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Effect of Overcrowding in [*n*]Radialenes on the Synthesis of Bis[4]radialenes

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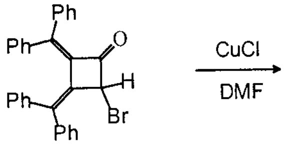
The crystallization of CuCl-assisted dimerization of 2-bromo-3,4-bis(diphenylmethylene)cyclobutanone revealed two polymorphs (**3** and **4)**. The dimer was intended to be a precursor to bis-radialenes. Attempts to dehydrogenate the compound to the true bis-radialene failed. This failure may be attributed to the overcrowding of the precursor. Dimerization was not observed in a similar reaction of 2,2-dibromo-3,4-bis(diphenylmethylene)cyclobutanone, and **5** was the only product obtained. The crystal structures of the three products are described. The overcrowding expressed by torsion angles is calculated, and experimental conformations of the central ring are compared for [3], [4], [5], and [6]radialenes.

Introduction

[*n*]Radialenes are carbocyclic systems containing *n*-cross-conjugated exocyclic double bonds. Stable [*n*]radialenes are of interest for their unique π-electron systems and ring strain.[1−10] The synthesis of polyphenyl-substituted derivatives of [3], [4], [5], and [6]radialenes have challenged organic chemists for many years. However, the only polyphenyl-substituted radialene synthesized is [4]radialene.[11] Syntheses of other poly-substituted radialenes go back to 1961,[12] and the first crystal structure of perchloro[4]radialene was published in 1970.[3] A comparison of the effect of substituent and ring size in [3], [4], [5], and [6] symmetric poly-substituted radialenes is given later in this publication. Two reviews on the synthesis and transformation of radialenes and on the structural chemistry of radialenes have recently been published.[13,14]



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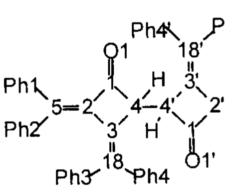

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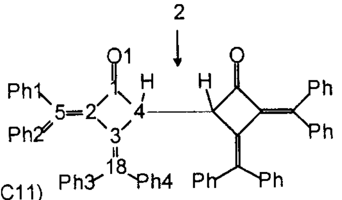
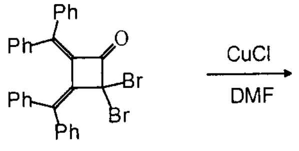


4

Ph1 (C6-C11)
Ph2 (C12-C17)
Ph3 (C19-C24)
Ph4 (C25-C30)



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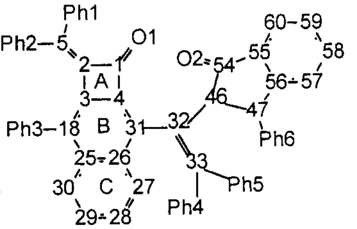

5

Ph1 (C6-C11)
Ph2 (C12-C17)
Ph3 (C19-C24)
Ph4 (C34-C39)
Ph5 (C40-C45)
Ph6 (C48-C53)

In the study on methylene analogues of cyclobutadienquinone,[15] Toda and co-workers have prepared **1** and **2.** In a later work on the preparation of various radialenes, Toda and co-workers found the following: 2-Bromo-3,4-bis(diphenylmethylene)cyclobutanone (**1**) undergoes CuCl-assisted dimerization, producing crystals of two different habits, colors, and melting points; **3** crystallizes as red prisms with a mp of 241 °C; and **4** crystallizes as red needles with a mp of 288 °C. Attempts to dehydrogenate **3** to produce the true bis-radialenes failed. A similar reaction with 2,2-dibromo-3,4-bis(diphenylmethylene)cyclobutanone **2** revealed a different product iden-

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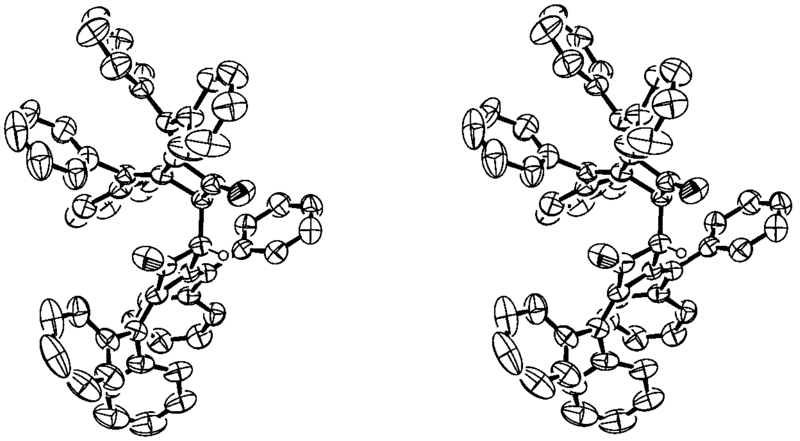
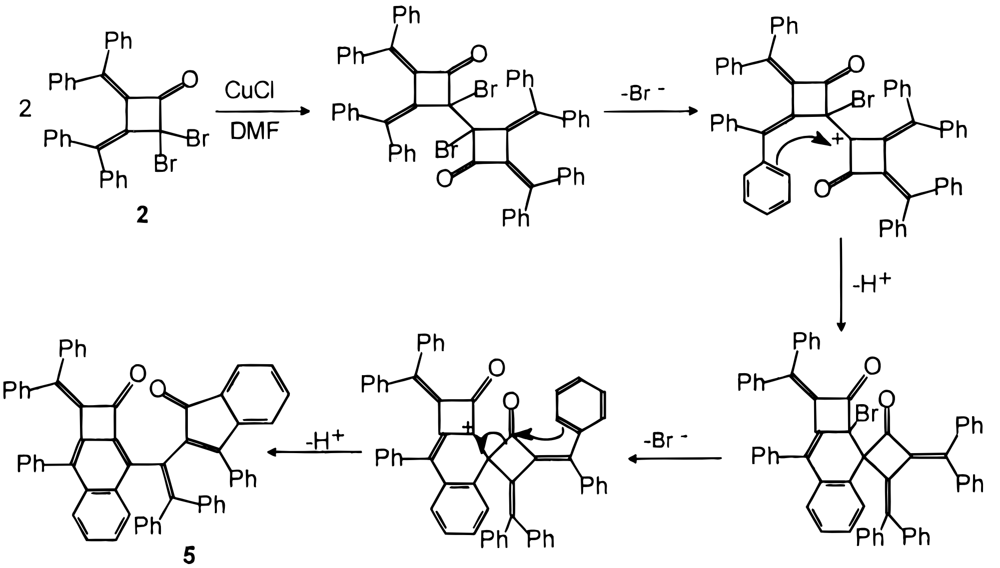


Figure 1. Stereoscopic drawing of **3.** The ellipsoids are drawn at 50% probability level (hydrogen atoms were omitted for clarity reasons).

Scheme 1



tified by X-ray diffraction methods to be **5** (orange prisms with a mp of 253 °C). A possible mechanism for the synthesis of **5** is shown in Scheme 1. The different molecular structures of the two conformational isomers **3** and **4** and of **5** are of interest regarding the unsuccessful attempts to synthesize a true bis[4]radialene.

Results and Discussion

Crystal Structures of Bis[4]radialenes 3 and 4. A comparison of bond lengths and angles of the two polymorphs is given in Table 1. The stereoscopic views of molecules **3** and **4** are shown in Figures 1 and 2, respectively. **3** crystallizes with the solvent molecule (ethyl acetate) (verified by NMR). The solvent molecule occupies an inversion center and must therefore be disordered. **4** crystallizes in the polar space group C_2, and the molecule occupies a crystallographic special position on a 2-fold axis. Although the absolute configuration of **4** was not determined, the asymmetric carbon atoms (C(4) and C(4′)) were assigned as *R*,*R* (or *S*,*S*) for **4** and (*R*,*S*) for **3**.

Crystal Structures of 5. Selected bond lengths and angles are given in Table 2. The stereoscopic view of **5** is shown in Figure 3. The two rigid fused rings determine the molecular structure of **5**. Rings A, B, and C are found to be coplanar, with a maximal bending of 5.1° between

Table 1. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) in 3 and 4

	3	**3**[a]	**4**
O(1)−C(1)	1.215(1)	1.200(1)	1.200(4)
C(1)−C(2)	1.488(1)	1.493(1)	1.511(5)
C(1)−C(4)	1.498(1)	1.553(1)	1.546(5)
C(2)−C(5)	1.361(1)	1.354(1)	1.351(5)
C(2)−C(3)	1.489(1)	1.482(1)	1.483(5)
C(3)−C(18)	1.343(1)	1.346(1)	1.340(5)
C(3)−C(4)	1.530(1)	1.530(1)	1.551(5)
C(4)−C(4′)	1.530(1)	1.530(1)	1.531(7)

	3	**3**[a]	**4**
O(1)−C(1)−C(2)	136.56(9)	137.17(9)	137.0(4)
O(1)−C(1)−C(4)	130.97(7)	131.60(9)	132.2(4)
C(2)−C(1)−C(4)	92.47(8)	91.21(7)	90.9(3)
C(5)−C(2)−C(3)	140.65(8)	138.88(7)	134.0(3)
C(5)−C(2)−C(1)	128.22(9)	128.55(7)	133.2(3)
C(1)−C(2)−C(3)	88.79(7)	89.75(7)	89.9(3)
C(18)−C(3)−C(2)	139.39(7)	132.26(8)	134.2(3)
C(18)−C(3)−C(4)	129.45(8)	134.33(8)	132.7(3)
C(2)−C(3)−C(4)	91.14(7)	92.54(6)	91.7(3)
C(1)−C(4)−C(4′)	116.42(8)	108.15(7)	115.0(2)
C(1)−C(4)−C(3)	86.94(7)	85.80(7)	86.2(3)
C(4′)−C(4)−C(3)	125.91(7)	119.48(7)	117.5(4)

[a] For these bond lengths read, for exampl, O(1′)−C(1′) etc.

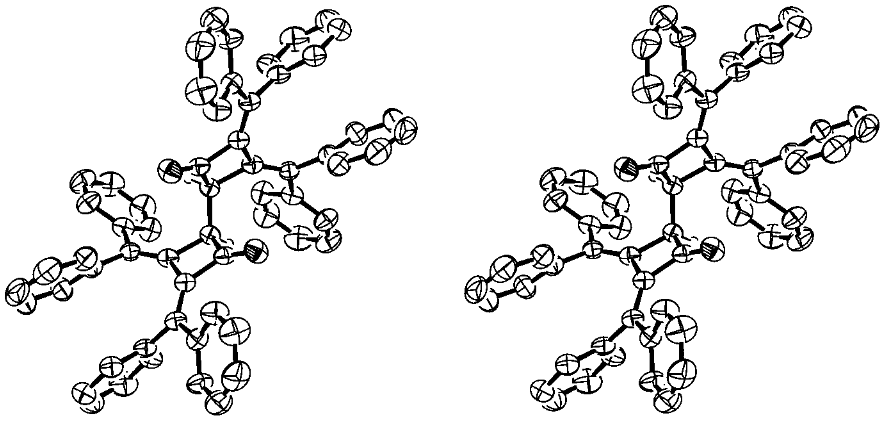


Figure 2. Stereoscopic drawing of **4**. The ellipsoids are drawn at 50% probability level (hydrogen atoms were omitted for clarity reasons).

Table 2. (5). Selected Bond Lengths (Å) and Bond Angles (deg)

O(1)−C(1)	1.205(4)
C(1)−C(4)	1.496(5)
C(1)−C(2)	1.509(5)
C(2)−C(5)	1.349(5)
C(2)−C(3)	1.495(5)
C(3)−C(18)	1.372(5)
C(3)−C(4)	1.414(5)
C(4)−C(31)	1.372(5)
C(5)−C(12)	1.488(5)
C(5)−C(6)	1.487(5)
C(18)−C(25)	1.448(5)
C(18)−C(19)	1.495(5)
O(1)−C(1)−C(4)	134.9(3)
O(1)−C(1)−C(2)	136.5(3)
C(4)−C(1)−C(2)	88.6(3)
C(5)−C(2)−C(3)	141.2(3)
C(5)−C(2)−C(1)	130.1(3)
C(3)−C(2)−C(1)	87.7(3)
C(18)−C(3)−C(4)	121.9(3)
C(18)−C(3)−C(2)	145.7(3)
C(4)−C(3)−C(2)	92.3(3)
C(31)−C(4)−C(3)	124.9(3)
C(31)−C(4)−C(1)	143.4(4)
C(3)−C(4)−C(1)	91.3(3)
C(2)−C(5)−C(12)	124.6(4)
C(2)−C(5)−C(6)	120.1(3)
C(12)−C(5)−C(6)	115.2(3)
C(3)−C(18)−C(25)	115.7(3)
C(3)−C(18)−C(19)	124.0(3)
C(25)−C(18)−C(19)	120.3(3)
C(4)−C(31)−C(26)	114.5(3)
C(4)−C(31)−C(32)	123.4(4)
C(26)−C(31)−C(32)	121.8(3)

rings B and C (the angle between the normal to the planes). This small bending may be attributed to the proximity of one of the phenyl groups (Ph6 in **5**) to the center of the cyclobutane ring. The shortest distances are between atoms C(48)−C(31) 3.240(6) Å and C(49)−C(1) 3.248(7) Å. It is expected that the close proximity will cause bending at the bridging bond between the four- and six-membered ring (C(3)−C(4)) in order to release the repulsion. In similar compounds that have no bulky substituents, such as benzocyclobutene-1,2-dione,[16] the angle between the four- and six-membered rings is only 1.8°. An alternative, less energy-consuming way for releasing the repulsion is bending at the bridging bond between the two six-membered rings (C(25)−C(26)). Therefore, the most severe bending takes place between planes B and C. Bending to a much higher extent was found in octabromonaphthalene[17] (25.9°) and in octakis(phenylthio)naphthalene[18] (26.6°).

Overcrowding in [3], [4], [5], and [6]Radialenes and in Bis[4]radialene. It is interesting to compare the effects of substituents and ring size in symmetrical polysubstituted [3],[19] [4],[20] [5],[21] and [6]radialenes[20] on their geometry. The molecular structure of polymethyl-substituted [*n*]radialenes with $n = 3$, 4, 5, and 6 are known. The average inner $Csp^2{-}Csp^2$ single bond lengths are 1.451(10), 1.506(5), 1.496(2), and 1.505(2) Å in the [3], [4], [5], and [6]radialenes described above, respectively. These bond lengths are somewhat longer than the average $Csp^2{-}Csp^2$ single bond lengths observed in nonconjugated compounds[22] (1.478(12) Å) and shorter by 0.05−0.06 Å than the $Csp^3{-}Csp^3$ single bonds in the equivalent parent ring compounds. The nonplanarity of the rings is more pronounced when overcrowding is increased.

The effect of overcrowding due to steric congestion is reflected by distortions of the molecule from its ideal geometry, where perturbations are absent. Overcrowding may, in principle, cause a variation in bond lengths, bond angles, and torsion angles. The variation in torsion angle is the least energy-consuming distortion and therefore may serve as a measure of the distortion resulted from overcrowding. The most sensitive parameters describing the effect of overcrowding in [*n*]radialenes are the inner-ring torsion angles, the outer-ring torsion angles, and the torsion angles at the exocyclic double bonds. In the discussion to follow, we will describe the effect of overcrowding in [3], [4], [5], and [6]radialenes on these torsion angles. Notation of the torsion angles is given in **7**, **14**, and **18** for each system.

Theoretical calculations using an MP2/6-31G(d,p) basis set with full geometry optimization for the parent molecules [3], [4], [5], and [6]radialenes was carried out[14] and will serve as a reference for the ideal geometry in the absence of overcrowding.

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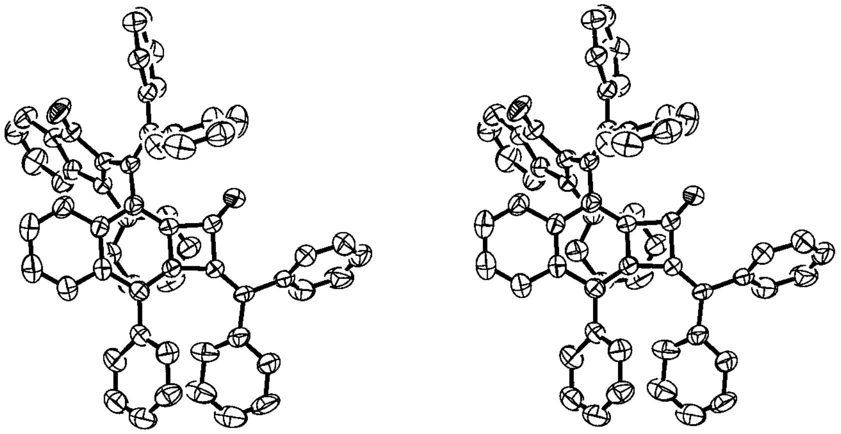

Figure 3. Stereoscopic drawing of **5.** The ellipsoids are drawn at 50% probability level (hydrogen atoms were omitted for clarity reasons).

[3]Radilenes. On the basis of theoretical calculations,[14] the minimum energy is obtained for a planar molecule. Indeed, due to the large unbonded distances between the sp^2 carbon atoms of the exocyclic double bonds, no overcrowding occurs. Thus, triisopropylidenecyclopropane[19] (hexamethyl[3]radialene) (**6**) is planar and all the above-mentioned torsion angles are less than 4°.

[4]Radialenes. Theoretical calculations[14] show that a planar four-membered ring in [4]radialene is the lowest energy conformation. For molecules bearing small substituents, such as the hydrazones in cyclobutanetetraone tetrakis(hydrazone)[23] (**7**), the four-membered ring is indeed planar. Similarly, the four-membered ring in 2,4-bis(diphenylmethylene)cyclobutane-1,3-dione[24] (**8**) is planar, regardless of the presence of two bulky substituents in the molecule, which are separated by the small oxygen atoms.

In all cases where bulkier substituents were introduced, the four-membered ring became puckered. Thus, when the substituents are 4,5-bis(carbomethoxy)-1,3-dithiol-2-ylidene)[25] (**9**), the inner-ring torsion angles are a = −13°, b = 13° (see **7** for notation) and the outer-ring torsion angles are c = −47°, d = 45.5° (average) (Chart 1). Overcrowding also affects the exocyclic double bonds. The torsion angles at these double bonds (e and f) range from −7° to +14°. In perchlorotetramethylenecyclobutane[3] (**10**), the equivalent torsion angles are a = −19°, b = 19°, c = −58°, and d = 59°. The torsion angles at the exocyclic double bonds range from −14° to +12°. Puckering increases with an increase in size of the substituents. For the dimethyl[19] case **11**, a = −22°, b = 22°, c = −62°, d = +62°, and torsion angles e and f range from −13° to +8°. For the diphenyl[11] case **12**, a = −24°, b = 24°, c = −62°, d = 63°, and torsion angles e and f range from −13° to +13°. For the phenylmethoxycarbonyl[26] case**13**, a = −26°, b = 26°, c = −67.5°, d = 63.5°, and e and f range from −11° to +18°.

[5]Radialenes. The minimum energy conformation in [5]radialene was theoretically calculated[14] to be a nearly planar five-membered ring (torsion angles of −5.75°, 15.08°, −18.64°, 15.08°, −5.75°). The structures of only one fully symmetrically substituted [5]radialene and of two others where one of the substituents is an oxygen atom are known. The first is 1,2,3,4,5-pentakis(prop-2-ylidene)cyclopentane[11] (**14**), and the other two are 2,3,4,5-tetrakis(1,3-benzodithiol-2-ylidene)cyclopentanone[27] (**15**) and tetrakis(di-*tert*-butylvinylidene)cyclopentanone[28] (**16**). The five-membered ring in the latter is practically planar, having an average torsion angle of 3°. This is an almost unperturbed system due to the presence of the allenic bonds, which cause an increase in the distances between the substituents and the central ring. However, in the other two compounds, cyclopentanone **15** and cyclopentane **14** adopt a twist envelope conformation having C_2 symmetry. In the less crowded cyclopentanone (**15**) the torsion angles are a = −8°, −11°, b = 24°, 26°, c = −38°, −39°, while in the decamethyl[5]radialene (**14**) the equivalent torsion angles are a = 14°, 16°, b = −38°, −39°, c = 47°. The differences in overcrowding are also marked at the outer-ring torsion angles with d = −17°, −21°, e = 52°, 53°, and f = −65°, −65° in the cyclopentanone (**15**) and d = −31°, 47°, e = −73°, 74°, and f = −73°, −74° in the cyclopentane (**14**). The most striking difference is in the torsion angles at the exocyclic double bonds, ranging from −9° to 16° for the former and from −8° to 23° for the latter, indicating severe twisting of the double bonds.

[6]Radialenes. Theoretical calculations[14] show that minimum energy is reached when the cyclohexane in [6]-radialene adopts a chair conformation somewhat more flattened than that of pure cyclohexane, with dihedral angles of 40° vs 54° in the latter. It was shown experimentally that in the uncrowded system, such as hexa(ethylidene)cyclohexane[29] (**17**), the inner-ring torsion angles are in very strong agreement with the calculated ones, a = −46°, b = 46°. The outer-ring torsion angles are c = −54°, d = 54°, and the exocyclic double bonds are not distorted (torsion angles e and f are less than 2°). In the crowded systems, such as 1,2,3,4,5,6-hexakis(isopropylidene)cyclohexane[20] (**18**), the cyclohexane ring adopts a chair conformation with inner-ring torsion angles a = −56°, b = 56° and outer-ring torsion angles c = −71°, d = 71°. The exocyclic double bonds are only

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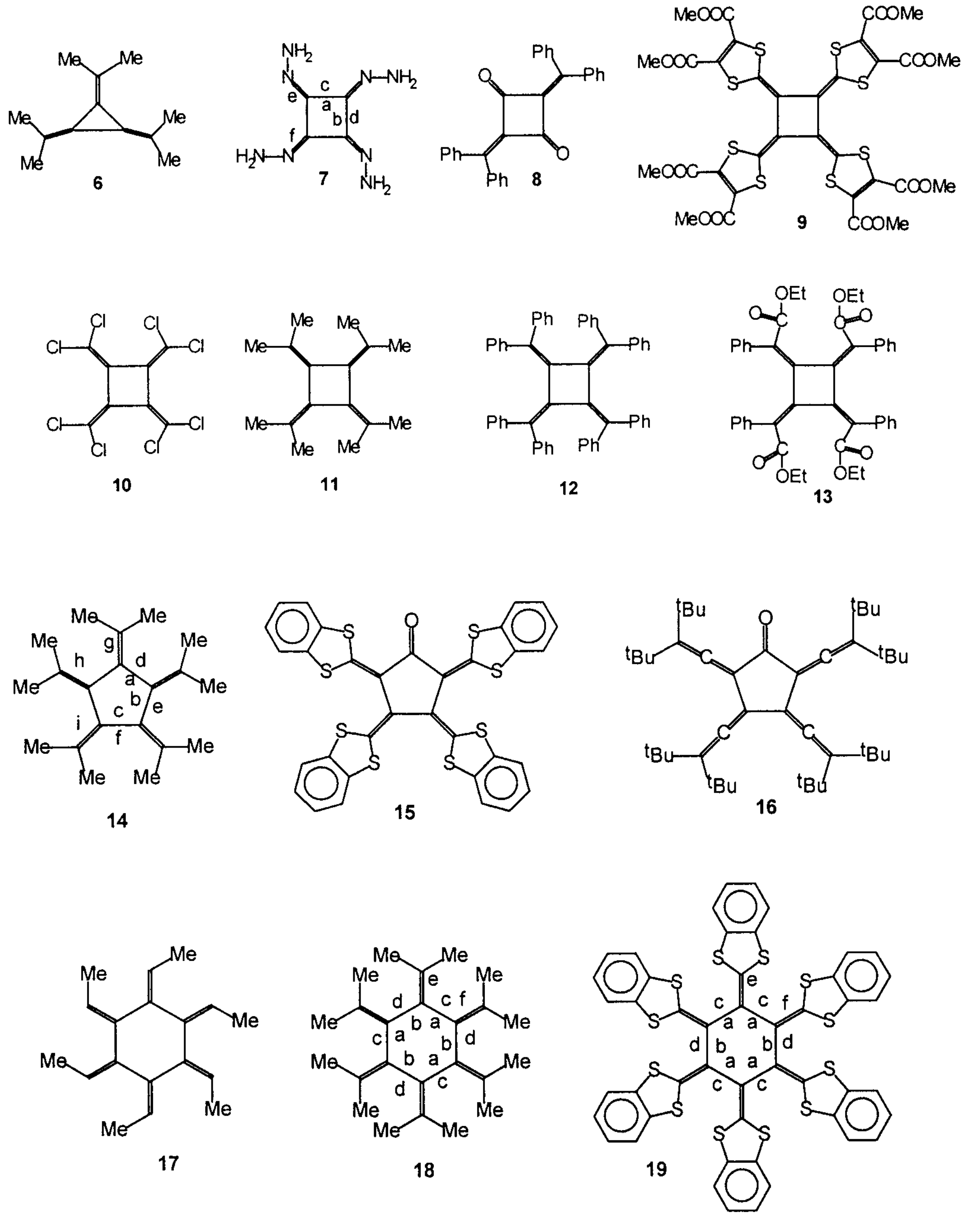
Chart 1



slightly distorted (torsion angles e and f are less than 5°). The structure of hexakis(4,5-benzo-1,3-dithiol-2-ylidene)cyclohexane[30] (**19**) is interesting. The six-membered ring adopts a boat conformation with inner-ring torsion angles a = −29°, b = 63° (see notation in **19**) and outer-ring torsion angles c = −42° (average), d = 85.5°-(average). The exocyclic double bonds are very distorted, with torsion angles reaching 30°.

Bis[4]radialene. Neither compound **3** or **4** is a bis[4]-radialene. The unsuccessful attempts to dehydrogenate the central bond connecting the two cyclobutanes to form the true bis[4]radialenes may be attributed to overcrowding at the cyclobutane rings. The accessibility of a dehydrogenating reagent might be prevented due to the shielding of the central HC−CH bond. Some of the typical distortions found in [*n*]radialenes as a result of overcrowding are also observed in **3** and **4**. The two compounds adopt different conformations. The observed O···O distance is 3.639(2) Å in **3** and 3.703(6) Å in **4**. The torsion angles at the joint between the two carbonyl groups (C(1)−C(4)−C(4′)−C(1′), see notation in **3**) are 70.8(3)° and −31.5(4)° in **3** and **4**, respectively.

The cyclobutane rings in both conformers adopt a puckered geometry. The puckering may be attributed either to the presence of an sp^3 carbon atom or to the steric repulsion between neighboring substituents at the exocyclic double bonds. Surprisingly, there is not even one known crystal structure of a compound consisting of a cyclobutane having three exocyclic double bonds and one sp^3 carbon atom to enable a comparison. However, a conformational analysis using a molecular mechanics calculations of a model molecule based on **3**, where the

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[30] Sugimoto, T.; Misaki, Y.; Kajita, T.; Yoshida, Z.-I.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *109*, 4106.

phenyl groups were replaced by hydrogens, shows[31] that the lowest energy conformation is when the cyclobutane ring adopts the planar conformation (inner-ring torsion angles are −0.3°, +0.3° consecutively). The range of the observed inner-ring torsion angles is −6.5° to 6.4° in the two four-membered rings in **3** and −8.7° to 8.7° in **4**, indicating that puckering is a result of the steric congestion imposed by the phenyl substituents. The outer-ring torsion angles that should be compared with those of [4]-radialenes are those involved with Csp^2 and/or O atoms (omitting torsion angles involving C(4) and C(4′) atoms). These torsion angles are −20.5(1)°, 22.7(2)°, 23.7(4)°, and 35.8(2)° in **3** and −25.8° and −39.4(4)° in **4**. These torsion angles are similar to those found for the other crowded [*n*]radialenes mentioned above. Molecular mechanics calculations[31] of the two conformers, **3** and **4**, restraining by fixing the experimental C(1)−C(4)−C(4′)−C(1′) torsion angle, clearly show the effect of overcrowding in these radialenes. The conformation of **4** was found to be 12.7 kcal/mol lower in energy than that of **3**. It was also found that more than 40% of the contribution to the energy is the van der Waals term, arising from the nonbonded close contacts.

Compound **5** is not a bis[4]radialene but rather a [4]-radialene. It is interesting to note that the four-membered ring is only very slightly puckered, all inner-ring torsion angles are less than 2.2°, and all outer-ring torsion angles are less than 9.0°. All the double bonds bearing diphenyl groups are only slightly distorted, with torsion angles less than 7.0°.

Experimental Procedure

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$, respectively.

Synthesis of 3 and 4. A solution of **1** (1.0 g) and CuCl (0.42 g) in DMF (20 mL) was left standing at room temperature for 4 h. The crude crystals formed by the addition of water were washed several times with water, dried, and recrystallized from $CHCl_3$ to produce a mixture of **3** and **4**. The two polymorphs were separated under a microscope according to their different external habits. **3** (red prisms, mp 241 °C, 0.17 g, 20%): IR 1770 cm^{-1}(C=O); UV 273 nm (ϵ 37900), 356 nm (ϵ 20900), and 442 nm (ϵ 16000); ^{1}H NMR δ 4.38 (2H, s, CH), 6.6−7.1(20H, m, Ph), and 7.1−7.65 (20H, m, Ph). Anal. Calcd for $C_{60}H_{42}O_2$: C, 90.65; H, 5.32. Found: C, 90.35; H, 5.12. **4** (red needles, mp 288 °C, 0.27 g, 31%): IR 1760 cm^{-1}(C=O); UV 273 nm (ϵ 40300), 347 nm (ϵ 19700), and 427 nm (ϵ 16300); ^{1}H NMR δ 3.80 (2H, s, CH), 6.85 (20H, brs, Ph), and 7.40 (20H, brs, Ph). Anal. Calcd for $C_{60}H_{42}O_2$: C, 90.65; H, 5.32. Found: C, 90.20; H, 4.83.

Synthesis of 5. A solution of **2** (2.0 g) and CuCl (1.0 g) in DMF (50 mL) was left standing at room temperature under nitrogen for 7 h. The reaction mixture was decomposed with water and then extracted with $CHCl_3$. The chloroform solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residual oil was chromatographed on silica gel. Elution with CCl_4 gave **5** (orange prisms, mp 253 °C, 0.45 g, 50%): IR 1765 and 1720 cm^{-1} (C=O); UV 252 nm (ϵ 57200), 292 nm (ϵ 51700), 348 nm (ϵ 42900), and 420 nm (ϵ 23200); ^{1}H NMR δ 6.50−7.75 (38H, m, Ar). Anal. Calcd for $C_{60}H_{38}O_2$: C, 91.11; H, 4.84. Found: C, 90.50; H, 4.46.

Data Collection, Structure Analysis, and Refinement. Diffraction intensities for all crystals were collected on a Phillips PW 11000 diffractometer, $\omega/2\theta$ mode, graphite monochromator, Mo Kα radiation. The crystal structures were solved by direct methods and refined by a full-matrix least squares procedure using F^2. All non-hydrogen atoms were refined with anisotropic hydrogen atoms with isotropic atomic displacement parameters. Final agreement factors and other refinement details are given below for each crystal structure. A list of computer programs used and data sources are provided in ref 32.

Crystal Data. 3: $C_{60}H_{42}O_2{\cdot}C_4H_8O_2$, $M = 883.10$. Triclinic, $a = 15.821(5)$, $b = 13.407(4)$, and $c = 13.363(4)$ Å, $\alpha = 116.93(3)$, $\beta = 108.60(3)$, and $\gamma = 81.70(2)°$, $V = 2395.0(13)$ Å^3, $\lambda = 0.71069$ Å, space group *P*1(bar), $Z = 2$, $D_x = 1.225$ g cm^{-3}. Red prismatic crystals of size 0.4 × 0.6 × 0.4 mm, μ(Mo Kα) = 0.070 mm^{-1}. A total of 6721 reflections measured ($2.5 < \theta < 23.1°$), 6440 used for refinement of 738 parameters. Final agreement factors are $R = 0.071$, wR = 0.180, for reflections with $[I > 2\sigma(I)]$, $R = 0.103$, wR = 0.227 for all the data. The atomic positions of the disordered ethyl acetate molecule were located from Fourier difference map but poorly refined.

4: $C_{60}H_{42}O_2$, $M = 794.94$. Monoclinic, $a = 20.023(7)$, $b = 8.842(3)$, and $c = 12.969(4)$ Å, $\beta = 100.83(3)°$, $V = 2255.21(13)$ Å^3, $\lambda = 0.71069$ Å, space group C_2, $Z = 4$, $D_x = 1.171$ g cm^{-3}. Red needle of size 0.4 × 0.3 × 0.3 mm, μ(Mo Kα) = 0.069 mm^{-1}. A total of 1897 reflections measured ($2.5 < \theta < 24.0°$), 1897 used for refinement of 364 parameters. Final agreement factors are $R = 0.044$, wR = 0.089, for reflections with $[I > 2\sigma(I)]$, R = 0.061, wR = 0.099 for all the data.

5: $C_{60}H_{38}O_2$, $M = 790.90$. Monoclinic, $a = 14.774(5)$, $b = 14.161(5)$, and $c = 21.698(8)$ Å, $\beta = 109.11(3)°$, $V = 4289(3)$ Å^3, $\lambda = 0.71069$ Å, space group $P2_1/c$, $Z = 4$, $D_x = 1.225$ g cm^{-3}. Orange prism of size 0.4 × 0.3 × 0.3 mm, μ(Mo Kα) = 0.073 mm^{-1}. A total of 6206 reflections measured ($2.8 < \theta < 24.0°$), 5866 used for refinement of 712 parameters. Final agreement factors are $R = 0.066$, wR = 0.163, for reflections with $[I > 2\sigma(I)]$, $R = 0.117$, wR = 0.224 for all the data.

Supporting Information Available: X-ray crystallographic data for the three compounds including atomic position and atomic displacement parameters as well as a complete list of bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] The conformation analysis was performed with the Cerius^2 software package, using Dreiding 2.21 force field. Mayo, S. L.; Olafson, B. D.; Goddard III, W. A. *J. Phys. Chem.* **1990**, *94*, 8897.

[32] The following computer program were used for crystal structure analysis. Program used to solve the crystal structures: SHELXS86 (Sheldrick, 1990). Program used to refine the crystal structures: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEP II (Johnson, 1976); TEXSAN 1.6 MSC.