°C, was prepared by recrystallization from $CHCl_3$. − IR (KBr): ν = 3020 (w), 2880 (s), 2840 (m), 1630 (w), 960 (m) cm^{-1}. − ^1H NMR ($CDCl_3$)[24]: δ = 5.37−5.30 (m, 4 H), 2.10−1.95 (m, 4 H), 1.90−1.70 (m, 8 H), 1.70−1.50 (m, 4 H), 1.50−1.20 (m, 20 H). − ^{13}C NMR ($CDCl_3$)[24]: δ = 128.75 (d), 47.46 (t), 45.98 (t), 37.07 (t), 33.62 (s), 29.36 (t). − $C_{28}H_{40}$ (376.62): calcd. C 89.29, H 10.71; found C 89.09, H 10.88.

Bis(tetrafluoroborate) **6**: A solution of disulfide **1** (0.085 g, 0.2 mmol) in 10 ml of CH_2Cl_2 was added under nitrogen to a suspension of 0.05 g (0.8 mmol) of dimethoxycarbonium tetrafluoroborate[25] in 5 ml of CH_2Cl_2 which was cooled to −30°C. The reaction mixture was stirred for 1 h at room temperature and then filtered. The solid residue was washed with 5 ml of dry EtOAc and then dried in vacuo to give 0.090 g (70%) of a white crystalline solid. This material was found to be > 95% pure (by ^1H-NMR analysis). − IR (KBr): ν = 2900 (s), 2840 (m), 1450 (w), 1050 (br. s), cm^{-1}. − ^1H NMR (CD_3SOCD_3): δ = 3.85 (br. s, 4 H), 3.40−3.00 (m, 8 H), 2.94 (s, 6 H, CH_3), 1.99 (br. s, 4 H), 1.80−1.50 (m, 28 H). − ^{13}C NMR (CD_3SOCD_3): δ = 41.87, 41.08, 40.18, 35.49, 33.63, 33.24, 32.67, 27.94. − $C_{30}H_{50}B_2F_8S_2$ (648.45): calcd. C 55.56, H 7.77; found C 55.46, H 7.64.

3-[2-(Methylthio)ethyl]-1-vinyladamantane (**7**) *and 1,3-Bis[2-(methylthio)ethyl]adamantane* (**8**): To a cooled (ice/water) suspension of NaH (0.150 g, 3 mmol) in dry THF (5 ml), was added under nitrogen a suspension of dimethylsulfonium tetrafluoroborate (**6**; 0.080 g, 0.12 mmol) in 10 ml of THF during 0.5 h. The resulting mixture was stirred at ambient temperature overnight and then was refluxed for 3 h. Excess of NaH was destroyed by careful addition of water. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic extracts were washed with saturated aqueous NaCl solution (2 × 30 ml) and then dried ($MgSO_4$). Filtration and concentration of the filtrate afforded 0.031 g of crude oily product which was analyzed by GLC (capillary column DB−210, 220°C) to be a mixture of compounds **7** and **8** (product ratio 1:1.3). This mixture was separated by column chromatography on silica gel using a 0 → 40% CH_2Cl_2/pentane gradient-elution scheme, thereby affording 0.010 g (46%) of **7** and 0.013 g (42%) of **8**.

7: IR (KBr): $\tilde{\nu}$ = 3060 (w), 2900 (s), 2840 (m), 1635 (w), 905 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 5.71 (dd, J_{cis} = 10.1 Hz, J_{trans} = 15.3 Hz, 1 H), 4.94−4.80 (m, 2 H), 2.54−2.40 (m, 2 H), 2.09 (s, 3 H), 2.08−2.01 (m, 2 H), 1.68−1.37 (m, 12 H), 1.29 (s, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 149.74 (d, 1 C), 109.49 (t, 1 C), 46.63 (t, 1 C), 43.80 (t, 1 C), 41.60 (t, 2 C), 41.42 (t, 2 C), 36.39 (t, 1 C), 36.29 (s, 1 C), 33.26 (s, 1 C), 28.84 (d, 2 C), 28.34 (t, 1 C), 15.65 (q, 1 C). − $C_{15}H_{24}S$ (236.41): calcd. C 76.20, H 10.23; found C 76.16, H 10.41.

8: IR (KBr): $\tilde{\nu}$ = 2900 (s), 2840 (m), 1460 (m) cm^{-1}. − ^1H NMR: δ = 2.52−2.38 (m, 4 H), 2.10 (s, 6 H), 2.06−1.97 (m, 2 H), 1.62−1.54 (m, 2 H), 1.51−1.32 (m, 12 H), 1.21 (s, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 46.92 (t, 2 C), 43.63 (t, 1 C), 41.60 (t, 4 C), 36.41 (t, 1 C), 33.27 (s, 2 C), 28.84 (d, 2 C), 28.19 (t, 2 C), 15.54 (q, 2 C). − $C_{16}H_{28}S_2$ (284.51): calcd. C 67.54, H 9.92; found C 67.42, H 9.83.

S,S,S′,S′-Tetroxide **9**: A mixture of 0.085 g (0.2 mmol) of disulfide **1** and 0.060 g (0.45 mmol) of *N*-chlorosuccinimide in 15 ml of CCl_4 was refluxed for 3 h under nitrogen. The reaction mixture was cooled, and succinimide was removed by filtration. The filtrate was concentrated in vacuo to give 0.098 g of crude product, which was utilized immediately in the next reaction. − The crude oily product was dissolved in 20 ml of CH_2Cl_2 and cooled to 0°C under nitrogen. To this stirred solution was added 0.150 g (0.95 mmol) of *m*-chloroperbenzoic acid, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was poured into 20 ml of water and extracted with CH_2Cl_2 (3 × 20 ml). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and then dried ($MgSO_4$). After filtration and concentration of the filtrate, 0.060 g (60%) of crude product was obtained.[26] Chromatography on silica gel by using a 0 → 20% EtOAc/$CHCl_3$ gradient-elution scheme gave **9** as a white crystalline solid: m.p. > 350°C. − IR (KBr): ν = 3020 (w), 2900 (s), 2840 (m), 1725 (m), 1620 (w), 1450 (m), 1300 (br. s), 1110 (br. s), 750 (br. s) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 6.74 (d, *J* = 15.9 Hz, 2 H), 6.28 (d, *J* = 15.9 Hz, 2 H), 3.00−2.90 (m, 4 H), 2.20−2.00 (m, 4 H), 1.76−1.14 (m, 28 H). − ^{13}C NMR ($CDCl_3$): δ = 158.48 (d, 2 C), 126.60 (d, 2 C), 50.06 (t, 2 C), 46.17 (t, 2 C), 41.13 (t, 1 C), 40.33 (t, 4 C), 36.61 (s, 2 C), 35.84 (t, 2 C), 35.51 (t, 2 C), 32.92 (s, 2 C), 28.27 (d, 4 C).

[1] F. Vögtle, J. Dohm, K. Rissanen, *Angew. Chem.* **1990**, *102*, 943; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 902; J. Dohm, M. Nieger, K. Rissanen, F. Vögtle, *Chem. Ber.* **1991**, *124*, 915.
[2] R. Lemmerz, M. Nieger, F. Vögtle, *J. Chem. Soc., Chem. Commmun.* **1993**, 1168; R. Lemmerz, M. Nieger, F. Vögtle, *Chem. Ber.* **1994**, *174*, 1147.
[3] R. M. Moriarty, M. S. C. Rao, S. M. Tuladhar, C. D′Silva, G. Williams, R. Gilardi, *J. Am. Chem. Soc.* **1993**, *115,* 1194.
[4] K. Mlinaric-Majerski, D. Pavlovic, M. Luic, B. Kojic-Prodic, *Chem. Ber.* **1994**, *27,* 1327.
[5] A. P. Marchand, K. A. Kumar, A. S. McKim, K. Mlinaric-Majerski, G. Kragol, *Tetrahedron* **1997**, *53*, 3467; G. Mehta, K. S. Rao, N. Krishnamurthy, V. Srinivas, D. Balasubramanian, *Tetrahedron* **1989**, *45*, 2743; K. Hayakawa, R. Naito, K. Kanematsu, *Heterocycles* **1988**, *27*, 2293.
[6] A. P. Marchand, G. M. Reddy, F Zaragoza, A. Bartsch, M. D. Eley, *Tetrahedron Lett.* **1993**, *34*, 5377; R. A. Bartsch, M. D. Eley, A. P. Marchand, R. Shukla, K. A. Kumar, G. M. Reddy, *Tetrahedron* **1996**, *52*, 8979.
[7] For overviews see: [7a] F. Vögtle, *Cyclophane Chemistry*, Wiley, Chichester, **1993**. – [7b] F. Diederich, "Cyclophanes" in *Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), Royal Society of Chemistry, Cambridge, **1991**.
[8] K. Mlinaric-Majerski, D. Pavlovic, Z. Marinic, *Tetrahedron Lett.* **1996**, *37*, 4829.
[9] The possibility that 1,3-divinyladamantane may be present in the crude reaction mixture cannot be confirmed (or denied) by analysis of the ^{1}H-NMR spectrum of this mixture. However, 1,3-divinyladamantane was not isolated, probably due to polymerization that may have occurred during chromatographic purification.
[10] L. A. Paquette, *Org. React.* **1977**, *25*, 1.
[11] C. Y. Meyers, A. M. Malte, W. S. Matthews, *J. Am. Chem. Soc.* **1969**, *91*, 7510.
[12] H. S. Gutowsky, C. H. Holm, *J. Chem. Phys.* **1956**, *25*, 1228.
[13] J. Sandström, *Dynamic NMR Spectroscopy,* Academic Press, New York, **1982**, and references cited therein.
[14] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
[15] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209; *J. Comput. Chem.* **1989**, *10*, 221.
[16] The MMX force field is an enhanced version of Allingers MM2 program: N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 8127.
[17] *PCMODEL*, Serena Software, Bloomington, Indiana, **1993**.
[18] *HYPERCHEM* version 4.5, Hypercube, Inc. Waterloo, Ontario, Canada, **1995**.
[19] B. A. Frenz and Associates, Inc. *SDP/VAX Structure Determination Package*, College Station Texas, USA, **1986**.
[20] G. M. Sheldrick in *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krueger, R. Goddard), Oxford University Press, Oxford, UK, **1985**.
[21] G. M. Sheldrick, *SHELX77, Program for Structure Determination*, University of Cambridge, Cambridge, UK, **1983**.
[22] A. L. Spek, *Acta Crystallogr.* **1990**, *A46,* C34.
[23] U. K. Johnson, *ORTEP,* Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, **1976**.
[24] ^{1}H-NMR and ^{13}C-NMR data are taken from the spectra at room temperature. Complete assignment of the structure was accomplished by analysis of the spectra obtained at −50°C; see ref.[8].
[25] Dimethoxycarbonium tetrafluoroborate was prepared according to: R. F. Borch. *J. Org. Chem.* **1969**, *34*, 627.
[26] The ^{1}H-NMR spectrum of the crude reaction mixture showed a small signal at $\delta = 4.8$ that suggests that an α-chloro sulfone could be present in a very small amount (< 5%).

[98025]