

Polyphenylbiphenyls and Polyphenylfluorenes

Ling Tong, Heidi Lau, Douglas M. Ho, and Robert A. Pascal, Jr.*

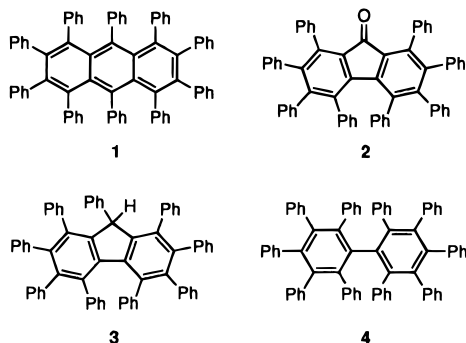
Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received January 28, 1998

Abstract: A series of highly congested polyphenylbiphenyls and polyarylfuorenes has been prepared and their X-ray structures determined. Decaphenylbiphenyl adopts a very unusual C_1 -symmetric geometry (rather than the more intuitive D_2 geometry) in which one of the central benzene rings is distorted into a boat conformation. AM1 calculations confirm that the C_1 geometry is the ground state but indicate that less highly substituted biphenyls should adopt D_2 geometries. The structure of 2,2',4,4',6,6'-hexaphenylbiphenyl supports the latter prediction; this material has crystallographic C_2 symmetry and (except for the orientation of the *para* phenyl groups) approximate D_2 symmetry in the solid state. Octaphenylfluorenone has been prepared in four steps from tetraphenylcyclopentadienone. Its X-ray structure shows the fluorenone core to be twisted and sterically shielded by the eight peripheral phenyl groups; nevertheless, phenylmagnesium bromide adds easily to the carbonyl group of its equally hindered dimethyl derivative, 2,3,5,6,7,8-hexaphenyl-1,4-di(*p*-tolyl)fluorenone. Reduction of the resulting fluorenone with $TiCl_3$ gives a nonaarylfluorene, 2,3,5,6,7,8,9-heptaphenyl-1,4-di(*p*-tolyl)fluorene, and its X-ray structure shows distortions similar to those of octaphenylfluorenone.

Introduction

Polyphenyl polycyclic aromatic hydrocarbons are remarkably robust even when possessing highly unusual geometries. Decaphenylanthracene¹ (**1**) and 9,10,11,12,13,14,15,16-octaphenyl-dibenzo[*a,c*]naphthacene² have strongly twisted acene cores, but their many phenyl groups form protective hydrocarbon sheaths about them which confer exceptional stability. Octaphenyl-naphthalene¹ is less distorted, but its stability and simple synthesis permits the construction of the albatrossenes,^{3,4} in which multiple octaphenyl-naphthalene subunits define large hydrophobic clefts. Other maximally arylated aromatic hydrocarbons, if easily prepared, could also serve as building blocks for very large organic structures. Among the obvious candidates are octaphenylfluorenone (**2**), nonaphenylfluorene (**3**), and decaphenylbiphenyl (**4**).



Compounds **2–4** may all be considered derivatives of biphenyl. Molecular mechanics calculations indicate that the

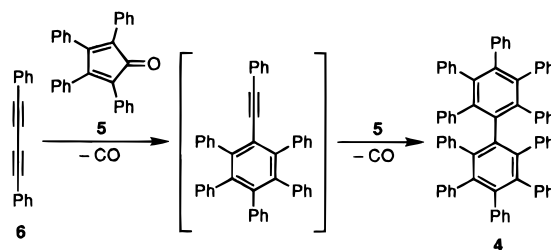
(1) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 741–745.

(2) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531–1532.

(3) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1997**, *38*, 7–10.

(4) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 7291–7302.

three are highly congested molecules in which the cores are well shielded by the surrounding “picket fence” of phenyl substituents. The crowding is most acute in **4**, where the four central *ortho*-phenyl groups must clash, and the molecule may only partly relieve steric congestion by rotation about its central carbon–carbon bond. Indeed, a CPK model of **4** is impossible to construct, and, given the degree of steric conflict, it was surprising to find that **4** had been prepared in 1965 in 60% yield by heating together two commercially available starting materials, tetraphenylcyclopentadienone (**5**) and 1,4-diphenyl-1,3-butadiyne (**6**).⁵ The second step in this double Diels–Alder reaction is sterically very demanding.⁶



In contrast with **4** and similar biphenyls, the “biphenyl” nuclei of the fluorenes **2** and **3** are constrained to be more nearly planar, although some degree of steric relief is provided by the replacement of two of the strongly interacting *ortho*-phenyl groups of **4** with the single linking atom (C-9) in a polyphenylfluorene. However, unlike the polyphenylbiphenyls, of which there are several examples, fluorenes with more than four phenyl substituents appear to be unknown.⁷ Can such compounds be unstable or unusually difficult to prepare?

The peralkyl and peraryl derivatives of common hydrocarbons and their ions are of fundamental interest to chemists: the

(5) Ogliaruso, M. A.; Becker, E. I. *J. Org. Chem.* **1965**, *30*, 3354–3360.

(6) Ogliaruso and Becker do not seem to have found this to be unusual; although they recognized that decaphenylbiphenyl is a very crowded molecule, its synthesis is reported almost without comment as “**4k**” in a series of “bishexaphenyl-benzenes”!

(7) Reid, W.; Freitag, D. *Chem. Ber.* **1966**, *99*, 2675–2676.

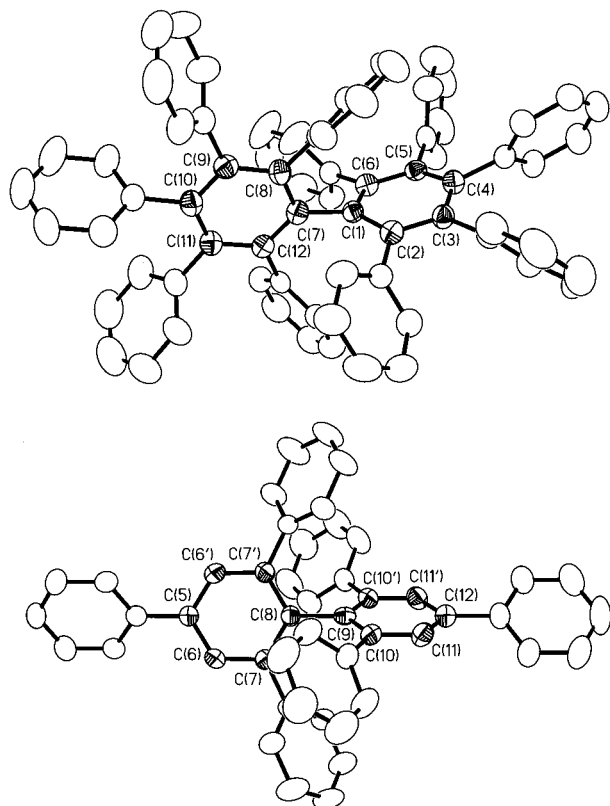


Figure 1. X-ray crystal structures of decaphenylbiphenyl (**4**, above) and 2,2',4,4',6,6'-hexaphenylbiphenyl (**9**, below). Thermal ellipsoids have been drawn at the 50% probability level.

structures and reactions of these species are important calibration points for theoretical work. Given our own long-standing interest in strained polycyclic aromatic hydrocarbons, the polyphenylbiphenyls and polyphenylfluorenes were attractive targets for synthetic and structural studies. We report herein the X-ray crystal structures of decaphenylbiphenyl and 2,2',4,4',6,6'-hexaphenylbiphenyl (which have surprisingly different geometries), computational studies of these and several related polyphenylbiphenyls, and the synthesis and structures of octaphenylfluorenone and several derivatives of nonaphenylfluorene.

Results and Discussion

Polyphenylbiphenyls. The preferred conformation of decaphenylbiphenyl (**4**) is not obvious, but the symmetry of its planar drawing suggests that some D_2 or D_{2d} geometry might be best. Ogliaruso and Becker's synthesis of **4** was repeated without difficulty, single crystals of the chloroform solvate of **4** were obtained, and X-ray data was collected. The structure was solved and refined in the monoclinic space group $P2_1/c$, and it is illustrated in Figure 1. The molecular conformation of **4** is unexpectedly asymmetric! Molecular mechanics calculations (SYBYL^{8,9}) had indicated that a D_2 geometry is the conformation of lowest energy, but the experimentally observed C_1 conformation is a distinct potential minimum of higher energy. There are no great distortions present in the calculated D_2 conformation, but in the observed C_1 structure, one of the central benzene rings is planar and the other is distorted into a

boat conformation! Why should this C_1 conformation be preferred, or is the observed structure merely due to the influence of crystal packing forces? A search of the Cambridge Structural Database¹⁰ showed that another extremely crowded biphenyl, dekakis(dichloromethyl)biphenyl,¹¹ exists in a similar C_1 conformation, suggesting that the unusual conformational preference of **4** is not just an artifact of crystal packing. Therefore, a more extensive computational study of **4** and related biphenyls was carried out in order to better define their conformational preferences.

All of the biphenyls examined bear phenyl substituents on the four carbons *ortho* to the central bond (see Table 1). AM1 calculations^{12,13} indicated that such biphenyls display two distinct conformational minima—the D_2 and C_1 conformations mentioned previously. These calculations indicate that whenever the four *ortho*-phenyls are buttressed by substituents *meta* to the central bond, the C_1 conformation is preferred, but when these positions are occupied by hydrogens, the D_2 conformation is best, although by only a very small margin (less than one kcal/mol; certainly too small to be the basis for a strong prediction). Thus decaphenylbiphenyl (**4**), 2,2',3,3',5,5',6,6'-octaphenylbiphenyl (**7**), and 3,3',4,4',5,5'-hexachloro-2,2',6,6'-tetraphenylbiphenyl (**8**) should exhibit C_1 structures, but 2,2',4,4',6,6'-hexaphenylbiphenyl (**9**) and 2,2',6,6'-tetraphenylbiphenyl (**10**) should exhibit D_2 structures. The geometry of the simplest member of this series, compound **10**, was also examined by means of ab initio calculations at the HF/STO-3G and HF/3-21G levels¹⁴ (Table 1). Once again, both the D_2 and C_1 conformations were found to be minima, with a strong preference for the D_2 geometry for **10** at the HF/STO-3G level and a slim, but perhaps more reliable, margin of 0.55 kcal/mol at the HF/3-21G level. (An ab initio calculation for **4** at this level is far beyond our current computational resources, but the excellent agreement between the AM1 calculations and the experimental results is reassuring.)

To test whether a D_2 conformation is indeed preferred in the less crowded biphenyls, 2,2',4,4',6,6'-hexaphenylbiphenyl (**9**) was prepared by a literature procedure,¹⁵ and its X-ray crystal structure was determined. Compound **9** crystallizes in the orthorhombic space group $Pnna$, and the molecule lies on a special position and possesses crystallographic C_2 symmetry. Only in the orientation of the *para* phenyl groups (which play no part in the steric conflict in these molecules) does **9** deviate from D_2 symmetry (see Figure 1). All of the aromatic rings of **9** are approximately planar; there are none of the severe distortions observed in **4**.

The structures of compounds **4** and **9** are best compared in the stereoviews in Figure 2. In compound **9**, the dihedral angle between the mean planes of the central rings is only 65.5°, while the corresponding rings in **4** are nearly perpendicular (86.5°). In **9**, both pairs of the interacting phenyl groups *ortho* to the

(10) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

(11) Biali, S. E.; Kahr, B.; Okamoto, Y.; Aburatani, R.; Mislow, K. J. *Am. Chem. Soc.* **1988**, *110*, 1917–1922.

(12) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

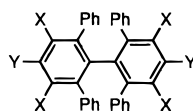
(13) Semiempirical and ab initio molecular orbital calculations were performed by using the SPARTAN program package (version 4.1; Wavefunction, Inc., Irvine, California, USA), and its built-in default thresholds for wave function and gradient convergence were employed. Frequency calculations were performed on the AM1-optimized equilibrium geometries to verify that these were true potential minima.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; pp 63–100.

(15) Fujioka, Y.; Ozasa, S.; Sato, K.; Ibuki, E. *Chem. Pharm. Bull.* **1985**, *33*, 22–29.

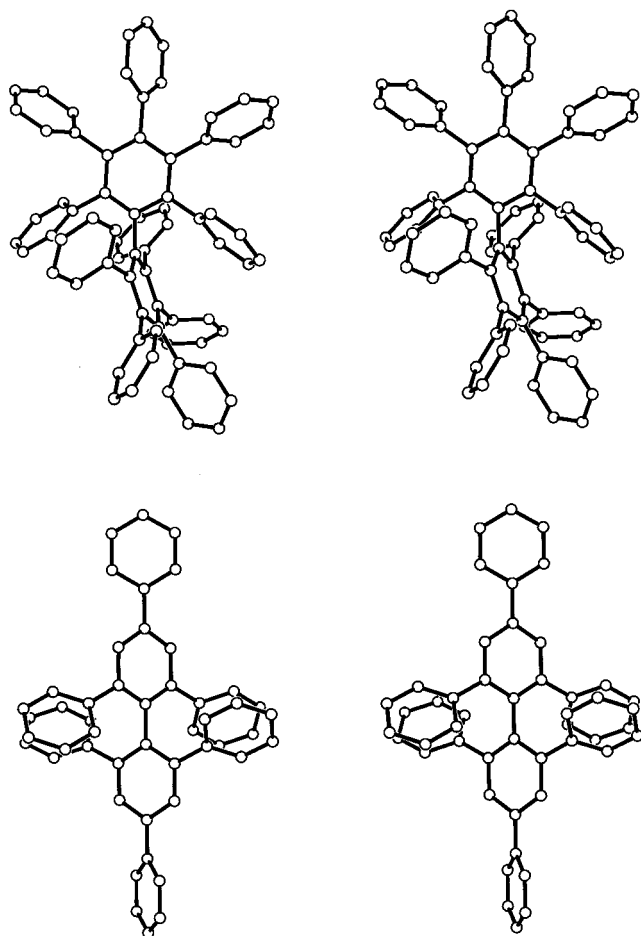
(8) Molecular mechanics calculations were performed by using the SYBYL⁹ force field implemented in the SPARTAN program package (versions 3.0 and 4.1; Wavefunction, Inc., Irvine, California, U.S.A.).

(9) Clark, M.; Cramer, R. D., III.; Van Opdenbosch, N. *J. Comput. Chem.* **1989**, *10*, 982–1012.

Table 1. Computational Data for Various Conformations of Polysubstituted Biphenyls

substituents	computational level ^a	symm	ΔH_f (AM1, kcal/mol) or E (HF, au ^b)	difference ($C_1 - D_2$, kcal/mol) ^c	central bond length (Å)
X = Y = Ph (4)	AM1	C_1	354.67	-2.00	1.476
	AM1	D_2	356.67		1.474
X = Ph, Y = H (7)	AM1	C_1	288.39	-1.20	1.476
	AM1	D_2	289.59		1.475
X = Y = Cl (8)	AM1	C_1	144.90	-2.67	1.476
	AM1	D_2	147.57		1.474
X = H, Y = Ph (9)	AM1	C_1	223.83	0.59	1.472
	AM1	D_2	223.24		1.470
X = Y = H (10)	AM1	C_1	168.38	0.72	1.473
	AM1	D_2	167.66		1.472
	HF/STO-3G	C_1	-1361.64463	4.66	1.526
	HF/STO-3G	D_2	-1361.65205		1.520
	HF/3-21G	C_1	-1370.73715	0.55	1.506
	HF/3-21G	D_2	-1370.73803		1.501

^a See note 13 for some computational details. ^b 1 au = 627.503 kcal/mol. ^c Negative values favor the C_1 conformation.

**Figure 2.** Stereoviews of the X-ray structures of compounds **4** (above) and **9** (below).

central bond are stacked face-to-face, but in **4**, one pair of *ortho* phenyls are face-to-face and the other pair adopts an edge-to-face orientation. This, indeed, is the characteristic difference between the D_2 and C_1 conformations in all of the calculated biphenyls as well. However, it remains difficult to understand why the D_2 conformation of **4** is not the preferred geometry: there is no single interaction in the calculated D_2 structure of **4** which is the obvious source of its destabilization. Nevertheless,

experimental and computational data agree, and observed preference must arise from small steric conflicts in the D_2 structure exacerbated by the buttressing groups in the positions *meta* to the central bond. It is noteworthy that the experimental central bond length in **4** [1.501(4) Å] is a bit shorter than that in the less crowded **9** [1.515(4) Å], which perhaps compensates in part for the distortion of the benzene ring in **4**. However, no significant difference between the central bond lengths of the pairs of D_2 and C_1 conformations of the various biphenyls is observed in the computational studies (Table 1).

A more extensive search of the Cambridge Structural Database found three additional examples of biphenyls with geometries similar to those of **4**: 2,2',4,4',6,6'-hexabromobiphenyl,¹⁶ 2,4,6-trinitro-2',4',6'-tris(*N*-pyrrolidiny)biphenyl,¹⁷ and 4,4',6,6'-tetranitro-2,2'-diphenic acid.¹⁸ The first two possess only small deviations from ideal D_2 and C_2 conformations, respectively, but the third is quite similar to **4**, although less highly distorted. AM1 calculations show discrete C_2 and C_1 conformations for this molecule, with the observed C_1 structure disfavored by 2.6 kcal/mol. However, the dimethyl ester of 4,4',6,6'-tetranitro-2,2'-diphenic acid¹⁹ as well as 6,6'-dinitro-2,2'-diphenic acid,²⁰ display undistorted, more nearly symmetric structures, so the observed preference for a higher energy C_1 conformation by solid 4,4',6,6'-tetranitro-2,2'-diphenic acid is likely to be the result of packing forces.

Polyphenylfluorenes. Given that a high-temperature Diels–Alder reaction sufficed for the synthesis of **4**, we chose similar reactions for key steps in the synthesis of octaphenylfluorenone (**2**, Scheme 1). Cycloaddition of tetraphenylcyclopentadienone (**5**) and 4-pentenoic acid in refluxing xylenes gave a highly crystalline adduct, which was then aromatized with bromine to give the (tetraphenylphenyl)propanoic acid **11** in 44% overall

(16) Field, L. D.; Skelton, B. W.; Sternhell, S.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 391–399.

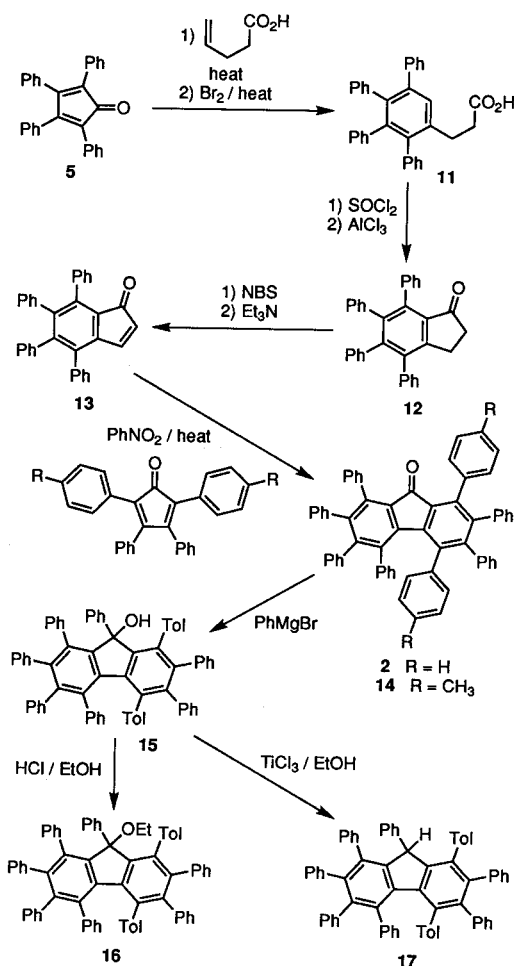
(17) Effenberger, F.; Agster, W.; Fischer, P.; Jogun, K. H.; Stezkowski, J. J.; Daltrozzo, E.; Kollmansberger-von Nell, G. *J. Org. Chem.* **1983**, *48*, 4649–4658.

(18) Popova, E. G.; Chetkina, L. A.; Bel'skii, V. K.; Andrievskii, A. M.; Poplovskii, A. N.; Dyumaev, K. M. *Zh. Struct. Khim.* **1987**, *28*, 129–132.

(19) Popova, E. G.; Chetkina, L. A.; Sobolev, A. N. *Zh. Struct. Khim.* **1991**, *32*, 130–133.

(20) Popova, E. G.; Chetkina, L. A.; Bel'skii, V. K.; Andrievskii, A. M.; Poplovskii, A. N.; Dyumaev, K. M. *Dokl. Akad. Nauk SSSR* **1989**, *304*, 127.

Scheme 1



yield. Surprisingly, the seemingly simpler reaction of **5** with 4-pentynoic acid to give **11** in one step gave yields no higher than 21% in several attempts. Cyclization of **11** to the indanone **12** was best accomplished by converting **11** to the acid chloride followed by an intramolecular Friedel–Crafts acylation (28% yield). Again, a one-step cyclization of **11** with hot polyphosphoric acid was much inferior (6% yield). NBS bromination of **12** followed by an elimination gave indenone **13** as a brilliant yellow solid (32% yield). The final Diels–Alder reaction of **13** and **5** was carried out in refluxing nitrobenzene to promote decarbonylation and dehydrogenation of the initial adduct. The yield of this reaction was low (11%), but single crystals of octaphenylfluorenone (**2**), suitable for X-ray analysis, formed upon cooling the reaction mixture, and additional **2** was precipitated by addition of methanol.

X-ray diffraction data were collected by using one of the crystals of **2** that formed upon cooling its synthetic reaction mixture. The structure was solved and refined without difficulty in the space group $P2_1/c$, and it is illustrated in Figure 3. Compound **2** lies on a special position and possesses crystallographic C_2 symmetry. The structure is generally similar to that of octaphenylcarbazole,²¹ but the fluorene core of **2** exhibits a somewhat greater twisting distortion from planarity. The twist is imparted by the very close interaction of the C(5) and C(5') phenyl groups; the *ipso* carbons of these phenyls [C(26) and C(26')] are only 3.12 Å apart, well within their van der Waal radii, and the torsional angle C(5)–C(6)–C(6')–C(5') is 33.2°.

(21) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1996**, *61*, 6748–6750.

The mean planes of all the phenyl groups are roughly perpendicular to the mean plane of the fluorene, so the carbonyl group is quite sheltered. Compound **2** proved to be profoundly insoluble, a surprising property, given that all of our other polyphenyl aromatics^{1–4,21} are quite soluble in common organic solvents. However, the X-ray structure shows the crystals to be especially close-packed (Figure 3), with many interlocking phenyl–phenyl interactions.

Because of the low solubility, further transformations of this material proved impossible. To continue the synthesis of a nonaarylfluorene, the dimethyl derivative **14** was prepared by Diels–Alder reaction of **13** and 2,3-diphenyl-1,4-di(*p*-tolyl)cyclopentadienone²² (39% yield). This material is quite soluble; presumably the methyls break up the close packing observed in the crystals of **2**. Addition of phenylmagnesium bromide to **14** gave nonaarylfluorene **15** (59% yield); the Grignard reagent has little difficulty in adding to the hindered carbonyl group. Finally, Ti(III) reduction of **15** gave the nonaarylfluorene **17** (61% yield). Interestingly, a standard procedure for reduction of 9-phenyl-9-fluorenone is to treat them with hydrogen halides in ethanol.²³ We verified that HCl in ethanol reduces 9-phenyl-9-fluorenone to the 9-phenylfluorene, as reported,²³ but treatment of **15** under the same conditions gave only the ethyl ether **16**.

Crystals of the nonaarylfluorene **17** were obtained from CH_2Cl_2 –acetone, its structure was solved and refined in the space group $P1$, and it is illustrated in Figure 4. The newly introduced C(9)-phenyl group is easily accommodated. Indeed, the fluorene nucleus is less distorted than in **2**, with a C(4)–C(4a)–C(4b)–C(5) torsion angle of only 19.3°, since the C(9)-phenyl need not lie directly between the C(1)-tolyl and C(8)-phenyl groups. However, there remain several close contacts between phenyl substituents: the distances between the *ipso* carbons C(29) and C(36), C(10) and C(60), and C(54) and C(60) are 3.09, 3.12, and 3.06 Å, respectively. The central “biphenyl” bonds in both **2** [C(6)–C(6')] and **17** [C(4a)–C(4b)] are of normal length, 1.501(9) Å and 1.510(5) Å, respectively.

Finally, the nonaphenylfluorenyl cation might be an unusually stable species due to steric shielding and delocalization of the charge throughout the fluorene nucleus, and this cation is a very likely intermediate in the transformations of **15** into **16** and **17**. However, attempts to prepare the cation by dissolving fluorene **15** in D_2SO_4 yielded a deep blue solution which gave only a very highly broadened ^{13}C NMR spectrum (unlike the sharp spectrum of the triphenylmethyl cation²⁴ recorded under the same conditions). Further attempts to obtain a crystalline nonaarylfluorenyl cation for X-ray analysis by treatment of **15** with acetic anhydride and perchloric acid²⁵ were also unsuccessful. In retrospect, it may be seen that the cation is more highly strained than the alcohol **15**, the ether **16**, or the hydrocarbon **17**, because sp^3 to sp^2 rehybridization at C(9) to form the cation will require the attached phenyl group to slide between the C(1) and C(8) phenyls, forcing them apart (see the space-filling view of **17** in Figure 4). By the same argument, the addition of any nucleophile to the cation to reform an sp^3 carbon will be favorable, perhaps enough so to prevent its easy isolation.

(22) Mehr, L.; Becker, E. I.; Spoerri, P. E. *J. Am. Chem. Soc.* **1955**, *77*, 986–989.

(23) Kohler, E. P.; Blanchard, L. W., Jr. *J. Am. Chem. Soc.* **1935**, *57*, 367–371.

(24) Olah, G. A.; Baker, E. B.; Comisarow, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 1265.

(25) Chance, J. M.; Geiger, J. H.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc.* **1990**, *112*, 3540–3547.

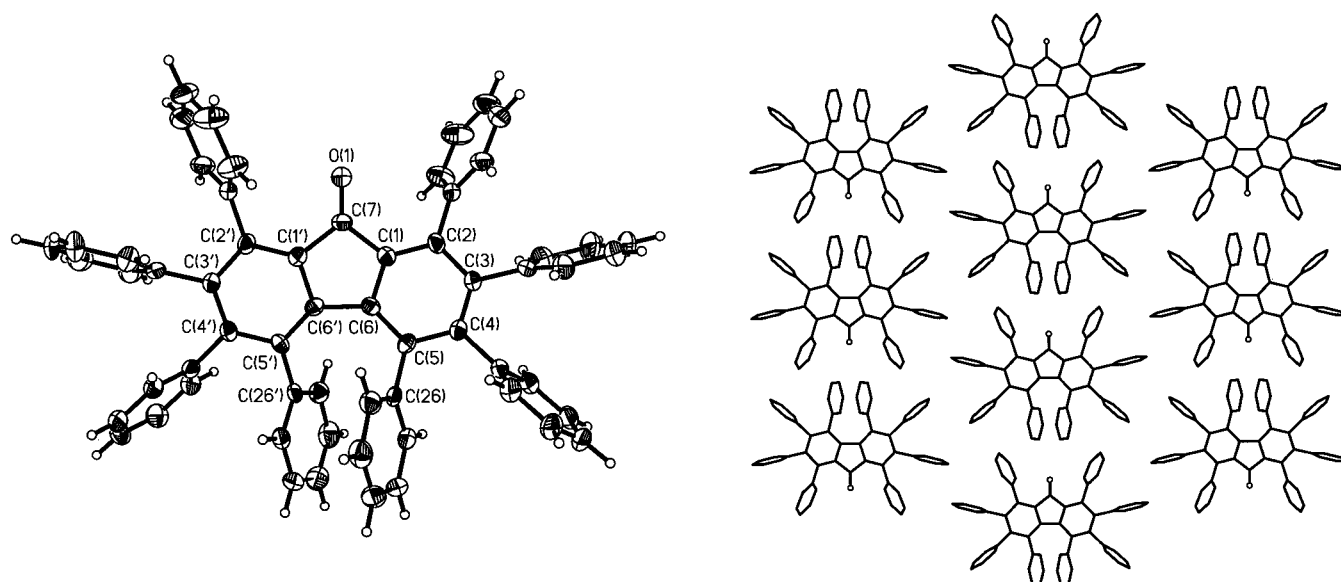


Figure 3. X-ray structure of octaphenylfluorenone (**2**). Thermal ellipsoids have been drawn at the 50% probability level. The close packing of **2** is illustrated (right side).

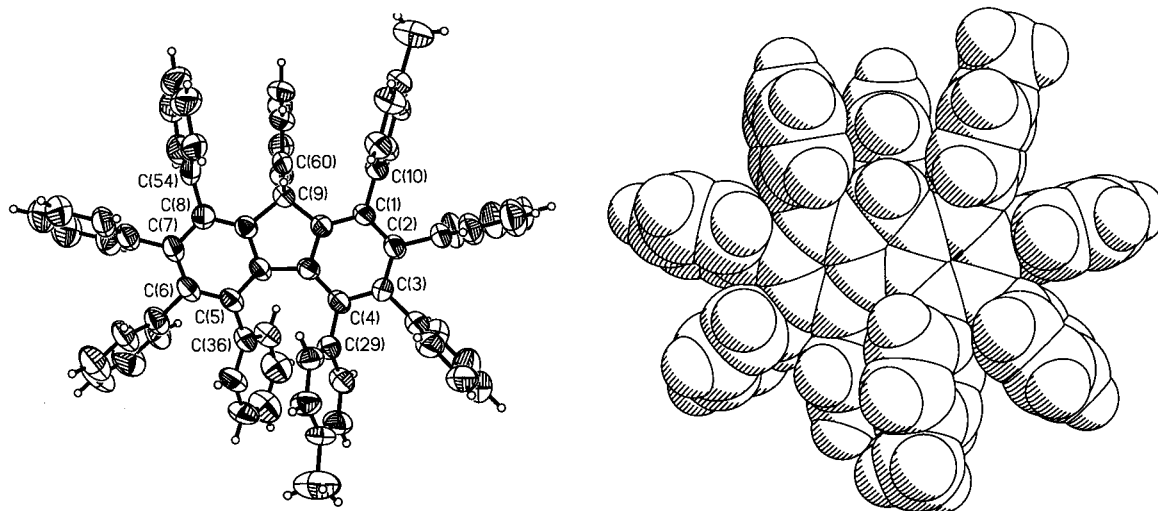


Figure 4. X-ray structure of 2,3,5,6,7,8-heptaphenyl-1,4-di(*p*-tolyl)fluorene (**17**). Thermal ellipsoids have been drawn at the 50% probability level.

Conclusion

The unique conformational dichotomy observed for the polyphenyl-biphenyls once again demonstrates that surprises await the unwary even for molecules having simple, "ordinary-looking" structures on paper, and that careful searches for all possible conformations must be made in computational studies if one is to accurately predict molecular structures. The polyphenylfluorenes held no such surprises, but their large size (C_{60} – C_{70}), well-defined conformations, short and versatile syntheses, and great stability indicate that they, like octaphenyl-naphthalene, will be suitable subunits for the assembly of very large organic structures.

Experimental Section

Decaphenylbiphenyl (4,2',3',5',6',2'',3'',5'',6''-octaphenyl-*p*-quaterphenyl) was prepared by the method of Ogliaruso and Becker;⁵ mp 225–227 °C (lit.⁵ 222–224 °C). Crystals suitable for X-ray analysis were obtained by the slow evaporation of a solution in chloroform-ethanol.

2,2',4,4',6,6'-Hexaphenylbiphenyl (9, 3',5',2'',6''-tetraphenyl-*p*-quaterphenyl) was prepared by the method of Fujioka et al.;¹⁵ mp

346–348 °C (lit.¹⁵ 345 °C, lit.²³ 348 °C). Crystals suitable for X-ray analysis were obtained by the slow evaporation of a solution in benzene-ethanol.

X-ray Crystallographic Analysis of Decaphenylbiphenyl (4). Formula $C_{72}H_{50}\cdot CHCl_3$; triclinic, space group $P\bar{1}$, $a = 11.073$ (1) Å, $b = 12.096$ (1) Å, $c = 23.303$ (3) Å, $\alpha = 88.649$ (8)°, $\beta = 88.657$ (10)°, $\gamma = 64.251$ (8)°, $V = 2810.2$ (6) Å³, $Z = 2$, $D_{\text{calcd}} = 1.223$ g/cm³. Intensity measurements were made at 298 K with $3^\circ \leq 2\theta \leq 50^\circ$ on a Siemens P4 diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and a crystal with dimensions of 0.05 mm \times 0.30 mm \times 0.50 mm. A total of 10 184 reflections were measured of which 9645 were unique ($R_{\text{int}} = 0.036$). The structure was solved by direct methods (SHELX-TL²⁶) and refined by full-matrix least-squares on F^2 (SHELXL-93²⁷). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were included with a riding model and isotropic displacement coefficients [$U(H) = 1.2U(C)$]. The chloroform in the lattice was disordered, and it was included in the refinement with a two-site model with distance and similarity restraints and a site occupancy parameter. The refinement converged to $R(F) = 0.050$, $wR(F^2) = 0.083$, and $S = 1.04$ for 3413 data with $I > 2\sigma(I)$,

(26) Sheldrick, G. M. *SHELXTL, Version 4.2*. Siemens Analytical X-ray Instruments, Madison, WI, 1991.

(27) Sheldrick, G. M. *SHELXL-93. Program for the Refinement of Crystal Structures*; University of Göttingen, Germany, 1993.

and $R(F) = 0.170$, $wR(F^2) = 0.108$, and $S = 0.74$ for 9645 data, 723 variables, and 24 restraints. Full details are provided in the Supporting Information.

X-ray Crystallographic Analysis of 2,2',4,4',6,6'-Hexaphenylbiphenyl (9). Formula $C_{48}H_{34}$; orthorhombic, space group $Pnna$; $a = 20.912$ (2) Å, $b = 16.579$ (1) Å, $c = 9.737$ (1) Å, $V = 3375.7$ (4) Å³, $Z = 4$, $D_{\text{calcd}} = 1.202$ g/cm³. Intensity measurements were made at 230 K with $4^\circ \leq 2\theta \leq 55^\circ$ on a Siemens P4 diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and a crystal with dimensions of 0.08 mm \times 0.35 mm \times 0.38 mm. A total of 4881 reflections were measured of which 3889 were unique ($R_{\text{int}} = 0.026$). The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-93). The positional and thermal parameters for all atoms were refined; the hydrogens were refined isotropically, and the carbons were refined anisotropically. The refinement converged to $R(F) = 0.052$, $wR(F^2) = 0.112$, and $S = 1.09$ for 1691 data with $I > 2\sigma(I)$, and $R(F) = 0.131$, $wR(F^2) = 0.137$, and $S = 0.83$ for 3888 data and 289 variables (one reflection was suppressed). Full details are provided in the Supporting Information.

3-(2,3,4,5-Tetraphenylphenyl)propanoic acid (11). 4-Pentenoic acid (2.65 g, 26.5 mmol) and tetraphenylcyclopentadienone (5, 11.2 g, 29 mmol) were heated in refluxing xylenes (30 mL) for 2 days. The product was chromatographed on a column of silica gel eluted successively with toluene, 1:2 toluene–ethyl acetate, and 20:1 toluene–methanol. The fractions containing 3-[(2,3,4,5-tetraphenyl-1,6-dihydro)phenyl]propanoic acid were combined, concentrated to dryness, and recrystallized from ethanol. This dihydro acid (5.61 g, 12.3 mmol) was heated in benzene (150 mL) in a 1 L round-bottom flask. After the compound had completely dissolved, the solution was cooled to room temperature. A solution of bromine (1.97 g, 12.3 mmol) in benzene (50 mL) was added dropwise. The resulting solution was heated at reflux overnight. Cooling and concentration gave compound **11** (5.26 g, 11.6 mmol, 44%), mp 145–150 °C. ¹H NMR (CDCl₃) δ 2.55 (t, $J = 7$ Hz, 2 H), 2.89 (t, $J = 7$ Hz, 2 H), 6.74–7.19 (m, 20 H), 7.42 (s, 1 H); MS m/z 454 (M⁺, 47), 436 (M – H₂O, 63), 393 (22), 358 (18), 315 (38), 157 (27), 91 (100); exact mass 454.1911, calcd for C₃₃H₂₆O₂ 454.1933. Compound **11** was also prepared by heating 4-pentynoic acid and **5** in xylenes, but the yield was only 21%.

4,5,6,7-Tetraphenyl-1-indanone (12). Compound **11** (2.78 g, 6.12 mmol), thionyl chloride (15 mL), and 1,1,1-trichloroethane (100 mL) were heated at reflux for 4 h. Unreacted thionyl chloride was largely removed by distillation of the reaction mixture to one-third of its original volume. After cooling, 1,1,1-trichloroethane (65 mL) and AlCl₃ (1.63 g, 12.2 mmol) were added, and the mixture was stirred at room-temperature overnight. The solution was heated at reflux for 1 h, allowed to cool, and poured into a mixture of 1 N HCl (100 mL) and ice (200 g). After stirring for 1 h, the organic phase was separated and washed 5 times with water. The organic layer was dried over Na₂SO₄ and concentrated to dryness. This material was chromatographed on a silica gel column eluted successively with toluene and 99:1 toluene–ethyl acetate. Concentration of the appropriate fractions gave compound **12** (0.760 g, 1.74 mmol, 28%), mp 171–173 °C. ¹H NMR (CDCl₃) δ 2.66 (t, $J = 6$ Hz, 2 H), 2.93 (t, $J = 6$ Hz, 2 H), 6.72–7.20 (m, 20 H); MS m/z 436 (M⁺, 4), 372 (10), 129 (28), 105 (100); exact mass 436.1834, calcd for C₃₃H₂₄O 436.1827. The direct cyclization of **11** to **12** was also accomplished by heating **11** in polyphosphoric acid at 190 °C for 2 days, but the yield was only 6%.

4,5,6,7-Tetraphenylindenone (13). Compound **12** (0.76 g, 1.74 mmol), *N*-bromosuccinimide (0.34 g, 1.9 mmol), and carbon tetrachloride (50 mL) were heated at reflux for 2 h while under illumination by a 250 W tungsten lamp. Triethylamine (5 mL) was then added, and heating was continued overnight. After cooling, the solution was washed three times with 1 N HCl; the organic layer was dried over Na₂SO₄ and concentrated to give a light brown solid. This material was chromatographed on a silica gel column eluted with 1:2 hexanes–toluene, and compound **13** was recovered as a bright yellow solid (0.24 g, 0.55 mmol, 32%), mp 229–230 °C. ¹H NMR (CDCl₃) δ 5.86 (d, $J = 6$ Hz, 1 H), 6.71–7.23 (m, 20 H), 7.44 (d, $J = 6$ Hz, 1 H); MS, m/z 434 (M⁺, 100), 357 (M – C₆H₅, 30); exact mass 434.1692, calcd for C₃₃H₂₂O 434.1671.

Octaphenylfluorenone (2). A solution of compounds **13** (26 mg, 0.060 mmol) and **5** (50 mg, 0.13 mmol) in nitrobenzene (0.5 mL) was heated to 210 °C for 40 h. The reaction mixture was allowed to cool slowly to room temperature, methanol (2 mL) was added, and the reaction mixture was left in the refrigerator overnight. The resulting bright yellow crystals of compound **2** (5 mg, 11%) were collected by filtration. These crystals are remarkably insoluble, but the larger ones were suitable for X-ray analysis. Mp > 400 °C; MS, m/z 788 (M⁺, 100), 711 (M – C₆H₅, 30); exact mass 788.3049, calcd for C₆₁H₄₀O 788.3079.

X-ray Crystallographic Analysis of Octaphenylfluorenone (2). Formula C₆₁H₄₀O; monoclinic, space group $P2_1/c$; $a = 15.031$ (2) Å, $b = 11.437$ (2) Å, $c = 12.326$ (1) Å, $\beta = 96.702$ (9)°, $V = 2104.4$ (5) Å³, $Z = 2$, $D_{\text{calcd}} = 1.245$ g/cm³. Intensity measurements were made at 223 K with $4^\circ \leq 2\theta \leq 50^\circ$ on a Siemens P4 diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and a crystal with dimensions of 0.10 mm \times 0.18 mm \times 0.25 mm. A total of 3868 reflections were measured of which 3720 were unique ($R_{\text{int}} = 0.065$). The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-93). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were included with a riding model and isotropic displacement coefficients [$U(H) = 1.2U(C)$]. The refinement converged to $R(F) = 0.078$, $wR(F^2) = 0.197$, and $S = 1.29$ for 1651 data with $I > 2\sigma(I)$, and $R(F) = 0.164$, $wR(F^2) = 0.308$, and $S = 0.96$ for 3713 data and 281 variables (7 reflections were suppressed). Full details are provided in the Supporting Information.

2,3,5,6,7,8-Hexaphenyl-1,4-di(*p*-tolyl)fluorenone (14). A solution of compound **13** (204 mg, 0.470 mmol) and 2,3-diphenyl-1,4-di(*p*-tolyl)cyclopentadienone²² (387 mg, 0.94 mmol) in nitrobenzene (2 mL) was heated to 210 °C for 48 h. After cooling, methanol (8 mL) was added slowly, and the resulting solution was left in the refrigerator overnight to yield bright yellow crystals of compound **14** (150 mg, 0.184 mmol, 39%); mp > 350 °C. ¹H NMR (CDCl₃) δ 2.09 (s, 3 H), 2.18 (s, 3 H), 6.14 (d, $J = 7$ Hz, 2 H), 6.26 (d, $J = 7$ Hz, 2 H), 6.39 (d, $J = 8$ Hz, 2 H), 6.44 (m, 4 H), 6.63 (m, 6 H), 6.70–6.81 (m, 14 H), 6.84 (d, $J = 8$ Hz, 2 H), 6.91 (d, $J = 8$ Hz, 2 H), 7.04 (s, 4 H); MS, m/z 816 (M⁺, 100), 739 (M – C₆H₅, 22); exact mass 816.3399, calcd for C₆₃H₄₄O 816.3392.

9-Hydroxy-2,3,5,6,7,8,9-heptaphenyl-1,4-di(*p*-tolyl)fluorene (15). A solution of compound **9** (50 mg, 0.061 mmol) in toluene (15 mL) was chilled in an ice bath. A solution of phenylmagnesium bromide (3 mL, 3 M in ether, 9 mmol) was added, and the resulting mixture was heated at reflux overnight. The reaction mixture was washed with water, dried over Na₂SO₄, and concentrated to dryness. The residue was fractionated by preparative TLC (silica gel GF; 3:1 toluene–hexanes) to yield compound **15** (32 mg, 0.036 mmol, 59%); mp 312.5–313.5 °C. ¹H NMR (CDCl₃) δ 2.12 (s, 3 H), 2.14 (s, 3 H), 2.74 (br s, 1 H), 5.74 (d, $J = 8$ Hz, 1 H), 5.86 (d, $J = 8$ Hz, 1 H), 6.29 (m, 3 H), 6.37–6.54 (m, 10 H), 6.60–6.88 (m, 24 H), 7.02 (t, $J = 7$ Hz, 1 H), 7.08 (m, 2 H), 7.24 (d, $J = 8$ Hz, 1 H); MS, m/z 894 (M⁺, 69), 876 (M – H₂O, 100), 817 (M – C₆H₅, 33), 799 (M – H₂O – C₆H₅, 31).

9-Ethoxy-2,3,5,6,7,8,9-heptaphenyl-1,4-di(*p*-tolyl)fluorene (16). Compound **15** (32 mg, 0.036 mmol) in ethanol (5 mL) was heated to boiling in a Pyrex screw-capped tube. Concentrated HCl (2 mL) was added, the tube was sealed, and it was heated at 110 °C overnight. After cooling, CH₂Cl₂ was added, and the mixture was washed with dilute NaOH, dried over Na₂SO₄, and concentrated to dryness. The residue was fractionated by preparative TLC (silica gel GF; 1:9 toluene–hexanes) to yield compound **16** (25 mg, 0.027 mmol, 76%); mp 305.5–307.5 °C. ¹H NMR (CDCl₃) δ 1.28 (t, $J = 7$ Hz, 3H), 2.07 (s, 3H), 2.14 (s, 3 H), 3.67 (m, 2 H), 5.60 (d, $J = 8$ Hz, 1 H), 5.73 (d, $J = 8$ Hz, 1 H), 6.18 (m, 3 H), 6.29 (m, 2 H), 6.39 (m, 3 H), 6.47 (m, 4 H), 6.52 (d, $J = 7$ Hz, 2 H), 6.59 (m, 2 H), 6.68 (m, 9 H), 6.75 (m, 11 H), 6.94 (m, 6 H), 7.12 (t, $J = 7$ Hz, 1 H); MS, m/z 922 (M⁺, 100), 877 (M – OEt, 86), 799 (M – EtOH – C₆H₅, 54); exact mass 922.4179, calcd for C₇₁H₅₄O 922.4177.

2,3,5,6,7,8,9-Heptaphenyl-1,4-di(*p*-tolyl)fluorene (17). Compound **15** (25 mg, 0.028 mmol) was dissolved in THF (1 mL), and TiCl₃ (0.5 g) was dissolved in ethanol (2 mL) with brief heating. The solutions were combined in a Pyrex screw-capped tube, and this was heated at

110 °C for 4 h. After the mixture cooled, water (1 mL) was added, and the mixture was poured into toluene and 1 N NaOH. The organic layer was separated, dried over Na₂SO₄, and concentrated to give pure compound **17** (15 mg, 0.017 mmol, 61%); mp 293.5–295 °C. ¹H NMR (CDCl₃) δ 2.10 (s, 3 H), 2.11 (s, 3 H), 5.16 (s, 1 H), 5.78 (d, *J* = 8 Hz, 1 H), 5.91 (d, *J* = 8 Hz, 1 H), 5.97 (br s, 2 H), 6.15 (d, *J* = 7 Hz, 1 H), 6.30 (m, 3 H), 6.36 (d, *J* = 8 Hz, 1 H), 6.41 (m, 4 H), 6.47 (t, *J* = 7 Hz, 1 H), 6.61 (m, 8 H), 6.71 (m, 10 H), 6.75 (m, 6 H), 6.86 (t, *J* = 7 Hz, 1 H), 6.96 (d, *J* = 7 Hz, 1 H), 7.18 (m, 2 H), 7.30 (d, *J* = 8 Hz, 1 H); ¹³C NMR (CDCl₃) δ 21.3, 21.4, 55.1, 124.7, 124.9, 125.0, 125.1, 125.6, 126.2, 126.4, 126.6, 126.7, 126.8, 127.0, 127.3, 127.85, 127.89, 128.0, 128.5, 129.2, 129.5, 130.2, 130.5, 130.7, 131.0, 131.5, 131.7, 131.8, 133.7, 135.0, 136.50, 136.53, 136.7, 137.7, 138.0, 138.2, 138.8, 139.0, 139.8, 140.5, 140.58, 140.64, 140.7, 140.8, 140.9, 141.0, 141.3, 148.4, 148.6 (49 of 51 expected resonances if there is free aryl group rotation); MS, *m/z* 878 (M⁺, 100), 801 (M – C₆H₅, 22), 787 (M – C₆H₄CH₃, 5), 723 (M – C₆H₅ – C₆H₆, 11), 709 (M – C₆H₄CH₃ – C₆H₆, 8); exact mass, 878.3911, calcd for C₆₉H₅₀ 878.3912. Crystals suitable for X-ray analysis were obtained by the slow evaporation of a solution in CH₂Cl₂–acetone.

X-ray Crystallographic Analysis of 2,3,5,6,7,8,9-Heptaphenyl-1,4-di(*p*-tolyl)fluorene (17). Formula C₆₉H₅₀·0.5C₃H₆O; triclinic, space group *P* $\bar{1}$, *a* = 13.771 (1) Å, *b* = 14.170 (1) Å, *c* = 14.233 (2) Å, α = 83.891 (9)°, β = 83.790 (10)°, γ = 81.373 (7)°, *V* = 2718.5 (5) Å³, *Z* = 2, *D*_{calcd} = 1.109 g/cm³. Intensity measurements were made at 298 K with 3° ≤ 2θ ≤ 45° on a Siemens P4 diffractometer using Mo Kα radiation (λ = 0.71073 Å) and a crystal with dimensions of 0.20 mm × 0.20 mm × 0.25 mm. A total of 7473 reflections were measured of which 7112 were unique (*R*_{int} = 0.032). The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on *F*² (SHELXL-93). The presence of a disordered solvent molecule in the lattice was evident, but this electron density was not well modeled

with discrete atoms. Therefore, the SQUEEZE/BYPASS²⁸ procedure implemented in PLATON-96²⁹ was used to account for the solvent electron density. A total electron count of 52.7 *e* in a total volume of 354.7 Å³ was found in a single potential solvent area, consistent with the presence of 1.6 acetones (32 *e*) per unit cell (52.7/32 = 1.6) and thus a formulation of 1:0.8 **17**:C₃H₆O ratio. NMR analysis indicated the presence of 0.5 molecules of acetone per molecule of **17**. The SQUEEZE-processed data was used for all subsequent cycles of refinement. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were included with a riding model and isotropic displacement coefficients [*U*(H) = 1.2*U*(C) or 1.5*U*(C_{methyl})]. The refinement converged to *R*(*F*) = 0.051, *wR*(*F*²) = 0.099, and *S* = 1.08 for 2316 data with *I* > 2σ(*I*), and *R*(*F*) = 0.159, *wR*(*F*²) = 0.129, and *S* = 0.68 for 7109 data and 624 variables (three reflections were suppressed). Full details are provided in the Supporting Information.

Acknowledgment. This work was supported by NSF Grant CHE-9707958, which is gratefully acknowledged.

Supporting Information Available: Crystal structure reports for compounds **2**, **4**, **9**, and **17**, which include full experimental details, tables of atomic coordinates, bond distances, bond angles, and thermal parameters, and selected figures (93 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA980322R

(28) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201.

(29) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.