Bond Angle Versus Torsional Deformation in an Overcrowded Alkene: 9-(2,2,2-Triphenylethylidene)fluorene

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Abstract: Competition between bond angle and torsional strain in sterically crowded alkenes generally causes twisting in tetrasubstituted alkenes, while most structurally characterized trisubstituted alkenes are planar. To investigate structural effects of steric repulsion between a planar aromatic ring and a vicinal triphenylmethyl (trityl) group, 9-(2,2,2-triphenylethylidene)fluorene (**1a**) was synthesized by reaction of 9-bromomethylenefluorene with triphenylmethyllithium. For comparison with a less strained analogue, 9-ethylidenefluorene (**1b**) was prepared by reaction of fluorenone with ethylmagnesium bromide. The X-ray crystal structures show that the difference between bond angles at the 9-fluorenyl carbon atom is much larger for **1a** (12.9°) than **1b** (2.6°). Bond angle and torsional deformations were compared theoretically (HF/6-31+G*) with the *tert*-butyl analogue (**1c**), 1,2,2-tri-*tert*-butylethene (**7**), and 2,4,4-trimethyl-2-pentene (**8**) and crystallographically with six known 1,1-diaryl-2-*tert*-alkylethenes (**2**). The trisubstituted alkenes formed three groups with 1) large angle distortion with moderate twisting (**1a**, **1b**, and **7**), 2) moderate bending with a large range of torsional angles (**2**), and 3) little bending or twisting (**1b** and **8**). For the entire series, there appears to be a delicate balance between angle and torsional deformation, but twisting appears to produce smaller relief from steric strain than angle bending. In the crystallographically characterized trisubstituted alkenes, the choice between the two is mainly determined by more subtle packing forces.

Keywords: alkenes · overcrowding · steric hindrance · strained molecules · structure elucidation

Introduction

Since the concept of bond-angle strain in organic compounds was introduced by Baeyer in 1895,[1] chemists have been fascinated by the various types of distortion produced by strain in molecules. Interest in strained alkenes has largely centered on probing the ability of a C–C π bond to tolerate torsional strain produced by twisting the ends of a normally planar C=C bond.[2] Angle bending competes with double bond twisting for distribution of strain produced by steric repulsion between bulky substituents in overcrowded alkenes.[2, 3] Tetrasubstituted alkenes mainly show torsional distortion because of steric repulsion between vicinal alkyl groups,[4] while most structurally characterized trisubstituted alkenes are planar.[7] We have found that the 9-alkylidenefluorenes (**1**) and related 1,1-diphenylalkene structures (**2**)[8] dramatically show a delicate balance between bond angle and torsional deformation (Scheme 1).

1 **2**

	R
a	CPh_3
b[9]	CH_3
c	$C(CH_3)_3$

	R
a[8a]	$CPh_2CH=C(CN)_2$
b[8a]	$C(Ipr)_2CH=C(CN)_2$
c[8a]	$C(CH_3)_2CH_2CPh_2OH$
d[8a]	$CPh_2CH=CH_2$
e[8b]	$C(CH_3)_2CH=CPh(C_6H_4$-*p*-$CN)$
f[8a]	$CCH_3(CH=CPh_2)[CH=C(CN)_2]$

Scheme 1. Structures of overcrowded trisubstituted alkenes **1a**, **1c** and **2a–f** and an unstrained model compound (**1b**).[8, 9]

Results and Discussion

Synthetic target 9-(2,2,2-triphenylethylidene)fluorene (**1a**) was expected to be stable because steric repulsion between the bulky trityl group and the fluorene unit should be lessened by insertion of the *syn* benzene ring between two of the trityl phenyls. The initial approach involving reaction of 9-lithiofluorene[10] with triphenylacetaldehyde[11] failed, apparently

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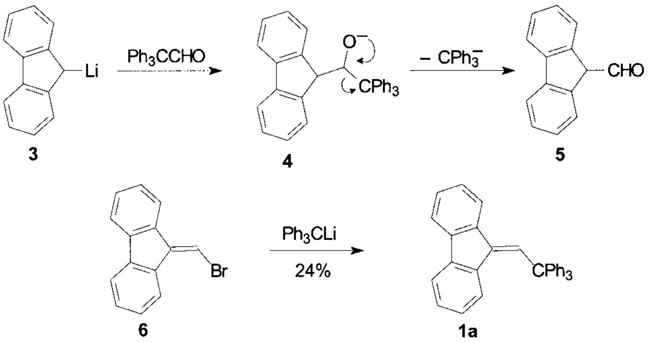
because the adduct **4** suffered fragmentation, as shown in Scheme 2. Triphenylmethane and 9-formylfluorene (**5**)[12] were detected as major products after the reaction mixture was quenched with water. Attempted reaction of triphenylacetaldehyde with 9-fluorenylidene triphenylphosphorane[13] also failed to yield target **1a**. The successful approach involved reaction of 9-bromomethylenefluorene (**6**) with carbon nucleophiles;[14] this reaction apparently proceeds by an addition–elimination mechanism. Reaction of **6** with triphenylmethyllithium gave overcrowded alkene **1a** in 24% yield after exhaustive purification (Scheme 2). Less strained analogue **1b**[9] was prepared by reaction of fluorenone with ethylmagnesium bromide, followed by dehydration of the intermediate alcohol.[9b] Various attempts by different methods failed to give pure 9-(2,2-dimethylpropylidene)fluorene (**1c**), which is expected to be the most overcrowded alkene in this series.



Scheme 2. Unsuccessful approach and successful synthesis of 9-(2,2,2-triphenylethylidene)fluorene (**1a**).

The structures of 9-(2,2,2-triphenylethylidene)fluorene (**1a**) and 9-ethylidenefluorene (**1b**) were determined by single-crystal X-ray diffraction. In both structures, there are two molecules in the asymmetric unit, but in each case their conformations are very similar. One of the two molecules is shown for **1a** and **1b** in Figures 1 and 2, respectively. Double-bond lengths, bond angles, and torsional angles for these and other trisubstituted alkenes are given in Table 1. Of particular significance is the difference between the C1-C13-C14 (α_2) and C12-C13-C14 (α_3) angles, which is on average 2.6° for **1b** (R = Me) and 12.9° for **1a** (R = CPh_3). This difference is caused by the much larger steric repulsion between the R group and the fluorene fragment compared to that of H14 with the fluorene fragment. This repulsion also enlarges the C13-C14-C15 angle (α_1) in **1a** to a mean value of 134.1°, compared to a mean value of 127.1° in **1b**.

We were unable to prepare crystals of **1c** (R = *tert*-butyl), but geometry optimization with the Gaussian 98 program[15] at the HF/6-31 + G* level showed that this structure (Figure 3) exhibits similar distortions to those observed in **1a** (Table 1). The dimensions obtained for **1a** and **1b** with this basis set are similar to those obtained from the two crystal structures, which suggests not only that this basis set is adequate for the calculations and that the quality of the structure determinations is acceptable, though not as high as we would hope due to the poor quality of the crystals, but also that packing effects in the two structures are small.

Further calculations were carried out with Gaussian 98 (HF/6-31 + G*) to investigate changes in energy and in dimensions observed when the C1-C13-C14-C15 torsion angle (τ_1) is varied. Accordingly, the step scan method was used, and τ_1 was varied from −20 to 50° in steps of 5°. For all three structures the differences between α_2 and α_3 were essentially maintained and only small decreases in the angles subtended at C13 and C14 are observed, as the two carbon atoms became more pyramidal as τ_1 increased. Variations in energy versus τ_1 are plotted in Figure 4 and show that the size of the increases are in the order **1b** > **1c** > **1a**. Note that the energy curve for **1a** is asymmetric around zero and has a minimum for τ_1 around 3.2°. This is not unexpected because the three phenyl rings, in a propeller conformation, are asymmetrically distributed with reference to the fluorene ring. However, the

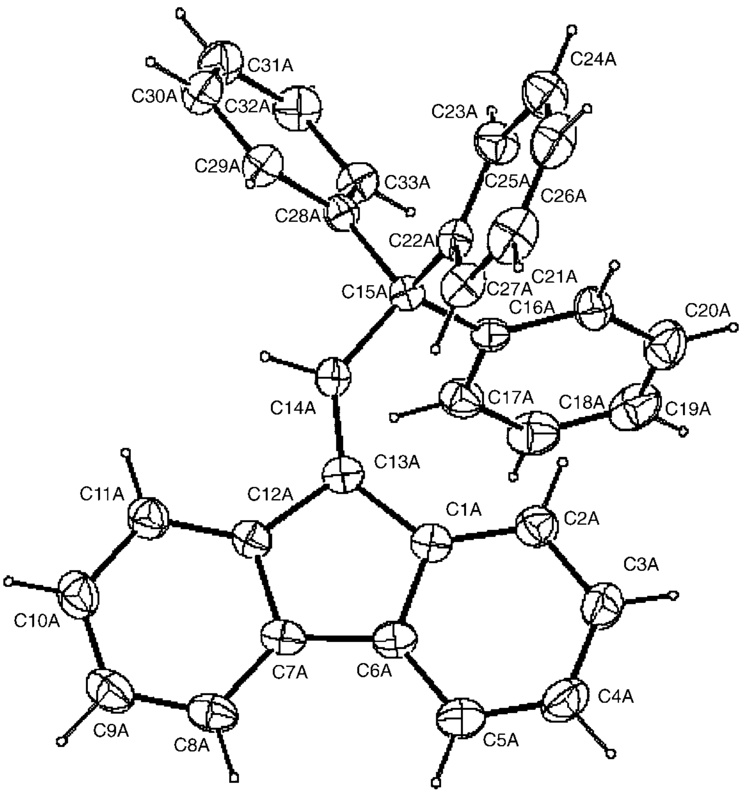


Figure 1. The structure of **1a** with ellipsoids at 30% probability. There are two molecules in the asymmetric unit with similar conformation.

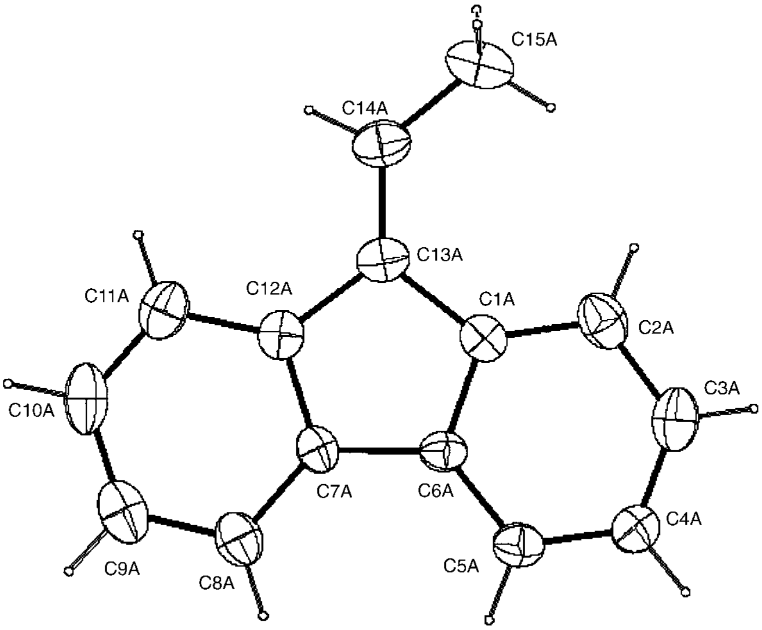


Figure 2. The structure of **1b** with ellipsoids at 20% probability. There are two molecules in the asymmetric unit with similar conformation.

Table 1. Crystallographically determined (X) and theoretical (T) C=C bond lengths [Å] and bond/torsional angles [°] in trisubstituted alkenes.

Alkene	Method	$d_{C=C}$[a]	α_1[b]	α_2[b]	α_3[b]	τ_1[c]	τ_2[c]
1a (mol 1)	X	1.348(3)	134.7(3)	134.5(3)	120.8(3)	3.3(6)	−176.1(3)
1a (mol 2)	X	1.342(3)	133.5(3)	134.3(3)	121.1(3)	5.2(5)	−171.5(3)
1b (mol 1)	X	1.356(6)	128.6(5)	128.6(5)	126.1(4)	0.2(8)	−175.5(4)
1b (mol 2)	X	1.347(6)	125.6(5)	128.5(5)	125.8(4)	0.7(7)	−175.7(4)
1a	T	1.331	134.8	134.6	121.0	3.2	−176.4
1b	T	1.330	127.7	130.1	124.9	0.0	−180.0
1c	T	1.329	133.5	134.5	121.3	1.3	−174.7
7[d]	T	1.342	142.2	124.8	115.4	2.6	−174.3
8[e]	T	1.342	127.6	126.4	120.6	0.0	−180.0
2a(SECWUS)	X	1.337	131.0	124.2	119.6	13.4	−167.7
2b(SECXAZ)	X	1.336	134.5	122.7	121.8	5.8	−175.4
2c(SEDBIM)	X	1.342	133.1	123.5	119.9	10.0	−174.0
2d(SECXIH)	X	1.331	132.7	123.9	120.7	5.6	−177.4
2e(NAJDUX-1)[f]	X	1.343	131.9	123.8	119.9	2.6	−178.7
2e(NAJDUX-2)[f]	X	1.346	129.6	124.3	121.1	11.3	−168.3
2f(SECXON-1)[f]	X	1.343	131.7	127.1	117.3	1.5	−179.0
2f(SECXON-2)[f]	X	1.354	130.9	126.4	119.1	0.4	−179.5

[a] C=C bond length corresponding to C13–C14 in **1**. [b] Bond angles defined as shown in Scheme 1. [c] Torsional angles corresponding to C1-C13-C14-C15 for τ_1 and C12-C13-C14-C15 for τ_2. [d] 2,2,5,5-Tetramethyl-2-(1,1-dimethylethyl)-3-hexene (or tri-*tert*-butylethene). [e] 2,4,4-Trimethyl-2-pentene. [f] Data given for two different 1,1-diarylalkene fragments.

energy curves for both **1b** and **1c** show energy minima at 0° and are symmetric around 0°.

We interpret the order of energies as being due to the relative importance of the double bond conjugation with the fluorene versus steric repulsions. Thus, for **1b** these repulsions are less important than conjugation and, therefore, changes in the torsion angle provide a larger contribution to the total energy than for **1c** and particularly **1a**, which has the greatest repulsion energy. It is interesting to note that the overall shape of the triphenylmethyl moiety in **1a** changes little, as measured by the torsion angles around C15–C16, C15–C22, and C15–C28, as the torsion angle around the double bond C13–C14 is varied. Clearly the overall shape of the CPh_3 unit is governed by the interactions between the phenyl rings in the propeller shape. The propeller shape in crystalline **1a** is described by the torsion angles C14-C15-C16-C17, C14-C15-C22-C23, and C14-C15-C28-C29 which are 45.1, 23.6, 60.7 and 40.1, 59.3 and 78.1°, respectively, in the two molecules of the asymmetric unit. Molecular mechanics calculations on molecules such as $HCPh_3$ and CH_3CPh_3 show broad minima with three similar torsion angles comparable with the propeller conformation in **1a**.

We next searched the Cambridge Crystallographic Database[16] for related trisubstituted ethenes for which good quality structural data was available. There are six examples of molecules (**2**) in which C13 is bonded to two unconnected phenyl rings, while C14 is bonded to a hydrogen atom and a tertiary alkyl group. The *R* values for these structures are all less than 6%, except for **2b** (8.8%). The C=C bond lengths, bond angles, and torsion angles for these six molecules are listed in Table 1. The angles at C13 (α_2 and α_3) and at C14 (α_1) and the torsion angles are dependent to some extent on the nature of the tertiary alkyl group, but it is noticeable that the difference between α_2 and α_3 is far less than in **1a**, ranging from 0.9 to 9.8° with a mean of 4.5°. This is apparently because steric strain can be alleviated by twisting of the unconnected phenyl rings. On the other hand, the α_1 angle is similar to that observed in **1a**, ranging from 128.8 to 134.5°, with a mean of 131.5°. Torsional angle τ_1 varies from 0.4 to 13.4° with a mean of 6.7°, which is somewhat in excess of values in **1a** and **1c**.

Two other molecules of interest were 1,1,2-tri-*tert*-butylethene (**7**) and 2,4,4-trimethyl-2-pentene (**8**). When **7** was studied by molecular mechanics previously,[3c] the optimized structure contained torsion angles around the double bond of 16.2 and −162.2°, while we obtained 2.6 and −174.3°, respectively, with HF/6-31+G* (all dimensions shown in Table 1). This comparison shows that steric effects were

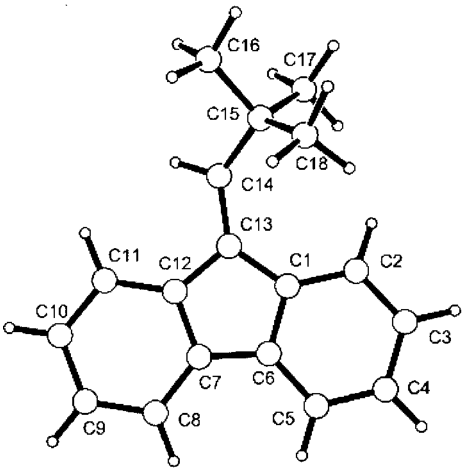


Figure 3. The structure of **1c** as established by ab initio methods.[15]

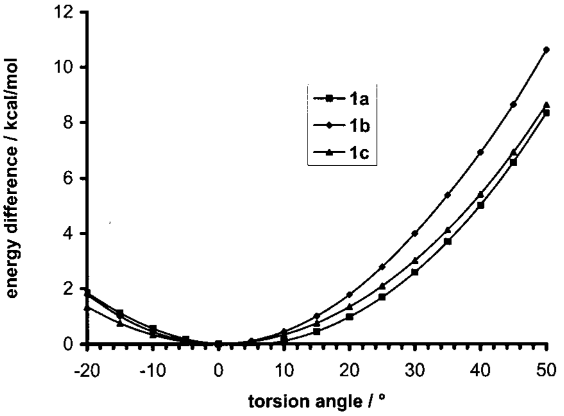


Figure 4. Plot of energy against torsion angle τ for the substituted fluorenes **1a**–**c**.

seriously overestimated in the force field used in the previous calculation. Geometry optimization of compound **8** gave rise to a planar molecule with C_s symmetry.

In order to compare the various distortions of these trisubstituted ethenes, and consider the correlation between angle bending and torsion twist, we have created an angle function φ, which is defined as $\alpha_1 - 127.1° + 0.5(\alpha_2 - \alpha_3)$. This gives a measure of the angle distortion at C13, as $0.5(\alpha_2 - \alpha_3)$ is the average angle deviation from $\alpha_2 = \alpha_3$, and $\alpha_1 - 127.1°$ is the distortion in the angle at C14 from the norm. The value of 127.1° was selected to be included in the function, as this is the average angle observed in **1b**, which has the smallest α_1 angle of the molecules under consideration. The angle function φ is plotted in Figure 5 against average torsion angle τ, defined as the average of τ_1 and $(\tau_2 + 180°)$, for all of the crystal and ground-state theoretical structures.

Figure 5 shows that the molecules can be divided into three distinct classes, dependent upon the value of the angle function φ and to a lesser extent the average torsion angle τ. The first group contains the fluorene molecules with R = CPh$_3$ (**1a**) and R = *tert*-butyl (**1c**), and 1,1,2-tri-*tert*-butylethene (**7**), which have large values of φ but smaller values of τ. These overcrowded alkenes have the highest steric strain of all the molecules, and it is noteworthy that this strain is relieved mainly by distortions in bond angles rather than torsion angles.[17] The approximate 3° variation in torsion angle for the two molecules of **1a** is offset by a small change in φ. This packing effect is consistent with the relatively flat energy surface seen for **1a** in Figure 4 in the range of $\tau = 0 - 8°$.

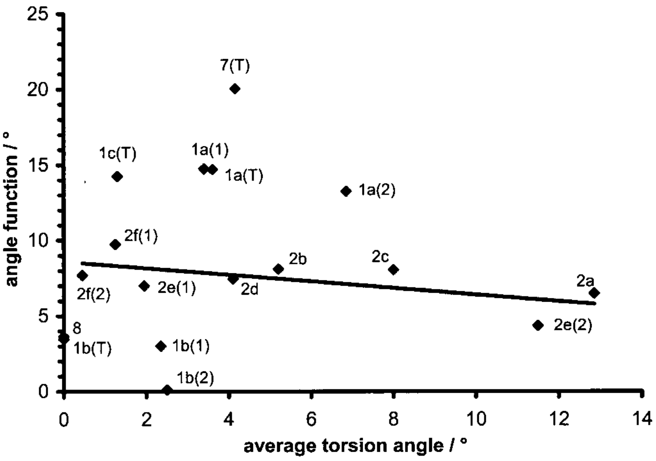


Figure 5. Plot of angle function (φ) against average torsion angle (τ) for all trisubstituted alkenes considered. Line for $\varphi = 8.60 - 0.22\tau$ is the least-squares fit for the series **2a**–**f**; calculated structures indicated by the notation T.

The second group includes the six crystal structures **2** with two unconnected phenyl rings bonded to C13; these have moderate values of φ, but a range of values of τ. For these molecules (and for **1a**) there is a negative correlation between φ and τ, indicating that an increase in τ results in a decrease in φ, and vice versa. There are eight data points for these alkenes because **2e** and **2f** each contain two 1,1-diarylethene fragments. The equation for the regression line for the eight points in series **2** is $\varphi = 8.60 - 0.22\tau$ as shown in Figure 5. This suggests that deformation of bond angles causes a four to fivefold greater increase in energy than twisting in this series. The third group contains fluorene **1b** and 2,4,4-trimethyl-2-pentene (**8**), which have low values of both τ and φ. In both compounds the two parameters are small because there is little steric repulsion at either end of the C=C bond. Crystal packing causes a 3° variation in φ for the two molecules of **1b** with negligible change in τ, but small deviation around $\varphi = 0$ costs little energy.

We also calculated the values of the angle function φ for the theoretical structures **1a**–**c** with a 40° range of fixed torsion angles ($\tau = -20$ to $+20°$). There is less than a 1° variation in φ. It is apparent that twisting causes very little relief of angle strain.

Conclusion

The view that emerges from these studies is that steric forces between bulky substituents in trisubstituted alkenes **1a** and **2a**–**f** strike a delicate balance between bond angle and torsional deformation. As shown in Figure 4 for **1a** and in Figure 5 for the entire series, twisting appears to produce smaller relief from steric strain than angle bending. These molecules are caught in a tug-of-war between two types of angle deformation (twisting and bending), and the choice between the two is in large part determined by more subtle packing forces. This unique set of overcrowded alkenes deepens our insight into the specific forces that determine the structures of the hydrocarbon frameworks of organic molecules. Moreover, the "steric gearing" observed between aromatic rings in **1a** makes this molecule of interest as a conformationally restricted scaffold in supramolecular chemistry.[18]

Experimental Section

Synthesis of 1a: A solution of triphenylmethane (1.80 g, 7.4 mmol) in anhydrous THF (60 mL) was cooled to $-78\,^{\circ}C$ under N_2 and a solution of *n*-butyllithium in hexane (1M, 6.0 mL) was added dropwise, producing an orange solution. The solution was stirred at $0\,^{\circ}C$ for 40 min, then the resulting blood-red solution of the trityl anion was recooled to $-78\,^{\circ}C$ and 9-bromomethylenefluorene (**6**)[14b] (1.32 g, 4.7 mmol) was added. The reaction mixture was slowly warmed to room temperature over 1.5 hours, then the resulting orange solution was stirred overnight. Water (15 mL) was added, and the resulting mixture was extracted with diethyl ether (3×25 mL). The combined diethyl ether solutions were dried over anhydrous Na_2SO_4, then concentrated to dryness by rotary evaporation. The residue was dried under vacuum, giving 3.08 g of an orange solid. Column chromatography on silica gel, eluting with hexane, followed by recrystallization from 1-butanol, gave 0.48 g (24 %) of **1a** as a white solid. M.p. 290–291 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.79$ (s, 1 H; C=CH), 7.74 (d, $^3J(H,H) = 7$ Hz, 1 H; H11),7.69 (d, $^3J(H,H) = 7$ Hz, 1 H; H8), 7.62 (d, $^3J(H,H) = 7$ Hz, 1 H; H5), 7.1–-7.4 (br m, Ph, 18 H; H4, H9, H10), 6.66 (t, $^3J(H,H) = 7$ Hz, 1 H; H3), 6.4 (d, $^3J(H,H) = 8$ Hz, 1 H; H2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.0$, 141.0, 140.8, 139.0, 138.5, 135.7, 130.4, 128.2, 126.7, 120.1, 119.5, 119.1, 61.8; IR(KBr): $\tilde{\nu} = 3053$, 2921, 2860, 2362, 1952, 1883, 1810, 1744, 1656, 1595, 1486, 1458, 750, 600 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 318 (14000), 306 (14000), 291 (12000), 282 (9600), 264 (30000), 252 nm (24000); Fluorescence ($CHCl_3$, λ_{ex} 318 nm): $\lambda_{em} = 456$ nm; MS (70 eV): *m/z* (%): 420 (100); elemental analysis calcd (%) for $C_{33}H_{24}$: C 94.25, H 5.75; found: C 94.03, H 5.64 %. ^1H NMR peak assignments are numbered according to Figure 1.

Synthesis of 1b: 9-Ethylidenefluorene (**1b**) was prepared by reaction of fluorenone with ethylmagnesium bromide, as described by Boyce et al.,[9b] except that the intermediate alcohol was treated with *p*-toluenesulfonic acid in boiling benzene to effect elimination of water. Chromatography on silica gel, eluting with hexane, gave 0.52 g (51 %) of a white solid. M.p. 76.5–78.0 °C (lit. 103–104 °C,[9b] 52–54 °C[9d]); ^1H NMR 300 MHz, $CHCl_3$, 25°C, TMS): $\delta = 7.90$ (d, $^3J(H,H) = 7$ Hz, 1 H; H11), 7.88 (d, $^3J(H,H) = 7$ Hz, 1 H; H2), 7.71 (d, $^3J(H,H) = 8$ Hz, 1 H; H8), 7.66 (d, $^3J(H,H) = 8$ Hz, 1 H; H5), 7.28–7.46 (m, 4 H; H3, H4, H9, H10), 6.88 (q, $^3J(H,H) = 8$ Hz, 1 H; C=CH), 2.42 (d, $^3J(H,H) = 7.7$ Hz, 3 H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 130.4$, 127.9, 127.3, 124.9, 124.5, 112.8, 112.7, 112.4, 112.3, 110.4, 109.6, 105.3, 104.9, 104.6, 38.9; MS (70 eV): *m/z* (%): 192 (100). ^1H NMR peak assignments are numbered according to Figure 2

Crystallographic data for 1a and 1b: Crystal data for **1a**: $a = 11.933(2)$, $b = 13.179(1)$, $c = 15.212(1)$ Å, $\alpha = 77.95(1)$, $\beta = 77.86(1)$, $\gamma = 89.35(1)^{\circ}$, $V = 2286$ Å^3, $M_r = 420.52$, triclinic, $P\bar{1}$, $Z = 4$, ρ_{calcd}1.222 $g\,cm^{-3}$, 5943 independent reflections were measured on a Siemens P4 diffractometer. Crystal data for **1b**: $a = 19.33(3)$, $b = 5.922(10)$, $c = 20.40(3)$ Å, $\beta = 111.92(1)^{\circ}$, $V = 2167$ Å^3, $M_r = 192.99$, monoclinic, $P2_1/n$, $Z = 8$, $\rho_{calcd} = 1.179$ $g\,cm^{-3}$, 2692 independent reflections measured on a Marresearch ImagePlate system. Both structures were solved by direct methods. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structures were refined on F^2 by using SHELXL.[19] Final *R* values were for **1a**, $R1 = 0.0488$, $wR2 = 0.0925$ for 3623 data, and for **1b** $R1 = 0.0820$, $wR2 = 0.2365$ for 1700 data, both with $I > 2\sigma(I)$. CCDC-182106 and CCDC-182107 CCDC contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

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[4] The elusive tetra-*tert*-butylethene is an extreme example; it is expected to have a large torsional angle and to lack bond-angle distortion, according to the results of molecular mechanics[3d] (see also ref. [2c], p. 247) and ab initio calculations.[3f] An exception is (*Z*)-1,2-diphenyl-2-butene,[5] in which the planar geometry of C=C bond may be stabilized by the π–π interactions[6] between the cofacially oriented phenyl rings.

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