Stepwise Introduction of π-Electron Cross-Conjugation: A Possible Access to [5]Radialenes?

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As starting points to the stepwise access to the corresponding [5]radialene, the unsaturated esters **14a** and **18a** have been prepared. These compounds have been isolated along with their isomers **14b** and **18b**, resulting from an intracyclic double-bond migration. Moreover a subsequent base-catalyzed process mediated the total isomerization of these mixtures to the latter more stable compounds **14b** and **18b**. The energy contents of the various compounds, and the corresponding tri- and tetrasubstituted higher homologues **19** and **20**, have been calculated at the *ab initio* level, using several minimal as well as extended basis sets, and the observed experimental results rationalized.

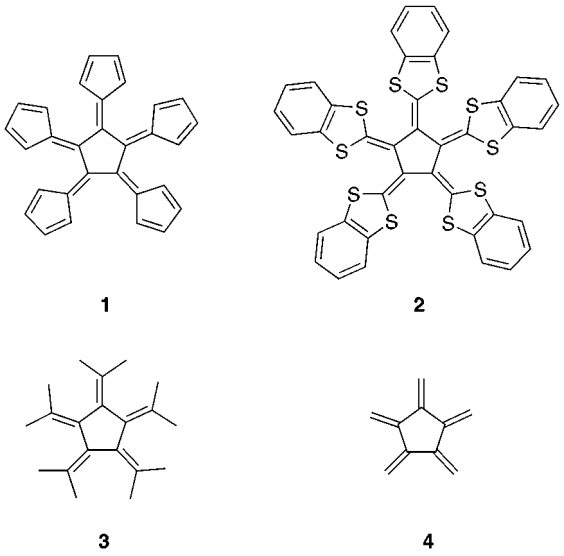
Radialenes are alicyclic compounds in which all ring atoms are sp^2-hybridized and carry exocyclic double bonds.[1] They are a class of compounds exhibiting very interesting structural and electronic properties;[1] the cooperative involvement of the latter has also been considered[1,2] in organic conducting, or ferromagnetic, solid-state.

Two main approaches for the synthesis of these compounds have been studied: (i) the olefin-forming reactions at an already existing cycloalkane ring; (ii) the metal-induced cyclooligomerization reactions of suitable [*n*]cumulenes. While a number of [3]-, [4]-, and [6]radialenes have been obtained, the preparations of [5]radialenes proved to be far more difficult. Thus, besides the aimed structures in this field, such as **1**,[3] the number of isolated [5]radialenes is presently limited to **2**[4] and **3**,[5] the parent compound **4** (Chart 1) itself being still unknown.

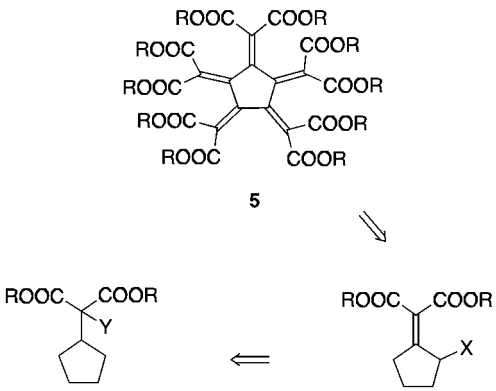
Clearly, a general and versatile synthetic method is needed here. We therefore decided to investigate the possibility to obtain the [5]radialene skeleton, i.e. compound **5**. The considered synthesis involved the stepwise introduction of a suitable substituent containing a double-bond forming radical **Y** by a sequence of reactions involving α-substitutions of the successively formed exocyclic double bonds (Scheme 1).

We wish to report here the experimental as well as the theoretical results of this study. We find that, as soon as two radial double-bonds have been formed, i.e. in compounds **14** and **18**, an unexpected rearrangement to regioisomers **14b** and **18b**, containing one endocyclic double-bond, takes place. Our theoretical *ab initio* calculations (the results of the semiempirical AM1 approach were not sufficiently accurate in this case) clearly address this phenomena to the higher stability of the latter endocyclic regioisomers. The higher homologues **19** and **20** of the series, containing three and four such double-bonds, also exhibit the same trends, in endocyclic vs radial exocyclic isomer stability.

Chart 1



Scheme 1



Experimental Section

General. NMR spectra were obtained with a Bruker AC 400 MHz spectrometer operating at 100.6 MHz for the ^{13}C resonance; other details of instrumentation have been reported recently.[6]

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Compounds **6**[7] and **7**[8] were prepared according to the literature methods.

1,3-Cyclopentanediol Bis(4-methylbenzenesulfonate) (15). Into a solution of 1,3-cyclopentanediol (cis + trans, mainly cis, mixture from Aldrich) (59.49 mmol) in dry pyridine (60 mL) at 0 °C was added *p*-toluenesulfonyl chloride (23.3 g, 122 mmol); the mixture was stirred overnight at room temperature under argon. The obtained suspension was poured into a mixture of ice−water (300 g) containing concentrated HCl (70 mL), and the resulting solid was filtered and dried; recrystallization from absolute ethanol yielded **15** (13.9 g, 68%) as a colorless solid; mp = 86−87 °C. ^{1}H NMR: (δ_H, $CDCl_3$) 1.76−1.8 (m, 2H), 1.91−1.95 (m, 2H), 2.08 (m, 2H), 2.41, (s, 6H), 4.92−4.94 (m, 2H), 7.3, (d, J = 8.2 Hz, 4H), 7.7 (d, J = 8.2 Hz, 4H); ^{13}C NMR: 21.52, 30.71, 40.54, 82.07, 127.59, 129.87, 133.63, 144.85. Anal. Calcd for $C_{19}H_{22}O_6S_2$: C, 55.60; H, 5.40; O, 23.38; S, 15.62. Found: C, 55.51; H, 5.26; O, 23.41; S, 15.53. Compound **15** is the cis stereoisomer.

Nucleophic Substitution by the Anion from Diethyl (Phenylthio)malonate (7). General procedure. The Preparation of Sulfides 8, 12, and 16. Sodium hydride (0.66 g, 16.5 mmol, 60% dispersion in mineral oil) was suspended in anhydrous THF (50 mL), or DMF (25 mL) for **12**, and diethyl (phenylthio)malonate (**7**) (4.02 g, 15 mmol) was added; the suspension was stirred under argon until hydrogen bubbling ceased. The needed amount of compound which had to be substituted (12 mmol, for **6** and **11**; 6 mmol for **15**) was added, and the mixture was refluxed (THF) for 24 h, or stirred at room temperature (DMF). The mixture was poured into water (200 mL) and extracted with dichloromethane (3 × 50 mL). The extracts were dried over $MgSO_4$ and the solvent evaporated; the compounds were purified by flash-chromatography. The following were obtained:

Diethyl cyclopentyl(phenylthio)propanedioate (8): eluted with dichloromethane as a colorless liquid (2.26 g, 56%). ^{1}H NMR: (δ_H, $CDCl_3$) 1.45 (t, J = 7 Hz, 6H), 1.75−1.95 (m, 6H), 2.13−2.18 (m, 2H), 2.86, (m, 1H), 4.38 (q, J = 7 Hz, 2H), 4.39 (q, J = 7 Hz, 2H), 7.55−7.63 (m, 3H), 7.80−7.82 (m, 2H). ^{13}C NMR: 13.78, 25.76, 28.65, 44.05, 61.49, 68.65 (quaternary carbon), 128.43, 129.40, 130.77, 136.86, 168.22. MS(CI), *m/e* = 337$(MH)^+$.

Diethyl 2-[2-[(phenylthio)dicarbethoxymethyl]cyclopentylidene]propanedioate (12): eluted with ethyl acetate/cyclohexane (20:80 v/v) as a colorless liquid (2.24 g, 38%). ^{1}H NMR: (δ_H, $CDCl_3$) 1.0−1.22 (m, 12H), 2.0−3.1 (m, 7H), 3.9−4.2 (m, 8H), 7.12−7.32, (m, 3H), 7.32−7.5 (m, 2H). Anal. Calcd for $C_{25}H_{32}O_8S$: C, 60.96; H, 6.55; O, 25.98; S, 6.51. Found: C, 60.76; H, 6.53; O, 25.55; S, 6.40. MS(CI), *m/e*: 493 $(MH)^+$.

Tetraethyl 2,2′-(1,3-cyclopentanediyl)bis[2-(phenylthio)propanedioate] (16): eluted with ethyl acetate/cyclohexane (35:65 v/v) as a liquid (2.6 g, 72%). ^{1}H NMR: (δ_H, $CDCl_3$) 1.08−1.20 (m, 12H), 1.50−2.12 (m, 6H), 2.51−2.62 (m, 2H), 4.02−4.20 (m, 8H), 7.15−7.36, (m, 6H), 7.50−7.55 (m, 4H). ^{13}C NMR: 13.87, 28.86, 30.37, 43.23, 61.71, 61.82, 68.20, 128.59, 129.64, 130.32, 137.05, 167.95.

Diethyl 2-Cyclopentylidenepropanedioate (10).[9] *m*-Chloroperoxybenzoic acid (the commercial sample containing ∼10% chlorobenzoic acid) was dissolved in CH_2Cl_2 and dried over $MgSO_4$, the solvent was evaporated, and the residue left under vacuum (0.1 mmHg) overnight) (90%, 1.3 g, 7 mmol) was added to CH_2Cl_2 (100 mL) containing sulfide **8** (2.35 g, 7 mmol) at 0 °C. The mixture was stirred an additional 1 h at 0 °C and diluted with more CH_2Cl_2 (100 mL). The dichloromethane solution was washed three times with saturated sodium bicarbonate (50 mL) and subsequently dried over $MgSO_4$. The solvent was evaporated and the corresponding sulfoxide (2.2 g) dissolved, without further purification, in toluene (100 mL) and refluxed (∼2 h). The solvent was evaporated under vacuum and the residue purified by flash-chromatography, eluting with dichloromethane. The compound **10** was obtained (the overall yield was not optimized) as a liquid (0.75 g, 50%) identical to the authentic sample.[9]

Diethyl 2-(2-Bromocyclopentylidene)propanedioate (11). NBS (2.31 g, 13 mmol) and dibenzoyl peroxide (0.05 g, 0.2 mmol) were added to CCl_4 (75 mL) containing **10** (2.94 g, 13 mmol), and the mixture was refluxed for 6 h. The suspension was cooled to room temperature, and the succinimide was filtered off. The filtrate was evaporated, and flash-chromatography of the residue, eluting with ethyl acetate/cyclohexane (15:85 v/v), led first to isolation of the corresponding 2,5-substituted dibromo compound (a liquid, 0.75 g, 15%); ^{13}C NMR: 13.88, 34.77, 48.01, 61.73, 127.52, 161.25, 163.70) and then to **11** as a liquid (2.38 g, 60%). ^{1}H NMR: (δ_H, $CDCl_3$) 1.21−1.34 (m, 6H), 1.81−2.29 (m, 4H), 2.4−2.6 (m, 1H), 2.85−3.05, (m, 1H), 4.10−4.40 (m, 4H), 5.45−5.55, (m, 1H). ^{13}C NMR 14.04, 22.38, 30.99, 37.12, 50.55, 61.15, 61.35, 122.83, 163.86, 164.32, 164.78. MS(CI), *m/e* = (305, 307) $(MH)^+$.

Preparations of Compounds 14a,b and 18a,b by Thermal Dehydrosulfenylation. General Procedure. The sulfides **12** (1.97 g, 4 mmol) and **16** (2.4 g, 4 mmol) were dissolved in anhydrous dichloromethane (40 mL), the solutions were cooled, with stirring, to −35 °C, and *m*-chloroperoxybenzoic acid (90%, 0.69 g, 4 mmol for **12**; 1.38 g, 8 mmol for **16**) was added slowly. The stirring was maintained for an additional 2 h at the same temperature. The reaction mixture was heated to room temperature, washed with a saturated sodium bicarbonate solution (3 × 20 mL), and dried over $MgSO_4$. The solvent was evaporated, and the sulfoxides **9** and **17** were dissolved, without further purification, in the appropriate solvent for the next thermal dehydrosulfenylation step. Using toluene first, the mixtures were refluxed 2 h and evaporated under vacuum, and the residue was purified by flash-chromatography. The following were obtained:

Tetraethyl 2,2′-(1,2-Cyclopentylidene)bis(propanedioate) (14a) and Diethyl 2-[2-(Dicarbethoxymethyl)cyclopent-2-enylidene]propanedioate (14b). Elution with ethyl acetate/cyclohexane (20:80 v/v) afforded the mixture **14a**,**b** as a light yellow liquid (0.76 g, 50%). ^{1}H NMR: (δ_H, $CDCl_3$) 1.15−1.32 (m), 1.80−1.89 (m), 2.52−2.56 (m), 2.65−2.71 (m), 2.96−3.02 (m), 3.13−3.15 (m), 4.09−4.30 (m), 4.42 (s), 6.84 (s). Anal. Calcd for $C_{19}H_{26}O_8$: C, 59.68; H, 6.85; O, 33.47. Found: C, 60.03; H, 6.88; O, 33.75. This mixture was dissolved in ethanol (20 mL), and KOH (0.1 g) was added. After 3 h stirring at room temperature, the solution was neutralized to pH 7 with dilute HCl, more water was added (100 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic extracts were dried over $MgSO_4$ and evaporated to dryness. The residue (quantitative yield) corresponded to pure **14b**. ^{1}H NMR: 1.15−1.28 (m, 12H), 2.60−2.70 (m, 2H), 2.90−3.0 (m, 2H), 4.0−4.25, (m, 8H), 4.41 (s, 1H), 6.83, (s, 1H). ^{13}C NMR: 13.88, 14.03, 31.17, 33.51, 54.95, 60.83, 62.01, 116.70, 129.96, 132.35, 156.25, 165.90, 166.29, MS(CI), *m/e*: 382 $(M)^+$.

Tetraethyl 2,2′-(1,3-Cyclopentylidene)bis(propanedioate) (18a) and Diethyl 2-[3-(Dicarbethoxymethyl)cyclopent-2-enylidene]propanedioate (18b). Elution with ethanol/dichloromethane (3:97 v/v) afforded the mixture **18a,b** as a light yellow liquid (0.87 g, 57%). ^{1}H NMR: (δ_H, $CDCl_3$) 1.0−1.05 (m), 2.41−2.70 (m), 2.90−3.0 (m), 3.20−3.30 (m), 3.95−4.25, (m), 4.41 (s), 6.83 (s). Anal. Calcd for $C_{19}H_{26}O_8$: C, 59.68; H, 6.85; O, 33.47. Found: C, 59.88; H, 7.06; O, 33.78. After the same procedure as for **14a**,**b** the pure isomer **18b** was quantitatively isolated. ^{1}H NMR: 1.15−1.32 (m, 12H), 2.65−2.71 (m, 2H), 2.96−3.02 (m, 2H), 4.09−4.20 (m, 8H), 4.42 (s, 1H), 6.84 (s, 1H). ^{13}C NMR: 13.92, 14.08, 31.21, 33.55, 54.99, 60.58, 62.02, 116.7, 130.08, 132.38, 156.24, 165.86, 166.30. The same thermal dehydrosulfenylation step was also effected using CH_2Cl_2 (with the inclusion of succinic anhydride),[10] and THF as solvent, as well as another run with toluene containing *p*-toluenesulfonic acid; in every case, the same mixtures of isomers **14a**,**b** and **18a**,**b** were isolated. The compositions of these **14a**/**14b** and **18a**/**18b** mixtures were estimated, by ^{1}H NMR, to be, respectively, 40/60 and 55/45.

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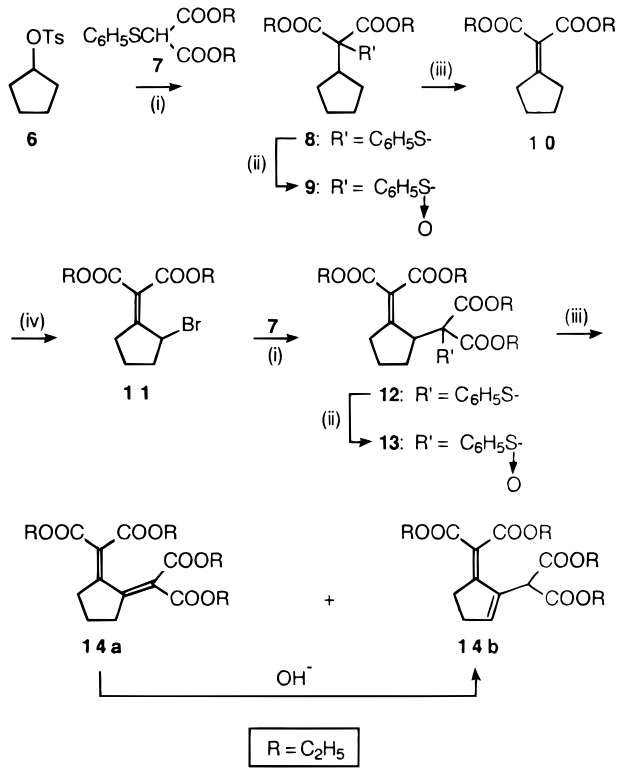
Table 1. AM1 and *ab Initio* Calculated Energy Contents[a] of Compounds 14a,b, 18a,b, 19a−c, and 20a,b

	ΔE(ΔG) energy (free energy) contents[a]			
compounds	AM1	MINI 1	6-31G	6-31G*
14a	0	0.68 (0.93)	4.20 (3.37)	4.54 (3.88)
14b	2.88	0	0	0
18a	0	1.66 (2.17)	3.31 (3.14)	5.86 (5.43)
18b	5.23	0	0	0
19a	0	1.49 (2.02)	−0.73 (0.36)	
19b	0.49	0	0	
19c	15.67	4.90 (6.98)	3.67 (6.56)	
20a	0	1.75 (2.03)		
20b	0.33	0		

[a] The energies are expressed in kcal mol^{-1} by reference (ΔE and $\Delta G = 0$) to the energy-minimized more stable isomers in each series.

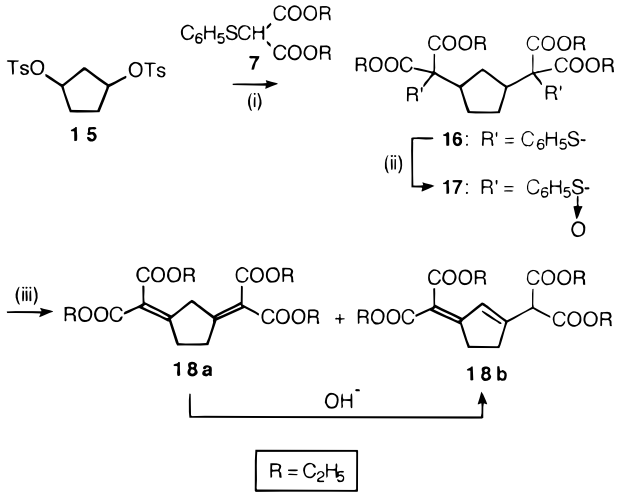
Scheme 2



Reagents and conditions: (i): NaH, THF; (ii): $ClC_6H_4CO_3H$; (iii): toluène reflux; (iv): NBS, CCl_4.

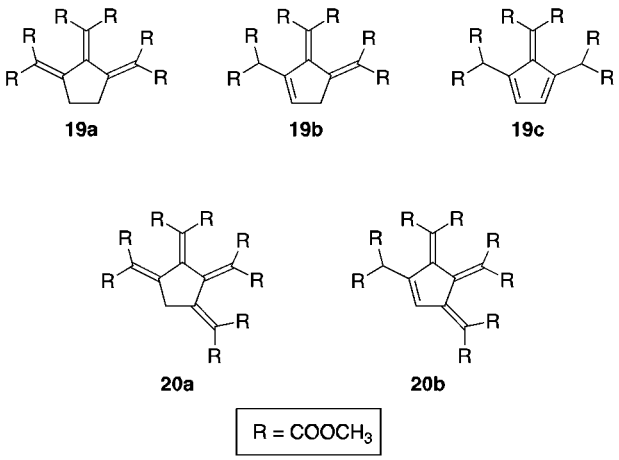
Calculations. Full geometry optimizations were performed for compounds **1**, **14a**,**b**, **18a**,**b**, **19a**−**c** and **20a**,**b** (Figures 1 and 2) at the semiempirical AM1[11] and at *ab initio* level within the MINI-1 minimal basis set of Huzinaga,[12] as well as the 6-31G double basis set and the 6-31G*[13] for compounds **14a**,**b** and **18a**,**b**; the 6-31G* basis set with polarization functions is known to give excellent results when applied to conjugated systems. The 6-31G basis set has also been used with compounds **19a**−**c**. For the higher 67-atom homologues **20a**,**b** at such a level of calculation (6-31G), a 421 basis function was needed; the corresponding calculations are as yet intractable and were not attempted. The equilibrium structures have first been investigated by an AM1 conformational analysis around the rotatable ester single bonds, either by fixed rotors or by reoptimizations of the other degrees of freedom. The highly overcrowded esters' environment resulted usually in a single minimum located on the maps. Such computed equilibrium structures are true minima, as shown by the positive eigen-

Scheme 3



Reagents and conditions: (i): NaH, THF; (ii): $ClC_6H_4CO_3H$; (iii): toluène reflux.

Scheme 4



values of the corresponding analytical second-derivative matrix. It is worth noting that the full geometry optimizations, found to be highly dependent on the basis set expansions, aimed primarly to minimize the significant electrostatic repulsions involving the ester-group oxygens and resulted in significant out-of-plane distorted conformations of the latters. The ΔG free-energy values (Table 1) were calculated as $\Delta G(T) = \Delta E + \Delta E(T) + P\Delta V - T\Delta S(T)$ (ΔE is the usual energy content and $\Delta E(T)$ its thermal dependence, $P\Delta V$ is negligible,[14] and $\Delta S(T)$ values were calculated, at 298.15 K, by the usual statistical mechanic formulas,[15a,b] by the Gaussian 94[16] program). The calculations have been effected on the CIP computers, mainly on a Cray FPS 522 EA and Digital Alpha 8400 8-processor server, using the Gaussian 94 (Rev. B and D) package.[16]

Results

Synthesis. The known starting alkene **10**[9] was alternatively synthesized from the tosylate **6**, by a three-step

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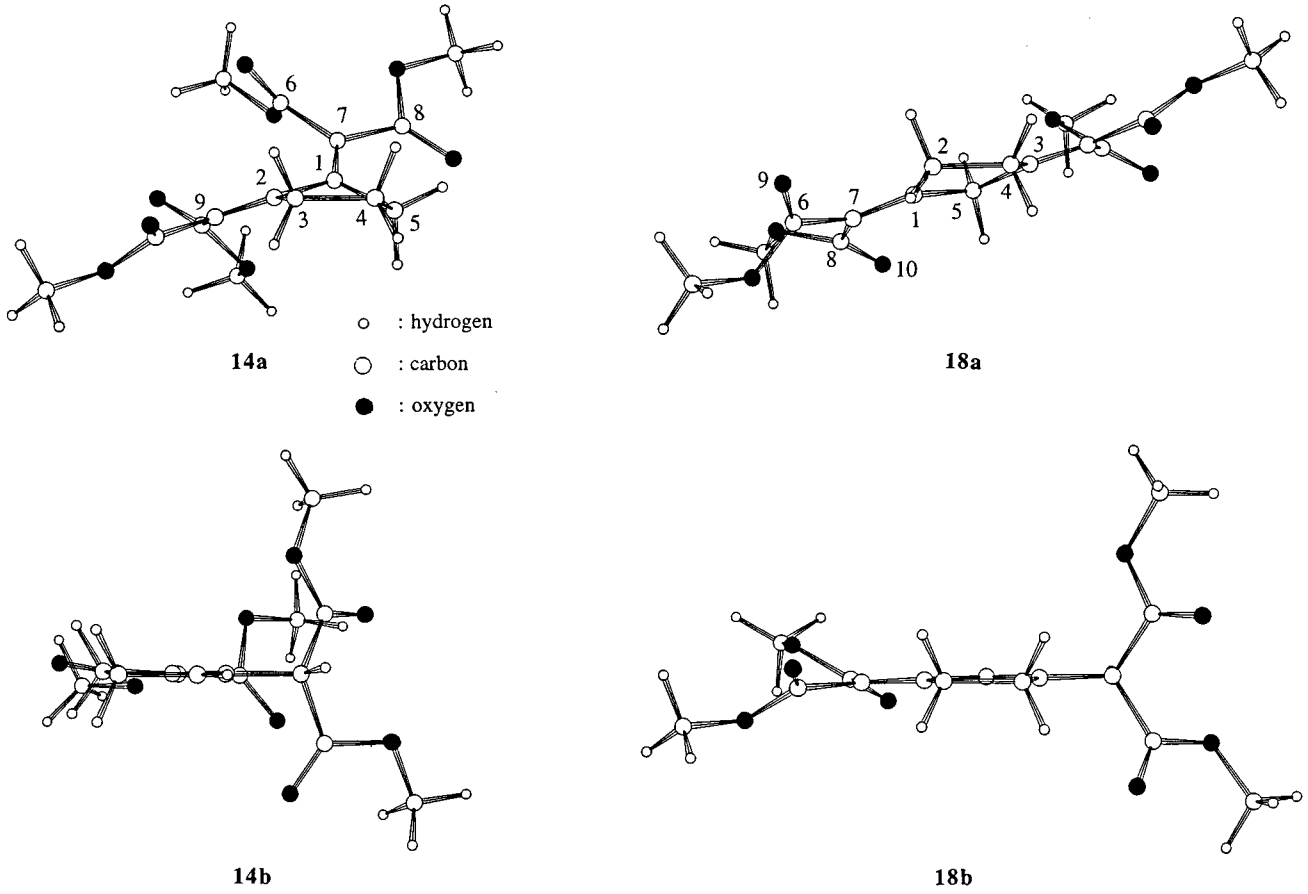


Figure 1. Views of the optimized energy-minimum conformations of the 1,2- and 1,3-disubstituted isomers **14a**,**b** and **18a**,**b**, obtained by the *ab initio* MINI-1 calculations. The values of the torsion angle $C_9-C_2-C_1-C_7$ remarkably increased as a function of the calculations accuracies from 42.60° (AM1), 49.04° (MINI-1), 55.33° (6-31G) to 57.95° (6-31G*) for **14a**. For **18a** the $O_9-C_6-C_7-C_1$ dihedral angle is found to be −129.09° (AM1), −117.35° (MINI-1), −127.24° (6-31G), −133.37° (6-31G*), and the $O_{10}-C_8-C_7-C_1$ angle is 29.12° (AM1), 21.51° (MINI-1), 24.96° (6-31G), and 28.38° (6-31G*).

procedure (Scheme 2): a nucleophilic substitution reaction involving the malonic phenylthio substituted ester **7**[8] and a subsequent oxidation by *m*-chloroperbenzoic acid yielded **9** containing a double-bond forming sulfoxide group;[17] a moderate heating of the latter compound led to **10**. The compound **13**, containing the same sulfoxide group, was then prepared by a similar sequence of reactions, from the bromo diester **11**. However, the thermal double-bond formation reaction from **13**, in boiling toluene, led to a mixture containing the desired compound **14a**, together with the endocyclic isomer **14b**. Modified experimental procedures, such as lower elimination-reaction temperature and/or addition of an acid to the medium (*p*-toluenesulfonic acid), invariably led to a mixture (around 40/60 compositions) of compounds **14a** and **14b**. Moreover, a base-catalyzed process, efficiently isomerized the former mixtures to the pure, undesired, more stable regioisomer **14b**.

This unexpected result prompted us to investigate a similar double-bond formation process, but in a 1,3 regiochemistry on the cyclopentane ring. Therefore we synthesized the disubstituted compound **17** (Scheme 3) from the ditosylate **15**. The corresponding disulfoxide **17** led, in boiling toluene, to a 55/45 mixture of the unsaturated compounds **18a** and **18b**; the latter mixture was also easily transformed to the pure and more stable isomer **18b**.

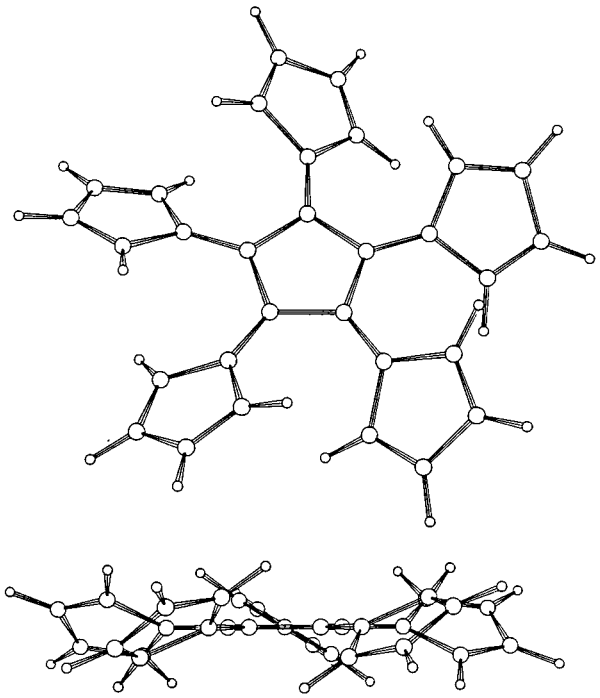
The knowledge of the respective thermodynamic stabilities of these various regioisomers was needed, in order to account for these results; we also were anxious to forsee the behavior of the higher, tri- and tetrasubstituted homologues of this series, before the corresponding syntheses were attempted. We therefore computed the properties of these compounds using the semiempirical AM1, as well as *ab initio* methods.

Calculations. We have calculated the relative energies of the energy-minimized geometries of the various 1,2- and 1,3-disubstituted isomers[18] **14a**,**b** and **18a**,**b** (Schemes 2 and 3, respectively), using the AM1 and *ab initio* methods (Table 1). The same calculations were also effected for the higher homologues **19** and **20** (Scheme 4), as well as for compound **1** (AM1). The calculated stabilities by the semiempirical AM1 method [19] were always in favor of the seemingly more stable radial double-bond isomers **14a** and **18a**. But the *ab initio* calculations led to values that are in closer agreement with the experimental results obtained for compounds **14** and **18**: the endocyclic isomers **14b** and **18b** are found to be more stable than the exocyclic ones **14a** and **18a**,

(17) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

(18) The less time-consuming calculations with the methyl esters were effected for **14**, **18**, **19**, and **20**.

(19) The widely used AM1 method and the corresponding ZDO approximation probably lead to an underestimation of the important electrostatic repulsion forces involved in the present highly overcrowded systems, and these effects are not counterbalanced by the parametrization of the other terms of the Fock matrix. However, as calculated by a referee, and we gratefully acknowledge him for this, the molecular mechanics force field PC model using VESCF charges correctly find **14b** to be more stable that **14a** by 7.3 kcal mol^{-1}, and **18b** to be more stable by 11 kcal mol^{-1} (both in ΔH); the twist angle between the two exocyclic double-bonds of **14a** (torsion angle $C_7-C_1-C_2-C_9$, Figure 1) is about 39° with this approach.



1

Figure 2. Upper and side views of the optimized conformation of the compound **1**, obtained by AM1 calculations.

though the values of the computed free energy differences, with the extended basis 6-31G* set, are still small ($\approx$5 kcal mol $^{-1}$). For the higher, not synthesized homologues **19** and **20** (Scheme 4), the radial double-bond-containing isomers **19a** and **20a** are also found to be less stable than the corresponding endocyclic isomers **19b**,**c** and **20b**, though by vanishingly small amounts of energy.

The views of the calculated (MINI 1 level) energy-minimized conformations for compounds **1** (AM1 level), **14a**,**b**, and **18a**,**b** are depicted in the Figures 1 and 2.

Similar trends, due to several rather severe overcrowding problems, are obtained for both the 1,2- and 1,3-disubstituted compounds **14a** and **18a**: (i) the steric hindrance of the two ester groups on the same sp^2 carbon result in important *out-of-plane distortions* of the latters as long as the corresponding alkene plane is considered (Figure 1, see the $O_9-C_6-C_7-C_1$ and $O_{10}-C_8-C_7-C_1$ dihedral angles for **18a**); this effect is also reflected by noticeable *out-of-plane deformations* of the central five-membered rings mediated by these squeezings of the radial double-bonds; (ii) additional dramatic distortions, related to the overcrowding of the esters on two neighboring radial alkenes, are observed for the 1,2-disubstituted compound **14a**; thus, the butadiene fragment (the torsion angle $C_9-C_2-C_1-C_7$, Figure 1) is highly twisted by almost 58°, as found by 6-31G* calculations; this effect is also illustrated by the nice propeller-like conformation of the pentafulvalene compound **1** (Figure 2).[20] On the other hand, the intracyclic double-bond migrations leading to **14b** and **18b** result in almost complete flattening of the central rings (Figure 1).

(20) The synthesis and thermal stability of compound **1** remains an open question for the moment; see for example: Sauter, H.; Gallenkamp, B.; Prinzbach, H. *Chem. Ber.* **1977**, *110*, 1382; a theoretical study of this aspect will be published in a forthcoming article.

Comparable, though more attenuated, effects on the conformation of the central rings, by the moving-in of the double-bonds, are also observed for **19a**,**c** and **20a**,**b** (see Supporting Information).

Discussion

Our present results identify a thermodynamic deadlock, with the isolation of the more stable endocyclic isomers **14b** and **18b**, in the projected double-bond step-by-step formation sequence. The calculations allow an adequate rationalization of these experimental results, considering the steric effects controlling the relative stabilities of the various isomers. The driving forces for these double-bond rearrangements are clearly mediated by the minimizations of the steric constraints and simultaneously by the conjugation enhancements within the *carbon−carbon bond* π-systems: (i) in the 1,3 regiochemistry on the central ring, as in **18a** (Figure 1), the radial double-bonds are hardly conjugated to the ester groups that are highly distorted out of the alkenes planes, and conjugation is obtained due to an intracyclic bond migration toward the formation of **18b**; (ii) in the 1,2 regiochemistry, as for **14a**, the butadiene fragment built on the exocyclic double-bonds are significantly twisted (see the $C_9-C_2-C_1-C_7$ angle for **14a**, Figure 1) due to the constraint of the neighboring ester groups, and the conjugation within the π-system is obtained by the intracyclic migration of one double-bond (see the simultaneous flattening of the central ring in **14b**, Figure 1). These effects therefore clarify the formation of **14b** and **18b** that precludes an acceptable synthesis of **14a** and **18a**. The synthesis of higher homologues, probably exhibiting the same endocyclic double-bond isomerization, as shown by calculations, was presently not attempted.

These results emphasize the difficulties related to the stepwise creation of cross-conjugation on a cyclopentane ring, as a way to [5]radialenes. Consequently, specific solutions to such problems will probably be needed for such a synthetic approach to this family of compounds. For example, if an alternative pentasubstitution of the central ring is first carried out, the subsequent formations of the missing unsaturations, leading to the desired structure, might be complicated by the formation of similar undesired endocyclic intermediates.

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Supporting Information Available: The views of the *ab initio* (MINI 1) computed energy-minimized conformations of the compounds **19a**−**c**, **20a**,**b** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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