J|A|C|S
ARTICLES

Octaphenylbiphenylene and Dodecaphenyltriptycene

Jun Lu, Jiajia Zhang, Xianfeng Shen, Douglas M. Ho, and Robert A. Pascal, Jr.*

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

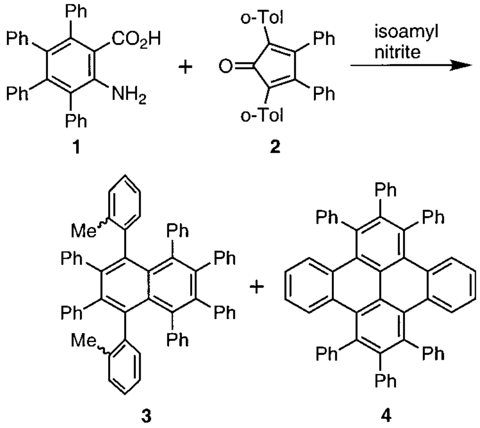
Received March 13, 2002

Abstract: Octaphenylbiphenylene, the expected dimer of tetraphenylbenzyne, has been prepared in low yield by diazotization of 3,4,5,6-tetraphenylanthranilic acid, and its X-ray structure has been determined. The X-ray structure of a second, abnormal dimer of tetraphenylbenzyne, 1,2,3,8,9,10-hexaphenyldibenzo-[*fg*,*op*]naphthacene has also been determined; this is a saddle-shaped polycyclic aromatic hydrocarbon. 1,2,3,4,5,6,7,8,13,14,15,16-Dodecaphenyltriptycene, perhaps the most crowded triptycene derivative yet prepared, has been made by the reaction of tetraphenylbenzyne with 1,2,3,4,5,6,7,8-octaphenylanthracene, which in turn was synthesized in two steps from commercial starting materials. The X-ray structure of the dodecaphenyltriptycene nonabenzene solvate is a remarkable channel containing structure in which more than 50% of the unit cell volume is occupied by the benzene molecules.

Introduction

Polyphenyl polycyclic aromatic molecules and even larger "polyphenylene nanostructures" have received increased attention in recent years.[1,2] By using both classical and modern synthetic techniques, one-, two-, or three-dimensional macromolecules possessing well-defined conformations and high stability can be constructed with relative ease, with potential applications ranging from electronic materials to molecular separations. We have been especially interested in the synthesis of perphenyl derivatives of simple polycyclic aromatics (for example, octaphenylnaphthalene,[3,4] decaphenylanthracene,[3] octaphenylfluorenone,[5] and decaphenylbiphenyl[5]), studies of which form the basis for understanding the structures and properties of more complex polyphenyl molecules.

Tetraphenylbenzyne, generated most conveniently by diazotization of 3,4,5,6-tetraphenylanthranilic acid (**1**), is a convenient precursor of polyphenyl aromatic hydrocarbons by means of Diels–Alder reactions with various dienes.[3,4,6] However, if the dienes are sterically hindered, then compound **1** and the products of its diazotization may react in unusual ways. Several years ago, we characterized one such product, 1,2,3,4,5,6,7,8-octaphenylcarbazole,[7] which appears to result from the reaction of tetraphenylbenzyne with a nitrogen-containing intermediate from the diazotization, but we did not observe any products formed by the dimerization of tetraphenylbenzyne itself. Our interest in such reactions was renewed unexpectedly by the solution of the structure of an "anomalous crystal". In 1998, we reported the synthesis of various methylated octaphenylnaphthalenes[4] (such as **3**) by the diazotization of **1** (or its methylated derivatives) in the presence of methylated tetracyclones (such as **2**). The assignment of the stereochemistry of **3** (cis or trans methyls) was not trivial, and we crystallized many samples in the hope of obtaining an X-ray structure, but none of the crystals was satisfactory.



A few years after these experiments were performed, our department acquired a more sensitive diffractometer, and a small crystal of **3** was found among the old samples that might suffice for diffraction experiments. To our great surprise, this crystal was found to contain a 1:2 complex of **3** and **4**, and the structures of these molecules are illustrated in Figure 1. Compound **4** is

---

* Corresponding author. E-mail: snake@chemvax.princeton.edu.

(1) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747–1785.

(2) Watson, M. D.; Fechtenkötter; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300.

(3) 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.

(4) Qiao, X.; Pelczer, I.; Pascal, R. A., Jr. *Chirality* **1998**, *10*, 154–158.

(5) Tong, L.; Lau, H.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1998**, *120,* 6000–6006.

(6) (a) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531–1532. (b) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1997**, *38*, 7–10. (c) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 7291–7302. (d) Pascal, R. A., Jr.; Barnett, L.; Qiao, X.; Ho, D. M. *J. Org. Chem.* **2000**, *65*, 7711–7717. (e) Zhang, J.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 10919–10926.

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

10.1021/ja0203723 CCC: $22.00 © 2002 American Chemical Society

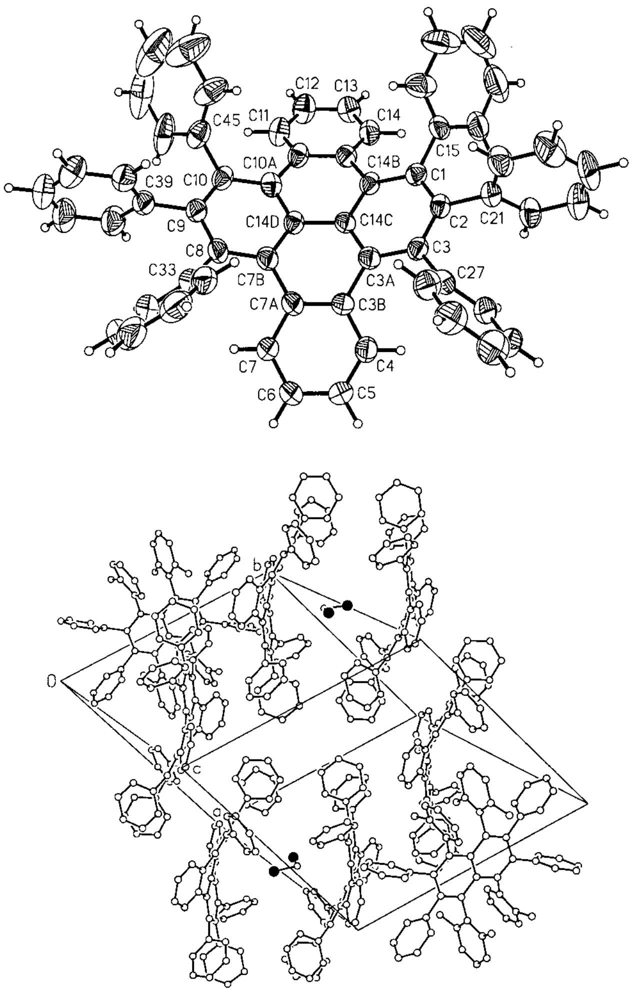
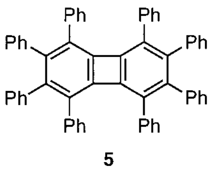
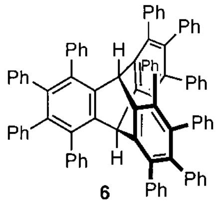


Figure 1. Molecular structure of 1,2,3,8,9,10-hexaphenyldibenzo[*fg*,*op*]-naphthacene (**4**, above), and a unit cell diagram of the X-ray structure of its complex with an octaarylnaphthalene [**3**·2(**4**)·CH_2Cl_2, below].

apparently a dimer of tetraphenylbenzyne, but it is not the "normal" 2+2 dimer octaphenylbiphenylene (**5**). In this paper we discuss the structure of **4** and its possible origin, and we report the synthesis and structure of **5**. In addition, we describe the synthesis of another aryne-derived polyphenyl aromatic compound, 1,2,3,4,5,6,7,8,13,14,15,16-dodecaphenyltriptycene (**6**), as well as the crystal structure of its remarkable benzene solvate.



5



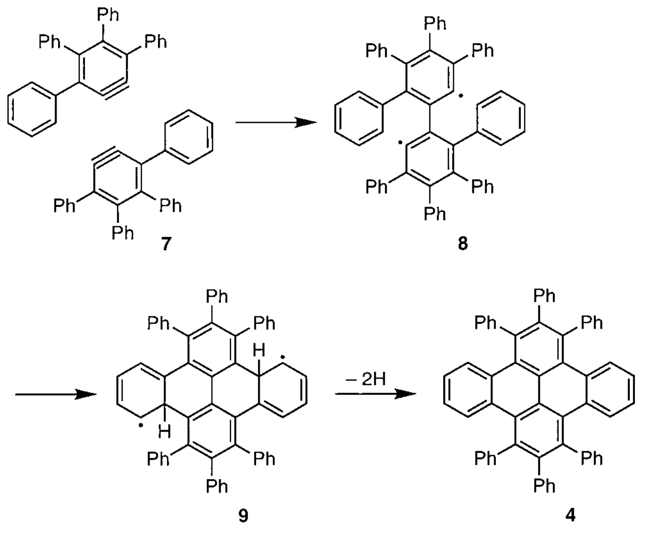
6

Results and Discussion

Dimers of Tetraphenylbenzyne. The X-ray structure of 1,2,3,8,9,10-hexaphenyldibenzo[*fg*,*op*]naphthacene (**4**) shows it to be a saddle-shaped polycyclic aromatic hydrocarbon possessing approximate C_{2v} symmetry (see Figure 1). This is unusual; almost all of the crowded polyphenyl polycyclic aromatic hydrocarbons that we have prepared exhibit twisting deformations from planarity,[3,5−8] which in this case would yield a D_2 symmetric structure. However, computational studies at the HF/3-21G level of theory[9] indicate that the C_{2v} conformation is more stable than the D_2 conformation by 13.0 kcal/mol, despite the fact that the latter requires less distortion from planarity. Indeed, the degree of deformation of the dibenzonaphthacene core in **4** is quite large; the average deviation of the carbon atoms from the mean plane of this C_{24} hexacycle is 0.63 Å, and the maximum deviation is 1.11 Å. For comparison, the same values for [7]circulene[10] (the paradigmatic saddle-shaped hydrocarbon) are 0.51 and 1.07 Å. No crystal structure exists for dibenzo[*fg*,*op*]naphthacene or any simple derivative, but HF/3-21G calculations indicate that the parent hydrocarbon should be strictly planar with D_{2h} symmetry.

The molecule of **4** is well-ordered in the crystal structure of the complex, but its companion, the dimethylated octaphenylnaphthalene **3**, is disordered across a crystallographic center of inversion. The disorder is such that it is not possible to assign unambiguously its geometry as cis or trans or a mixture of the two, which had been the original purpose of the diffraction experiment! The structure refined best with a 55:45 ratio of cis and trans isomers included in the disorder model, but this result is not conclusive, and none of the metrical parameters from this part of the structure should be taken to be particularly reliable.

In the 1996 report[7] from this research group of the formation of octaphenylcarbazole by diazotization of tetraphenylanthranilic acid (**1**), it was noted that "no trace of [octaphenylbiphenylene (**5**)] was observed, even though many fractions... were screened by mass spectrometry." This result had seemed strange, but the later observation of **4** provided, for a time, a rationalization for the absence of **5**. If the initial dimerization of tetraphenylbenzyne (**7**) gives the diradical **8**, then subsequent addition of the radicals to nearby phenyl groups would lead to intermediate **9**, and its dehydrogenation would yield **4** (oxidants such as isoamyl nitrite are present in the reaction mixture). The small difference in the masses of **4** ($C_{60}H_{38}$, $M = 758$) and **5** ($C_{60}H_{40}$, $M = 760$) might explain the failure of the previous mass spectrometry-based search for **5**.



In the hope of generating **4** more cleanly, we conducted several diazotization reactions with **1** in the absence of any

---

(8) Smyth, N.; Van Engen, D.; Pascal, R. A., Jr. *J. Org. Chem.* **1990**, *55*, 1937−1940.

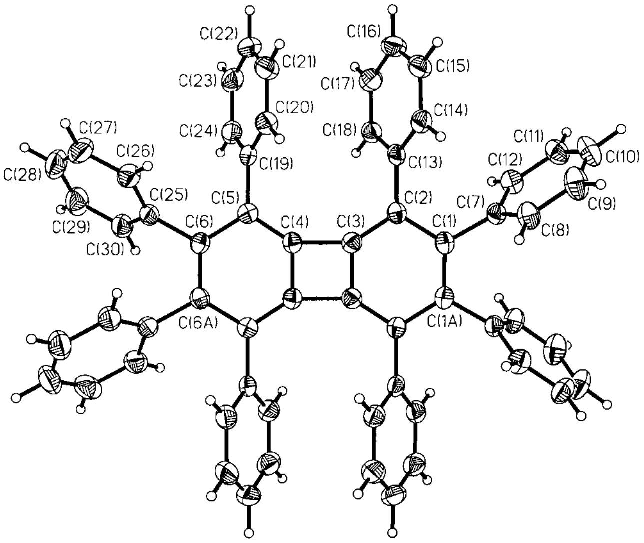


Figure 2. Molecular structure of octaphenylbiphenylene (**5**). Thermal ellipsoids have been drawn at the 50% probability level.

reactive diene. Compound **1** was added to refluxing solutions of isoamyl nitrite in dichloroethane and heated for an hour, just as in our past syntheses of octaarylnaphthalenes.[3,4,6b−d] In those syntheses, we used excesses of isoamyl nitrite ranging from 1.5 to 5 equiv; 1 to 10 equiv were used in the present experiments. Several products were characterized by NMR and mass spectrometry, including octaphenylcarbazole, 1,2,3,4-tetraphenylbenzene, and 2,3,4,5-tetraphenylnitrobenzene. When large excesses of the nitrite were used, the last of these became the dominant product. However, only one dimer of tetraphenylbenzyne was isolated. Spectroscopic data indicated that this material was the previously undetected octaphenylbiphenylene (**5**), and this was confirmed by an X-ray structure determination (Figure 2). The yields of **5** were very low, and never more than 5%. We were surprised to find compound **5** at all; there is no apparent difference between the diazotization conditions employed in 1996[7] (when we failed to observe **5**) and the present experiments.

Compound **5** crystallized in the orthorhombic space group *Pbcn*, and it lies on a special position, so that the molecule has exact C_2 symmetry (and approximate D_2 symmetry). Except for the presence of the four-membered ring, **5** seems to be relatively unstrained, and the geometry of its biphenylene nucleus is extremely similar to those of the parent hydrocarbon[11] and its octamethyl derivative.[12,13] For example, the central C(3)−C(4) bond distance in **5** is 1.521 (4) Å (see Figure 2), while the average values for this bond in the determinations of biphenylene itself and octamethylbiphenylene are 1.512 and 1.521 Å, respectively. However, these smaller molecules are essentially planar, but **5** exhibits a small twist along its long axis: the torsion angle C(1A)−C(1)−C(6)−C(6A) is 6.3°. This twist is greater than that predicted for HF/3-21G calculations (1.3°), but still very modest.

In addition to compound **5**, the mass spectra of some fractions from various diazotization reactions contained the characteristic *m*/*z* 758 ion, which presumably indicates the presence of the alternative dimer **4**, but in none of these was this the principal component, and compound **4** was never isolated in pure form. Moreover, not even a tiny amount of pure **4** could be obtained from the few available crystals of its 2:1 complex with **3**; the two compounds cochromatographed upon TLC in several solvent systems. Thus, for the present, **4** must remain a minor, anomalous product known only by means of its fortuitous crystallization with the naphthalene **3**.

Dodecaphenyltriptycene. Among the most dramatic demonstrations of benzyne's utility is Wittig's one-step synthesis of triptycene in 28% yield from anthracene,[14] a task that had required seven steps in Bartlett's original synthesis.[15] When anthranilic acid is used as a benzyne precursor, the yield of triptycene can be as high as 75%.[16] We have previously prepared polyphenyl versions of several common aromatic hydrocarbons—including naphthalene, anthracene,[3] biphenyl, fluorene,[5] and now biphenylene—and the synthesis of a polyphenyl version of triptycene seemed to be a natural extension of this work. Furthermore, our experience with the crystal structures of very large, polyphenyl aromatics indicates that most of these molecules form complex, channel-containing solids,[3,6b−d] and we suspected that a polyphenyl triptycene, with three built-in molecular clefts around a central axis, would likely form crystals with especially large channels.

Addition of tetraphenylbenzyne (**7**) to the central ring of decaphenylanthracene is sterically precluded by the C-9 and C-10 phenyl substituents, but addition of **7** to 1,2,3,4,5,6,7,8-octaphenylanthracene (**12**, Scheme 1) to give 1,2,3,4,5,6,7,8,13,14,15,16-dodecaphenyltriptycene (**6**) seemed to be a reasonable goal. Compound **12** has been reported by Hart and Ok,[17] but their synthesis requires seven steps from commercial starting materials, and the key reaction, a double amination of 1,5-dihydrobenzo[1,2-*d*:4,5-*d*′]bistriazole, proved to be very troublesome in our hands. However, a two-step synthesis of octaphenylanthracene **12** (and thus a three-step synthesis of **6**) from commercial starting materials was easy to imagine (Scheme 1). We found this new synthesis to be short and convenient, but it does not give high yields.

There are several close analogues in the literature for the first step, a double Diels−Alder addition of benzoquinone to tetracyclone under conditions that promote decarbonylation and dehydrogenation of the initial adduct, and the yields are often good.[18] However, in this particular case, the isolated yield of pure, crystalline octaphenylanthraquinone (**11**) was never above 10%. Fortunately, the starting materials are inexpensive, and in an initial synthetic step, the losses are not so painful. Quinone **11** was resistant to catalytic hydrogenation, and hydride reagents gave mixtures of oxygenated reduction products,[19] but it was reduced to the desired anthracene **12** by boiling in hydriodic

---

(9) 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.

(10) (a) Yamamoto, K.; Harada, T.; Nakazaki, M.; Nakao, T.; Kai, Y.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 7171−7172. (b) Yamamoto, K.; Harada, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M.; Kai, Y.; Nakao, T.; Tanaka, M.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 3578−3584.

(11) Fawcett, J. K.; Trotter, J. *Acta Crystallogr.* **1966**, *20*, 87−93.

(12) Jones, J. B.; Brown, D. S.; Hales, K. A.; Massey, A. G. *Acta Crystallogr., Sect. C* **1988**, *44*, 1757−1759.

(13) Le Magueres, P.; Lindeman, S. V.; Kochi, J. K. *Organometallics* **2001**, *20*, 115−125.

(14) (a) Wittig, G. *Org. Synth.* **1959**, *39*, 75−77. (b) Wittig, G. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, pp 964−966.

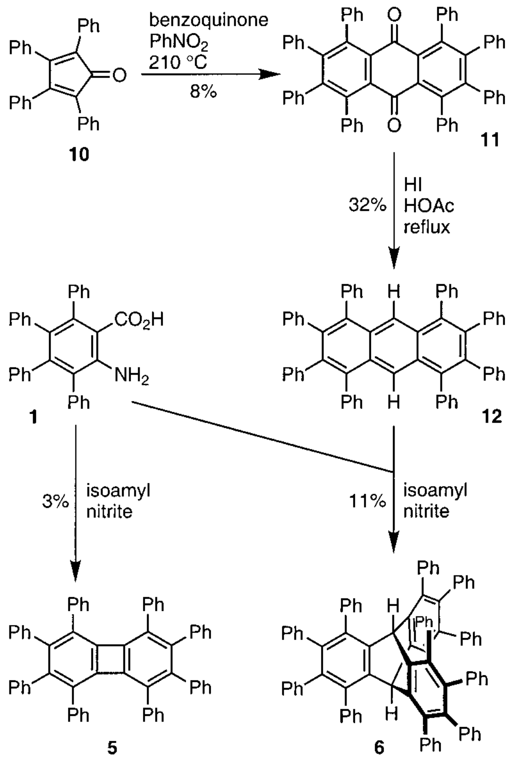
(15) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649−2653.

(16) Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549.

(17) Hart, H.; Ok, D. *J. Org. Chem.* **1986**, *51*, 979−986.

(18) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem Rev.* **1965**, *65*, 261−367.

Scheme 1



acid and acetic acid for prolonged periods.[20] Two weeks of reaction gave **12** in 32% yield. Addition of tetraphenylbenzyne to **12** gave the desired dodecaphenyltriphenylene **6** in 11% yield, a satisfactory result given the steric crowding in the product.[21]

Compound **6** is soluble in a variety of organic solvents and it crystallizes readily, always forming structures with substantial amounts of included solvent. Two such structures are reported here: the dichloromethane and benzene solvates. Crystallization from CH_2Cl_2−MeOH gave monoclinic crystals, space group $P2_1/c$, with $Z = 8$; that is, there are two independent molecules of **6** in the asymmetric unit. In addition, 20.5% of the unit cell volume is occupied by dichloromethane molecules which are disordered to varying degrees, but this is not an unusual degree of solvation for a molecular solid. More impressive are the crystals obtained from benzene; these are orthorhombic, space group $Pna2_1$. The asymmetric unit contains a single molecule of **6** along with *nine* molecules of benzene; the included solvent occupies 50.5% of the unit cell volume. With 12 phenyl substituents, **6** is by far the most highly substituted triptycene to have been crystallographically characterized, and its molecular structure is illustrated in Figure 3. The Cambridge Structural Database[22] (CSD) contains only three triptycene derivatives with as many as six substituents.[23,24] One other triptycene with 12 substituents is known, Hart's "supertriptycene",[25] in which there are six 9,10-anthradiyl moieties fused to a central triptycene, but he reports that the solvent molecules included in the crystals made it impossible to solve the crystal structure.[26] It seems that we were more fortunate!

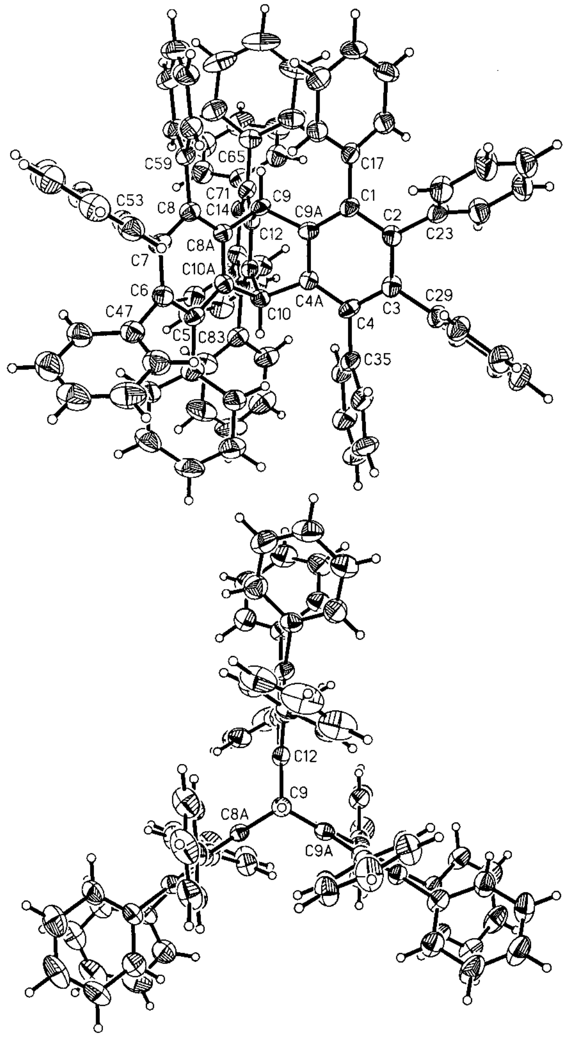


Figure 3. Molecular structure of 1,2,3,4,5,6,7,8,13,14,15,16-dodecaphenyltriptycene (**6**), taken from the X-ray structure of its benzene solvate (**6**·$9C_6H_6$). Thermal ellipsoids have been drawn at the 50% probability level.

The 12 phenyl groups of **6** are accommodated with little distortion of the triptycene core.[21] For example, the 12 crystallographically independent bridgehead−arene bonds in the dichloromethane solvate of **6** average 1.531 ± 0.007 Å, and this value is 1.531 ± 0.008 Å for the six independent bonds in the benzene solvate. For comparison, two existing X-ray structures of triptycene itself yield average distances of 1.53 ± 0.03 Å[27] and 1.526 ± 0.014 Å[28] for the same bonds. In all three determinations of **6**, the 12 phenyl rings are interlocked in the same fashion, so that the molecules have approximately D_3, and not D_{3h}, symmetry. There is a roughly cylindrical cavity above each of the bridgehead hydrogens of **6**, but this is too small to be occupied by a guest solvent molecule, and substitution of

---

(19) Zhang, J.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1999**, *40*, 3859−3862.

(20) Konieczny, M.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4813−4816.

(21) A referee noted that the low yield in the synthesis of **6** seems inconsistent with the molecule's apparent lack of strain. However, such low strain applies only to the ground state of **6** in which the phenyl groups are nicely interdigitated; in the transition state leading to the formation of **6**, there may be substantial conflicts between the phenyls of the precursors.

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

(23) Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675−6679.

(24) Toyota, S.; Endo, M.; Teruhi, M.; Noda, Y.; Oki, M.; Yamasaki, M.; Shibahara, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2088−2096.

(25) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1990**, *112*, 3687−3688.

(26) Hart, H. *Pure Appl. Chem.* **1993**, *65*, 27−34.

(27) Anzenhofer, K.; de Boer, J. J. *Z. Kristallogr.* **1970**, *131*, 103−113.

(28) Veen, E. M.; Postma, P. M.; Jonkman, H. T.; Spek, A. L.; Feringa, B. L. *Chem. Commun.* **1999**, 1709−1710.

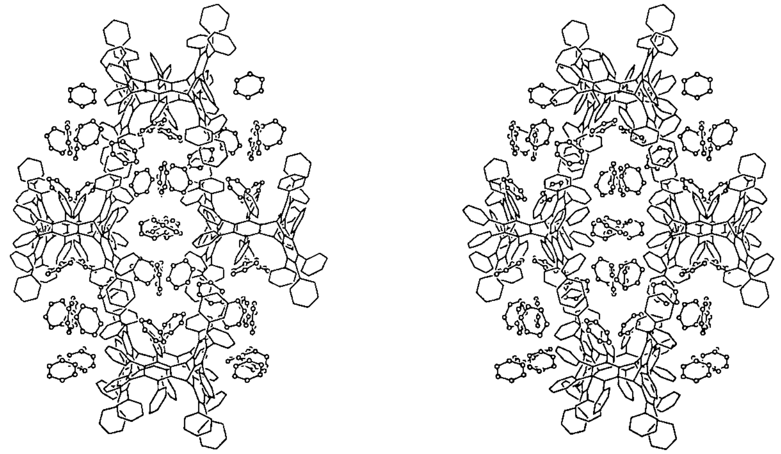


Figure 4. Stereoview of the crystal structure of **6**·9C_6H_6 viewed down the crystallographic *a* axis. The molecules of **6** are shown as simple line drawings; the benzene molecules as ball-and-stick drawings.

the bridgehead hydrogens with larger atoms would undoubtedly be difficult.

As noted above, the crystals of **6** from benzene are highly solvated. The solvent is located mainly in infinite channels parallel to the *a* axis, which are illustrated in Figure 4. These channels have roughly elliptical cross sections with major and minor axes of 25 and 10 Å, respectively. A careful examination of the structure shows that six of the nine crystallographically independent benzene molecules are arranged in three infinite columns within the channels, and the remaining three benzenes are found in the three V-shaped clefts of the dodecaphenyltriptycene. The vast majority of the benzene−benzene and benzene−phenyl contacts are of the edge-to-face or edge-to-edge variety; there are few interactions that may be characterized as π-stacking.

Table 1. Exceptional Examples of Crystallographically Characterized Organic Binary Solvates (**A**·*n***S**)[a]

	solvent	reported formula	non-H_A/non-$H_{n\mathrm{S}}$	vol % solvent[b]	CSD refcode[c]
a	benzene	$C_{17}H_{20}O_{10}·C_6H_6$	27/24 = 1.12	60.0	CEPJOW
b	benzene	$C_{92}H_{62}·9C_6H_6$	92/54 = 1.70	50.5	*d*
c	benzene	$C_{72}H_{60}Si_6·7C_6H_6$	78/42 = 1.86	47.1	BASVIA
d	benzonitrile	$C_{44}H_{30}N_4O_8·7C_5H_5N$	56/56 = 1.00	63.2	NIPXIT
e	*tert*-butanol	$C_{18}H_{20}O_2·4C_4H_{10}O$	20/20 = 1.00	64.3	XEHPEF
f	chloroform	$C_{48}H_{40}O_6·12CHCl_3$	54/48 = 1.13	57.9	FUJGOG
g	chloroform	$C_{24}H_{12}N_6·4CHCl_3$	30/16 = 1.88	56.6	HUFWAG
h	chloroform	$C_{26}H_{40}N_4·4CHCl_3$	30/16 = 1.88	50.2	WAQMIK
i	2-chlorophenol	$C_{40}H_{26}N_8·5C_6H_5ClO$	48/40 = 1.20	57.3	YOVVEK
j	cyclohexane	$C_{60}·12C_6H_{12}$	60/72 = 0.82	81.9[e]	YOLSOH
k	DMA	$C_{160}H_{136}O_{24}·18C_4H_9NO$	184/108 = 1.70	52.9	VURBUF
l	DMSO	$C_{52}H_{40}O_{12}·18C_2H_6SO$	64/72 = 0.89	71.3	RETKAC
m	DMSO	$C_{52}H_{40}O_{12}·12C_2H_6SO$	64/48 = 1.33	64.1	GIYTAJ
n	DMSO	$C_{52}H_{40}O_{12}·10C_2H_6SO$	64/40 = 1.60	58.5	GIYSUC
o	ethyl acetate	$C_{44}H_{30}N_4O_8·5C_4H_8O_2$	56/30 = 1.87	53.0	NIPXEP
p	propionic acid	$C_{20}H_{16}N_4O_4Si·4C_3H_6O_2$	29/20 = 1.45	57.7	YINJOU
q	propionic acid	$C_{53}H_{32}N_4O_4·8C_3H_6O_2$	61/40 = 1.52	51.2	VOJFEF
r	pyridine	$C_{52}H_{40}O_{12}·14C_5H_5N$	64/84 = 0.76	68.6	RETKEG
s	pyridine	$C_{32}H_{32}O_8·6C_5H_5N$	40/36 = 1.11	59.3	NEYLOS
t	pyridine	$C_{18}H_{142}N_4O_8S_2·4C_5H_5N$	46/24 = 1.92	54.3	GOWVAP
u	pyridine	$C_{88}H_{112}O_8·8C_5H_5N$	96/48 = 2.00	46.5	LAYKUR
v	TFA	$C_{25}H_{35}N_3O_4·4C_2HF_3O_2$	32/28 = 1.14	51.3	DEXQIG
w	TFA	$C_{28}H_{18}N_2O_6·4C_2HF_3O_2$	36/28 = 1.29	46.1	QEFCEJ
x	TFA	$C_{40}H_{26}N_4·4C_2HF_3O_2$	44/28 = 1.57	43.1	FIZFEZ

[a] Criteria for inclusion in this table: (1) the structures are binary solvates with the composition **A**·*n***S**, where **A** and **S** are neutral organic molecules containing no metal atoms and $n \geq 4$; (2) the ratio of non-H atoms in **A** to those in *n***S** is 2 or less; and (3) the atomic coordinates of the structure (at least for the primary molecule **A**) have been deposited in the CSD (ref 21). [b] This quantity is the percent "solvent accessible volume" as calculated by the VOID/SOLV option in PLATON (ref 34) when only the primary molecule (**A**) is included in the crystallographic input file. [c] See ref 30 for the full citations. [d] This work. [e] The deposited coordinates for this structure are idealized C_{60} and cyclohexane molecules, and no *R* factor is given, so the volume calculation must be considered approximate at best.

Nearly all of our crystals of very large polyphenyl aromatic compounds (with >100 carbons[6b−d,29]) contain solvent of crystallization as part of the structure, but in none does the primary molecule occupy less than 50% of the unit cell volume, which is the case for **6**·9C_6H_6. The fact that the benzene molecules are, for the most part, well-ordered is also unusual. Wondering how common were such highly solvated structures, we conducted a search of the CSD for two-component organic crystals which contained large proportions of solvent of crystallization. The results are presented in Table 1.[30] A detailed analysis of these structures is inappropriate here (the interested reader can access them easily by way of the CSD refcodes), but one observation stands out. In the great majority of these exceptionally solvated crystals, both components are polar molecules capable of hydrogen bonding (at least as donors or acceptors). Thus, for example, the chloroform molecules in entries **f**, **g**, and **h**[30e,h,o] donate hydrogen bonds to oxygen or nitrogen atoms in the primary organic components. A pure hydrocarbon binary system, such as the present case (entry **b**), with 50% solvent by volume is extremely unusual. Only two other structures in Table 1 lack any polar functionality, the dodecaphenylcyclohexasilane benzene solvate (**c**)[27a] and the C_{60} cyclohexane solvate (**j**).[30s] It is interesting that both **b** and **c** contain large polyphenyl molecules. Perhaps their large surface area permits the formation of particularly favorable van der Waals interactions between the primary molecules and the included benzene, and their relative rigidity in turn helps to support the benzene molecules in an ordered array.

Conclusion

In sum, tetraphenylbenzyne undergoes "expected" reactions with itself, to form octaphenylbiphenylene (**5**), and with 1,2,3,4,5,6,7,8-octaphenylanthracene (**12**), to form dodecaphenyltriptycene **6**. Compounds **5** and **6** are two new members of the growing class of polyphenyl derivatives of simple polycyclic aromatics. The yields in these syntheses are lower than those

---

(29) Pascal, R. A., Jr.; Hayashi, N.; Ho, D. M. *Tetrahedron* **2001**, *57*, 3549−3555.

Table 2. Crystallographic Data for Compounds **3**−**6**

	3·2(**4**)·CH_2Cl_2	**5**·2CH_2Cl_2	**6**·CH_2Cl_2	**6**·9C_6H_6
chemical formula	$C_{60}H_{44}$·2$C_{60}H_{38}$	$C_{60}H_{40}$·2CH_2Cl_2·CH_2Cl_2	$C_{92}H_{62}$·CH_2Cl_2	$C_{92}H_{62}$·9C_6H_6
formula weight	2367.69	930.77	1252.34	1870.39
crystal size (mm^3)	0.15 × 0.10 × 0.05	0.22 × 0.05 × 0.05	0.20 × 0.12 × 0.05	0.42 × 0.35 × 0.07
space group	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)
a, Å	13.8946 (6)	18.6482 (5)	19.2738 (4)	24.155 (2)
b, Å	15.1490 (9)	24.2381 (8)	28.5548 (5)	17.016 (1)
c, Å	17.4672 (10)	10.5573 (3)	32.3310 (5)	26.221 (2)
α, deg	75.587 (2)	90	90	90
β, deg	67.113 (3)	90	125.4847 (8)	90
γ, deg	70.637 (3)	90	90	90
V, $Å^3$	3165.0 (3)	4771.9 (2)	14488.9 (5)	10778 (1)
Z	1	4	8	4
ρ_{calcd}, g/cm^3	1.242	1.296	1.148	1.153
m, mm^{-1}	0.111	0.289	0.136	0.065
T, K	200 (2)	200 (2)	200 (2)	200 (2)
θ_{max}, deg	22.5	25.0	22.5	22.5
no. of reflcns				
total	25504	20081	82861	29102
unique	8242	4217	18933	13354
obsd [$I > 2s(I)$]	5443	2767	12780	9682
$R(F)$ (obsd data)[a]	0.097	0.063	0.075	0.060
$wR(F^2)$ (obsd data)[a]	0.208	0.153	0.207	0.118
S (obsd data)[a]	1.21	1.08	1.17	1.11
$R(F)$ (all data)[a]	0.147	0.104	0.112	0.099
$wR(F^2)$ (all data)[a]	0.235	0.180	0.227	0.139
S (all data)[a]	1.09	1.02	1.04	1.06

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; Σ = goodness-of-fit on $F^2 = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined.

for the parent hydrocarbons, due probably to the steric restrictions imposed by the many phenyl groups. However, the extra phenyl groups also give an opportunity for unusual reactivity, as in the formation of dimer **4** in which three new carbon−carbon bonds have been made. All of these polyphenyl aromatic compounds are prone to form solvated crystals, of which **6**·9C_6H_6 is an exceptional example.

Experimental Section

Octaphenylbiphenylene (5). A solution of isoamyl nitrite (0.15 mL, 1.1 mmol) in 1,2-dichloroethane (10 mL) was heated to reflux under argon. A mixture of 3,4,5,6-tetraphenylanthranilic acid[3] (**1**, 246 mg, 0.56 mmol) in dichloroethane (30 mL) was added dropwise over 1 h, and heating was continued for 3 h. Ethanol (8 mL) and 1% NaOH (32 mL) were added to quench the reaction, and the resulting mixture was extracted with chloroform (100 mL). The extract was washed twice each with saturated $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a silica gel column (solvent, 3:1 hexanes−benzene), and the fraction with R_f 0.28 (silica gel TLC; solvent, 3:1 hexanes−benzene) was collected. Further purification by preparative TLC in the same solvent gave compound **5** (11 mg, 0.014 mmol, 2.6%); mp 265−267 °C. ^1H NMR ($CDCl_3$) δ 6.44−6.50 (m, 16 H), 6.62−6.65 (m, 8 H), 6.71 (t, $J = 6$ Hz, 4 H), 6.79−6.84 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 125.5, 126.2, 126.7, 126.9, 129.3, 131.7, 132.3, 137.2, 140.3, 141.7, 148.0 (11 of 11 expected resonances observed); MS (EI) *m/z* 760 (M^+, 100), 736 (M − C_2, 30), 682 (M − C_6H_6, 2), 660 (M − C_2 − C_6H_6, 36); exact mass 760.3138, calcd for $C_{60}H_{40}$ 760.3130.

Octaphenylanthraquinone (11). Tetracyclone (**10**, 10.00 g, 26.0 mmol) and *p*-benzoquinone (1.41 g, 13.0 mmol) were heated in refluxing nitrobenzene (20 mL) for 22 h. After cooling, methanol (~40 mL) was added, and the resulting dark precipitate was collected by filtration. This material was air-dried, and then it was extracted with hot benzene for 5 h (Soxhlet). The extract was concentrated and then chromatographed on a silica gel column (solvent, benzene), and the fraction with R_f 0.37 was collected. Crystallization of this material from benzene−methanol gave pure compound **11** (824 mg, 1.01 mmol, 7.8%); mp 391−392 °C. ^1H NMR ($CDCl_3$) δ 6.71 (dd, $J = 8$, 2 Hz, 8 H), 6.80−6.84 (m, 12 H), 6.92−6.98 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 125.9, 126.1, 126.7, 126.9, 130.3, 130.7, 135.4, 137.8, 138.7, 139.7, 146.3, 188.6 (12 of 12 expected resonances); MS (EI) *m/z* 816 (M^+, 100); exact mass 816.2985, calcd for $C_{62}H_{40}O_2$ 816.3030.

1,2,3,4,5,6,7,8-Octaphenylanthracene (12). Compound **11** (220 mg, 0.270 mmol) was added to acetic acid (100 mL), and the mixture was heated to reflux. Hydriodic acid (10 mL) was added, and heating was continued for 2 weeks under argon, with the addition of more hydriodic acid on three occasions (5 mL each). The hot solution was poured into 8% sodium bisulfite (200 mL), and the resulting yellow precipitate was collected by filtration and washed with water. This material was chromatographed on a silica gel column (solvent, toluene), and the fraction with R_f 0.92 was collected and concentrated to dryness to give compound **12** (67.2 mg, 0.086 mmol, 32%); mp 369−370 °C (lit.[17]

---

(30) References for the structures in Table 1: (a) BASVIA: Drager, M.; Walter, K. G. *Z. Anorg. Allg. Chem.* **1981**, *479*, 65−74. (b) CEPJOW: Radcliffe, M. D.; Gutierrez, A.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1984**, *106*, 682−687. (c) DEXQIG: Abele, S.; Vogtli, K.; Seebach, D. *Helv. Chim. Acta* **1999**, *82*, 1539−1558. (d) FIZFEZ: Hall, D. M.; Hwang, H.-Y.; Insole, J. M.; Walker, N. P. C. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1763−1769. (e) FUJGOG: Kohnke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 892−894. (f) GIYSUC, GIYTAJ: Shivanyuk, A.; Bohmer, V.; Paulus, E. F. *Gazz. Chim. Ital.* **1997**, *127*, 741−747. (g) GOWVAP: Bock, H.; Nagel, N.; Eller P. *Z. Naturforsch., Teil B* **1999**, *54*, 501−514. (h) HUFWAG: Alfonso, M.; Stoeckli-Evans, H. *Acta Crystallogr., Sect. E (Structure Rep. Online)* **2001**, *57*, o242−o244. (i) LAYKUR: Czugler, M.; Tisza, S.; Speier, G. *J. Inclusion Phenom. Macrocycl. Chem.* **1991**, *11*, 323−331. (j) NEYLOS: MacGillivray, L. R.; Atwood, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6931−6932. (k) NIPXIT, NIPXEP: Bhyrappa, P.; Wilson, S. R.; Suslick, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 8492−8502. (l) RETKAC, RETKEG:, Shivanyuk, A.; Paulus, E. F.; Bohmer, V.; Vogt, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1301−1303. (m) VOJFEF: Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696−4698. (n) VURBUF: Cram, D. J.; Blanda, M. T.; Paek, K.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 7765−7773. (o) WAQMIK: Lloyd, J.; Vatsadze, S. Z.; Robson, D. A.; Blake, A. J.; Mountford, D. P. *J. Organomet. Chem.* **1999**, *591*, 114−126. (p) XEHPEF: Gorbitz, C. H.; Hersleth H.-P. *Acta Crystallogr., Sect. B* **2000**, *56*, 1094−1102. (q) YINJOU: Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119−12120. (r) YOVVEK: Krupitsky, H.; Stein, Z.; Goldberg, I.; Strouse, C. E. *J. Inclusion Phenom. Macrocycl. Chem.* **1994**, *18*, 177−192. (s) YOLSOH: Jansen, M.; Waidmann, G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 14−18.

mp 415−417 °C). ^{1}H NMR (CDCl$_3$) δ 6.69−6.72 (m, 8 H), 6.76−6.80 (m, 12 H), 6.87−6.89 (m, 8 H), 6.92−6.97 (m, 12 H); ^{13}C NMR (CDCl$_3$) δ 125.3, 126.0, 126.7, 127.5, 130.6, 131.6, 136.6, 139.0, 139.1, 139.9, 140.9 (11 of 12 expected resonances); MS (FAB) *m*/*z* 786 (M$^+$, 100), 711 (22), 551 (82).

1,2,3,4,5,6,7,8,13,14,15,16-Dodecaphenyltriptycene (6). A solution of compound **12** (67 mg, 0.085 mmol) in 1,2-dichloroethane (15 mL) was heated to reflux. Isoamyl nitrite (19 mL, 0.14 mmol) in dichloroethane (1 mL) was added, and then compound **1** (62 mg, 0.14 mmol) in dichloroethane (15 mL) was added over 25 min. After 2 h, ethanol (6 mL) and 1% NaOH (10 mL) were added to quench the reaction, and the resulting mixture was extracted twice with chloroform. The combined extracts were washed with saturated NaHCO$_3$, dried over Na$_2$SO$_4$, and concentrated to dryness. The residue was subjected twice to preparative TLC (solvents, 1:1 hexanes−benzene and 5:1 hexanes−ethyl acetate) to give compound **6** (R_f 0.53, 5:1 hexanes−ethyl acetate), which was recrystallized from CH$_2$Cl$_2$−MeOH (10.7 mg, 0.0092 mmol, 11%); mp >450 °C. ^{1}H NMR (CDCl$_3$) δ 6.38 (s, 2 H), 6.55−6.58 (m, 12 H), 6.61−6.70 (m, 24 H), 6.72−6.79 (m, 18 H), 6.95 (tt, J = 7, 2 Hz, 6 H); ^{13}C NMR (CDCl$_3$) δ 47.0, 125.1, 125.9, 126.7, 127.4, 131.1, 132.0, 137.1, 138.6, 141.2, 143.6 (11 of 12 expected resonances); MS (FAB) *m*/*z* 1168 (M + H [^{12}C$_{91}$^{13}C$_1$], 100), 788 (38).

General X-ray Crystallographic Procedures. X-ray data were collected by using graphite monochromated Mo Ka radiation (0.71073 Å) on a Nonius KappaCCD diffractometer. The diffraction data were processed by using the program DENZO.[31] All structures were solved by direct methods with Siemens SHELXTL,[32] and all were refined by full-matrix least squares on F^2 with SHELXTL. All non-hydrogen atoms were refined anisotropically, and hydrogens were included with a riding model. The structure of **6**·CH$_2$Cl$_2$ contained some highly disordered solvent of crystallization; this was treated by using the SQUEEZE/BYPASS procedure[33] implemented in PLATON-96.[34] Specific crystal, reflection, and refinement data are contained in Table 2, and full details are provided in the Supporting Information.

Computational Studies. All ab initio calculations were performed by using GAUSSIAN 98,[35] and its built-in default thresholds for wave function and gradient convergence were employed. Analytical frequency calculations established that all of the conformations discussed represent true potential minima.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-0077990, which is gratefully acknowledged.

Supporting Information Available: A crystallographic information file (CIF), containing the full X-ray structural data for structures **3**·2(**4**)·CH$_2$Cl$_2$, **5**·2CH$_2$Cl$_2$, **6**·CH$_2$Cl$_2$, and **6**·9C$_6$H$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0203723

---

(31) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.
(32) Sheldrick, G. M. *SHELXTL*, Version 5; Siemens Analytical X-ray Instruments:, Madison, WI, 1996.
(33) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194−201.
(34) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.
(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian*; Gaussian, Inc.: Pittsburgh, PA, 1998.