Synthesis of 1,3-Diphenyl-6-alkyl/aryl-Substituted Fulvene Chromophores: Observation of $\pi-\pi$ Interactions in a 6-Pyrene-Substituted 1,3-Diphenylfulvene

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Ⓢ Supporting Information

ABSTRACT: The synthesis, structural, and electronic properties of nine 1,3-diphenyl-6-alkyl/aryl substituted pentafulvenes were studied. Pyrene ring $\pi-\pi$ interactions were revealed from analysis of the experimental crystal packing of 1,3-diphenyl-6-(1-pyrene)fulvene and supporting DFT calculations. Photophysical properties derived from UV−vis and fluorescence emission measurements demonstrated tunable and low HOMO−LUMO band gaps for the series. The presented results point to a model synthetic approach for incorporation of extended π systems and donor-π-acceptor groups for fulvene-based electronic materials.
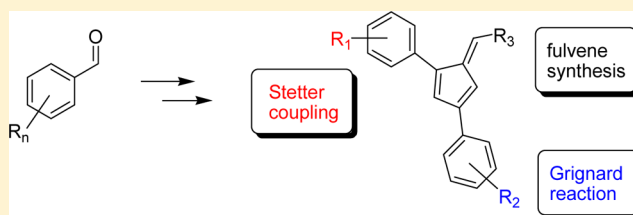
Pentafulvenes have been investigated as important structural units in synthesis areas spanning natural products[1] and medicine,[2,3] cyclic conjugated systems,[4,5] and organometallic complexes with catalytic and other properties.[6] Ring and exocyclic C6-substituted pentafulvenes are receiving increased research attention in the design of materials with electronic properties such as donor-π-acceptor systems and n-type semiconductors.[7−9] The synthesis of pentafulvene-based polymers and supramolecular architectures, some of which exhibit luminescent properties, has been reported.[10] Important in this type of work are synthetic methods that give entry into substitutional variability for tuning of electronic properties while maintaining a framework that will allow for incorporation of the pentafulvene structural unit into polymers or extended networks. In the course of our research on the synthesis of C_2-symmetric *ansa*-metallocenes,[11,12] the crystallinity and intense color of some of the pentafulvene precursors prompted us to consider more carefully their absorption properties and a possible synthetic design for their incorporation into electronic materials. Herein, we report the synthesis, spectroscopic properties, and select single crystal X-ray structures of several new 1,3-diphenyl-6-alkyl/aryl fulvenes. This work represents a modular approach to the selective and stepwise attachment of electronically functional substituents in positions favorable for applications as monomeric units or for incorporation into polymers and supramolecular assemblies.

Fulvenes **4−12** were obtained using an overall four-step reaction sequence (Scheme 1). Stetter coupling of benzaldehyde with methyl vinyl ketone gave 1-phenyl-1,4-pentanedione **1**, which was purified by vacuum distillation. Conversion of **1** to 3-phenyl-cyclopenten-1-one **2** was carried out employing base-

promoted cyclization. The Grignard addition of PhMgCl to **2**, with ensuing dehydration, afforded 1,3-diphenyl-1,3-cyclopentadiene **3**, which was purified by crystallization from hot EtOH.[13] The final, key step[14] is the reaction of **3** with numerous functionalized aldehydes producing a diverse fulvene substrate pool **4−12**. The overall procedure is high-yielding and operationally simple, requires no chromatography, and is easily amenable to scale up to multigram quantities of fulvenes. The fulvenes produced in the reaction of **3** with functionalized aldehydes crystallize from the ethanol and can be obtained as pure crystalline solids by recrystallization from common organic solvents. Structure elucidation and purity of fulvenes **4−12** were confirmed using a combination of spectroscopic techniques, including single crystal X-ray analysis for fulvenes **4−6**,[15] **8**, and **11** (see Supporting Information).

Organic materials incorporating pyrene in the molecular architecture are of current interest,[16,17] and herein, we highlight the molecular and crystal structure of the 6-(1-pyrene)-substituted fulvene **11** (Figure 1). Dark prismatic crystals of **11** were obtained from THF layered with MeCN. Molecules of **11** crystallized out in the centrosymmetric space group, *Pbca*, with one molecule per asymmetric unit.[18] Alternating short and long bond distances as well as alternating intraring bond angles for the fulvene ring of **11** were observed and are consistent with data for other substituted pentafulvenes reported previously (Figure 1).[7−10,19−21] The pyrene ring of **11** is tilted out of the fulvene ring plane by the largest angle [50.51°(4)] compared to the other aromatic ring 6-substituted fulvenes in this series [**6**,

Scheme 1. Synthesis of 1,3,6-Substituted Fulvenes
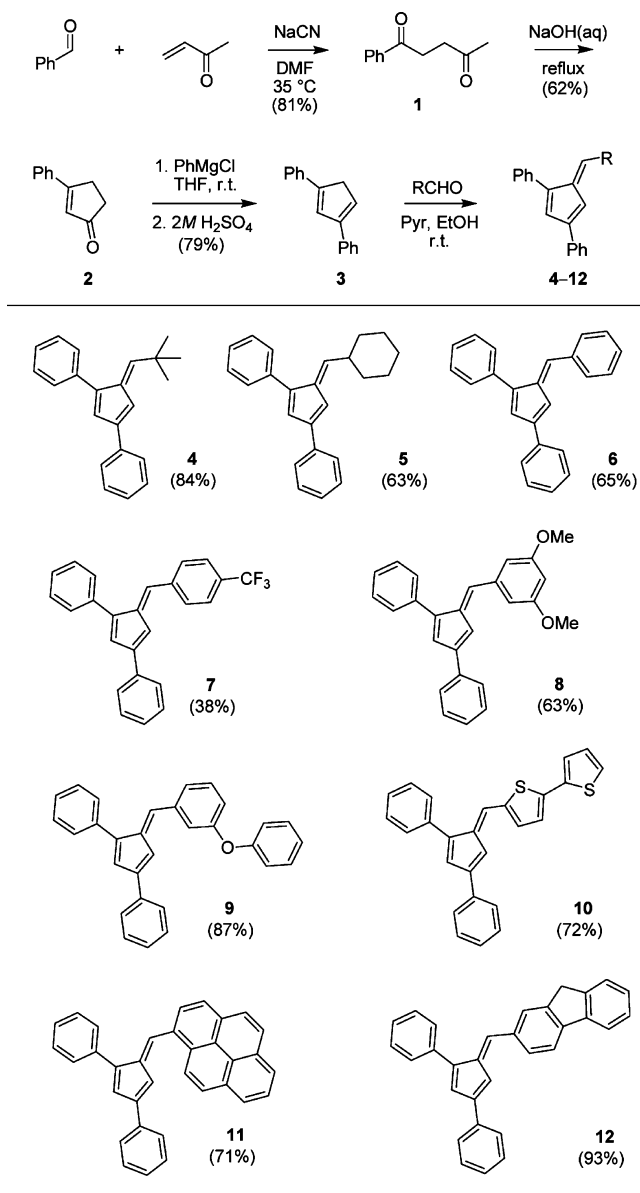
44.60°(5); and **8**, 45.75°(4)], and it is significantly larger than this angle reported for 1,2,3,4-tetramethyl-6-(1-pyrene)fulvene (13.68°).[22] Pyrene rings have been observed to form $\pi-\pi$ interactions in the solid state as well as in organic and organometallic compounds with attached pyrene units.[23−26] These interactions play an important role in supramolecular chemistry and in organic- and organometallic-based molecular electronics.[27−31] One of the most notable features in the crystal structure of **11** is the organization of molecules into layers in which all pyrene rings adopt a head-to-tail[19] $\pi-\pi$-stacked arrangement (Figure 1). In the *c* direction, molecules of **11** are arranged in a H-T—T-H—H-T—T-H bilayer-type repeating sequence [head (H) = pyrene ring (red), tail (T) = 1,3-diphenylfulvene rings (blue), Figure 1]. Adjacent fulvene molecules running along the *b* direction are packed such that the planes from attached pyrene rings are oriented nearly perpendicular (87.2°) to each other giving a herringbone appearance to the pattern. In the H—H region, pyrene rings in the bottom of the bilayer are aligned almost face to face and

head to tail to their complementary pyrene rings in the top of the bilayer, forming $\pi-\pi$-stacked dimers. A tetrameric packing motif results in which the space between π-stacked pyrene rings is shrouded by 1,3-diphenylfulvene rings from the top and bottom of the bilayer. The closest contacts between pyrene ring C atoms of adjacent molecules (see packing motif, Figure 1) range from 3.629 to 3.664 Å which gives an average centroid-to-centroid distance of 3.64 Å. However, the centroids of the pyrene rings of π-stacked dimers of **11** are slipped 1.15 Å end to end and 0.51 Å edge to edge when viewed down the normals of pyrene rings (Figure 1). The angles between pyrene ring normals and centroid-to-centroid vectors are 18.4° in the end-to-end direction and 8.1° in the edge-to-edge direction. This results in a somewhat slipped $\pi-\pi$ interaction between coplanar pyrene rings with an interplane contact distance of 3.46 Å, well within the distance expected for a noncovalent $\pi-\pi$ interaction.[24] In the crystal structure of fulvene **11**, the pyrene ring overlap is intermediate between perfect face-to-face alignment and fully slipped alignment where some of the ring atoms are positioned directly above or below the centroid of the opposite ring.

In an effort to better understand the $\pi-\pi$ stacking, density functional theory (DFT) calculations were performed on **11**. The calculations were performed with Gaussian 09[32] using Grimme's generalized gradient approximation functional (keyword B97D)[33] and the standard 6-31G(d,p) basis set.[34] This functional has been shown in the past[35] to be an appropriate selection for π-stacked systems. No basis set superposition error correction was performed, so the targeted energy value, the energy of interaction of the dimer of **11**, should be considered an upper limit. The resultant energy-minimized dimer was found to be 93.7 kJ mol^{-1} more stable than isolated molecules of **11**. Although this should be regarded as an upper limit, because of the relative simplicity of the calculation, it does point to a significant energetic tendency for the dimer to form, at least in the gas phase. Significant differences in the calculated dimer structure were observed and include fully slipped π-stacked pyrene rings, non-coplanar pyrene rings, and different relative orientations for the 1,3-diphenylfulvene rings (see Supporting Information for pictorial representations of calculated versus observed dimers). Although slipped, face-to-face $\pi-\pi$ interactions exist in the solid state structure of **11**, no such face-to-face interactions were observed in the reported crystal structure of 1,2,3,4-tetramethyl-6-(1-pyrene)fulvene.[22] The noted differences between the calculated and observed dimer structures of **11** as well as the lack of any $\pi-\pi$ stacking interactions in the crystal structure of 6-(pyrene)-1,2,3,4-tetramethylfulvene could point to a directing influence of 1,3-diaryl substituents in enforcing dimeric $\pi-\pi$ stacking interactions for these types of fulvenes, which is one focus of ongoing research.

The fulvene series **4−12** produced intensely colored, high-melting point solids ranging across the visible spectrum from orange and red to black based on the nature of substitution on the exocyclic C6 position on the fulvene core. In order to understand electronic-structure property relationships for **4−12**, solution studies including ultraviolet−visible excitation with complementary fluorescence emission were performed in THF with concentrations ranging from 0.4 to 0.6 mmol L^{-1}. Absorbance studies on the fulvene series are compiled graphically in Figure 2, and selected optical properties are also shown in Table 1. All fulvenes produced more than two strong, distinct absorptions due to $\pi-\pi^*$ transitions from their
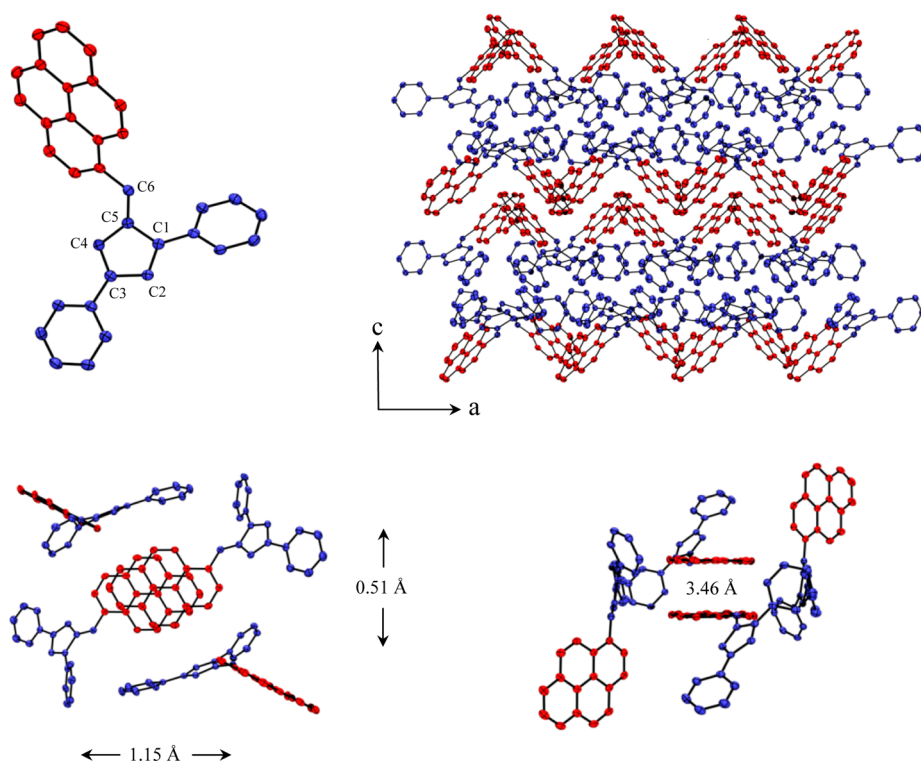
Figure 1. Crystal and molecular structure of fulvene **11**, showing the ORTEP view (upper left, viewed normal to and with numbering scheme for the fulvene ring), crystal packing viewed along the *b* direction (upper right), and the slipped π−π stacking arrangement of pyrene rings viewed normal to the pyrene ring planes (lower left), and in the plane of pyrene rings (lower right). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å): C1−C2 1.353(2), C2−C3 1.467(2), C3−C4 1.363(2), C4−C5 1.459(2), C5−C6 1.357(2). Selected bond angles (deg): C5−C1−C2 107.09(12), C1−C2−C3 110.06(12), C2−C3−C4 108.07(12), C3−C4−C5 108.74(12), C4−C5−C1 106.00(11).
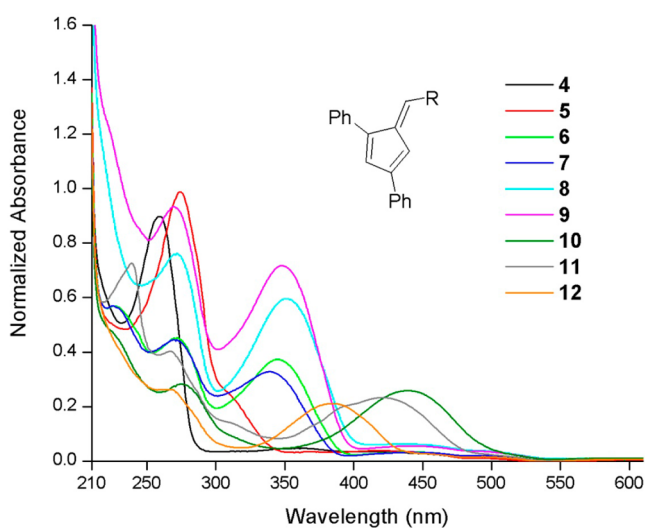

Figure 2. Solution absorbance spectra of fulvene compounds **4−12** in THF.

Table 1. Selected Solution Electronic Properties of Fulvenes 4−12

	excitation				
entry	λ_{max} (nm)	$\log(\varepsilon)^a$	emission^b λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)	ΔE (eV)^c
4	400	3.11	460	60	2.32
5	365	3.03	420	55	2.36
6	438	3.10	500	62	2.04
7	450	2.98	516	66	2.01
8	436	3.04	509	73	2.07
9	440	3.03	506	66	2.06
10	439	4.36	503	64	2.34
11	422	3.87	480	58	2.45
12	384	4.06	451	67	2.73

$^a\varepsilon$ reported in L mol^{-1} cm^{-1}. $^b\lambda_{max}$ reported in nm based on λ_{max} excitiation. ^{c}Estimated by onset of absorption.

structural contributions. Nonaromatic substituted fulvenes **4** and **5** produced the most intense absorption bands at only 260 and 280 nm, respectively. For fulvenes **6−12**, absorptions beyond 300 nm are a consequence of through-space aromatic conjugation with the fulvene core.

The lowest-energy onset absorption extended to nearly 600 nm for the series, indicating that these fulvenes overall possess low HOMO−LUMO band gaps (ΔE ranging from 2.01 to 2.73 eV) making them attractive precursory organic-based elec-

tronics. Extended fused ring fulvenes **11** and **12** produced the largest band gaps among the series, with absorption onsets slightly less than 500 nm. The maximum absorption wavelength (λ_{max}) was employed to excite each of the fulvenes in the series. All fulvenes in this study possessed weak emission signals, indicating most of the excitation energy is lost to primarily nonradiative-decay processes such as structural, translational, or rotational molecular vibrations. Overall, emission bathochromic shifts upon excitation appear within a narrow range of 55−73 nm with no direct correlation with fulvene structure. These small Stokes shifts indicate negligible intramolecular charge transfer.

Trifunctional 1,3,6-aryl and 1,3,6-alkyl/aryl pentafulvenes can be obtained using a modular approach based on the synthetic scheme for 1,3-diphenylcyclopentadiene and a subsequent fulvene synthesis step. The ability to tailor the synthesis provided a diverse pool of functionalized fulvene compounds. The commercial availability of alkyl and aryl aldehydes as well as various Grignard reagents makes this synthetic approach an attractive one for the design of new electronic materials and ligands containing or derived from a conjugated pentafulvene core. Incorporation of polyaromatic hydrocarbons, alkynes, and other heteroalkyl- and heteroaromatic-based functional groups may lead to highly conjugated and processable organic and organometallic materials. It is anticipated that the correct choice and placement of functional groups could result in materials with properties including donor-π-acceptor behavior, intense absorption in the visible and near-infrared (low band gap) regions, and fluorescence. Electronic-structure property relationships suggest that these fulvene-based compounds could also serve as valuable repeat structures for extended macromolecular systems possessing one or more of these properties.

■ EXPERIMENTAL SECTION

Syntheses of compounds **1**, **2**, and **3** were carried out using modified literature procedures.[13] The procedures are outlined below and include spectroscopic data that were not available in the original reports. Fulvene syntheses using **3** as the cyclopentadiene starting material were carried out using the method of Stone and Little.[14] Reactions were carried out under an atmosphere of nitrogen unless otherwise noted. All glassware was oven-dried prior to use. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR data were obtained under ambient temperature conditions, and chemical shifts were reported in parts per million (δ). Chemical shifts were referenced using the peak for residual CHCl$_3$ (δ 7.25) or TMS (δ 0.00) for ^{1}H NMR and the peak for CDCl$_3$ (δ 77.0) for ^{13}C NMR. ^{19}F NMR was referenced to CFCl$_3$ (δ 0.00). Coupling constants for all spectra are reported in hertz. Samples for absorbance and emission spectra were collected in THF using a path length of 1 cm in Spectrosil quartz cuvettes (3 mL). HRMS data were obtained using a double focusing sector instrument operating in EI mode.

1-Phenyl-1,4-pentanedione 1. Freshly distilled benzaldehyde (31.2 g, 294 mmol) in DMF (150 mL) was added dropwise over 10 min to a vigorously stirred suspension of NaCN (1.5 g, 30.6 mmol) in DMF (100 mL) at 35 °C under N$_2$. The color of the reaction mixture turned yellow and faded to a dark orange as the addition of benzaldehyde neared completion. The reaction mixture was allowed to stir for 10 min, and freshly distilled methyl vinyl ketone (16.0 g, 228 mmol) in DMF (150 mL) was added dropwise over 20 min with continued vigorous stirring at 35 °C under N$_2$. The resulting dark red−brown reaction mixture was allowed to stir for 4 h at 35 °C under N$_2$ exposed to air and combined with twice the volume of water. The pale yellow suspension was extracted by vigorous stirring over two, 1 L portions of CHCl$_3$. The combined organic fractions were filtered through a cotton plug and concentrated under a rotary vacuum. Residual DMF was removed, by Kugelrohr vacuum distillation (100 °C, 2 Torr) followed by distillation of **1** (150 °C, 2 Torr), as a viscous light yellow liquid (32.7 g, 81%), which was >95% pure (^{1}H NMR, GC−MS). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.97 (m, 2H, *o*-Ph), 7.49 (m, 3H, *m*- and *p*-Ph), 3.25, 2.86 (t, 4H, C$\underline{H}_2$), 2.23 (s, 3H, Me). ^{13}C NMR (75 MHz, CDCl$_3$): δ 206.8, 198.1 (CO), 136.4, 132.8, 128.2, 127.7 (Ph), 36.7, 32.1, 29.7 (C$\underline{H}_2$ and Me). MS (EI, 70 eV): *m/z* 176 (M$^+$), 161 (M$^+$ − Me), 133 (M$^+$ − COCH$_3$), 105 [M$^+$ − (CH$_2$)$_2$COCH$_3$], 77 (Ph$^+$).

3-Phenylcyclopent-2-en-1-one 2. A pale yellow suspension of 1-phenyl-1,4-pentanedione **1** (30.7 g, 174 mmol) in 0.5 M NaOH (400 mL) was vigorously stirred under reflux conditions for 4 h resulting in a brown-colored reaction mixture. The reaction mixture was cooled in an ice bath with vigorous stirring, and hydrochloric acid (200 mL, 3

M) was added until the mixture was acidic to pH paper. The resulting brown precipitate was vacuum filtered and washed with water (200 mL). The brown solid was air dried and subsequently dried in a vacuum desiccator giving 3-phenylcyclopent-2-en-1-one **2** as a crude, brown solid (25.2 g, 92%). The crude product was recrystallized by dissolving in boiling hot absolute EtOH (110 mL) and cooling (−5 °C). Vacuum filtration, washing with cold absolute EtOH (30 mL), and vacuum drying afforded **2** as a yellow crystalline solid (14.3 g, 52%). An additional crystalline crop of product was obtained by concentration of the filtrate to 50 mL, cooling (−5 °C), and seeding with crystals from the first crop (2.7 g, total combined yield 17.0 g, 62%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.66, 7.46 (m, 5H, P$\underline{h}$), 6.57 (t, 1H, C$\underline{H}$), 3.05, 2.59 (m, 4H, C$\underline{H}_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 209.2 (C̲O), 173.8, 134.1 (Ph ipso-C and Ph-C), 131.2, 128.9, 127.5, 126.8 (C̲H), 35.3, 28.6 (C̲H$_2$). MS (EI, 70 eV): *m/z* 158 (M$^+$), 129, 115, 102, 91, 77, 64.

1,3-Diphenylcyclopentadiene 3. A solution of 3-phenylcyclopent-2-en-1-one **2** (8.42 g, 53.2 mmol) in THF (80 mL) under N$_2$ was added dropwise over 15 min to vigorously stirred PhMgCl in THF (2 M, 35 mL, 70 mmol) under N$_2$. The resulting brown reaction mixture was allowed to stir at room temperature for 16 h under N$_2$ exposed to air, and THF was removed by rotary vacuum to give a brown residue. The brown residue was taken up and vigorously stirred in a mixture of water (300 mL) and Et$_2$O (300 mL). Addition of 6 M H$_2$SO$_4$ (15 mL, 90 mmol) resulted in a brown Et$_2$O layer and a clear water layer, which was stirred for an additional 5 min. The brown Et$_2$O layer was separated and washed sequentially with saturated NaHCO$_3$ (3 × 200 mL), water (2 × 200 mL), and saturated brine (1 × 200 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under vacuum to afford a golden-colored oil, which was recrystallized by dissolving in boiling hot absolute EtOH (300 mL) and cooling (−5 °C). Vacuum filtration, washing with cold absolute EtOH (20 mL), and vacuum drying afforded **3** as colorless crystalline flakes that appear golden in bulk (9.16 g, 79%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18−7.66 (m, 11H, P$\underline{h}$ and PhC$\underline{H}$CPh), 6.63 (m, 1H, PhCC$\underline{H}$CH$_2$), 3.58 (m, 2H, C$\underline{H}_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.8, 146.6, 136.1, 135.6 (C̲), 128.7, 128.6, 127.4, 127.0, 126.9, 126.1, 125.9, 125.1 (C̲H), 41.8 (C̲H$_2$). MS (EI, 70 eV): *m/z* 218 (M$^+$), 202, 189, 165, 141, 139, 115, 101.

1,3-Diphenyl-6-(*tert*-butyl)fulvene 4. To a vigorously stirred mixture of 1,3-diphenylcyclopentadiene (3.86 g, 17.7 mmol) in absolute EtOH (30 mL) under N$_2$ were added pivaldehyde (2.20 mL, 20.3 mmol) and pyrrolidine (2.20 mL, 26.4 mmol), and the reaction mixture was maintained at room temperature for 26 h. After 20 h, GC−MS analysis of the reaction mixture showed less than 1% 1,3-diphenylcyclopentadiene remaining. The precipitate from the reaction mixture was vacuum filtered, washed with cold absolute EtOH (3 × 30 mL), and vacuum dried to give **4** as a bright orange, microcrystalline solid (4.26 g, 84%). Crystals suitable for single-crystal X-ray diffraction were obtained from EtOH by slow evaporation. Mp: 96−97 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.35 [s, 9H, C(M̲e)$_3$], 6.86, 7.05, 6.49 (3H, fulvene ring and exocyclic C$\underline{H}$), 7.26−7.71 (m, 10H, P$\underline{h}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 31.3 [C(M̲e)$_3$], 36.0 [C̲(Me)$_3$], 114.2, 126.1, 126.6, 126.8, 127.7, 128.2, 128.6, 129.6, 135.5, 136.4, 141.3, 142.3, 145.0, 154.3 (C̲H and ring-C̲). HRMS-EI: *m/z* calcd for C$_{22}$H$_{22}$ [M]$^+$, 286.17215; found, 286.17163.

1,3-Diphenyl-6-cyclohexylfulvene 5. Cyclohexane carboxaldehyde (1.88 mL, 15.6 mmol), pyrrolidine (1.75 mL, 21.3 mmol), and 1,3-diphenylcyclopentadiene (3.1 g, 14.2 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **5** as a bright orange, microcrystalline solid (2.79 g, 63%). Crystals suitable for single-crystal X-ray diffraction were obtained from THF layered with EtOH. Mp: 89−90 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.18−1.88 (m, 10H, Cy-C$\underline{H}_2$), 2.83 (m, 1H, Cy-C$\underline{H}$), 7.28−7.72 (m, 10H, P$\underline{h}$), 6.94, 6.89 (2H, fulvene ring-C$\underline{H}$), 6.35 (d, 1H, fulvene exocyclic C$\underline{H}$Cy, ^2J = 10 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ 25.6, 25.8, 33.2, 40.4 (C̲y), 113.7, 126.0, 126.8, 127.6, 127.9, 128.3, 128.6, 129.2, 135.5, 136.2, 140.5, 142.7, 144.4, 148.9 (C̲H and C̲). HRMS-EI: *m/z* calcd for C$_{24}$H$_{24}$ [M]$^+$, 312.18780; found, 312.18685.

1,3,6-Triphenylfulvene 6.[15] Benzaldehyde (1.88 mL, 15.6 mmol), pyrrolidine (1.75 mL, 21.3 mmol), and 1,3-diphenylcyclopentadiene (3.1 g, 14.2 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **6** as a cherry-red, microcrystalline solid (1.89 g, 65%). Crystals suitable for single-crystal X-ray diffraction were obtained from 50:50 C_6H_6/MeOH at −5 °C. Mp: 121−22 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.26−7.74 (overlapping m, 16H, Ph, and fulvene exocyclic CH-Ph), 7.00, 7.04 (2H, fulvene ring-CH). ^{13}C NMR (75 MHz, CDCl$_3$): δ 114.6, 126.1, 127.1, 128.0, 128.1, 128.4, 128.6, 128.7, 129.1, 129.4, 131.0, 135.2, 136.0, 137.1, 138.5, 141.6, 144.3, 146.8 (CH and C). HRMS-EI: m/z calcd for $C_{24}H_{18}$ [M]$^+$, 306.14085; found, 306.14108.

1,3-Diphenyl-6-(4-trifluoromethylphenyl)fulvene 7. 4-(Trifluoromethyl)benzaldehyde (3.40 mL, 25.7 mmol), pyrrolidine (2.30 mL, 27.5 mmol), and 1,3-diphenylcyclopentadiene (4.00 g, 18.3 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **7** as a maroon microcrystalline solid (2.60 g, 38%). Mp: 115−116 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.22−7.74 [overlapping m, 15H, Ph, fulvene exocyclic CH-(p-CF$_3$)Ph, and p-(CF$_3$)Ph CH], 7.02, 6.93 (2H, fulvene ring-CH). ^{13}C NMR (75 MHz, CDCl$_3$): δ 125.6 (q, CF$_3$, J_{CF} = 3.9 Hz), 113.9, 126.2, 127.3, 128.3, 128.5, 128.8, 128.9, 129.4, 130.6, 134.8, 135.6, 135.9, 140.5, 141.6, 146.3, 147.8 (CH and C). ^{19}F NMR (376 MHz, CDCl$_3$): δ −62.6 (CF$_3$). HRMS-EI: m/z calcd for $C_{25}H_{17}F_3$ [M]$^+$, 374.12824; found, 374.12882.

1,3-Diphenyl-6-(3,5-dimethoxyphenyl)fulvene 8. 3,5-Dimethoxybenzaldehyde (1.88 mL, 15.6 mmol), pyrrolidine (1.75 mL, 21.3 mmol), and 1,3-diphenylcyclopentadiene (3.1 g, 14.2 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **8** as a dark red solid (2.79 g, 63%). Dark-red prismatic crystals suitable for single-crystal X-ray diffraction were obtained by cooling (−5 °C) a concentrated solution of **8** in CH$_2$Cl$_2$. Mp: 124−125 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.84 (s, 6H, OMe), 6.51 (t, 1H, MeOCCHCOMe), 6.77 (d, 2H, MeOCCHCCHCOMe), 6.99, 7.04 (2H, fulvene ring-CH), 7.18−7.74 [overlapping m, 11H, Ph, and fulvene exocyclic CH-(3,5-dimethoxyphenyl)]. ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.4 (OMe), 101.4, 108.4, 114.6, 126.1, 127.0, 128.0, 128.2, 128.4, 128.7, 129.4, 135.1, 135.9, 138.4, 138.8, 141.6, 144.6, 146.7, 160.8 (CH and C). HRMS-EI: m/z calcd for $C_{26}H_{22}O_2$ [M]$^+$, 366.16198; found, 366.16105.

1,3-Diphenyl-6-(3-phenoxyphenyl)fulvene 9. 3-Phenoxybenzaldehyde (1.09 g, 5.51 mmol), pyrrolidine (0.57 mL, 6.89 mmol), and 1,3-diphenylcyclopentadiene (1.03 g, 4.59 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **9** as a dark-red microcrystalline solid (1.59 g, 87%). Mp: 132−133 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.02−7.68 [overlapping m, 20H, Ph, fulvene exocyclic CH-(3-phenoxyphenyl), and 3-phenoxyphenyl CH], 6.97, 6.93 (2H, fulvene ring-CH). ^{13}C NMR (75 MHz, CDCl$_3$): δ 114.3, 119.3, 120.1, 123.7, 125.5, 126.1, 127.1, 128.0, 128.2, 128.4, 128.6, 129.3, 129.9, 130.0, 135.0, 135.8, 137.5, 138.6, 141.6, 144.7, 146.9, 156.8, 157.8 (CH, CO and C). HRMS-EI: m/z calcd for $C_{30}H_{22}O$ [M]$^+$, 398.16707; found, 398.16659.

1,3-Diphenyl-6-[5-(2,2'-bithiophene)]fulvene 10. (2,2'-Bithiophene)-5-carboxaldehyde (4.90 g, 25.7 mmol), pyrrolidine (2.30 mL, 27.5 mmol), and 1,3-diphenylcyclopentadiene (4.00 g, 18.3 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **10** as a dark red−brown microcrystalline solid (5.20 g, 72%). Mp: 130−134 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.90−7.80 (overlapping m, 18H, Ph, fulvene ring-CH, fulvene exocyclic CH-bithiophene and bithiophene CH). ^{13}C NMR (75 MHz, CDCl$_3$): δ 113.3, 124.1, 124.8, 125.7, 126.2, 127.0, 127.3, 127.9, 128.1, 128.4, 128.7, 129.3, 130.0, 135.0, 135.3, 136.1, 136.8, 139.5, 141.0, 142.0, 143.0, 146.4. HRMS-EI: m/z calcd for $C_{26}H_{18}S_2$ [M]$^+$, 394.08500; found, 394.08411.

1,3-Diphenyl-6-(1-pyrene)fulvene 11. 1-Pyrenecarboxaldehyde (1.30 g, 5.51 mmol), pyrrolidine (0.57 mL, 6.89 mmol), and 1,3-diphenylcyclopentadiene (1.03 g, 4.59 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-

butyl)fulvene **4** to obtain **11** as a black microcrystalline solid (1.45 g, 71%). Dark-red prismatic crystals of **11**, suitable for single-crystal X-ray diffraction, were obtained from THF layered with MeCN. Mp: 195−196 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.26−8.36 (overlapping m, 20H, Ph, fulvene exocyclic CH-pyrene, and pyrene CH), 7.11, 6.99 (2H, fulvene ring-CH). Selected ^{13}C NMR (75 MHz, CDCl$_3$): δ 115.8, 123.8, 124.7, 125.7, 125.8, 126.1, 126.2, 127.1, 127.4, 128.0, 128.25, 128.33, 128.34, 128.4, 128.6, 128.7, 129.4, 129.5, 130.1, 130.9, 131.3, 131.4, 131.9, 135.2, 136.1, 136.5, 141.1, 146.0, 146.9. HRMS-EI: m/z calcd for $C_{34}H_{22}$ [M]$^+$, 430.17215; found, 430.17145.

1,3-Diphenyl-6-(2-fluorenyl)fulvene 12. 2-Fluorenecarboxaldehyde (2.95 g, 15.2 mmol), pyrrolidine (1.71 mL, 20.9 mmol), and 1,3-diphenylcyclopentadiene (3.01 g, 13.9 mmol) were used employing the procedure outlined for the preparation of 1,3-diphenyl-6-(*tert*-butyl)fulvene **4** to obtain **12** as a dark red−brown microcrystalline solid (5.48 g, 93%). Mp: 179−180 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.30−7.88 (overlapping m, 18H, Ph, fulvene exocyclic CH-fluorene, and fluorene CH), 7.00, 7.13 (2H, fulvene ring-CH), 3.98 (s, 2H, CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 36.9 (CH$_2$), 114.6, 120.1, 120.4, 125.2, 126.1, 126.9, 127.0, 127.3, 127.4, 127.7, 127.9, 128.4, 128.7, 129.4, 130.1, 135.4, 135.7, 136.2, 139.2, 141.0, 141.8, 142.9, 143.6, 143.7, 143.9, 146.6 (CH and C). HRMS-EI m/z calcd for $C_{31}H_{22}$ [M]$^+$, 394.17215; found, 394.17395.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure of electronic absorption spectra and figures depicting ^{1}H, ^{13}C, and ^{19}F NMR spectra, text describing crystallographic details, tables of crystallographic data and cifs for fulvenes **4−6**, **8**, and **11**, and text and data related to DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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