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Highly Strained Molecules

Isolation of Bicyclopropenylidenes: Derivatives of the Smallest Member of the Fulvalene Family**

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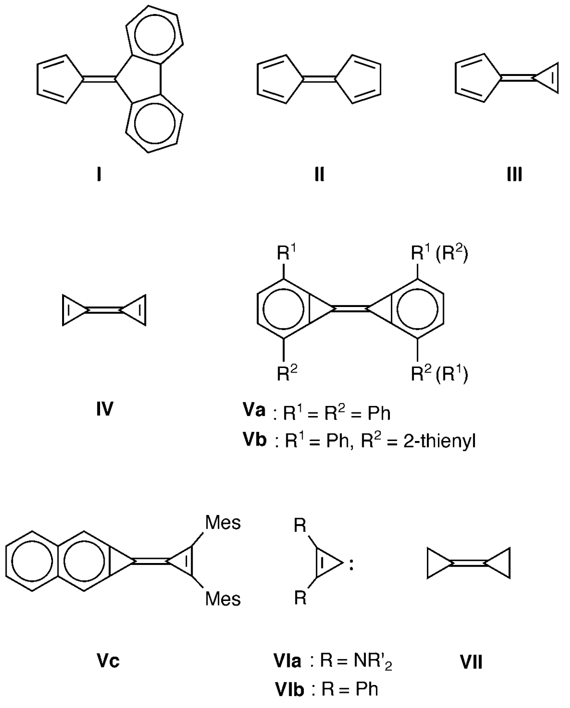
Dedicated to Professor Edgar Niecke on the occasion of his 70th birthday

The class of hydrocarbons obtained by formally cross-conjugating two rings through a common exocyclic double bond is known as the fulvalenes, a terminology introduced by Brown.[1] Although the synthesis of compound **I** (Scheme 1) was reported as early as 1915 by Courtot,[2,3] the first non-benzannulated fulvalene, a derivative of pentafulvalene **II**, was prepared in 1954.[4] A decade later, derivatives of triapentafulvalenes **III**,[5] larger-ring[6] and heterocycle-containing fulvalenes, such as the widely studied tetrathiafulvalenes (TTF),[7] were isolated. However, despite intensive effort,[6,8] the experimental demonstration of the existence of derivatives of the smallest and most strained member, namely triafulvalene (bicyclopropenylidene) **IV**, has not been achieved to date. Even compounds **Va–c**,[9,10] which feature thermodynamically highly stabilizing benzo substituents,[11] were only characterized by ^{1}H NMR spectroscopy and mass spectrometry. The difficulty in isolating triafulvalene **IV** has been predicted by theoretical calculations,[8] Radom and co-workers[8a] even concluding that these compounds have an antiaromatic character. Herein we show that kinetically protected triafulvalenes can be prepared and isolated as thermally stable compounds. They feature a small HOMO–LUMO gap (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital), and consequently are very reactive, as exemplified by the spontaneous room temperature addition of water to the central C=C bond.



Scheme 1. Benzannulated compound **I**, pentafulvalene **II**, triapentafulvalene **III**, triafulvalene **IV**, benzannulated derivatives **V**, cyclopropenylidenes **VI**, and bicyclopropylidene **VII**.

Triafulvalenes **IV** are formally the dimers of cyclopropenylidenes **VI**. According to the Carter and Goddard formulation,[12] the strength of the C=C bond that results from the dimerization of singlet carbenes should correspond to that of a canonical C=C bond (usually that of ethene) minus twice the singlet–triplet energy gap (E_{ST}) for the carbene. The comparison of the calculated E_{ST} value for the isolated diaminocyclopropenylidenes **VIa**[13] and matrix-characterized diphenylcyclopropenylidene **VIb**,[14] 250 and 179 kJ mol^{-1}, respectively, suggests that aryl-substituted triafulvalenes should be more likely to exist. However, the dimerization of singlet carbenes is believed to follow a non-least-motion pathway[15] that involves the attack of the occupied in-plane lone pair of σ electrons of one singlet carbene center on the out-of-plane vacant p_π orbital of a second carbene, and in cyclopropenylidenes **VI** the latter orbital is difficult to access because of the 2π-electron system. Thus, there is an energy barrier for the dimerization of cyclopropenylidenes **VI** that arises from electronic factors, this barrier would be enhanced by the presence of bulky substituents, which are necessary to kinetically protect the central π bond of triafulvalenes **IV**.[10] Based on this analysis, we planned a two-step approach involving the coupling of two dichlorocyclopropene units followed by reduction of the resulting bis(chlorocyclopropenyl) moiety.

Starting from the commercially available tetrachlorocyclopropene **1**, a bulky 2,4,6-triisopropylphenyl group (Tip) was first incorporated into the framework by using a Friedel–

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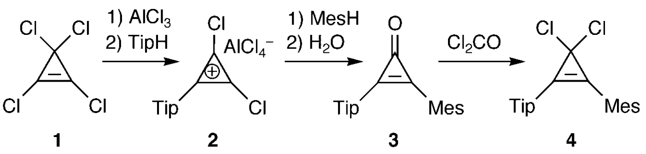
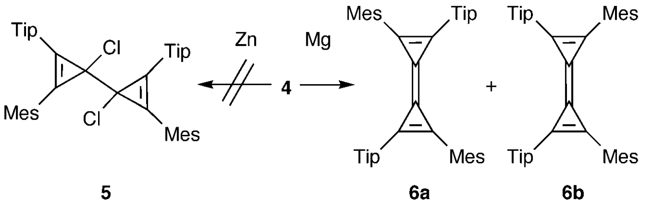
Crafts reaction, as described by West et al.[16] We were not able to introduce a second Tip group, but successfully introduced a mesityl group (Mes). Treatment of cyclopropenone **3** with phosgene led to **4**, which was isolated in 69% yield with respect to **1** (Scheme 2). To prepare the bis(chlorocyclopropenyl) derivative **5**, we first tested zinc as a coupling reagent, as reported by Breslow et al.,[17] for the diphenyl analogue, but a complex mixture was formed and we were not able to isolate any products. However, when a solution of **4** in THF was treated with an excess of magnesium at room temperature, we directly obtained the desired triafulvalene derivatives **6a** and **6b** (94% total yield), instead of the expected bis(cyclopropenyl) derivatives **5** (Scheme 3). The observed *E*/*Z* ratio (60:40) reflects the relative thermodynamic stability of **6a** and **6b** based on steric repulsion between the bulky substituents.



Scheme 2. Synthesis of dichlorocyclopropene **4**.



Scheme 3. Synthesis of triafulvalenes **6a** and **6b**.

The signal for the central sp^2 carbon atoms in the ^{13}C NMR spectrum was observed at $\delta = 85.0$ ppm for **6a** and $\delta = 85.3$ ppm for **6b**, which is remarkably shifted to higher field compared to the shifts observed for bicyclopropylidenes **VII** (115–120 ppm).[18] Although perfect separation of **6a** and **6b** was not successful because of their similar and high solubility in all solvents, a few single crystals of **6a** were obtained from a pentane/THF mixture at −78°C. An X-ray diffraction analysis[19] shows that the triafulvalene skeleton is almost perfectly planar, the sums of bond angles around the two central carbon atoms C1 and C16 are 359.64° and 359.48°, and the C2-C1-C16-C18 torsion angle is 3.01° (Figure 1). The dihedral angles between the cyclopropene rings and each Mes and Tip groups are between 28.26° and 54.61°, which suggests that, if operative, the conjugative interactions between the fulvalene skeleton and its substituents are weak. As predicted by theoretical calculations,[8] there is a considerable fulvalenic bond length compression, because of the high s character of the σ-bond component of the central double bond; indeed, the C1–C16 distance is only 1.303(5) Å. The C1–C2 and C1–C3 (1.459(5) and 1.479(5) Å), as well the C2–C3 bond lengths (1.330(5) Å) are slightly shorter than typical C–C single and double bonds, respectively, which confirms the highly localized nature of the π system.

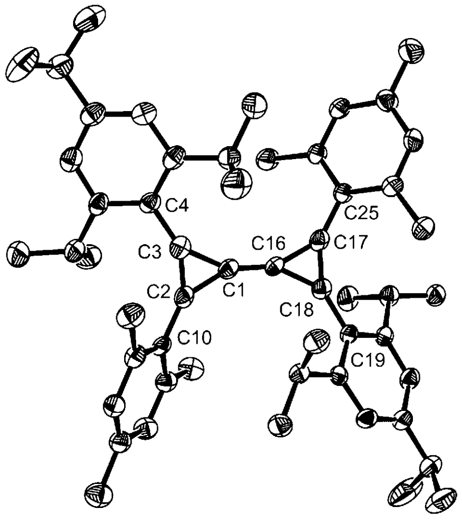


Figure 1. X-ray crystal structure of **6a** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–C16 1.303(5), C1–C2 1.459(5), C1–C3 1.479(5), C2–C3 1.330(5), C2–C10 1.456(5), C3–C4 1.452(5), C16–C17 1.457(5), C16–C18 1.455(5), C17–C18 1.323(5), C17–C25 1.451(5), C18–C19 1.458(5); C2-C1-C3 53.8(2), C1-C2-C3 63.8(3), C1-C3-C2 62.3(3), C17-C16-C18 54.1(2), C16-C17-C18 62.9(3), C16-C18-C17 63.1(3).

Derivatives **6** are indefinitely stable at room temperature, both in the solid state and in solution, under an inert atmosphere,. Crystals of **6a** melt at 130°C, and no decomposition was observed by heating a benzene solution at reflux for 48 h. Solutions and crystals of **6a** are dark purple, and indeed the UV/Vis spectrum showed a distinct absorption band at 502 nm ($\varepsilon = 2500$). This band is unusually red-shifted compared to the absorption maxima of ethylene (171 nm), 1,3-butadiene (217 nm), *trans*-1,3,5-hexatriene (274 nm), and even that of diaminotriafulvene (298 nm).[20] Ab initio calculations (at the HF/6-31G(d,p)//B3LYP/6-31G(d) level) performed on the tetraphenyltriafulvalene as a model readily rationalized this phenomenon. The frontier orbitals are depicted in Figure 2. The HOMO, a combination of the three C=C π orbitals, is remarkably high-lying (−5.29 eV), which reflects the high electron density in the triafulvalene plane. The LUMO, which is a combination of the C=C π* orbitals of the two three-membered rings, is relatively low-lying.

The existence of a small HOMO–LUMO energy gap not only rationalized the unusual UV/Vis spectrum, but also suggests that triafulvalenes should be very reactive. Indeed, triafulvalenes **6** are extremely air-sensitive, and decompose within a minute to give a complex mixture of unidentified products. When a mixture of **6a** and **6b** was treated with oxygen-free water in THF, H$_2$O addition to the central C=C bond occurred to afford the corresponding adducts **7a** and **7b** as racemic mixtures in 82% overall yield (Scheme 4). The structure of these compounds was determined by ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography for **7b**. This is certainly one of the very rare examples of spontaneous

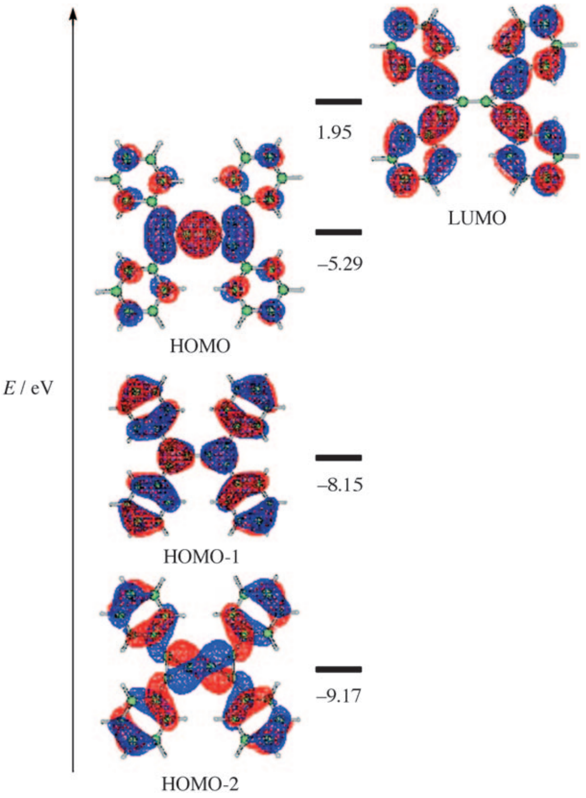
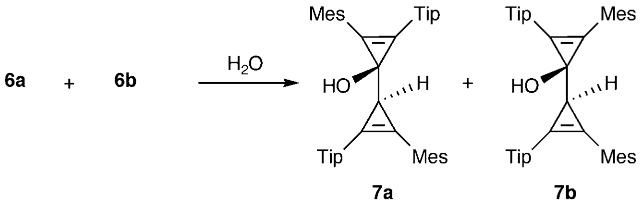


Figure 2. Molecular orbitals of tetraphenyltriafulvalene calculated at the HF/6-31G(d,p)//B3LYP/6-31G(d) level of theory.



Scheme 4. Spontaneous addition of water to triafulvalenes **6a**/**6b**.

addition of water to the C=C bond of a hydrocarbon derivative.

More than half a century after the discovery of the first fulvalene derivative, this work demonstrates that by providing sufficient kinetic protection of the inter-ring C=C bond, triafulvalenes can also be isolated. The high degree of strain means that these molecules should feature unique chemical reactivity. Moreover, because of the similarities with tetrathiafulvalenes (TTF), namely an electron-rich C=C bond and a small HOMO–LUMO gap, the availability of triafulvalenes opens a new avenue for the discovery of materials with useful electrochemical and photochemical properties.

Experimental Section

All manipulations were performed under an atmosphere of dry argon by using standard Schlenk techniques. Structures annotated with atom labels used in the ^{13}C NMR spectra are given in the Supporting Information.

Synthesis of dichlorocyclopropene **4**: Tetrachlorocyclopropene (2.1 g, 11.7 mmol) was added to a solution of aluminum trichloride (1.6 g, 11.7 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The solution was warmed to room temperature and stirred for 2 h. 1,3,5-triisopropylbenzene (2.5 g, 12.0 mmol) was added at −78 °C to this solution and the reaction mixture stirred at room temperature overnight. 1,3,5-trimethylbenzene (2.0 g, 16.6 mmol) was then added at −78 °C, and after stirring at room temperature overnight, water (30 mL) was added. The organic layer was washed with water and dried over $MgSO_4$. After filtration, the volatile components were removed under vacuum to give **3**[21] as a white powder, which was used without further purification. A 20 % solution of phosgene in toluene (5 mL) was added to a solution of **3** in CH_2Cl_2 (20 mL) at 0 °C, and the reaction mixture was stirred at room temperature overnight. The volatile components were removed under vacuum, and the solid residue washed with hexane (5 mL) to give **4** as a white powder (3.5 g, 69 %); m.p. 98.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.19$ (d, $J = 6.9$ Hz, 12 H), 1.24 (d, $J = 6.6$ Hz, 6 H), 2.00 (s, 3 H), 2.50 (s, 6 H), 2.77 (sept, $J = 6.9$ Hz, 2 H), 3.24 (sept, $J = 6.6$ Hz, 1 H), 6.61 (s, 2 H), 7.19 ppm (s, 2 H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 21.5$ (CH_3Mes), 22.0 (CH_3Mes), 24.4 (CH_3Tip), 25.0 (CH_3Tip), 32.1 (CHTip), 35.1 (CHTip), 64.5 (CCl_2), 121.6 (*ipso*), 129.5 (*ipso*), 132.3 (C_{ring}Tip) 122.0 (*m*), 132.1 (C_{ring}Mes), 130.1 (*m*), 141.1 (*o*), 142.1 (*p*), 149.6 (*o*), 151.5 ppm (*p*).

Synthesis of triafulvalenes **6a** and **6b**: THF (15 mL) was added to a mixture of **4** (2.15 g, 5.0 mmol) and magnesium (250 mg, 10.3 mmol), and the solution was stirred at room temperature for 18 h. After evaporation of THF, the residue was extracted with hexane (50 mL). The remaining excess magnesium and magnesium salts were removed by filtration, and the solvent was removed under vacuum to afford a black powder (1.68 g, 94 %). Recrystallization of the residue from THF and pentane gave **6a** as dark purple crystals. ^{1}H and ^{13}C NMR signals of **6a** and **6b** were assigned by 2D NMR techniques. **6a**: m.p. 130.0 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.15$ (d, $J = 6.7$ Hz, 24 H), 1.23 (d, $J = 6.8$ Hz, 12 H), 2.09 (s, 6 H), 2.38 (s, 12 H), 2.81 (sept, $J = 6.8$ Hz, 2 H), 3.56 (sept, $J = 6.7$ Hz, 4 H), 6.75 (s, 4 H), 7.19 ppm (s, 4 H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 21.4$ (CH_3Mes), 21.5 (CH_3Mes), 23.7 (CH_3Tip), 24.6 (CH_3Tip), 31.2 (CHTip), 35.4 (CHTip), 85.0 (C=C), 120.9 (*m*), 126.4 (*ipso*), 126.7 (*ipso*), 126.8 (C_{ring}Tip), 127.1 (C_{ring}Mes), 129.3 (*m*), 138.5 (*p*), 138.8 (*o*), 149.5 (*o*), 150.1 ppm (*p*); UV/Vis (hexane): λ_{max} 502 nm; **6b**: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.15$ (d, $J = 6.7$ Hz, 24 H), 1.23 (d, $J = 6.8$ Hz, 12 H), 2.09 (s 6 H), 2.32 (s, 12 H), 2.81 (sept, $J = 6.8$ Hz, 2 H), 3.63 (sept, $J = 6.7$ Hz, 4 H), 6.71 (s, 4 H), 7.24 ppm (s, 4 H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 21.4$ (CH_3Mes), 21.6 (CH_3Mes), 23.9 (CH_3Tip), 24.6 (CH_3Tip), 31.1 (CHTip), 35.3 (CHTip), 85.3 (C=C), 121.0 (*m*), 124.9 (C_{ring}Tip), 126.2 (*ipso*), 126.4 (*ipso*), 127.4 (C_{ring}Mes), 129.1 (*m*), 138.5 (*p*), 138.7 (*o*), 149.9 (*p*), 150.0 ppm (*o*).

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