DOI: 10.1002/chem.200501169

Sequential Formation of Yellow, Red, and Orange 1-Phenyl-3,3-Biphenylene-Allene Dimers Prior to Blue Tetracene Formation: Helicity Reversal in *trans*-3,4-Diphenyl-1,2-bis(fluorenylidene)cyclobutane

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Abstract: 1-Phenyl-3,3-biphenylene-allene (**2**), the base-catalyzed rearrangement product of 9-phenylethynylfluorene (**1**) yields a yellow, head-to-tail dimer **6** that, upon gentle warming, is converted to the red tail-to-tail isomer *trans*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane (**7**), in which the two fluorenylidene moieties severely overlap. The helical sense of the fluorenylidene moieties in **7** matches that of the phenyl substituents, and the interplanar angle between the fluorenylidene moieties is 41°. At 80 °C, **6** isomerizes to orange *cis*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane (**8**), which at 110 °C is converted to orange *trans* diastereomer **9**, whereby the helicity of the overlapping fluorenylidene moieties is reversed from that in **7** such that they are aligned with the ring hydrogen atoms, and the interplanar angle between the fluorenylidene moieties is now 60°. At 180 °C, **6** rearranges to dispirodihydrotetracene **3** and blue, electroluminescent diindenotetracene **4**, which is readily oxidized to peroxide **5**. In the solid state, both **3** and **4** adopt structures with C_i symmetry (only an inversion center) such that the central polycyclic framework is nonplanar. Deprotonation of yellow head-to-tail allene dimer **6** with *t*BuOK in DMSO and reprotonation with HOAc yields the [1,3]-hydrogen migration product **10**, in which the proton originally on the cyclobutane ring is now sited at C9 on the exocyclic fluorenyl substituent. Analogously, deprotonation and reprotonation of orange dimer **9** furnishes [1,3]-hydrogen migration product **11**. Side product **17**, formed during the synthesis of **1** from 9-phenylethynylfluoren-9-ol, BF_3 and Et_3SiH, was shown to be a silyl-indene spiro-linked to C9 of fluorene. All products were characterized by NMR spectroscopy and X-ray crystallography, and the mechanisms of these interconversions are discussed.

Keywords: allenes · dimerization · helical structures · isomerization · tetracenes

Introduction

In a recent communication,[1] we reported that, upon heating, 9-phenylethynylfluorene (**1**) rearranges to the corresponding allene **2**, which dimerizes and subsequently yields the dispirofluorenyldihydrotetracene **3** and the diindeno[1,2,3-*de*:1′,2′,3′-*mn*]tetracene **4**. In air, the latter compound is readily oxidized to peroxide **5**. Alkyne **1**, dispirotetracene **3** and peroxide **5** were all unambiguously characterized by X-ray crystallography.[1,2]

In 1965, Kuhn and Rewicki observed that, when allene **2** is heated in refluxing heptane, yellow and red dimers are formed.[3] The yellow product was subsequently identified as head-to-tail dimer **6**,[4] but the identity of the red product **7** remained unresolved. We now describe the sequential formation and X-ray crystallographic characterization of six dimers of allene **2**, which are yellow (**6**), red (**7**), orange (**8**), orange (**9**), pale yellow (**10**) and pale yellow (**11**), as well as the structure of blue tetracene **4**. Moreover, we offer a rationalization of the processes leading to successive isomeric allene dimers, and ultimately to the tetracenes.

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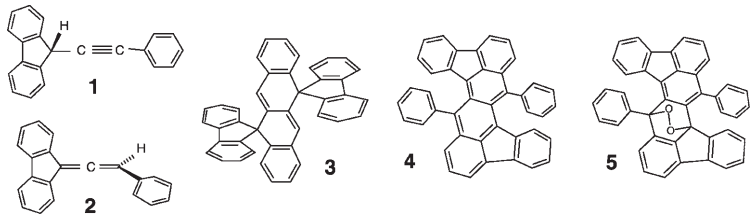


Results and Discussion

When alkyne **1** is stirred in pentane at 0 °C for 5–7 h in the presence of triethylamine, a yellow precipitate of **6** gradually forms. X-ray quality crystals of **6** were obtained from diethyl ether/hexane; the structure (Figure 1) confirms the original assignment.[4a] As shown in Scheme 1, the yellow dimer, 3-(9-fluorenylidene)-2-phenyl-4-phenylmethylenespiro[cyclobutane-1,9′-fluorene] (**6**) has a head-to-tail 1,2-dialkylidenecyclobutane structure in which one spiro-bonded fluorenylidene moiety is linked through a long (1.605 Å) C3–C4 bond to a benzylidene unit. In the exocyclic phenylmethylene substituent the phenyl group is positioned *exo* and the interplanar angle C5-C1-C2-C18 between the two exocyclic double-bonded fragments is 38°.

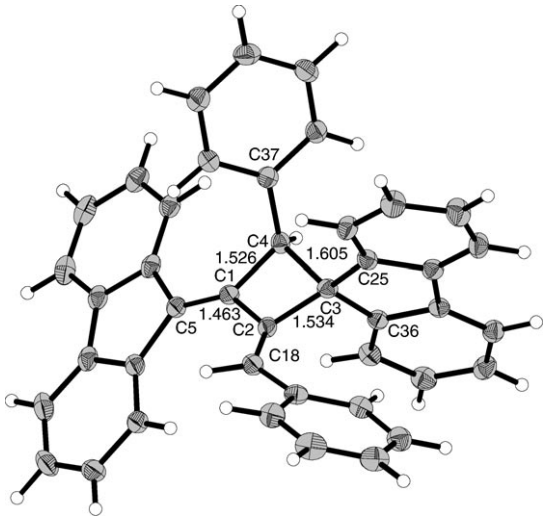
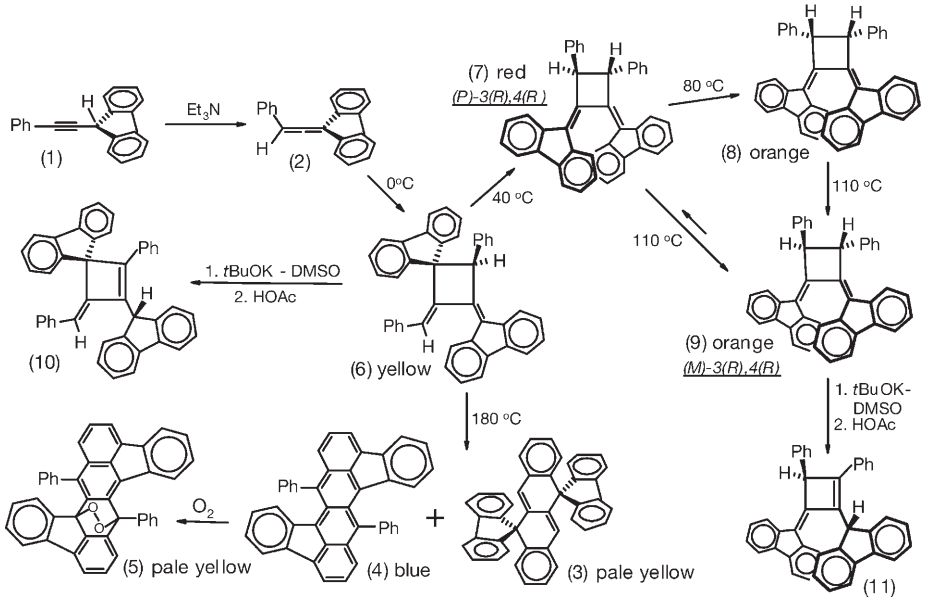


Figure 1. Molecular structure of yellow head-to-tail dimer **6**; thermal ellipsoids are drawn at the 50% probability level.

In contrast, when the same reaction was performed at room temperature, **6** was again the major product, but traces of the previously unidentified red compound **7** were found. However, when alkyne **1** and triethylamine were heated together in refluxing dichloromethane at 40 °C, red dimer **7** was more abundant and could be separated from yellow isomer **6** by chromatography on silica. Recrystallization from dichloromethane/pentane furnished crystals suitable for an X-ray diffraction study, and the identity of **7** was revealed as *trans*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane. Figure 2 depicts the palindromic[5] helical molecule of pseudo-C_2 symmetry such that the two phenyl substituents in the cyclobutane ring adopt a *trans* configuration; the two exocyclic fluorenylidene fragments overlap considerably and are twisted out of the ring plane and in the same helical sense as the phenyl groups. Thus, for the enantiomer of **7** depicted in Scheme 1 and Figure 2, the fluorenylidene moieties at C1 and C2, when viewed along the twofold axis passing through the midpoints of C1–C2 and C3–C4 successively, give rise to a *P* helix[6] while C3 and C4 each have *R* configurations. The four-membered ring is almost flat, and the length of the C3–C4 bond linking the two sp^3 ring carbon atoms is now only 1.587 Å. The dihedral angle between the fluorenylidene planes is 41°.



Scheme 1. Sequential formation of allene dimers and tetracenes.

In a subsequent experiment, yellow head-to-tail dimer **6** was held at 80 °C overnight to yield, after chromatographic separation, orange dimer **8**, which was identified by NMR spectroscopy as *cis*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane. In this case, each of the exocyclic fluorenylidene moieties exhibited eight ^{1}H NMR signals, which clearly shows that the molecule is no longer C_2-symmetric; likewise, the methyne protons in the cyclobutane ring appeared as doublets ($J = 8.4$ Hz) at 5.40 and 5.29 ppm. These data were paralleled in the ^{13}C NMR spectrum, which again indicated the reduced symmetry of the mole-

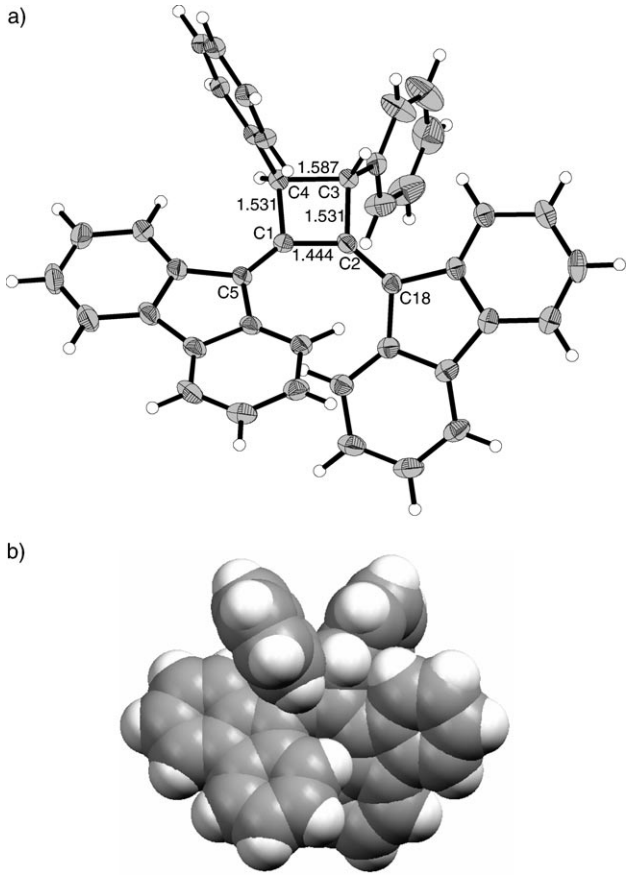


Figure 2. a) Molecular structure of red *trans* dimer **7**; thermal ellipsoids are drawn at the 50% probability level. b) Space-filling view of red *trans* dimer **7**, emphasizing the overlap of the fluorenylidene moieties.

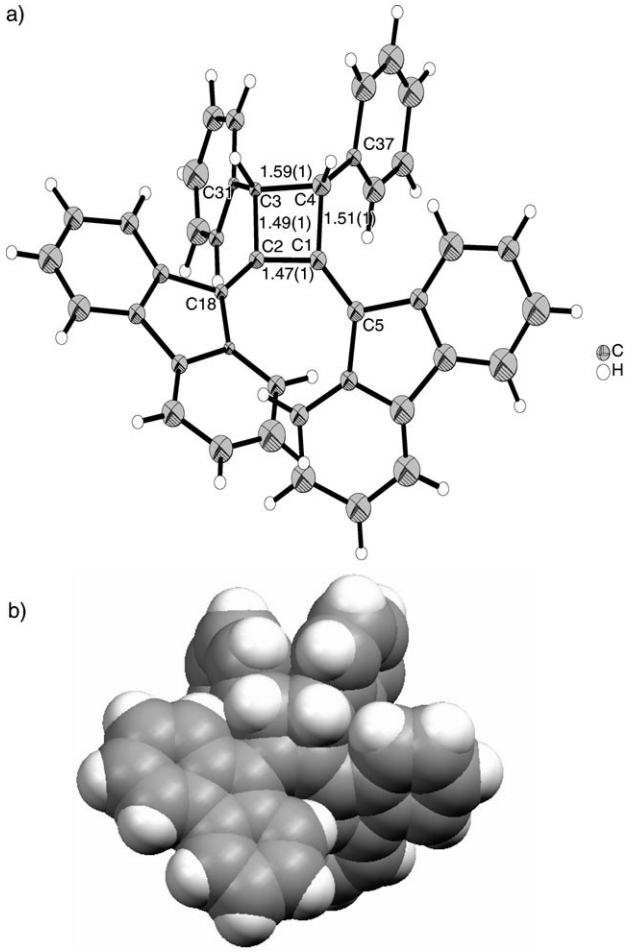


Figure 3. a) Molecular structure of orange *cis*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane (**8**). Only one of the four independent molecules in the unit cell is shown. b) Space-filling view of orange *cis* dimer **8**, emphasizing the severe overlap of the fluorenylidene moieties.

cule, whose structure was unequivocally confirmed by X-ray crystallography (Figure 3). The monoclinic unit cell ($Z=8$) contains four independent molecules, and the dihedral angle between the fluorenylidene planes is now $62\pm2°$.

Finally, thermolysis of yellow head-to-tail dimer **6** in refluxing toluene at 110°C yields yet a fourth allene dimer, namely, **9**, an orange material that is relatively insoluble in diethyl ether and thus readily separable from the small quantity of red dimer **7** that is also formed. Recrystallization from dichloromethane/diethyl ether/hexane gave crystals of X-ray quality, and the resulting structure is depicted in Figure 4. The molecule of **9** has almost perfect C_2 symmetry, with atom connectivity identical to that found in red dimer **7**, but the helicity of the two exocyclic fluorenylidene fragments has now been reversed. Thus, for the structure depicted in Scheme 1 and Figure 4, the fluorenylidene moieties in **9** now give rise to an *M* helix while C3 and C4 maintain their *R* configurations. That is, the fluorenylidene moieties are now oriented such that they are aligned with the hydrogen atoms in the cyclobutane ring, which adopts a markedly nonplanar "butterfly-type" conformation in which the C3–C4 bond length is now 1.594 Å (average of three independent molecules in the unit cell). When a pure sample of orange dimer **9** was held at 110°C for 8 h, interconversion of the two *trans* diastereomers was observed with an equilibrium ratio for **7**:**9** of approximately 1:6, as determined by NMR spectroscopy. Clearly, orange isomer **9**, in which the dihedral angle between the bulky fluorenylidene groups is now 60°, is markedly favored over its red *trans* counterpart **7** and *cis* isomer **8**.

As noted at the outset, we had previously proposed that the blue diphenyldiindeno[1,2,3-*de*:1′,2′,3′-*mn*]tetracene (**4**) arose via rearrangement of an allene dimer,[1] and this has now been confirmed by thermolysis of yellow head-to-tail dimer **6** in dimethyl sulfoxide at 180°C for 6 h. The dark blue crystals thus obtained were characterized by X-ray diffraction, and the structure is illustrated in Figure 5a. In the solid state, the molecule is not fully planar but rather adopts a centrosymmetric (C_i) conformation such that the indenyl moieties are curved away from the central tetracene framework by 18°; the phenyl substituents each make a dihedral angle of 57° with the planar tetracene unit. This places one hydrogen atom (H12) in each of the exterior six-membered rings of the fluorenyl units almost directly above a peripheral phenyl substituent, which results in a ^{1}H NMR shielding

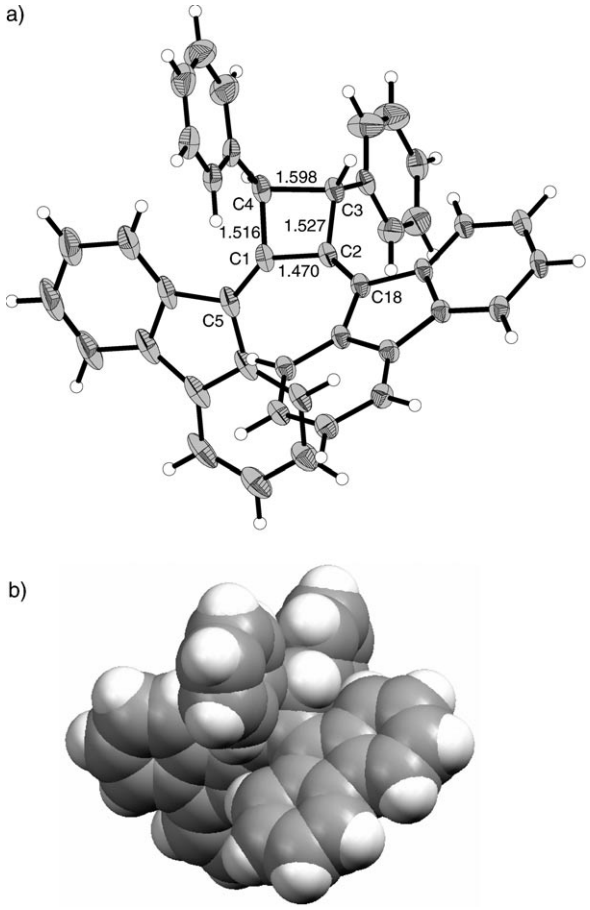


Figure 4. a) Molecular structure of orange *trans* dimer **9**; thermal ellipsoids are drawn at the 50% probability level. b) Space-filling view of orange *trans* dimer **9**, emphasizing the inversion of helicity of the fluorenylidene moieties relative to that in the structure of red *trans* dimer **7**.

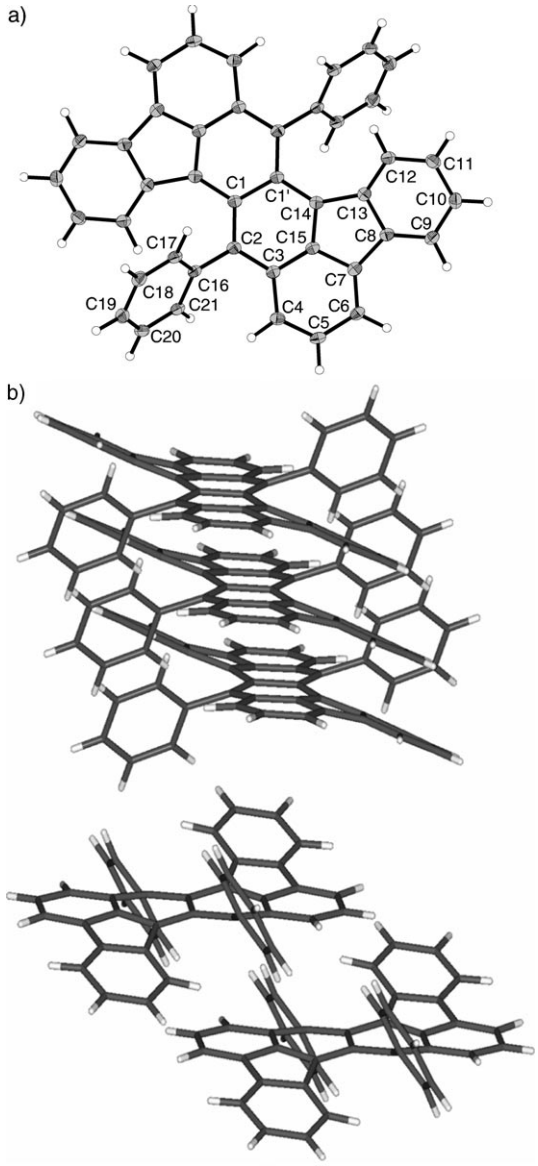


Figure 5. a) Top view of the molecular structure of blue tetracene **4**; thermal ellipsoids are drawn at the 50% probability level. b) Front and side views showing the π stacking of blue tetracene **4**.

of 1.3 ppm relative to its *para*-situated counterpart (H9) in the same ring.[1] In the solid state, π stacking between tetracenes is evident (Figure 5b).

The blue tetracene **4** can be kept in the dark under a nitrogen atmosphere for an extended period; however, when exposed to oxygen and sunlight, it is gradually converted to the pale yellow peroxide **5**, whose structure is shown in Figure 6. It has long been known that linear polyaromatics such as naphthacene and pentacene readily undergo addition of dioxygen,[7] perhaps via excitation to the triplet state, which facilitates reaction with ground-state triplet dioxygen. However, a recent report[8] describes the reaction of a tetrakis(trimethylsilyl)pentacene with oxygen when exposed to sunlight, and the possible involvement of a radical cation was discussed. One could also envisage a third possibility, namely, formation of singlet oxygen through sensitization by **4** followed by a [4+2] cycloaddition.

In a preliminary communication,[1] we reported the structure of dispirodihydrotetracene **3** as a cocrystal with peroxide **5**. We have now obtained single crystals of **3**, and the structure appears in Figure 7a. In the previous determination,[1] the molecule exhibited a "twisted-saddle" C_2-type conformation (Figure 7b), whereby the spiro-bonded fluorenyl moieties are each folded to the same side of the tetracene framework by about 17°. However, as a single compound, **3** adopts C_i symmetry (as does **4**) such that the tetracene skeleton resembles a chaise-longue in which the terminal rings are bent in opposite directions out of the central plane through 14°, and the spiro-bonded fluorenyl units are also folded out of this plane, by 18°, but now lie on opposite sides of this central framework. Although both tetracenes **3** and **4** adopt C_i conformations in the solid state, they have considerable flexibility, since their NMR spectra are entirely consistent with time-averaged C_{2h} symmetry.

In their 1965 paper,[3] Kuhn and Rewicki also noted that deprotonation of yellow head-to-tail dimer **6** with potassium *tert*-butoxide in DMSO immediately produced a blue anion-

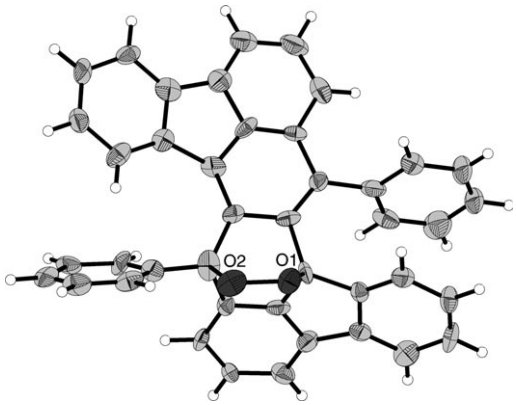


Figure 6. Molecular structure of tetracene peroxide **5**.

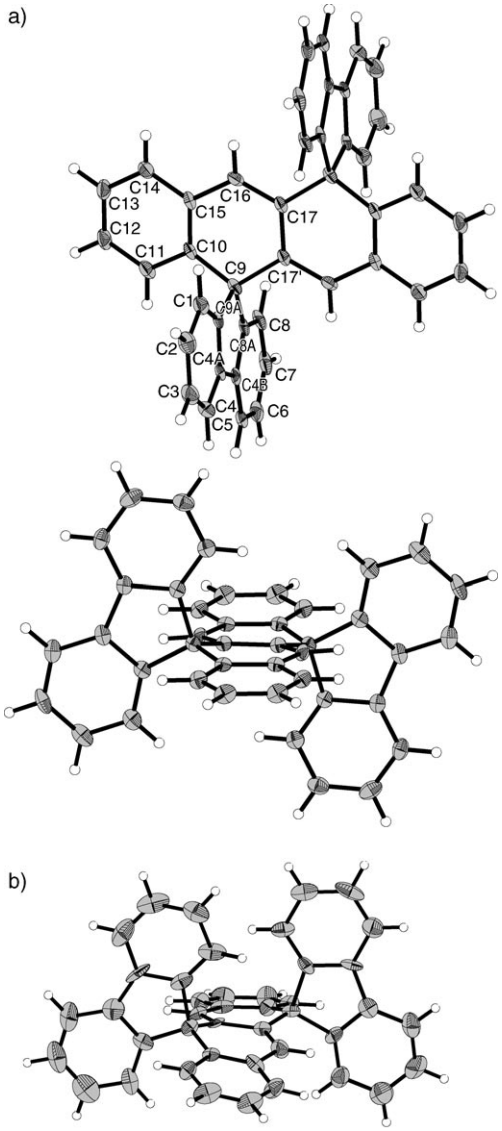


Figure 7. a) Top and side views of spirotetracene **3**; thermal ellipsoids are drawn at the 50% probability level. b) Molecular structure of the dispirotetracene **3** when cocrystallized with **5**.

ic species; subsequent reprotonation with acetic acid yielded isomeric, but unidentified, pale yellow product **10**. Upon repeating this procedure, a sample of **10** was obtained, the structure of which was elucidated by NMR spectroscopy and confirmed by X-ray crystallography. In the ^{1}H NMR spectrum of **6**, all eight protons in each of the fluorenyl moieties were distinguishable, as anticipated for a molecule of such low symmetry. However, after the deprotonation/reprotonation sequence, each of the fluorenyl groups exhibited only four proton environments, which implies the existence of a time-averaged molecular mirror plane; likewise, the ^{13}C NMR spectra of **6** and **10** paralleled the ^{1}H NMR results. These observations suggested that the intermediate blue species was best represented as a 14π fluorenide anion, and that reprotonation had occurred at the C9 position of the exocyclic fluorenyl substituent to give 1-(9-fluorenyl)-2-phenyl-4-phenylmethylenespiro[cyclobutene-3,9′-fluorene] (Scheme 1). The X-ray crystallographic structure of **10** (Figure 8) clearly reveals the formation of a cyclobutene ring bearing a 9-fluorenyl substituent in the rearranged product.

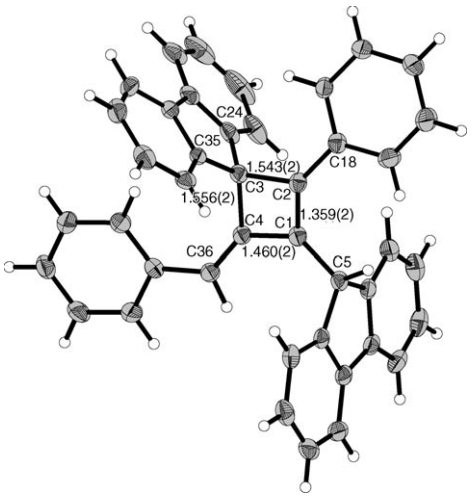


Figure 8. Molecular structure of [1,3]-hydrogen migration product **10**; thermal ellipsoids are drawn at the 50% probability level.

Moreover, Rewicki and Kuhn[3] reported that they were unable to deprotonate the unidentified red allene dimer, now known to be *trans*-3,4-diphenyl-1,2-bis(fluorenylidene)-cyclobutane (**7**). However, we found that when orange isomer **9** was allowed to react with potassium *tert*-butoxide in DMSO for an extended time (1–3 h), a greenish blue anionic species was formed; subsequent reprotonation with acetic acid yielded the [1,3]-hydrogen migration product 1-(9-fluorenyl)-2,3-diphenyl-4-fluorenylidenecyclobutene (**11**), analogous to that produced from yellow dimer **6**. The structure of **11** appears as Figure 9. Apparently, deprotonation of **9** is sterically hindered relative to the situation in head-to-tail isomer **6**, and thus anion formation is a much slower process. Red dimer **7** behaves similarly when treated with potassium *tert*-butoxide in DMSO for 1 h; moreover, repro-

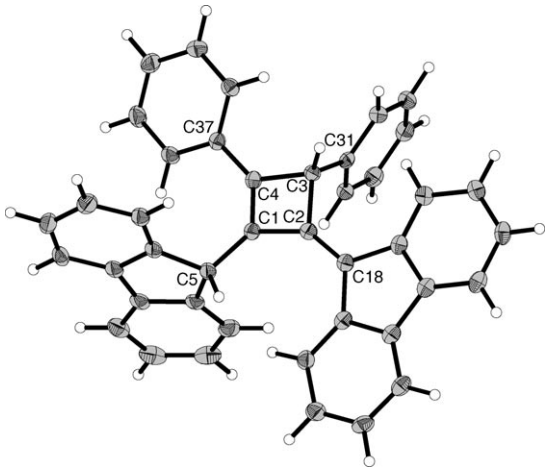
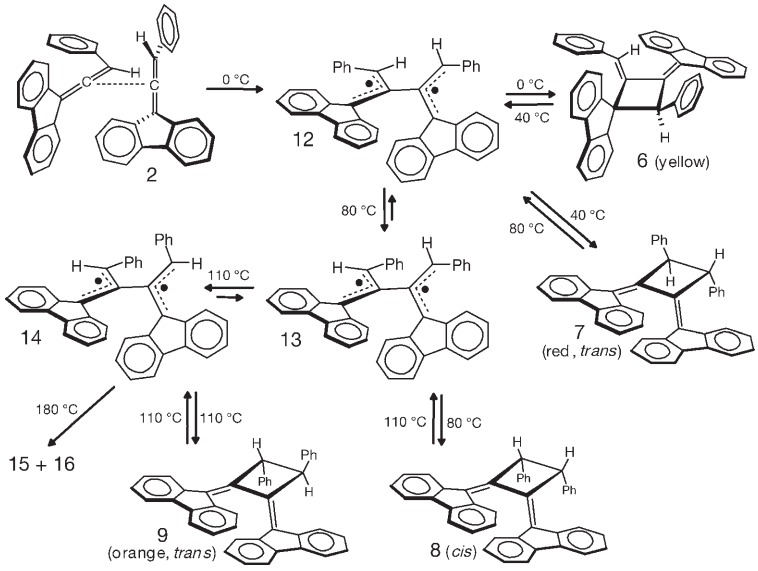


Figure 9. Molecular structure of [1,3]-hydrogen migration product, **11**; thermal ellipsoids are drawn at the 50% probability level.

tonation with acetic acid yielded not only the [1,3]-hydrogen migration product **11**, but also small quantities of orange dimer **9**, as befitting its status as the thermodynamically more stable atropisomer of *trans*-3,4-diphenyl-1,2-bis(fluorenylidene)-cyclobutane.

Mechanistic considerations: Having established not only the molecular structures of the four allene dimers **6–9**, but also the fact that they are sequentially produced, one must offer a rationale for these observations. Evidently, the initial yellow head-to-tail dimer **6** is the kinetic product, and so must arise from the allene starting material **2** via a low-energy pathway that does not involve extensive molecular reorganization. Although a $[_{\pi}2_{s}+_{\pi}2_{a}]$ cycloaddition mechanism for allene dimerization is orbital-symmetry-allowed, a stepwise process involving a diallylic diradical intermediate is more commonly invoked.[9–12] The orthogonal arrangement of substituents in allenes, together with the obvious preference of large groups to minimise steric hindrance, suggests that the initial geometry of approach of two molecules of **2** is favored by a C_2-type trajectory, as depicted in Scheme 2.[13] Thus, at the moment of generation, the most favorably oriented p orbitals through which radical coupling can occur are located on unlike termini, and a least-motion rotation about the central bond suffices to bring these centers close enough for bond formation to occur, and leads directly to the initially observed yellow dimer **6**.



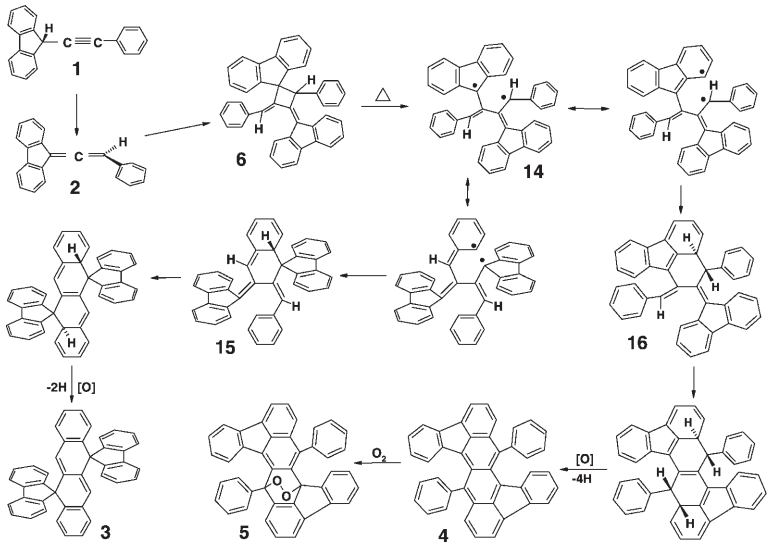
Scheme 2. Proposed mechanism for the formation of allene dimers **6–9**.

Further heating converts **6** to red dimer **7**, in which both fluorenylidene units are now exocyclic. One can readily envisage cleavage of the long C3–C4 bond (1.605 Å) in **6** to regenerate the tetramethylene ethane diradical having a phenyl and a biphenylene group, which can exist in three isomeric forms: *endo*,*endo* (**12**), *endo*,*exo* (**13**) and *exo*,*exo* (**14**). Now, following the allene dimerization mechanism proposed by Christl,[13] conrotatory ring closure of *endo*,*endo* form **13** leads to red *trans* dimer **7**, while, at successively higher temperatures *endo*,*exo* and *exo*,*exo* isomers **13** and **14** lead to the orange *cis* and orange *trans* products **8** and **9**, respectively.

Experiments are currently in progress on analogous molecules having trifluoromethyl substituents in the phenyl rings, which will allow rate data to be conveniently obtained through ^{19}F NMR measurements. These studies are aimed at elucidating the kinetic parameters for this series of isomerizations, and may help to further clarify the situation.

As noted above, prolonged thermolysis of yellow allene dimer **6** yields the dispirodihydrotetracene **3** and diindenotetracene **4**. It is relevant to note the important studies by Capdeveille and Rigaudy,[11] and also by Christl and coworkers,[12] who demonstrated the intermediacy of biallyl diradicals that can be delocalized onto the *ortho* positions of neighboring aromatic rings and thus allow formation of six-membered rings.

In Scheme 3, we show how these ideas can account for the generation of the observed products **3–5**. Cleavage of the long C3–C4 bond (1.605 Å) of initially formed [2+2] dimer **6** leads ultimately to diradical **14**, from which one can envisage coupling either between an *ortho*-phenyl site and the C9 position of a neighboring fluorenyl ring (to give **15**), or between an *ortho*-fluorenyl position and the benzylic site (leading to **16**). Subsequent disrotatory electrocyclization of



Scheme 3. Proposed mechanism for the formation of tetracenes **3** and **4**.

the 6π system in **15** and **16** generates the required molecular frameworks, and aerial oxidation yields the observed products **3** and **4** and, eventually, **5**.

Spectroscopic data: The striking color change (red to orange-yellow) observed during the transformation of **7** via **8** into **9** is an interesting phenomenon. In the visible region, the spectra of these compounds show strong absorptions at 457 ($\varepsilon = 11\,300$), 446 ($\varepsilon = 25\,000$) and 431 nm ($\varepsilon = 27\,000$), respectively. Thus, dimer **7** absorbs mainly in the blue and green regions, and thus appears red; in contrast, **8** and **9** absorb primarily in the blue and violet regions, and thus appear orange-yellow. One can perhaps relate these colors to the different degrees of conjugation between the two fluorenylidene moieties. In red isomer **7**, the dihedral angle C5-C1-C2-C18 between these substituents is 41°, but this opens up to 62° in **8**, and 60° in **9**. Assuming that a greater deviation from coplanarity increases the HOMO–LUMO gap, one would anticipate absorption at higher energy in **8** and **9**, and this is indeed the case.

One of our original goals was to investigate the luminescence behaviour of diindenotetracene **4**, and the relevant data are shown in Figure 10. This compound absorbs strongly in red and yellow regions, and thus appears blue; in contrast, intense emission is observed in the red region at 665 nm.

An interesting final observation concerns the synthesis of 9-phenylethynylfluorene (**1**) from 9-phenylethynylfluoren-9-ol by treatment with boron trifluoride and triethylsilane.[14] The mechanism presumably involves coordination of the hydroxyl group to boron, transfer of fluorine from boron to silicon and delivery of a hydride from silicon to carbon to furnish the desired alkyne **1**, possibly via single cyclic transition state. In our hands, the reaction works reasonably satisfactorily (50–60% yield of isolated product) and the alkyne has been characterized by X-ray crystallography.[2] However, there is always a side product that, according to the ^{1}H NMR spectrum, contains a fluorenyl group, a disubstituted phenyl fragment and a triethylsilyl substituent. The identity of this material was resolved unequivocally by X-ray crystallography (Figure 11), which revealed the it to be 2′-triethylsilylspiro-[fluorene-9,1′-1*H*-indene] (**17**), in which the fluorenyl moiety is spiro-linked to a triethylsilyl-substituted indenyl ring. One might venture to suggest that the Et_3SiF now present in the system might react with some already formed allene **2** (by rearrangement of alkyne **1**) to

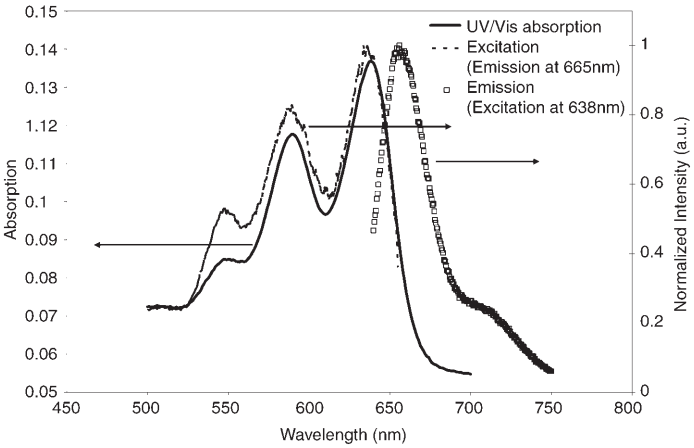


Figure 10. Luminescence data for blue tetracene **4** (10^{-4} M, THF). UV/Vis absorption (solid line), fluorescent excitation (broken line), and fluorescent emission (□) spectra.

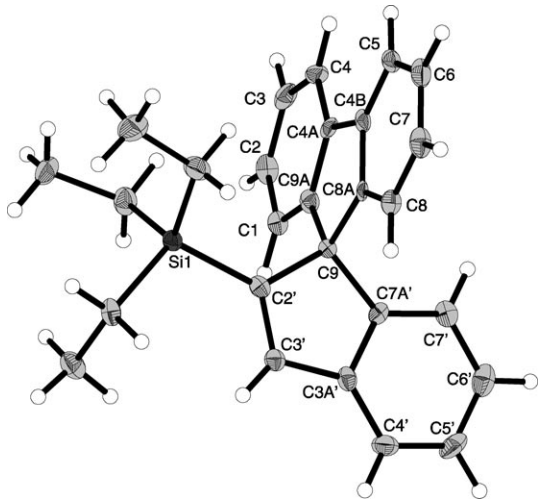
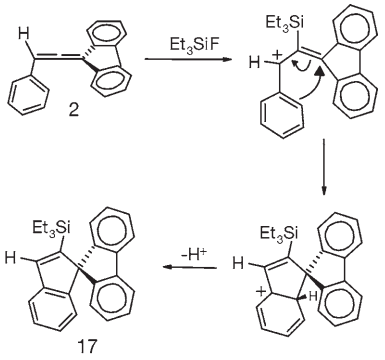


Figure 11. Molecular structure of spiro-cyclized product **17**; thermal ellipsoids are drawn at the 50% probability level.

generate a β-silyl stabilized cation, as depicted in Scheme 4. Subsequent Nazarov-type cyclization would lead directly to the observed product **17**. Related structures having spiro-



Scheme 4. Proposed Nazarov cyclization mechanism to form the spiro product **17**.

bonded fluorenyl and indenyl fragments include the 3′-phenyl analogue that arises upon acidification of 9-(2,2-diphenylvinyl)fluoren-9-ol.[15] Moreover, we note that treatment of 1,1-diphenyl-3,3-biphenyleneallene with bromine in CCl_4 gives 2′-bromo-3′-phenylspiro[fluorene-9,1′-1*H*-indene].[16]

To conclude, it has been established that dimerization of allene **2** proceeds in several steps, the products of each of which can be isolated and fully characterized. At higher temperatures, expansion of the four-membered ring to a six-membered ring, subsequent electrocyclization and, finally, elimination of hydrogen leads to tetracene formation. The generality of this process and the optical properties of a wide variety of tetracenes are currently being explored. We have also synthesized push–pull allene dimers[17] bearing ferrocenyl and other organometallic fragments, and the structures, dynamics and reactivity of these compounds will be the subject of a future report.

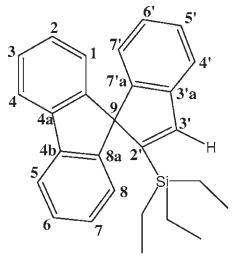
Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300 MHz or 500 MHz spectrometer. Assignments were based on standard 2D NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and HMBC, NOESY). Electrospray mass spectrometry was performed on a Micromass Quattro micro instrument. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer and were calibrated with polystyrene. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. Melting points were determined on an Electrothermal ENG. instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

Syntheses of 1 and 17: Triethylsilane (5.7 mL, 36.1 mmol) was added slowly to 9-phenylethynylfluoren-9-ol (8.5 g, 30.1 mmol) in dry dichloromethane (250 mL) at 0 °C. $BF_3{\cdot}OEt_2$ (4.4 mL, 36.1 mmol) was added dropwise, and the solution became green-brown. After stirring for 30 min at 0 °C, the reaction was quenched with distilled water (100 mL), and the mixture was extracted with diethyl ether several times. The organic layers were washed with water and with brine successively, dried over $MgSO_4$, filtered and concentrated to give a brown solid that was purified by chromatography on silica gel with dichloromethane/pentane (1/9) as eluent. 9-Phenylethynylfluorene (**1**) was isolated as a yellow solid (4.1 g, 15.4 mmol; 51 %), m.p. 127–130 °C, lit.: 129–131 °C.[3] A second product, 9*H*-fluorene-9-spiro-1′-[2′-triethylsilylindene] (**17**), m.p. 89–94 °C, was also obtained (300 mg, 0.8 mmol; 2.7 %). A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/hexane.

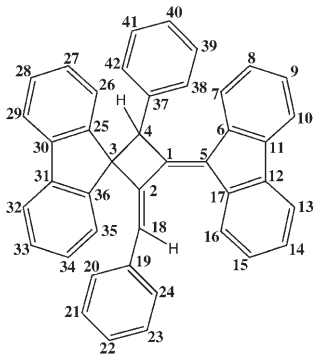
Data for 1: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.83$ (d, 2H, $J = 7.5$ Hz, H4, H5), 7.81 (d, 1H, $J = 7.5$ Hz, H1, H8), 7.50 (d, 2H, 7.5 Hz, phenyl *o*-H), 7.48 (t, 2H, $J = 7.5$ Hz, H3, H6), 7.44 (t, 2H, $J = 8.0$ Hz, H2, H7), 7.34–7.32 (m, 3H, phenyl *m*-H, *p*-H), 5.02 ppm (s, 1H, H9); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 144.1$ (C8a, C9a), 140.6 (C4a, C4b), 131.9 (phenyl *o*-C), 128.3 (phenyl *m*-C), 128.1 (phenyl *p*-C), 128.0 (C3, C6), 127.7 (C2, C7), 125.2 (C1, C8), 123.6 (C3′a), 120.2 (C4, C5), 87.3 (C2′), 82.2 (C3′), 40.0 ppm (C9); elemental analysis calcd (%) for $C_{21}H_{14}$: C 94.70, H 5.30; found: C 94.37, H 5.53.

Data for 17: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.79$ (d, 2H, $J = 7.5$ Hz, H4, H5), 7.40 (d, 1H, $J = 7.5$ Hz, H4′), 7.35 (s, 1H, H3′), 7.35 (td, 2H, $J = 7.5$, 1.0 Hz, H3, H6), 7.22 (t, 1H, $J = 7.5$ Hz, H5′), 7.11 (t, 2H, $J = 7.5$ Hz, H2, H7), 6.96 (t, 1H, $J = 7.5$ Hz, H6′), 6.82 (dd, 2H, $J = 7.5$, 1.0 Hz, H1, H8), 6.57 (d, 1H, $J = 7.5$ Hz, H7′), 0.66 (t, 9H, $J = 8.0$ Hz, CH_3), 0.09 ppm (q, 6H, $J = 8.0$ Hz, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 152.1$ (C7a′), 151.9 (C2′), 146.1 (C8a, C9a), 145.2 (C3a′), 144.0 (C3′), 142.3 (C4a, C4b), 127.7 (C3, C6), 127.4 (C2, C7), 127.1 (C5′), 126.1 (C6′), 124.1 (C1, C8), 122.3 (C7′), 120.8 (C4′), 120.1 (C4, C5), 72.4 (C9), 7.2 (CH_3), 2.9 ppm (CH_2); elemental analysis calcd (%) for $C_{27}H_{28}Si$: C 85.21, H 7.42; found: C 84.99, H 7.67.



Synthesis of 6: Triethylamine (200 μL, 0.29 mmol) was added to a suspension of 9-phenylethynylfluorene (**1**; 1.31 g, 4.92 mmol) in pentane (25 mL) at 0 °C, and the suspension was stirred for 5 h at 0 °C and then overnight in a cold water bath. The precipitate was collected by filtration, washed with cold pentane and dried to give 3-(9-fluorenylidene)-2-phenyl-4-phenylmethylenespiro[cyclobutane-1,9′-fluorene] (**6**; 956 mg, 1.80 mmol; 73 %) as a yellow powder, m.p. 175–178 °C, lit.: 184–186 °C.[3] A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/pentane.

Data for 6: ^{1}H NMR (500 MHz, $CDCl_3$); numbering is in accord with the crystal structure: $\delta = 8.65$ (d, 1H, $J = 8.0$ Hz, H16), 7.85 (d, 1H, $J =$

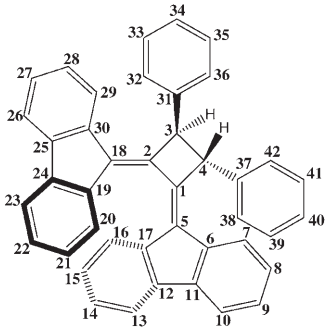


7.5 Hz, H13), 7.81 (d, 1H, $J = 7.5$ Hz, H29), 7.78 (d, 1H, $J = 7.5$ Hz, H10), 7.71 (d, 1H, $J = 7.5$ Hz, H26), 7.69 (s, 1H, H18), 7.67 (d, 1H, $J = 7.5$ Hz, H32), 7.56 (br s, 1H, H38 or H42), 7.43 (td, 1H, $J = 7.5$, 1.0 Hz, H14), 7.40 (td, 1H, $J = 7.5$, 1.0 Hz, H27), 7.34 (td, 1H, $J = 7.5$, 1.0 Hz, H15), 7.27 (td, 1H, $J = 7.5$, 1.0 Hz, H9), 7.25 (td, 1H, $J = 7.5$, 1.0 Hz, H28), 7.21 (br s, 1H, H39 or H41), 7.20 (d, 1H, $J = 8.0$ Hz, H7), 7.12 (t, 1H, $J =$

7.5 Hz, H40), 7.09 (td, 1H, $J=7.5$, 1.0 Hz, H33), 7.03 (brs, 1H, H39 or H41), 6.99 (td, 1H, $J=7.5$, 1.0 Hz, H8), 6.89 (t, 1H, $J=7.5$ Hz, H22), 6.79 (t, 2H, $J=7.5$ Hz, H21, H23), 6.55 (d, 2H, 7.5 Hz, H20, H24), 6.52 (td, 1H, $J=7.5$, 1.0 Hz, H34), 6.49 (brs, 1H, H38 or H42), 6.09 (d, 1H, $J=$ 8.0 Hz, H35), 5.16 ppm (s, 1H, H4); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=$ 150.1 (C25), 144.2 (C2), 143.9 (C1), 141.7 (C36), 141.4 (C31), 140.6 (C12), 140.0 (C11), 139.8 (C30), 138.4 (C6), 137.9 (C17), 137.8 (C37), 134.7 (C19), 131.5 (C5), 130.3 (C38, C42), 128.8 (C20, C24), 128.4 (C14), 128.1 (C18), 128.0 (C28), 127.8 (C9), 127.8 (C27), 127.6 (C22), 127.5 (C15), 127.4 (C21, C23), 127.4 (C33), 127.2 (C8), 127.1 (C40), 126.5 (C35), 126.1 (C34), 125.2 (C7), 124.1 (C16), 122.8 (C26), 120.1 (C13), 119.9 (C29), 119.7 (C22), 119.4 (C32), 63.4 (C3), 61.7 ppm (C4).

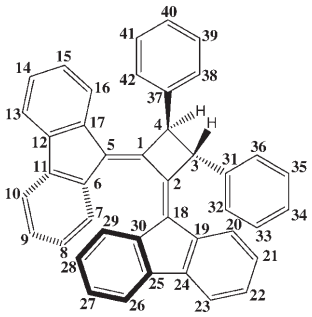
Syntheses of 7 and 9: When yellow dimer **6** was dissolved in dichloromethane and heated at reflux for 1.5 h, the presence of a red product was evident. After removal of solvent and redissolution in cyclohexane (3 mL), **6** (55 mg, 0.10 mmol) was heated at reflux overnight. After removing the solvent, NMR examination of the crude material indicated a 13:1 ratio of yellow dimer to red dimer. Chromatographic separation and recrystallization from dichloromethane/pentane (1/9) gave X-ray quality crystals of *trans*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane (**7**), m.p. 223–226 °C, lit.: 227–229 °C.[3] Analogously, yellow dimer **6** (100 mg, 0.19 mmol) suspended in toluene (5 mL) was heated at reflux for 3 d, and the product was concentrated to give a brown oil and triturated with diethyl ether to give orange dimer **9** (52 mg, 0.1 mmol; 52%), m.p. 196–200 °C. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/diethyl ether/hexane.

Data for 7: ^{1}H NMR (500 MHz, $CDCl_3$); numbering is in accord with the crystal structure: $\delta=7.68$ (d, 2H, $J=7.5$ Hz, H10, H26), 7.62 (d, 2H, $J=$ 7.0 Hz, H13, H23), 7.29 (d, 2H, $J=8.0$ Hz, H7, H29), 7.24 (t, 2H, $J=$ 7.5 Hz, H9, H27), 7.22 (d, 4H, $J=7.5$ Hz, phenyl *o*-H), 7.18 (t, 4H, $J=$



7.5 Hz, phenyl *m*-H), 7.14 (t, 4H, $J=7.0$ Hz, H14, H22, phenyl *p*-H), 7.09 (d, 2H, $J=7.5$ Hz, H20, H16), 6.87 (td, 2H, $J=7.5$ Hz, H8, H28), 6.86 (td, 2H, $J=7.5$ Hz, H15, H21), 4.73 ppm (s, 2H, H3, H4); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=143.9$ (C1, C2), 141.2 (C31, C37), 140.5 (C12, C24), 140.4 (C11, C25), 138.0 (C17, C19), 136.7 (C6, C30), 135.9 (C5, C18), 128.8 (phenyl *m*-C), 128.7 (C9, C27), 128.0 (C14, C22), 127.5 (phenyl *o*-C), 127.0 (C8, C28, phenyl *p*-H), 126.5 (C15, C21, C16, C20), 126.3 (C7, C29), 119.6 (C13, C23), 119.3 (C10, C26), 61.2 ppm (C3, C4); elemental analysis calcd (%) for $C_{42}H_{28}\cdot 0.5\ CH_2Cl_2$: C 88.75 H 5.08; found: C 88.11, H 5.57.

Data for 9: ^{1}H NMR (500 MHz, $CDCl_3$); numbering is in accord with the crystal structure: $\delta=7.75$ (d, 2H, $J=7.5$ Hz, H13, H23), 7.74 (dd, 2H, $J=$ 8.0, 1.5 Hz, H10, H26), 7.52 (d, 2H, $J=8.0$ Hz, H16, H20), 7.49 (d, 4H, $J=7.0$ Hz, phenyl *o*-H), 7.32 (t, 6H, $J=7.5$ Hz, H14, H22, phenyl *m*-H), 7.29 (t, 2H, $J=7.5$ Hz, H9, H27), 7.27 (d, 2H, $J=7.0$ Hz, H7, H29), 7.24 (t, 2H, $J=7.5$ Hz, phenyl *p*-H), 7.05 (td, 2H, $J=7.5$, 0.5 Hz, H8, H28), 7.03 (td, 2H, $J=7.5$, 1.0 Hz, H15, H21), 4.80 ppm (s, 2H, H3, H4); ^{13}C NMR (125 MHz, $CDCl_3$) 143.0 (C1, C2), 142.0 (C31, C37), 140.6 (C11, C25), 140.3 (C12, C24), 138.6 (C6, C30), 136.8 (C17, C19), 134.8 (C5, C18), 129.5 (phenyl *m*-C), 128.7 (C14, C22), 128.4 (C7, C29), 127.5 (C15, C21), 127.4 (C8, C28), 127.3 (phenyl *o*-C), 127.2 (phenyl *p*-C), 126.3 (C16, C20), 124.8 (C9, C27), 120.1 (C10, C26), 119.6 (C13, C23),



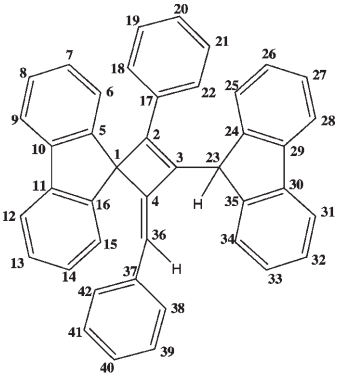
62.5 ppm (C3, C4); elemental analysis calcd (%) for $C_{42}H_{28}$: C 94.70 H 5.30; found: C 93.98, H 5.57.

Synthesis of 8: Yellow dimer **6** (330 mg, 0.62 mmol) suspended in toluene (5 mL) was heated at 85 °C for 30 h. After removing the solvent, the crude product was purified by chromatography on alumina with dichloromethane/cyclohexane (1/9) as eluent. *cis*-3,4-Diphenyl-1,2-bis(fluorenylidene)cyclobutane (**8**) was isolated as an orange solid (33.9 mg, 0.06 mmol; 10%), m.p. 214–218 °C (decomp). A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/diethyl ether.

Data for 8: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.75$ (d, 1H, $J=7.5$ Hz), 7.72 (d, 2H, $J=7.5$ Hz), 7.66 (d, 1H, 7.5 Hz), 7.63 (dd, 1H, $J=7.0$, 1.0 Hz), 7.38 (d, 1H, $J=7.5$ Hz), 7.38 (brs, 1H), 7.34–7.10 (m), 7.13 (td, 1H, $J=$ 7.5, 0.5 Hz), 7.08–6.95 (m, 5H), 6.94–6.85 (m, 2H), 6.77 (td, 1H, $J=7.5$, 1.0 Hz), 6.65 (brs, 0.5H), 6.45 (brs, 1H), 6.18 (brs, 1H), 5.42 (d, 1H, $J=$ 8.5 Hz), 5.31 ppm (d, 1H, $J=8.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=$ 145.6, 141.4, 140.6, 140.3, 140.3, 140.2, 138.7, 138.3, 137.4, 137.4, 137.1, 136.3, 135.2, 134.8, 129.7 (brs), 129.0 (brs), 128.7, 128.6, 128.4 (brs), 128.3, 127.9, 127.8 (brs), 127.5, 127.5, 127.2 (brs), 127.2, 126.8, 126.6, 126.5, 126.4, 126.3, 125.6, 125.2, 120.0, 119.5, 119.4, 119.4, 58.2, 56.3 ppm; elemental analysis calcd (%) for $C_{42}H_{28}\cdot 0.25\,CH_2Cl_2\cdot 0.5\,Et_2O$: C 89.62, H 5.89; found: C 89.89, H 5.62.

Synthesis of 10: Potassium *tert*-butoxide (126 mg, 1.13 mmol) was added portionwise to a solution of yellow dimer **6** (500 mg, 0.94 mmol) in dimethyl sulfoxide (10 mL), and the solution turned dark blue. After stirring at room temperature for 1 h, the reaction was quenched with a solution of acetic acid (20 mL; 2 mL acetic acid in 50 mL water) and extracted twice with diethyl ether. The organic phases were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to give a yellow solid. The crude material was triturated with diethyl ether to give **9** (343 mg, 0.64 mmol; 68%) as a pale yellow solid, m.p. 194–196 °C, lit.: 233–235 °C (with sintering at 190 °C).[3] A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/diethyl ether/hexane.

Data for 10: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.95$ (d, 2H, $J=7.5$ Hz), 7.89 (d, 2H, $J=7.5$ Hz), 7.83 (d, 2H, $J=7.5$ Hz), 7.52 (t, 2H, $J=7.5$ Hz), 7.46 (d, 2H, $J=7.5$ Hz, H), 7.43 (td, 2H, $J=7.5$ Hz), 7.38 (td, 2H, $J=$ 7.5 Hz), 7.22 (td, 2H, $J=7.5$ Hz), 7.15–6.95 (m, 5H), 6.80–6.65 (m, 4H),



6.25–6.10 (m, 2H), 5.70 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.6 (br s), 146.3, 145.9 (C5, C16), 144.8 (C24, C35), 141.5 (C29, C30), 141.1 (C10, C11), 135.3, 132.6 (br s), 128.6 (C_{phenyl}), 128.1 (C8, C13, C_{phenyl}), 128.0 (C27, C32), 127.9, 127.9 (C7, C14, C26, C33), 127.8 (C_{phenyl}), 127.6, 125.8 (C36, C_{phenyl}), 126.6, 125.2 (C25, C34), 124.1 (C6, C15), 120.4 (C28, C31), 120.3 (C9, C12), 113.6 (br s), 65.8 (C1), 46.9 ppm (C23); elemental analysis calcd (%) for $C_{42}H_{28}\cdot 0.5\,CH_2Cl_2$: C 88.75, H 5.08; found: C 88.31, H 5.33.

Synthesis of 11: Potassium *tert*-butoxide (101 mg, 0.90 mmol) was added portionwise to a solution of orange dimer **9** (300 mg, 0.56 mmol) in dimethyl sulfoxide (6 mL), and the solution turned dark green-blue. After stirring at room temperature for 3 h, the reaction was quenched with a solution of acetic acid (10 mL; 2 mL acetic acid in 50 mL water), and extracted twice with diethyl ether and dichloromethane. The organic phases were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to give a yellow solid. The crude material was triturated with diethyl ether to give **11** (286 mg, 0.53 mmol; 95%) as a pale yellow solid, m.p. 132–135°C (decomp). A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/diethyl ether/hexane.

Data for 11: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 7.5 Hz), 7.92 (d, 1H, J = 8.0 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.81 (d, 1H, J = 7.5 Hz), 7.74 (d, 1H, J = 7.0 Hz), 7.73 (d, 1H, J = 7.5 Hz), 7.59 (d, 2H, J = 8.0 Hz), 7.51 (t, 1H, J = 7.5 Hz), 7.41 (t, 1H, J = 7.5 Hz), 7.38–7.32 (m, 4H), 7.31–7.21 (m, 2H), 7.16–7.09 (m, 2H), 6.91 (t, 1H, J = 7.5 Hz), 6.80 (t, 2H, J = 7.5 Hz), 6.48 (d, 2H, J = 7.5 Hz), 5.96 (s, 1H), 5.37 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2, 147.8, 144.9, 144.3, 142.5, 141.5, 141.4, 140.8, 140.1, 139.1, 137.8, 131.7, 128.8, 128.5, 128.3, 128.3, 128.0, 128.0, 127.6, 127.5, 127.1, 126.9, 126.6, 126.6, 125.5, 125.3, 124.8, 124.6, 120.5, 120.1, 120.0, 119.4, 53.9, 49.3 ppm; elemental analysis calcd (%) for $C_{42}H_{28}\cdot 1.5\,Et_2O$: C 89.58, H 6.68; found: C 90.33, H 6.24.

Syntheses of 3, 4 and 5: 9-Phenylethynylfluorene (636 mg, 2.39 mmol) and tetracyclone (963 mg, 2.51 mmol) were added together, and the mixture was heated over a free flame with an air condenser attached for 30 min. The solution was cooled, and 5 mL of benzene was added to prevent solidification of the tetracyclone. The mixture was subjected to column chromatography (100% hexanes to 100% CH_2Cl_2), which resulted in the recovery of tetracyclone and isolation of two major fractions: pale yellow dispiro[fluorene-9,5′-11′*H*-naphthacene-11′,9″-fluorene] (**3**; 164 mg, 0.31 mmol, 13%), m.p. 250–253°C, and deep blue 8,16-diphenyldiindeno[1,2,3-*de*:1′,2′,3′-*mn*]naphthacene (**4**; 570 mg, 1.1 mmol, 45%), m.p. 167–170°C (decomp).

Alternatively, yellow dimer **6** (1.0 g, 1.88 mmol) suspended in dimethyl sulfoxide (20 mL) was heated at reflux for 5 h, during which time a blue coloration of the solution was observed. The solution was cooled, water (20 mL) was added and the mixture was extracted with diethyl ether and dichloromethane. The organic phases were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to give a dark oil. Chromatographic separation with toluene/cyclohexane (1/9) and recrystallization from dichloromethane/pentane, gave X-ray quality crystals of dispirofluorenyldihydrotetracene **3** and diindeno[1,2,3-*de*:1′,2′,3′-*mn*]tetracene **4**. When **4** was left in air and exposed to daylight for several hours, it was gradually oxidized to give pale yellow 8,16-diphenyl-8*H*-8,16*b*-epidioxydiindeno[1,2,3-*de*:1′,2′,3′-*mn*]naphthacene (**5**), m.p. 261–264°C.

Data for 3: ^{1}H NMR (500 MHz, CD_2Cl_2); numbering is in accord with the crystal structure: δ = 7.87 (4H, d, J = 7.5 Hz, H16), 7.43 (4H, dd, J = 7.4, 7.4 Hz, H15), 7.20 (4H, dd, J = 7.5, 7.4 Hz, H14), 7.16 (4H, d, J = 7.4 Hz, H13), 6.97 (2H, dd, J = 7.5, 7.6 Hz, H2), 6.86 (2H, d, J = 8.2 Hz, H1), 6.76 (2H, dd, J = 7.5, 7.5 Hz, H3), 6.28 (2H, d, J = 7.7 Hz, H4), 5.95 ppm (2H, H6); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 153.5, 142.6, 140.6, 128.1, 127.9, 126.7 (C), 128.7 (C14), 128.4 (C15), 128.1 (C1), 127.8 (C3), 127.6 (C2), 126.5 (C4), 125.9 (C13), 120.8 (C16), 69.0 ppm (C6); HRMS: *m/z*: calcd for $C_{42}H_{26}$ [M^+]: 530.2035; found: 530.2010.

Data for 4: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.96 (4H, d, J = 8.0, 6.3 Hz, H1, H3), 7.86 (2H, d, J = 7.4 Hz, H4), 7.67 (4H, br s, Ph), 7.61 (2H, dd, J = 7.6, 6.8 Hz, H2), 7.46 (6H, br s, Ph), 7.10 (2H, dd, J = 7.2, 7.2 Hz, H5), 6.77 (2H, dd, J = 7.6, 7.5 Hz, H6), 6.57 ppm (2H, d, J = 8.0 Hz, H7); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 141.3, 140.9, 138.4, 138.2, 130.5, 128.2 (C), 134.5, 128.7 (phenyl CH), 128.6 (C2), 127.4 (C1), 127.3 (C6), 126.5 (C7), 125.8 (C5), 120.9 (C4), 120.0 ppm (C3); HRMS: *m/z*: calcd for $C_{42}H2_4$ [M^+]: 528.1878; found: 528.1873.

Data for 5: ^{1}H NMR (600 MHz, CD_2Cl_2); numbering is in accord with the crystal structure: δ = 8.42 (1H, d, J = 8.4 Hz, phenyl *p*-H), 8.20 (1H, d, J = 7.7 Hz, H1), 8.15 (1H, d, J = 7.8 Hz, H4), 8.06 (1H, d, J = 7.8 Hz, H12), 7.96 (2H, d, J = 7.0 Hz, phenyl *o*-H), 7.89 (1H, d, J = 7.7 Hz, H9), 7.67 (1H, d, J = 7.0 Hz, H11), 7.64 (2H, dd, J = 7.1, 7.6 Hz, phenyl *m*-H), 7.62 (1H, dd, J = 7.6, 7.6 Hz, H5), 7.51 (1H, dd, J = 7.9, 7.6 Hz, H13), 7.40 (1H, dd, J = 7.9, 7.5 Hz, H2), 7.29–7.27 (2H, m, H6, H10), 7.21 (1H, dd, J = 7.6, 7.6 Hz, H14), 7.13–7.10 (2H, m, H3, H7), 6.96 (2H, d, J = 7.1 Hz, phenyl *o*-H), 6.82 (1H, d, J = 7.5 Hz, H15), 6.69 (1H, d, J = 8.0 Hz, phenyl *p*-H), 6.58 ppm (2H, dd, J = 7.8, 7.7 Hz, phenyl *m*-H). The numbering for protons 1–3 and 9–11, as well as 4–7 and 12–15 may be interchanged. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 144.3, 142.5, 141.0, 138.7, 136.6, 134.6, 133.6, 132.1 (C), 132.5, 129.7, 129.4, 129.3, 128.8, 128.0, 127.9, 127.3, 124.4, 123.8, 123.6, 122.9, 122.4, 121.6, 121.0 (CH), 128.9, 127.5, 126.5, 123.9 ppm (2CH); HRMS: *m/z*: calcd for $C_{42}H2_4O_2$ [M^+]: 560.1776; found: 560.1776.

X-ray measurements for 3, 4, 6–10, 11, and 17: X-ray crystallographic data (Table 1) were in each case collected from a suitable sample mounted with grease on the end of a thin glass fiber. Data were collected on a D8 Bruker diffractometer equipped with a Bruker SMART APEX CCD area detector (employing the program SMART)[18] and an X-ray tube utilizing graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). A full sphere of the reciprocal space was scanned by phi-omega scans. Data processing was carried out by use of the program SAINT,[19] while the program SADABS[20] was utilized for scaling of diffraction data and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct-methods procedure in the Bruker SHELXL[21] program library and refined by full-matrix least-squares methods on F^2. In **4** and **6** all hydrogen atoms were located in the difference Fourier map and allowed to refine freely with isotropic temperature factors, as were the hydrogen atoms in the main molecule of **11**, where the solvent hydrogen atoms were added at calculated positions, and refined using a riding model. In the remaining structures all hydrogen atoms were treated in this way. Anisotropic temperature factors were used for all non-hydrogen atoms, except in **8** where the carbon atoms could only be refined with isotropic temperature factors.

After completing the initial structure solution for **7**, it was found that 27% of the total cell volume was filled with disordered solvent, which could not be modelled in terms of atomic sites. From this point on, residual peaks were removed and the solvent region was refined as a diffuse contribution without specific atom positions by using the PLATON module SQUEEZE,[22] which subtracts electron density from the void regions by appropriately modifying the diffraction intensities of the overall structure. An electron count over the solvent region provides an estimate for the number of solvent molecules removed from the cell. The number of electrons thus located, 1474 per unit cell, was included in the formula, formula weight, calculated density, μ and F(000). This residual electron density was assigned to two molecules of diethyl ether per molecule of **7** (1474/18 = 81.89 electrons per molecule of **7**; two molecules of diethyl ether would give 84 electrons). A dramatic improvement was observed in all refinement parameters and residuals when this procedure was applied. SQUEEZE was also used to treat disordered solvent in the structures of **8** and **10**.

CCDC-273672 (**6**), CCDC-273673 (**7**), CCDC-273674 (**9**), CCDC-273675 (**3**), CCDC-273676 (**10**), CCDC-273677 (**17**), CCDC-273678 (**4**), CCDC-273679 (**11**) and CCDC-273680 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data.

	3	**4**	**6**	**7**	**8**	**9**	**10**	**11**	**17**
formula	$C_{42}H_{26}\cdot 2C_4H_{10}O$	$C_{42}H_{24}$	$C_{42}H_{28}$	$C_{42}H_{28}\cdot 2C_4H_{10}O$[c]	$C_{42}H_{28}$	$C_{42}H_{28}\cdot {}^1/_2\,C_4H_{10}O$[c]	$C_{42}H_{28}\cdot {}^1/_3C_4H_{10}O$[c]	$C_{42}H_{28}\cdot C_4H_{10}O$	$C_{27}H_{28}Si$
M	678.87	528.61	532.64	670.80	532.64	569.70	557.33	606.76	380.58
crystal system	triclinic	triclinic	monoclinic	trigonal	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
space Group	$P\bar{1}$	$P\bar{1}$	Cc	$R\bar{3}$	$P2_1$	$Pbcn$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.7183(17)	6.2886(9)	18.2159(16)	44.0683(19)	15.233(6)	38.173(3)	8.5223(9)	8.8824(12)	9.7574(15)
b [Å]	11.473(2)	7.7305(11)	19.8116(17)	44.0683(19)	8.987(4)	16.7503(11)	17.7609(19)	11.3304(15)	10.3304(16)
c [Å]	18.316(3)	13.2639(19)	8.5724(7)	9.6514(9)	41.163(16)	28.754(2)	20.117(2)	16.048(2)	21.297(3)
α [°]	93.463(3)	93.099(2)	90	90	90	90	90	86.752(2)	95.133(3)
β [°]	97.648(4)	98.409(2)	110.5690(10)	90	100.163(7)	90	99.502(2)	84.894(2)	92.099(3)
γ [°]	113.730(3)	100.014(2)	90	120	90	90	90	88.268(2)	97.908(3)
V [Å^3]	1838.2(6)	626.07(15)	2896.4(4)	16232.1(18)	5547(4)	18386(2)	3003.3(5)	1605.6(4)	2115.1(6)
Z	2	1	4	18	8	24	4	2	4
ρ_{calcd} [g cm^{-3}]	1.226	1.402	1.221	1.235	1.276	1.235	1.233	1.255	1.195
T [K]	100(2)	100(2)	100(2)	100(2)	113(2)	100(2)	100(2)	105(2)	100(2)
μ [mm^{-1}]	0.073	0.080	0.069	0.074	0.072	0.071	0.067	0.073	0.121
$2\theta_{max}$ [°]	44.00	52.22	52.00	52.00	48.00	45.00	52.00	52.00	48.00
reflns measured	16975	4398	22248	39446	23392	101709	21816	11912	27278
reflns used (R_{int})	4509 (0.0666)	2193 (0.0176)	2858 (0.0300)	6976 (0.0289)	14670 (0.0800)	12007 (0.0506)	5759 (0.0256)	5916 (0.0197)	6614 (0.0489)
parameters	488	238	491	379	674	1135	379	538	511
final R values [$I>2\sigma(I)$]:									
$R1$[a]	0.0547	0.0383	0.0269	0.0410	0.1082	0.0430	0.0430	0.0400	0.0947
$wR2$[b]	0.1140	0.0987	0.0671	0.1035	0.2623	0.1008	0.1108	0.0921	0.2545
R values (all data):									
$R1$[a]	0.0838	0.0444	0.0276	0.0521	0.1400	0.0577	0.0505	0.0504	0.1023
$wR2$[b]	0.1260	0.1029	0.0678	0.1075	0.2916	0.1064	0.1146	0.0981	0.2570
GOF on F^2	1.059	1.048	1.035	1.055	1.032	1.041	1.070	1.026	1.178

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] The diethyl ether molecule(s) could not be located in the unit cell. PLATON SQUEEZE was used to compensate for the spread electron density.

Acknowledgement

We thank Science Foundation Ireland and University College Dublin for generous financial support, Dr. Noël Lugan, Laboratoire de Chimie de Coordination, Toulouse, for advice on the use of the program SQUEEZE to resolve solvent disorder in crystal structures, and our colleagues Dr. Mike Casey and Dr. Declan Gilheany for useful discussions. We are especially grateful to Professor Manfred Christl (Universität Wurzbürg) for very helpful comments on the manuscript. C.M.S. is the recipient of a post-doctoral fellowship from the Natural Sciences and Engineering Research Council of Canada.

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[6] Taking the C1–C2 bond axis as a locant, the relative orientations of the fluorenylidene moieties can be defined as being clockwise (*R*) or counterclockwise (*S*). Thus, the enantiomer of **7** depicted in Figure 2 could be labelled (3*R*,4*R*)-*trans*-3,4-diphenyl-(1:2*R*)-bis-(fluorenylidene)cyclobutane. See, for example, K. C. Nicolaou, C. N. C. Boddy, J. S. Siegel, *Angew. Chem.* **2001**, *113*, 723–726; *Angew. Chem. Int. Ed.* **2001**, *40*, 701–704.

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Received: September 23, 2005
Revised: December 11, 2005
Published online: February 10, 2006

