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Electronic and Structural Properties of the Cyclobutenodehydroannulenes

Yi Li, Yves Rubin, François Diederich,* and Kendall N. Houk*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received June 26, 1989*

Abstract: Two series of cyclobutene-annelated dehydro[*n*]annulenes (n = 18, 24, 30) **10–12** and **13–15** were obtained by oxidative coupling of 1,2-diethynyl-1-cyclobutenes **8** and **9**. The properties of these macrocycles are analyzed in an experimental and computational study and compared to those of the parent 1,3,7,9,13,15-hexadehydro[18]annulene (**18**) and 1,3,7,9,13,15,19,21-octadehydro[24]annulene (**19**). The analysis of the electronic absorption and ^{1}H NMR spectra shows that the trimers **10** and **13** both possess planar diatropic [18]annulene perimeters, while the tetramers **11** and **14** both possess planar paratropic [24]annulene perimeters. The chromophores in the pentamers **12** and **15** are conformationally more flexible, and the diatropic character of these [30]annulenes is strongly reduced. Cyclobutene annelation stabilizes all macrocycles. In particular, the fusion of cyclobutene rings stabilizes dramatically the planar [24]annulene perimeter in the tetramers **11** and **14** and is responsible for their preferred formation in the oxidative coupling reactions. AM1 and MM2 computational studies reproduce well the experimentally observed conformational preferences of the parent dehydroannulenes **18** and **19** and the cyclobutene-fused **10–11** and **13–14**. The calculations show that the peculiar stereochemistry of the 1,2-diethynyl-1-cyclobutene unit defines the unique properties of the cyclobutenoannulenes. With its large C(1′)–C(1)–C(2)-angle of 136°, the 1,2-diethynyl-1-cyclobutene unit is accommodated in a nearly strain-free way into the planar tetramers **11** and **14**, whereas its incorporation into the planar trimers **10** and **13** generates considerable angle strain. The enhanced kinetic stability of the cyclobutene-fused dehydroannulene perimeters is explained by energetically more difficult bending and out-of-plane distortions, normally required to reach reaction transition states.

Since the first report on [18]annulene by Sondheimer and Wolovsky in 1959,[1] annulene chemistry has been a central field of interest in physical–organic research.[2,3] Today, research in this area focuses predominantly on the generation of new planar annulene perimeters, especially porphyrin analogues.[4–6]

For both [4*n* + 2] and [4*n*]annulenes ($n > 1$), it has been recognized that, in the absence of transannular steric interactions or angle strain, the rigidity of the ring skeleton is an essential structural prerequisite for stability.[7–10] Several approaches have been considered to reduce the conformational flexibility of the thermally unstable and highly reactive parent [*n*]annulenes. The annelation by arenes, e.g. benzene in **1**,[11] provides rigidity and planarity to an annulene perimeter. However, the more effective benzenoid delocalization is superposed over the annulenoid delocalization, and the macrocyclic diatropism is weakened. In the extreme case of kekulene,[12] a perfectly stable planar molecule with an inner [18]annulene and an outer [30]annulene perimeter, all experimental evidence shows that macrocyclic delocalization is overwhelmed by benzenoid aromaticity. Stabilization of annulenes without disturbing the macrocylic delocalization can be generated by bridging the perimeter to enforce rigidity and planarity, e.g. in **2**,[13] and in **3a–d**.[14–16] (Chart I).

The rigidity of the annulenes also increases upon introduction of acetylene bonds into the π-electron perimeter.[3] Both [4*n* + 2] and [4*n*] systems have been stabilized by introducing diacetylene and butatriene units for enhanced perimeter rigidity and by protecting these units kinetically with bulky *tert*-butyl groups, e.g. in **4**.[17] A large variety of annulenes, including the biological derivatives, the porphyrins, are planarized and stabilized by the incorporation of five-membered aromatic heterocycles, e.g. pyrrols (**5**, **6**) and furans (**7**).[8] In **5–7**, the heterocyclic π-electron systems are integrated into the macrocyclic π-systems.

In this paper, we present evidence for the considerable stabilization of large planar annulenes by annelation to small cycloalkenes.[18–20] In the two series **10–12** and in **13–15**, cyclobutenes are fused with their alkene bonds to the macrocyclic perimeters (Scheme I). Similar to the bridging in **2** and **3a–d**, these *external* one-bond fusions do not alter the macrocyclic π-system. Mills–Nixon effects[21] have not been found to be very effective in ben-

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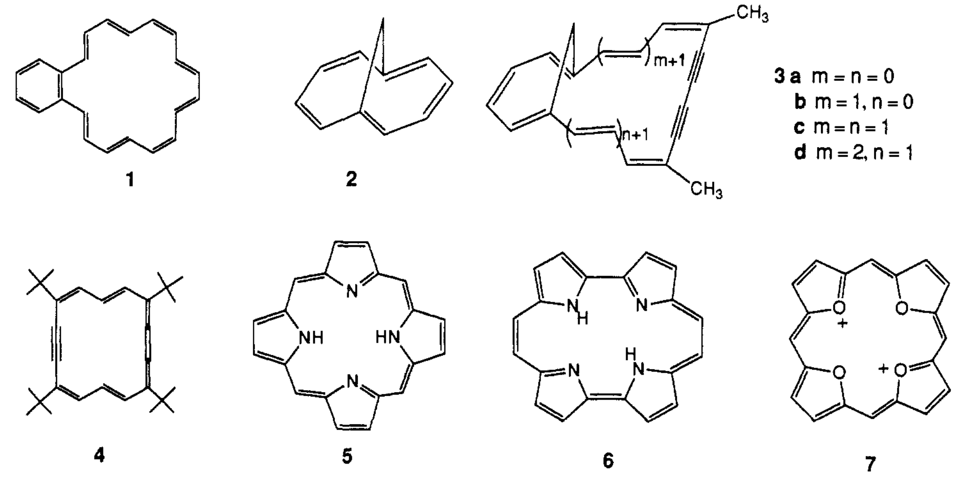
Chart I



zenoid and annulenoid systems.[22] We show that small cycloalkene fusion can provide a unique control of the size and stability of selected annulene perimeters as compared to others.

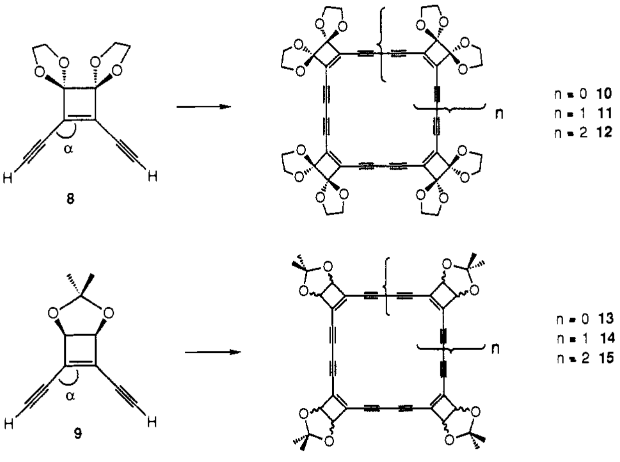
Results and Discussion

Properties of the Parent Dehydroannulenes. With **18**[23,24] and **19**,[25] described almost two decades ago, ideal comparison compounds are available to identify the properties in **10**–**15** specifically resulting from cyclobutene annelation. In the oxidative coupling of *cis*-hex-3-en-1,5-diyne (**16**), Sondheimer and Okamura exclusively obtained the yellow trimer **18** (20%), the absence of higher cyclic oligomers being specifically noted by the authors (Scheme II).[23] The trimer **18** is highly unstable in the crystalline state. It decomposes within a few hours at room temperature and explodes at ca. 85 °C. The [18]annulene **18** is diatropic according to ^{1}H NMR criteria. The presence of a planar perimeter in **18** is also supported by the electronic absorption spectrum (Table I) which shows a characteristic vibrational structure with strong absorptions between λ = 300–350 nm and an end absorption around $\lambda \approx$ 420 nm.[23] A very similar electronic absorption spectrum was recently measured for a novel hexadehydro[18]annulene for which the planar annulene perimeter was shown by X-ray analysis.[26]

Sondheimer et al. prepared the bright yellow tetramer **19** in 20% yield starting from the "dimer" **17**.[25] This octadehydro[24]annulene, like **18**, is also described as being very unstable (explosion point at ~130 °C) and detonates with a flash on being rubbed. According to the ^{1}H NMR spectra, **19** must be characterized as atropic. The electronic absorption spectra of **19** and the precursor **17** closely resemble each other (taken into account that **19** is made up of two units of **17**). The spectrum of **19** (Table I) is characterized by a lack of long-wavelength transitions, low extinction coefficients, and reduced vibrational structure. On the basis of the lack of paratropicity in the ^{1}H NMR spectrum and the electronic absorption spectrum, characteristic of a nonplanar, conformationally flexible chromophore, Sondheimer et al. assigned a cyclooctatetraene (COT) type structure to **19**.[25]

Properties of the Cyclobutenodehydroannulenes 10–15.[27] The results obtained in the oxidative cyclizations of the cyclobutenediynes **8** and **9** are strikingly different from the results in the similar reaction of **16**. Hay coupling of **8** affords the pale yellow trimer **10** (3.8%), the orange-red tetramer **11** (5.1%), and the bright yellow pentamer **12** (0.8%). All three compounds are kinetically quite stable, and crystals can be kept for weeks at room temperature and ambient atmosphere without noticeable decomposition. Similarly, the coupling of **9** yields the pale-yellow trimer **13** (2.1%), the red tetramer **14** (6.6%), and the yellow pentamer **15** (1.8%) as mixtures of diastereoisomers. In this series, the trimer **13** is slightly unstable in the solid state. It slowly decomposes at room temperature and is best kept in dilute solution. Crystals of the tetramer are stable at room temperature and ambient atmosphere for months, while crystals of the pentamer are stable if kept at 0 °C.

Scheme I



Scheme II

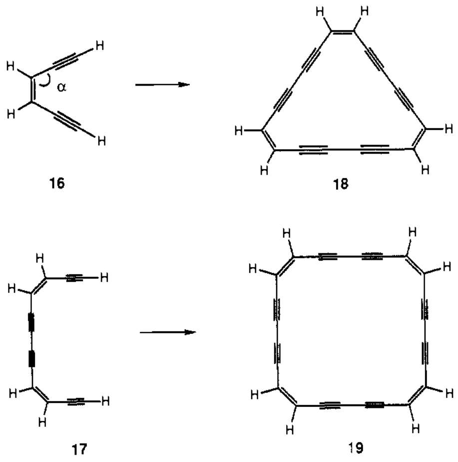


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Table I. Electronic Absorption Spectra of **10**–**12** in Dichloromethane, of **13**–**15** and **18**[a] in Cyclohexane, and of **19**[b] in Ether

compd	λ_{max}, nm
10	238 (ϵ 39 000), 252 (34 600), 299 sh (6 500), 306 sh (16 000), 318 sh (34 600), 322 (36 700), 340 (74 600), 364 (10 800), 372 sh (7400), 387 (9200), 395 (13 800), 413 sh (1400)
11	239 (ϵ 100 700), 247 sh (87 400), 270 sh (25 300), 298 sh (27 100), 311 sh (40 000), 314 (41 000), 332 (75 600), 356 (142 200), 390 sh (6510), 425 sh (4320), 455 sh (3640), 500 sh (3510)
12	242 (ϵ 55 500), 276 sh (38 200), 286 sh (37 300), 310 (35 100), 328 (35 300), 357 (36 200), 384 (36 500), 428 sh (14 100)
13	237 (ϵ 28 400) 250 (25 500), 312 sh (17 300), 330 (35 800), 346 (65 100), 365 sh (14 500), 372 sh (11 700), 396 (12 400), 407 (13 400), 427 sh (1650)
14	230 (ϵ 84 000), 242 sh (62 000), 303 sh (24 100), 312 (31 900), 318 (32 600), 334 (81 900), 339 (68 600), 360 (189 600), 407 sh (4510), 437 (3460), 445 sh (3380), 479 (2600), 490 sh (2290), 520 sh (1350)
15	231 (ϵ 46 100), 246 (46 000), 259 sh (38 400), 301 (34 000), 312 (33 800), 332 (36 000), 357 (39 300), 376 sh (34 200), 389 (34 500), 431 sh (11 200), 455 sh (8200)
18	227 (ϵ 25 500), 236 (21 500), 260 (5 900), 315 sh (41 000), 317 (41 500), 333 (75 800), 357 (13 000), 366 (7400), 378 (15 500), 388 (17 600), 405 sh (790)
19	243 (ϵ 50 600), 248 (50 400), 307 sh (27 400), 317 sh (29 500), 329 (38 900), 341 (38 300), 352 (45 100)

[a] Taken from ref 23. [b] Taken from ref 25.

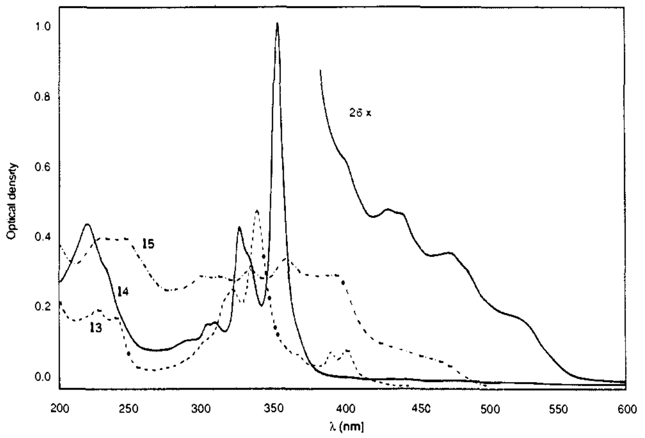

Figure 1. Electronic absorption spectra of **13**–**15** recorded in cyclohexane, $T = 293$ K, $d = 1$ cm, $c = 7.3 \times 10^{-6}$ M for **13** (- - -), $c = 5.2 \times 10^{-6}$ M for **14** (—), and $c = 8.5 \times 10^{-6}$ M for **15** (-····-); $c = 1.4 \times 10^{-4}$ M for the long wavelength absorptions of **14**.

All cyclobutenoannulenes **10**–**15** are kinetically stabilized as compared to the parent compounds **18** and **19**, with the highest stability being observed for the tetramers **11** and **14**. We believe that the properties in the series **13**–**15** reflect better the intrinsic kinetic stability of the cyclobutenodehydroannulene perimeters than those in the series **10**–**12**. The acetonide protective groups in **13**–**15** provide less steric shielding of the π-systems than the ethylene ketal groups in **10**–**12**. That stability results predominantly from cyclobutene-annelation rather than from steric shielding of the π-electron perimeter is demonstrated by the stability of the octol[27] obtained upon deprotection of the tetraacetonide **14**. The red crystals of this cyclobutene-fused octadehydro[24]annulene can also be kept without decomposition at ambient atmosphere and room temperature.[27]

The electronic absorption spectra of **13**–**15** are shown in Figure 1 and Table I. They are very similar to those measured in the series **10**–**12**.[28] The spectra of **10** and **13** closely resemble the spectra of **18** and the new hexadehydro[18]annulene mentioned above, and we conclude that the trimers **10** and **13** possess planar π-electron perimeters.

The electronic absorption spectra of **11** and **14** differ strikingly from the spectrum reported for **19**. The strong bands of **11** and **14** between λ = 300 and 370 nm show a close shape similarity to the corresponding absorptions of the planar trimers **10**, **13**, and **18**. From this shape similarity and the appearance of long-wavelength absorptions at λ = 400–550 nm, which account for the red color, we conclude that the tetramers **11** and **14**, in contrast to **19**, possess planar, conformationally rather rigid [24]annulene perimeters. The considerable bathochromic shift of the longest wavelength transitions in the tetramers **11** and **14** as compared to the trimers **10** and **13** (Figure 1) is qualitatively reproduced by the smaller HOMO–LUMO gap calculated by AM1 for the cyclobuteno-fused tetramer (Table III).

Table II. Chemical Shifts (in ppm) of the Proton Resonances of Compounds **8**–**15** as Determined by ^{1}H NMR ($T = 296$ K)

	monomer **8**[a]	[18]annulene **10**[a]	[24]annulene **11**[a]	[30]annulene **12**[a]
δ[b]	4.04	4.27	3.95	4.07

	monomer **9**[c]	[18]annulene **13**[c]	[24]annulene **14**[c]	[30]annulene **15**[c]
δ(3,4-H)[d]	5.12	5.97	4.95	5.28
δ(CH$_3$)	1.47	1.54	1.36	1.53
δ(CH$_3$)	1.35	1.19	1.62	1.44

[a] In CD$_2$Cl$_2$. [b] Chemical shifts refer to the center of the AA′BB′ multiplet. [c] In CDCl$_3$. [d] 3,4-H refers to the numbering in the cyclobutene ring.

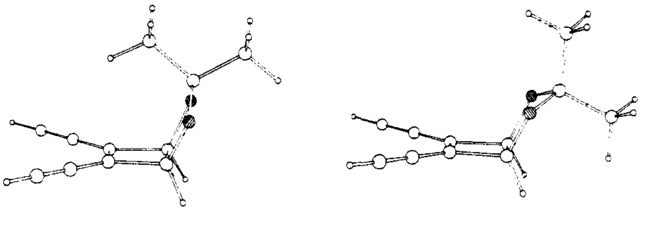

Figure 2. MM2-optimized endo and exo conformations of the acetonide **9**. The endo structure is 0.6 kcal/mol higher in energy than the exo conformer.

The spectra of the pentamers **15** and especially of **12** resemble in their shape more the one reported for **19** (Table I). We take the lower extinction coefficients, the considerably reduced vibrational structure, and the lack of long-wavelength transitions as strong evidence for conformationally much more flexible, possibly nonplanar chromophores in these [30]annulenes.

Although all protons in **10**–**12** and in **13**–**15** are at a remote distance of the π-systems, their ^{1}H NMR resonances provide additional evidence for planar [18]- and [24]annulene perimeters (Table II). The comparison of the proton resonances in the macrocycles to the resonances in the cyclization components **8** and **9** suggests that the [18]annulenes **10** and **13** have diatropic character and the [24]annulenes **11** and **14** paratropic character. Interestingly, the *exo*- and *endo*-methyl groups in the acetonides **13** and **14** are shifted into opposite directions by the magnetic anisotropy. The protons 3,4-H of the cyclobutene rings and the *exo*-methyl group of **13** stay within the deshielding region of the diatropic trimer **13** and, correspondingly, in the shielding region of the paratropic tetramer **14** (Table II). A reverse effect is seen for the *endo*-methyl groups, since their protons, in one conformation of the 1,3-dioxolane ring, come well above the annulene ring system where the opposite magnetic anisotropy is effective. Such locations of the methyl groups in **13** and **14** are supported by MM2 calculations of the conformations of the acetonide **9**

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(28) For a preliminary communication of parts of this work, see: Rubin, Y.; Diederich, F. *J. Am. Chem. Soc.* **1989**, *111*, 6870–6871.

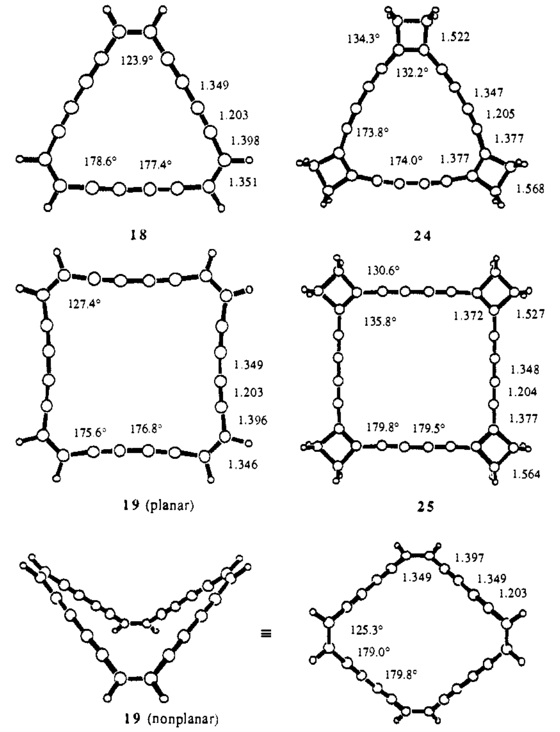


Figure 3. AM1 optimized geometries of various dehydroannulenes.

(Figure 2). For the pentamers **12** and **15**, weak shifts of the macrocyclic resonances indicate a considerably reduced diatropic, possibly atropic character.

In summary, the experimental data support the following specific effects due to cyclobutene annelation: Oxidative coupling reactions of the cyclobutene-1,2-diynes **8** and **9** generate macrocyclic trimers, tetramers, as well as pentamers, whereas the simple enediyne **16** only yields a trimer. The tetramers **11** and **14**, two [24]annulenes, form in the highest yields. The cyclobutene annelation increases the stability of all macrocycles. We ascribe this stabilization to a reduction of conformational flexibility of the annulene perimeters as a result of the small ring fusion. The most dramatic stabilization is observed for the two [24]annulenes **11** and **14**, which are among the most stable [24]annulenes ever reported.[29] Both tetramers **11** and **14** are planar paratropic annulenes in striking contrast to the parent cyclodehydro[24]-annulene **19**, an atropic, nonplanar chromophore believed to prefer a cyclooctatetraene-like geometry.[25] In the following computational study, we show that the peculiar stereochemistry of the 1,2-diethynyl-1-cyclobutene unit defines the unique properties of the cyclobutenoannulenes.

Computational Studies

Due to the large size of the molecules, semiempirical AM1 molecular orbital calculations[30] were performed on the parent dehydroannulenes and the cyclobutene-annelated derivatives. Calculations were carried out using the GAUSSIAN 86 program[31] with proper symmetry constraints for the geometry optimizations. The optimized geometries are shown in Figure 3, and relevant bond lengths and bond angles, calculated heats of formation, and HOMO–LUMO energies are given in Table III.

The angular strain caused by bond angle distortion is one of the major factors that affect the conformation and the stability of the dehydroannulene perimeters. The ideal C═C—C bond angles in the planar trimer **18** and tetramer **19** are 120° and 135°, respectively (144° for the planar pentamer). The nonplanar COT-type tetramer should have an ideal bond angle around 120°. The angular strain of a planar trimer of tetramer is dependent upon how close the C═C—C bond angles α in the coupling monomers, e.g. in **8** or **16**, are to the ideal macrocyclic angles. As shown in Table III, the annelation of the double bond by four-membered and three-membered rings enlarges the C═C—C bond angle α from 125° to 136° and 151°, respectively. Thus, the parent monomer **16** should prefer the formation of the planar trimer over the tetramer. Severe angle strain exists in the planar tetramer, and a nonplanar conformation should be more stable. On the other hand, the cyclobutene-annelated monomers **20** and **22** (and correspondingly **8** and **9**) have the bond angles α closest to the ideal angle of the planar tetramer, which should favor the formation of planar tetramer over the trimer. (Chart II).

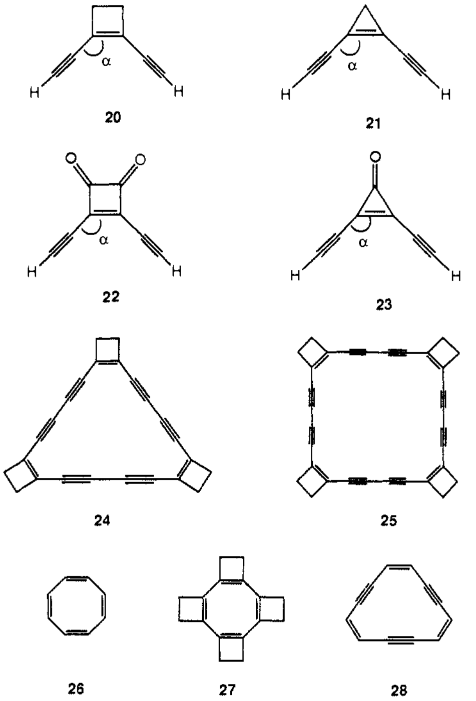
AM1 calculations (Table III) indicate that the parent trimer **18** adopts a planar conformation with an interior C═C—C bond angle of 124° which is very close to the value of 125° in the monomer **16**. The edge that consists of triple bonds is nearly linear,

Table III. AM1 Geometries, Heats of Formation, and HOMO–LUMO Energies for Various Annulenes and Their Synthetic Precursors

compound	C═C bond length, Å	C═C—C bond angle, deg	ΔH_f, kcal/mol	HOMO, eV	LUMO, eV
16	1.346	125.4	120.0	-9.34 (9.10)[a]	-0.09
20	1.369	136.3	149.3	-8.91	-0.26
21	1.328	151.1	178.5	-9.06	-0.48
22	1.375	136.1	111.4	-9.96	-1.50
23	1.357	148.6	153.7	-9.91	-1.09
18	1.351	123.9	347.8	-8.80	-1.07
19 (planar, D_{4h})	1.346	127.4	465.2	-8.41	-1.41
19 (nonplanar, D_{2d})	1.349	125.3	462.7	-8.64	-1.12
24 (D_{3h})	1.377	132.2	441.0	-8.41	-1.24
25 (D_{4h})	1.372	135.8	579.1	-8.04	-1.58
26 (planar)	1.336	135.0	75.5	-8.05	-0.88
26 (nonplanar)	1.338	126.4	63.4	-8.71 (8.7)[a]	+0.09
27 (D_{4h})	1.370	135.0	177.5	-7.26	-1.15
28 (D_{3h})	1.351	122.9	197.1	-8.29 (7.69)[b]	-1.14
benzene	1.395	120.0	21.9	-9.65 (9.25)[a]	+0.55

[a] The first ionization potential; ref 34a. [b] Reference 34b.

Chart II



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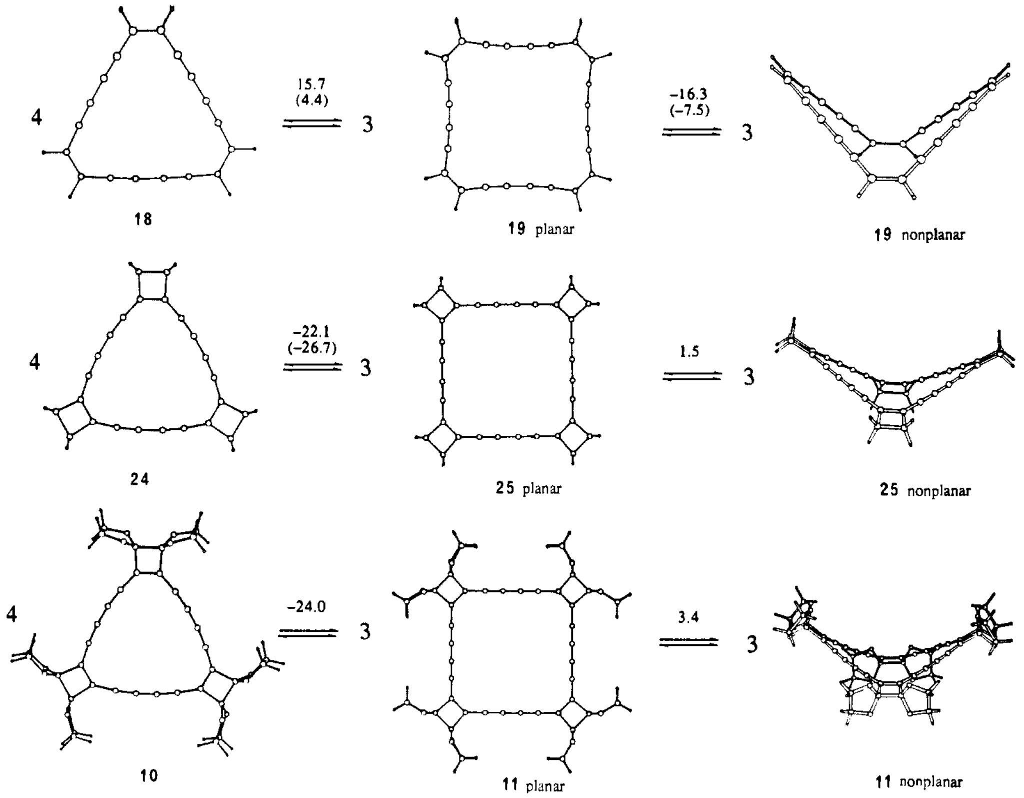

Figure 4. MM2 steric energies (kcal/mol) for the isodesmic transformations between the planar trimers and the planar tetramers and between the planar and nonplanar tetramers. The AM1 results are shown in parentheses.

indicating little angular strain. In the optimized planar tetramer **19**, however, triple bonds are significantly bent in order to minimize the distortion of the interior C═C—C bond angle. Indeed, the nonplanar conformation is predicted to be 2.5 kcal/mol more stable than the planar conformation.

For the cyclobutene-annelated species, the trimer seems to be considerably strained. The triple bonds in **24** are apparently bent in order to compensate for the angular strain which would be caused by a deviation of the interior C═C—C angle further down from the calculated 132°. On the other hand, the optimized D_{4h} symmetry structure of **25** indicates that there is no significant bond angle distortion in the planar cyclobutene-fused dehydro[24]-annulene perimeters. The optimization of the nonplanar COT-type structure for **25** failed because the nonplanar structure converges slowly to the planar conformation.

The performance of the AM1 method was tested on the interconversion barrier of 1,3,5,7-cyclooctatetraene (COT, **26**). Although the calculated heat of formation of the nonplanar COT differs by about 10 kcal/mol from the experimental values, the calculated barrier of 12.1 kcal/mol via a planar D_{4h} conformation is in good agreement with the experimental value of 13.7 kcal/mol.[32] The effect of cyclobutene annelation on the conformation of the tetramers **11**, **14**, and **25** resembles that for the COT derivative **27**.[33] Both experimental and theoretical studies have reported that cyclobutene annelation enhances the planarity of COT.[33] Our AM1 calculations also indicate that the nonplanar conformer of **27** collapses into the planar one upon optimization. Furthermore, there is a reasonable accord between the AM1-calculated HOMO energies and the measured first ionization potentials for molecules where experimental data are available (Table III).[34]

The strain energies of the parent and cyclobutene-fused dehydroannulenes were also evaluated by molecular mechanics calculations (MM2).[35] Despite the fact that the standard MM2 program does not take into consideration the effect of conjugate interactions, the MM2 results on the parent (**18** and **19**) and the cyclobutene-annelated systems (**24** and **25**) are in good agreement with the AM1 calculations and the experimental results as shown in Figure 4. Presumably, bond angle distortions are the source of strain energy that affect most the stability of the described [18] and [24]annulene perimeters. The same should also be true for compounds **10** and **11** in which two ethylene ketal groups are attached to each cyclobutene ring. MM2 calculations indicate that the ketal-protected compounds follow the same trend as the unprotected compounds. The trimer **10** is more strained than the tetramer **11** which prefers a planar conformation (Figure 4).

The experimental results suggested a significant stabilization of both the trimers **10** and **13** and the tetramers **11** and **14** as compared to the parent compounds **18** and **19**. The most dramatic stabilization was observed for the cyclobutene-fused tetramers. Although the total strain energy of the systems increases due to the cyclobutene-annelation (Table III), there is little angular strain introduced during the coupling process to form the planar tetramers **11** and **14**. Therefore, the triple bonds in those molecules undergo essentially no bending distortion and they are less likely the subject of attack by either nucleophiles or electrophiles. In addition, annelation with cyclobutene rings also reduces the tendency of the tetramers to undergo out-of-plane distortions. Such rigidity may make it difficult for the systems to undergo structural distortions which are aften required in order to reach a reaction transition state.[16] Both arguments may account for the intrinsic high kinetic stability of the tetramers **11**, **14**, and the octol formed by the deprotection of **14**. Also, the latter argument can also be seen at the origin of the experimentally observed

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enhanced kinetic stability of the trimers **10** and **13** as compared to **18**.

Conclusions

The electronic and structural properties of 1,3,7,9,13,15-hexadehydro[18]annulene (**18**) and 1,3,7,9,13,15,19,21-octadehydro[24]annulene (**19**), and the corresponding cyclobutene-annelated derivatives **10–15** were compared in an experimental and computational study. On the basis of analysis of their electronic absorption and ^{1}H NMR spectra, the trimers **10** and **13** are assigned a planar diatropic [18]annulene perimeter and the tetramers **11** and **14** a planar paratropic [24]annulene perimeter. The chromophores in the pentamers **12** and **15** are conformationally more flexible, and the diatropic character of these [30]annulenes is strongly reduced. Cyclobutene annelation kinetically stabilizes all macrocycles as compared to the parent dehydroannulene perimeters **18** and **19**. In particular, the fusion of cyclobutene rings stabilizes dramatically the planar [24]-annulene perimeter in the tetramers **11** and **14** and is responsible for their preferred formation in the oxidative coupling reactions. The crystalline tetramers **11** and **14** are stable for months at room temperature and ambient Los Angeles atmosphere. AM1 and MM2 computational studies reproduce well the experimentally observed conformational preferences of all annulene perimeters considered in this study. The calculations show that the peculiar stereochemistry of the 1,2-diethynyl-1-cyclobutene unit defines the unique properties of the cyclobutenoannulenes. With its larger C═C—C angle α of 136°, the 1,2-diethynyl-1-cyclobutene unit is accommodated in a nearly strainfree way into the planar tetramers **11** and **14**, whereas its incorporation into the planar trimers **10** and **13** generates considerable angle strain. The enhanced kinetic stability of the cyclobutene-fused dehydroannulene perimeters is explained by energetically more difficult bending and out-of-plane distortions, normally required to reach reaction transition states. The computational studies suggest that diethynylcyclopropenone (**21**) derivatives with their very large C═C—C angle α of ~150° should be ideally suited to generate even larger dehydroannulene perimeters in oxidative coupling reactions. With protected derivatives of **21**, currently under preparation, planar [30]-, [36]-, and [42]annulene perimeters should be accessible as potential precursors to the cyclo[*n*]carbons C_{30}, C_{36}, and C_{42}.

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Registry No. **8**, 123002-93-7; **9**, 124562-53-4; **10**, 123002-94-8; **11**, 123002-95-9; **12**, 123002-96-0; **13**, 124562-54-5; **14**, 124562-55-6; **15**, 124562-56-7; **16**, 16668-67-0; **18**, 16668-69-2; **19**, 30047-26-8; **20**, 124562-57-8; **21**, 124581-11-9; **22**, 123002-91-5; **23**, 124562-58-9; **24**, 124581-12-0; **26**, 629-20-9; **27**, 83489-77-4; **28**, 18460-92-9.

Supplementary Material Available: Listing of Cartesian coordinates of optimized geometries calculated by AM1 (6 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Low-Temperature Conformational Transition within the [Zn-Cytochrome *c* Peroxidase, Cytochrome *c*] Electron-Transfer Complex

Judith M. Nocek,[†] Nong Liang,[†] Sten A. Wallin,[†]
A. Grant Mauk,[‡] and Brian M. Hoffman*,[†]

Department of Chemistry, Northwestern University
Evanston, Illinois 60208
Department of Biochemistry
University of British Columbia
Vancouver, British Columbia, V6T 1W5 Canada

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Whereas protein systems that incorporate redox partners held at fixed distance and orientation are of extreme interest for studying the fundamentals of long-range electron transfer (ET),[1-3] interprotein ET typically involves protein complexes that associate through electrostatic and hydrophobic interactions, for example, [cytochrome *c* peroxidase, cytochrome *c*],[4] [cytochrome *c*, cytochrome b_5],[5] [plastocyanin, cytochrome *c*],[6] [flavodoxin, cytochrome *c*],[7] and [hemoglobin, cytochrome b_5].[8] Although such complexes are thought to exhibit a preferred binding mode, they are not necessarily restricted to a unique, static docking geometry[9,5b] as might be inferred from the earlier molecular graphics modeling studies. We now show that studies of interprotein triplet-state quenching may be used to probe the dynamics of docking rearrangements within ET complexes: we report that the [ZnC*c*P, Fe^{3+}C*c*] complex[10] undergoes a remarkable conformational transition at low temperature.

The intrinsic triplet decay traces for ZnP incorporated into C*c*P, as measured with the [ZnC*c*P, Fe^{2+}C*c*] complex[11,12] in ethylene glycol (EGOH)/KP$_i$ buffer, are rigorously single-exponential for ≥5 half-lives, and the decay rate constant (k_D) decreases smoothly[13] from $k_D = (126 \pm 4)$ s^{-1} at 293 K to $k_D = (66 \pm 2)$

[†] Northwestern University.

[‡] University of British Columbia.

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(12) Emission experiments were performed by using a xenon flash (baseline pulse width = 80 μs) excitation source (excitation at 430 ± 10 nm); emission was detected by using a red-extended PMT (Hamamatsu R446).

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