

Preparation and Conformation of Octaethylbiphenylene

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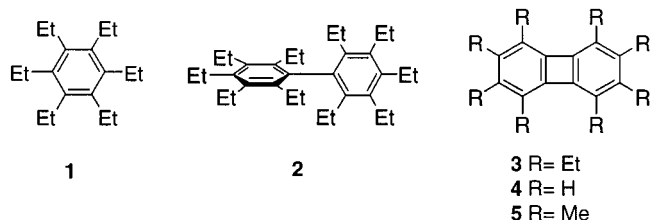
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Dimerization of tetraethylbenzynes (generated by reaction of 1,2-dibromo-3,4,5,6-tetraethylbenzene (**8**) with 1 equiv of BuLi) afforded in low yield octaethylbiphenylene (**3**), together with a major product which was characterized as 2,3,4,5,3',4',5'-heptaethyl-2'-vinylbiphenyl (**9**). X-ray diffraction indicates that biphenylene **3** adopts in the crystal a conformation of approximate C_{2h} symmetry with the ethyl groups within each phenylene ring arranged in an alternated *up–down* fashion. Notably, pairs of vicinal ethyl groups located at *peri* positions are oriented in a *syn* arrangement in the crystal. Low temperature NMR spectroscopy is consistent with the presence in solution of either the crystal conformation or a fully alternated conformation lacking any *syn* interaction. Molecular mechanics (MM3), semiempirical (AM1, PM3), and ab initio calculations indicate that the crystal conformation is a high energy form, and that the lowest energy conformation is the fully alternated form. The topomerization barrier of the methylene protons of the ethyl groups of **3** is 9.4 ± 0.1 kcal mol⁻¹, which is between the rotational barriers of **8** and 1,2,3,4-tetraethylbenzene **7** (9.9 ± 0.1 and 8.2 ± 0.1 kcal mol⁻¹, respectively). The similarity in rotational barriers suggests that a given tetraethylphenylene subunit does not markedly affect the rotational barrier of the ethyl groups of the other subunit.

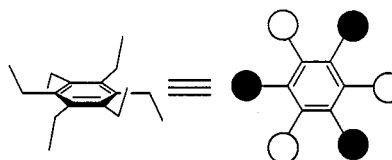
Introduction

Multiarmed organic compounds contain several “arms” (usually alkyl chains) connected to a central core.^{1,2} These systems pose synthetic challenges due to their crowded nature and have been used as scaffolds for the preparation of novel host systems.³ The smallest nonconical alkyl arm is the ethyl group, and thus hexaethylbenzene (**1**) can be viewed as the prototype of a multiarmed organic molecule. An X-ray diffraction study showed that in the crystal the molecule adopts a conformation with the ethyl groups alternately disposed in a perpendicular fashion “above” and “below” the benzene plane (Scheme 1).⁴ Molecular mechanics calculations indicated that this arrangement is the lowest in energy and that the relative energy of the conformers of **1** increases with the number of “*syn*” interactions, i.e., with the number of pairs of vicinal ethyl groups oriented both “*up*” or “*down*”.⁴



Decaethylbiphenyl (**2**) consists of two sets of mutually perpendicular pentaethylphenyl subunits.^{5,6} In the low

Scheme 1



energy conformations of **2** the *up–down* alternation of the ethyl groups of each ring is disrupted (and a *syn* interaction introduced) to avoid the repulsive interactions between *ortho* methyl groups at different rings.^{5a} A different kind of stereochemical situation will result if the two polyethylated rings are coplanar. Such an arrangement is present in octaethylbiphenylene (**3**) in which two tetraethylphenylene subunits are ideally oriented in parallel, and interact laterally. In this article we report the preparation, conformation, and rotational barrier of the multiarmed biphenylene **3**.

Results and Discussion

Synthesis. The central core of **3** (the parent biphenylene **4**) is of chemical interest due to the formal presence

(3) See for example: Gilmore, C. J.; MacNicol, D. D.; Murphy, A.; Russell, M. A. *Tetrahedron Lett.* **1983**, 24, 3269. MacNicol, D. D.; Mallison, P. R.; Murphy, A.; Robertson, C. D. *J. Incl. Phenom.* **1987**, 5, 233.

(4) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R.; Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, 103, 6073. For a study of the side chain rotations of **1** in the solid-state see: Barnes, J. C.; Chudek, J. A.; Hunter, G.; Blake A. J.; Dyson, P. J.; Johnson, B. F. G.; Weissensteiner, W. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 2149.

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(6) For a recent study on a crowded biphenyl see: Tong, L.; Lau, H.; Ho, D. M.; Pascal, R. A. *J. Am. Chem. Soc.* **1998**, 120, 6006.

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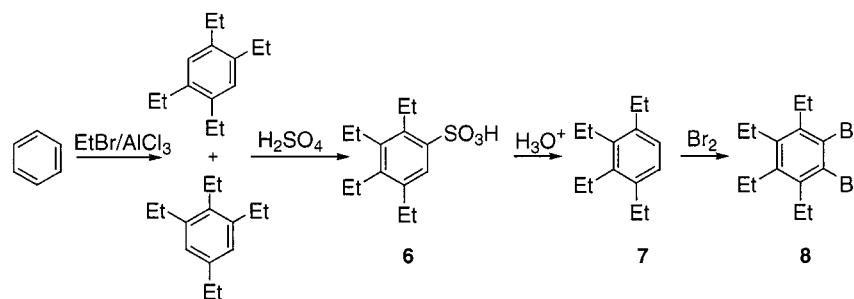
[†] The Hebrew University of Jerusalem.

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(1) Menger, F. M. *Top. Curr. Chem.* **1986**, 136, 1.

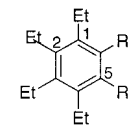
(2) For a review on the conformation of alkyl groups, see: Berg, U.; Sandström, J. *Adv. Phys. Org. Chem.* **1989**, 25, 1.

Scheme 2



of the “antiaromatic” cyclobutadiene ring, and the strain induced by the four-membered ring on the fused benzene rings.⁷ We have shown previously that the crowded polyethylated derivative **2** can be prepared by exhaustive ethylation of biphenyl using Friedel–Crafts conditions.^{5a} However, it is unlikely that this method would be successful for the preparation of **3**. The strategy chosen for the preparation of octaethylbiphenylene was patterned after Hart’s synthesis of octamethylbiphenylene⁸ (**5**) using the dimerization of a benzyne intermediate as a means of forming the biphenylene nucleus.^{9,10}

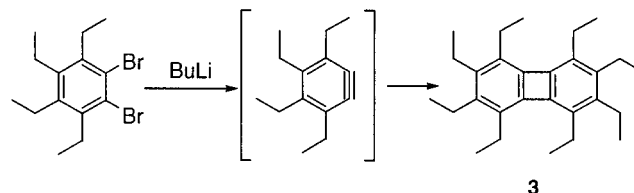
1,2,3,4-Tetraethylbenzene (**7**) was prepared by a minor modification of the literature procedure.^{11a,b} Ethylation of benzene with a large excess of EtBr/AlCl₃ was conducted until the reaction mixture mainly consisted (as judged by GC MS) of a mixture of tetraethylated derivatives. ¹H NMR analysis indicated that the major components of this mixture were the 1,2,3,5- and 1,2,4,5-tetraethyl derivatives. Jacobsen rearrangement of the isomeric mixture was achieved by treatment with concentrated H₂SO₄ yielding 2,3,4,5-tetraethylbenzenesulfonic acid (**6**).^{11b} Desulfonation (steam/H⁺) of **6** afforded 1,2,3,4-tetraethylbenzene (**7**) (Scheme 2). Tetraethylbenzene was dibrominated according to the literature procedure¹² (Br₂/AcOH) to afford 1,2-dibromo-3,4,5,6-tetraethylbenzene (**8**). NMR data for **7** and **8** are presented in Table 1. Addition of BuLi to a solution of **8** in THF at –78 °C or 0 °C generated the benzyne intermediate which yielded the yellow biphenylene **3** in low yield (Scheme 3), together with a major product which was characterized as 2,3,4,5,3',4',5'-heptaethyl-2'-vinylbiphenyl (**9**) (see below). Although small amounts of **3** were obtained, they were sufficient for conducting our stereochemical studies. Hart has reported that addition of the dibromide (1,2-dibromotetramethylbenzene (**10**)) to a solution of BuLi affords 2,3,4,5,2',3',4',5'-octamethylbiphenyl (**11**) instead

Table 1. NMR Data for Tetraethylbenzene Derivatives^a


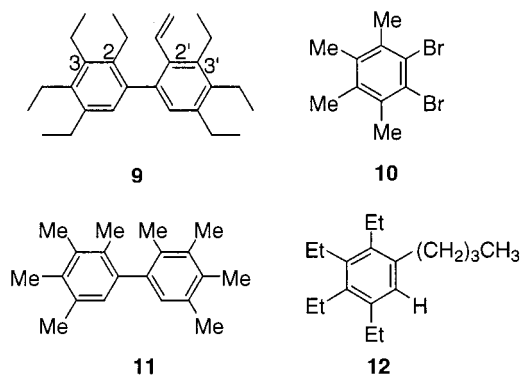
	¹³ C			¹ H ^b		
	7	8	3	7	8	3
1	139.58	141.55	130.63			
2	130.62	140.79	139.60			
5	126.21	126.23	149.79	7.00		
1-CH ₂	21.77	28.36	22.86	2.64	2.92	2.48
1-CH ₃	15.65	13.96	16.26	1.23	1.18	1.15
2-CH ₂	25.73	23.13	22.86	2.68	2.67	2.48
2-CH ₃	15.60	13.52	16.26	1.16	1.17	1.13

^a All data refer to CDCl₃ solutions at 300 K. The signals were assigned by a careful analysis of HMQC and HMBC ¹H–¹³C correlation spectra, and the atoms are numbered according to the structure below. ^b In the proton spectrum, all methyls are triplets and all methylenes, quartets; *J* = 7 Hz.

Scheme 3



of **5**.⁸ In the case of **8**, slow addition of the dibromide to BuLi yielded (as shown by NMR and GC MS analyses) a mixture of 1-*n*-butyl-2,3,4,5-tetraethylbenzene (**12**) (originating from the nucleophilic addition of BuLi to tetraethylbenzene) and **7**.



Static Stereochemistry of Octaethylbiphenylene. By analogy with **1**, it will be assumed that in all the ideal conformers of **3** the ethyl groups are perpendicular to the biphenylene plane. The stereochemistry of **3** can be analyzed by viewing the molecule as consisting of a

(7) For reviews on biphenylene see (a) Vögtle, F. *Fascinating Molecules in Organic Chemistry*; Wiley: New York, 1992; p 110. (b) Shepherd, M. K. *Cyclobutarenes: The Chemistry of Benzocyclobutene, Biphenylene and Related Compounds*; Elsevier: Amsterdam, 1991.

(8) Hart, H.; Teuerstein, A. *Synthesis* **1979**, 693. The anions and cations derived from **5** have been the subject of several studies. See for example: Bausch, J. W.; Gregory, P. S.; Olah, G. A.; Prakash, G. K. S.; Schleyer, P. v. R.; Segal, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 3633.

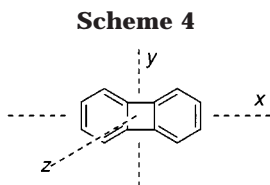
(9) In the absence of dienophiles, benzyne can dimerize to biphenylene. For a review on the chemistry of benzyne and related compounds, see: Hart, H. In *The chemistry of functional groups: Supplement C. The Chemistry of Triple Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1994; Ch. 18.

(10) Diazotization of 3,4,5,6-tetraphenylanthranic acid generated a mixture of products containing 1,2,3,4,5,6,7,8-octaphenylcarbazole, but no octaphenylbiphenylene could be isolated. See: Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1996**, *61*, 6748.

(11) (a) Smith, L. I.; Guss, C. O. *J. Am. Chem. Soc.* **1940**, *62*, 2625.

(b) Smith, L. I.; Guss, C. O. *J. Am. Chem. Soc.* **1940**, *62*, 2631.

(12) Smith, L. I.; Guss, C. O. *J. Am. Chem. Soc.* **1940**, *62*, 2635.



planar biphenylene frame (of D_{2d} symmetry) with eight perpendicular ethyl groups attached to it. Since each ethyl group can be oriented either “up” or “down” a large number of isomers is possible. The symmetry of these conformers, necessarily, must correspond to the symmetry of the central frame, or to one its subgroups. For the following analysis the biphenylene skeleton will be oriented in a coordinate system as shown in Scheme 4. Since the ethyl groups are perpendicular to the biphenylene plane, none of the potential conformers can possess a symmetry plane coplanar with the xy plane. Under these restrictions, the allowed symmetries for the conformers of **3** must correspond to the following subgroups of the D_{2h} point group: D_2 , $C_{2h}(x)$, $C_{2h}(y)$, $C_{2v}(z)$, $C_2(x)$, $C_2(y)$, $C_2(z)$, $C_s(xz)$, $C_s(yz)$, C_i , C_1 .¹³ On the basis of the desymmetrization graph of the D_2 point group,¹⁴ the number of conformers of each symmetry was calculated using the configurational matrix method.¹⁵ This analysis indicates that a total of 76 forms (34 enantiomeric pairs and 8 achiral forms) are possible, with 4 forms possessing D_2 , 4 forms C_{2h} , 2 forms C_{2v} , 12 forms C_2 , 2 forms C_i , and 48 forms C_1 point group symmetries.

Molecular Mechanics Calculations. To estimate the relative energies of the low energy conformers of **3**, we resorted to MM3 calculations.¹⁶ It has been shown for the parent **1** that the calculated relative steric energy of the conformers increases with the number of *syn* interactions.⁴ For comparison purposes we calculated first the relative steric energies of the six possible “up-down” arrangements of **7** and **8**.

The calculations on **7** and **8** indicate that the lowest energy conformer of both compounds corresponds to the fully alternated form of C_2 symmetry (Figure 1). The conformers of **7** and **8** possessing a single *syn* interaction are calculated as lying 0.9–1.5 and 1.6–1.8 kcal mol⁻¹, respectively, above their all-alternated forms.

Two types of *syn* interactions are possible for **3**: across two vicinal *peri* positions of different rings (a *syn-peri* interaction) or within two *ortho* positions of the same ring (a *syn-ortho* interaction). In the conformers of **3** necessarily the total number of *syn* interactions (*syn-peri* + *syn-ortho*) must be equal to zero or to an even number. For the MM3 calculations we restricted ourselves to conformers with at most two of such interactions since these were the expected low energy forms. The calculated relative energies of these selected conformers are collected in Figure 2. The MM3 calculations indicate that a *syn-peri* or *syn-ortho* interaction destabilizes a given conformation by 1.1–1.6 kcal mol⁻¹. The lowest energy conformer (global minimum) corresponds to the fully

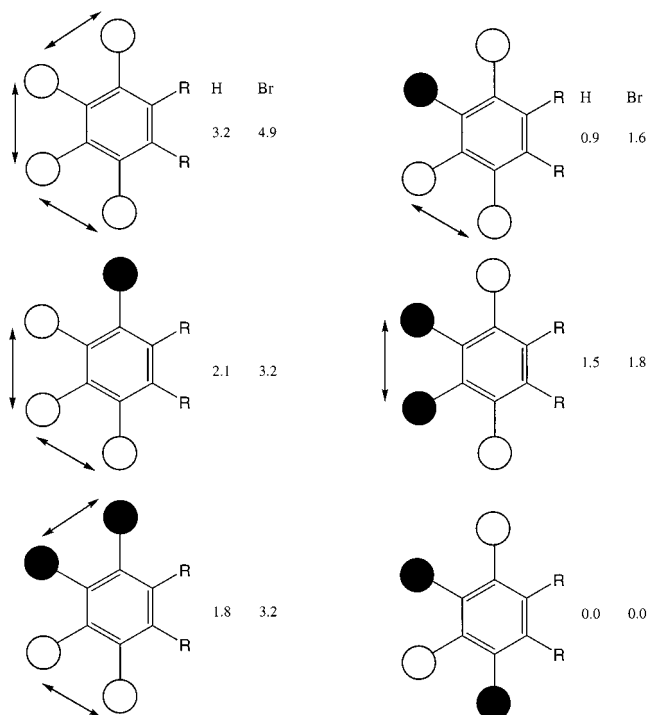


Figure 1. Calculated (MM3) relative steric energies of the six possible conformers of **7** and **8**. Filled and empty spheres represent ethyl groups perpendicular to the molecular plane and pointing “above” or “below” it, respectively. Double-headed arrows denote *syn* interactions.

alternated *up-down* conformer of D_2 symmetry (form “a” in Figure 2) lacking any *syn* interaction. Form “b” with two *syn-peri* interactions is 2.3 kcal mol⁻¹ higher in energy than the global minimum. In most cases the calculated conformers possessed the maximum attainable symmetry. In the case of “b”, the form of C_{2h} symmetry corresponds to a hilltop with two imaginary frequencies, but the local minimum of C_i symmetry (obtained by a minor distortion of the C_{2h} form) possesses both a geometry and energy ($\Delta E < 0.05$ kcal mol⁻¹) practically identical to it. We will therefore in the following discussion refer to conformer “b” as possessing C_{2h} symmetry.

Crystal Structure of Octaethylbiphenylene. The crystal structures of the parent **4**^{17,18} and its octamethyl derivative **5**¹⁹ have been reported in the literature. The structures display significant bond alternation. The four-membered ring is rectangular with short exocyclic C–C bonds. These structural features have been interpreted for **4** as indicating a major contribution of the canonical form (I) to the resonance hybrid (Scheme 5).^{7a,20}

A single crystal of **3** was grown from dichloromethane/methanol and submitted to X-ray crystallography. In the crystal the ethyl groups within each ring are arranged in an alternated *up-down* disposition. Although the symmetry of the crystal conformation is C_i the deviation

(13) The coordinate axis (or axes) collinear with the C_2 axis (in the C_{2h} , C_{2v} , and C_2 point groups) or coplanar with the mirror plane (in the C_s point group) are given in parentheses.

(14) Donaldson, J. D.; Ross, S. D. *Symmetry and Stereochemistry*; Wiley: New York, 1972.

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(18) For an early electron diffraction study of biphenylene see: Waser, J.; Schomaker, V. *J. Am. Chem. Soc.* **1943**, *65*, 1451.

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

(20) Stanger has shown in an ab initio study that bond distortions in benzene result in bond fixation (Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277). Bridging the *peri* positions of biphenylene can result in substantial distortions of the biphenylene skeleton. See: Vögtle, F.; Schulz, J. E.; Rissanen, K. *J. Chem. Soc., Chem. Commun.* **1992**, 120.

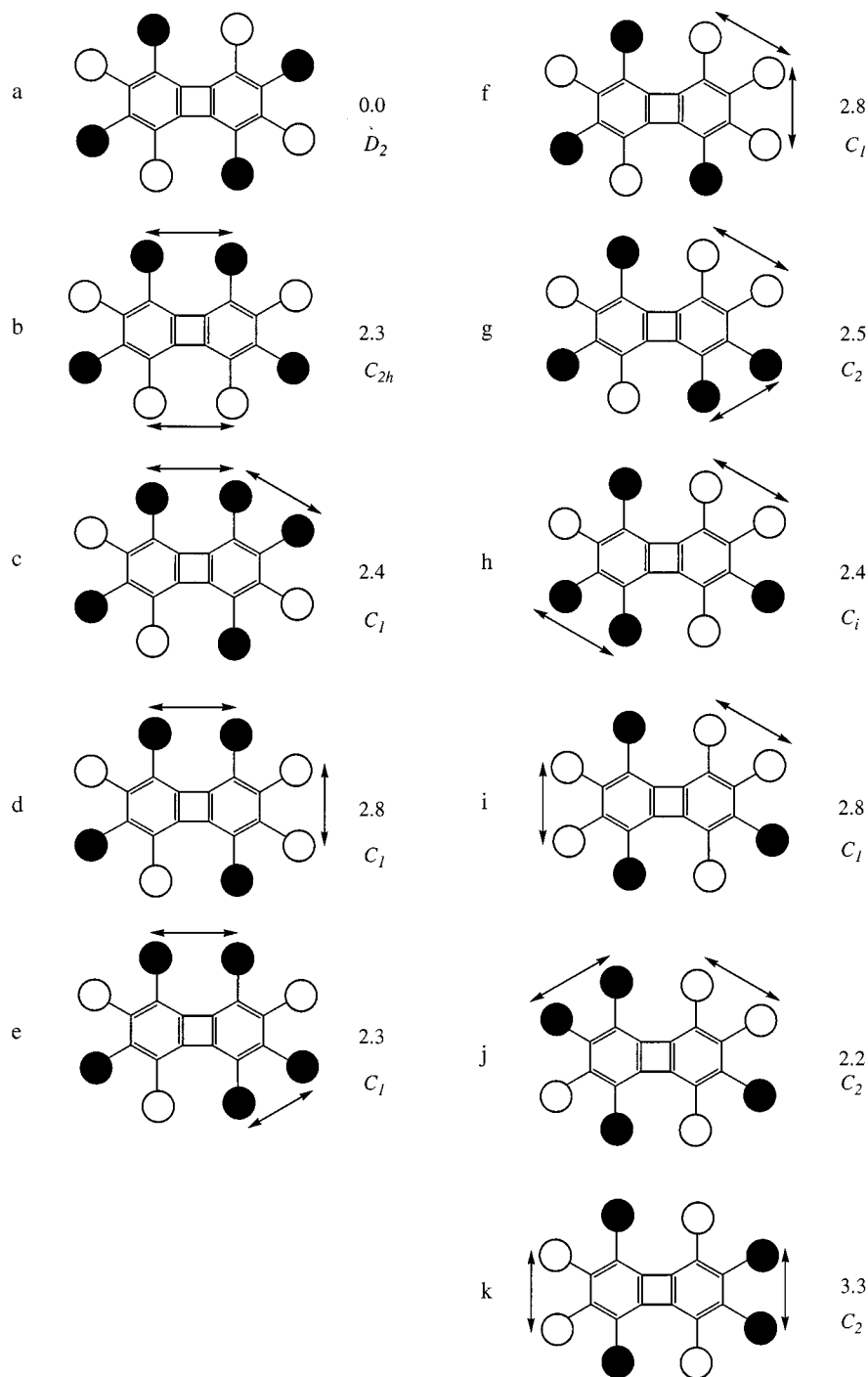
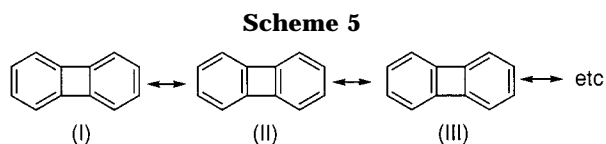
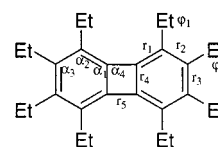


Figure 2. Relative steric energies (MM3, in kcal mol⁻¹) of selected conformers of **3**.



from C_{2h} symmetry is small. Notably, the crystal conformation does not correspond to the fully alternated form (a) which was predicted by the MM3 calculations as the global minimum, but corresponds to form "b" with two *syn-peri* interactions (Figures 3 and 4). Selected bond lengths and angles are collected in Table 2. The distance between the methyls at the pairs of proximal *syn-peri* ethyl groups is 3.92 Å indicating van der Waals contacts between the methyls.²¹ As observed in the crystal struc-

tures of **4**¹⁸ and **5**¹⁹ the phenylene rings of **3** display a marked bond fixation (the difference in the bond lengths between r_2 and r_1 is 0.072–0.067 Å) and small α_2 bond angles (115.0(1)–115.2(1)°).



Slow-Exchange Spectrum and Rotational Barrier of **3.** To estimate the rotational barrier of a 1,2,3,4-

(21) The commonly accepted value for the van der Waals radius of a methyl group is 2.0 Å (Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441).

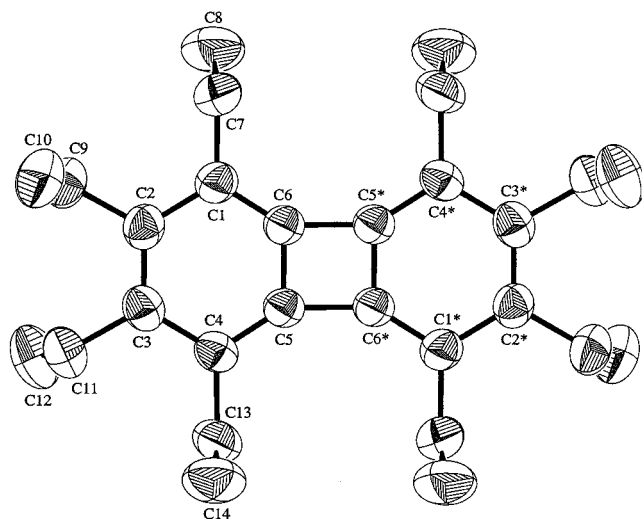


Figure 3. X-ray structure and numbering scheme of octaethylbiphenylene (**3**). Atoms marked with an asterisk are symmetry-related to the corresponding atoms without the asterisk. The crystal conformation corresponds to form "b" in Figure 1.

tetraethylphenyl subunit we examined first the slow exchange and temperature-dependent NMR spectra of **7** and **8**. The room temperature ^1H and ^{13}C NMR spectra of **7** and **8** were assigned by means of the COSY, HMBC, and HMQC techniques (see Table 1). Upon lowering the temperature of samples of **7** and **8** in CDCl_2F ,²² the methylene signals broadened and decoalesced. In the case of **8**, the low temperature ^1H NMR spectrum displayed four signals for the methylene signals (two signals partially overlapping). The diastereotopicity of the methylene protons is in agreement with perpendicular arrangements of the ethyl groups. The number of signals experimentally observed in the slow-exchange spectra of both compounds are in agreement with the calculated global minima, i.e., with frozen conformations (on the NMR time scale) of C_2 symmetry with an alternated *up-down* arrangement of the ethyls. Total line shape simulations of the temperature-dependent NMR spectra²⁴ enabled the determination of the rotational barriers of the ethyl groups in each compound. In both cases identical barriers (within experimental error) were found for the rotation of the external and internal ethyl groups. The topomerization barriers measured ($\Delta G^\ddagger = 9.9 \pm 0.1$ and 8.2 ± 0.1 kcal mol⁻¹ for **8** and **7**, respectively; for full kinetic results, see Table 3), are ascribed, by analogy to **1**,⁴ **2**,^{5a} and several pentaethyl derivatives,^{5b} to the noncorrelated rotation of the ethyl groups.

The room temperature ^{13}C and ^1H NMR spectra of **3** were determined, and the proton and carbon signals were assigned by 2D NMR techniques. The ^1H NMR spectrum (600 MHz, CDCl_3 , see Table 1) displayed two pairs of quartets for the methylene groups of the ethyl groups, indicating (precluding accidental isochrony) fast rotations of the ethyl groups on the NMR time scale. Upon cooling

in CD_2Cl_2 , the ^1H NMR signals of the methylene ethyl groups of **3** broadened and eventually decoalesced. Three methylene signals (in a 2:1:1 ratio) were observed in the low temperature ^1H NMR spectrum, in agreement (precluding accidental isochrony) with the presence of a single major conformer significantly populated. This spectrum is in agreement with forms "a" and "b" (of D_2 and C_{2h} symmetries, respectively) as well as with symmetric structures of D_2 , C_{2h} or C_{2v} symmetries (cf., Scheme 6). Assuming that in the solution conformation no *syn-ortho* interaction is present, the potential conformers can be further restricted to the fully alternated (a) and crystal (b) forms.

The ^{13}C spectrum showed one set of lines at room temperature; however, some of them were broadened (maximum width 20 Hz). Upon heating, or upon cooling to below 260 K, all lines sharpened, and no extra lines could be detected. The best explanation for such behavior is the presence of a small amount of a minor species, which participates in the equilibrium but is too sparsely populated to be detected in the ^{13}C at low temperature (a so-called "hidden partner").²³ Line shape analysis of the temperature-dependent ^1H NMR spectra indicated that the rotational barrier of the two types of ethyl groups were identical within experimental error.²⁴ The height of the rotational barrier of **3** (9.4 ± 0.1 kcal mol⁻¹) is between the values determined for **7** and **8**. The similarity in rotational barriers of **3**, **7**, and **8** suggests that a given tetraethylphenylene subunit in **3** does not markedly affect the rotational barrier of the ethyl groups of the other subunit.

Semiempirical and ab Initio Calculations. The *syn* arrangement observed in the crystal conformation of **3** can represent either the lowest energy conformation, or a high energy form that is nevertheless preferred in the crystal due to packing forces. van der Waals interactions are strongly repulsive when the distance between two nonbonded atoms is smaller than the sum of their van der Waals radii, and mildly attractive when the distance is larger than the sum of the radii. In some cases, the preferred conformation of a molecule is mainly dictated by attractive van der Waals interactions.^{25,26} A classic example is 1,3,5-tribromo-2,4,6-trineopentylbenzene (**13**), in which in its lowest energy conformation the three neopentyl groups are arranged in a mutual *syn* orientation (cf, Scheme 7).²⁵ MM3 calculations indicate that the lowest energy conformer of **3** is the fully alternated form "a". However, it could be possible that the relative high energy calculated for the crystal form "b" is due to poor parametrization of the empirical force field program which underestimates the attractive interactions (if indeed present) between the *peri* ethyl groups. A recent computational study indicated that all the molecular mechanics methods examined (including MM3) correctly reproduce the conformational preferences of **14**.²⁷ We tested whether the MM3 force field as implemented in the Alchemy 2000 program satisfactorily reproduce the conformational behavior of **13**. The calculations predict

(22) Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

(23) Anet, F. A. L.; Basus, V. J. *J. Magn. Reson.* **1978**, *32*, 339. See also: Adams, S. P.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 1602; Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1839; Hassner, A.; Maurya, R.; Friedman, O.; Gottlieb, H. E.; Padwa, A.; Austin, D. *J. Org. Chem.* **1993**, *58*, 4539.

(24) The line shape calculations were performed using a computer program based on the equations in the following paper: Alexander, S. *J. Chem. Phys.* **1962**, *37*, 967.

(25) Carter, R. E.; Nilsson, B.; Olsson, K. *J. Am. Chem. Soc.* **1975**, *97*, 6155.

(26) Berg, U.; Petterson, I. *J. Org. Chem.* **1987**, *52*, 5177. Nishio, M.; Hirota, M. *Tetrahedron* **1987**, *52*, 5177. Anderson, J. E.; Brucapdeville, V.; Kirsch, P. A.; Lomas, J. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1077. For a review see: Sauer, R. R. *J. Chem. Educ.* **1996**, *73*, 114.

(27) Gundertofte, K.; Liljefors, T.; Norby, P.-O.; Petterson, I. *J. Comput. Chem.* **1996**, *17*, 429.

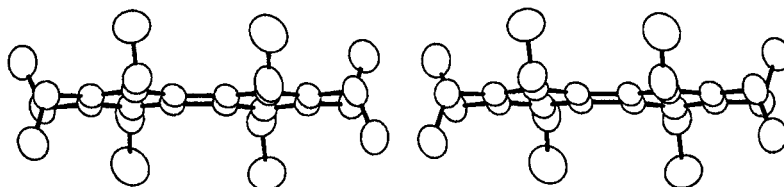


Figure 4. Stereoview (side view) of the crystal conformation of **3**. Pairs of vicinal ethyl groups at the *peri* positions are oriented *syn*.

Table 2. Experimental (X-ray) and Calculated Geometrical Parameters for **3 and Calculated Energy Differences^a**

	r_1	r_2	r_3	r_4	r_5	α_1	α_2	α_3	α_4	ΔE
X-ray	1.365(2)	1.432(2)	1.393(2)	1.414(2)	1.520(2)	123.0(1)	115.2(1)	121.8(1)	90.1(1)	
	1.365(2)	1.437(2)			1.514(2)	123.1(1)	115.0(1)	121.7(1)	98.9(1)	
MM3	1.378	1.439	1.419	1.404	1.521	123.4	115.3	121.3	90.0	2.3
AM1	1.363	1.439	1.393	1.460	1.485	122.1	116.1	121.8	90.0	1.57
PM3	1.359	1.438	1.391	1.446	1.488	122.5	115.6	121.9	90.0	0.57
RHF 6-31G*	1.361	1.436	1.387	1.412	1.519	122.9	115.5	121.6	90.0	2.54 1.90 ^b

^a Bond lengths in Å, bond angles in degrees. Calculated energy difference (in kcal mol⁻¹) between the crystal (b) and fully alternated (a) conformations. ^b Single point MP2(full) calculations using the optimized RHF/6-31G* geometries.

Table 3. Dynamic NMR-Derived Rates for the Topomerization Processes of **3, **7**, and **8****

T/K^a	k/sec ⁻¹	$\Delta G^\ddagger/\text{kcal mol}^{-1}$
7^{b,d}		
159.4	25	8.1 ± 0.1
164.7	40	8.2 ± 0.1
175.0	280	8.1 ± 0.1
196.2	3000	8.2 ± 0.1
217.2	20000	8.3 ± 0.1
8^{b,d}		
180.4	4	9.9 ± 0.2
196.2	40	9.9 ± 0.1
212.0	230	10.0 ± 0.1
233.0	3000	9.8 ± 0.1
264.5	30000	10.0 ± 0.2
3^{c,d}		
176.0	15	9.2 ± 0.2
196.8	130	9.5 ± 0.1
216.7	1400	9.4 ± 0.1

^a Temperatures believed to be accurate to ±0.5 K. ^b In CDCl₂F. ^c In CD₂Cl₂. ^d Coalescence of the signals of the diastereotopic methylene protons.

correctly that the *all-syn* form of C_{3v} symmetry is 1.3 kcal mol⁻¹ more stable than the *syn-anti* form of C_s symmetry. A similar conformational behavior is also predicted for the parent hydrocarbon **14**, although the energy gap favoring the *all-syn* form is narrower (0.5 kcal mol⁻¹).

To obtain an additional estimate of the energy gap between the “a” and “b” forms of **3**, we conducted semiempirical (AM1, PM3) and restricted Hartree–Fock ab initio calculations at the 6-31G* level.²⁷ In addition, single point MP2(full) calculations were conducted using the optimized RHF-6-31G* geometries. The results of the calculations are collected in Table 2. In general the semiempirical methods underestimate the bond length between the two phenylene subunits (X-ray: 1.514–1.520 Å, AM1: 1.485 Å, PM3: 1.488 Å) as previously observed in the MNDO calculations of the parent biphenylene.²⁸ The MM3 and RHF 6-31G* ab initio calculations satisfactorily reproduce all the structural parameters of the crystal structure. The calculated geometries of the C_{2h} and D_2 forms (RHF 6-31G*) are shown in Figure 5. All

the computational methods used indicate that the all-alternated form “a” is the one lower in energy. The most reliable computational method (MP2(full)) indicates that the energy gap between the C_{2h} “crystal” conformation and the all-alternated D_2 form is about 1.90 kcal mol⁻¹ which is similar to the gap calculated by the MM3 program (2.3 kcal mol⁻¹). It can be concluded therefore that form “b” does not correspond to the lowest energy conformer, and that its presence in the crystal is probably due to packing forces.

On the basis of the calculations which indicate that the all-alternated form “a” is the lower energy form, the solution conformation detected in the slow-exchange NMR spectrum is assigned to this form. The rotational barrier determined by NMR can be ascribed to the enantiomerization of the conformer “a” via noncorrelated rotation of the eight ethyl groups.

Side Products. Mass spectral analysis indicated that the main product obtained in the reaction depicted in Scheme 3 possessed the same molecular weight as **3**. The chemical behavior of tetraethylbenzynes is different from that of its lower homologue tetramethylbenzynes, which under analogous reaction conditions, yields exclusively octamethylbiphenylene. The main product was characterized as 2,3,4,5,3',4',5'-heptaethyl-2'-vinylbiphenyl (**9**) on the basis of its NMR spectra. The positions of the aromatic hydrogens and the vinyl group on the biphenyl skeleton were unambiguously determined by a detailed analysis of long-range CH correlations in the HMBC spectrum. The latter, together with other 2D NMR techniques enabled the signal assignments presented in Table S1 (Supporting Information). Notably, the two methylene protons of the ethyl group at the 2 position are noticeably anisochronous (δ in CDCl₃, 2.27 and 2.47 ppm), in agreement with the presence of a chiral frozen conformation on the NMR time scale. Interestingly, a *single* vinyl group is present in the biphenyl **9**. The formation of this product can be rationalized assuming that the [2+2] reaction of the two benzyne precursors to yield **3** proceeds in a stepwise (nonconcerted) fashion, in which the two σ bonds are not formed simultaneously (Scheme 8). The biradical can either form a new σ bond between the two phenyl radicals yielding biphenylene **3**,

(28) Saitmacher, K.; Vögtle, F.; Peyerimhoff, S.; Hippe, D.; Büllsbach, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 466.

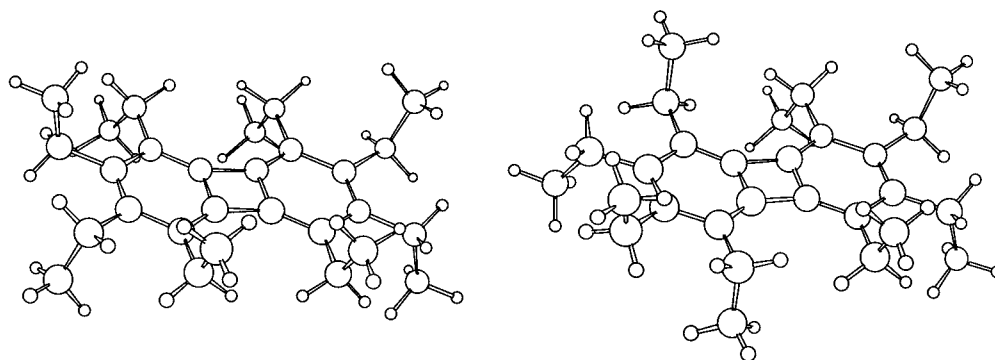
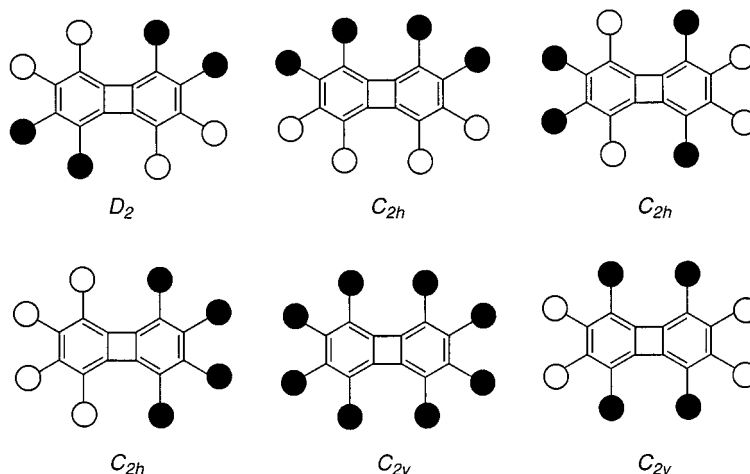
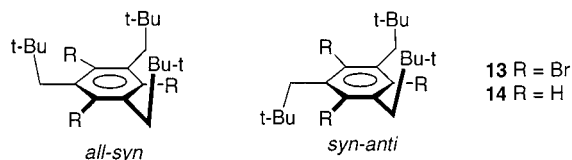


Figure 5. Calculated geometries (RHF 6-31G*) of the D_2 ("a", right) and C_{2h} ("b", left) conformers of **3**. The crystal conformation "b" possesses a higher energy than the fully alternated form "a".

Scheme 6



Scheme 7



or can undergo a series of intramolecular hydrogen atom transfer reactions (an intramolecular disproportionation) generating biphenyl **9**. It is likely that the isomer with the vinyl group at the 2' (*ortho*) position of the biphenyl is formed preferentially since it is the isomer most stable thermodynamically. The planar vinyl group is less bulky than an ethyl substituent, and the isomer in which the less bulky substituent is located at the most crowded position should be energetically favored.

Experimental Section

NMR Spectroscopy. NMR spectra were run on a Bruker DMX-600 spectrometer operating at 600.1 (^1H) and 150.9 (^{13}C) MHz.

Calculations. The crystal coordinates were used as input for the calculations involving conformer *b*. MM3(94) calculations were performed using the Alchemy 2000 program.²⁹ All stationary points were characterized as minima by the absence of imaginary frequencies in the frequency matrix. Semiempirical *ab initio* calculations were conducted using the Chem3D and Gaussian 98 Programs,³⁰ respectively. Geometry optimizations in the *ab initio* calculations were conducted using tight optimization criteria.

Crystallography. The X-ray diffraction data were measured with an ENRAF-NONIUS CAD-4 computer-controlled

diffractometer. Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation with a graphite crystal monochromator in the incident beam was used. All crystallographic computing was done on a VAX 9000 computer using the TEXSAN structure analysis software. Crystal data for **3**: $C_{28}H_{40}$, FW = 376.62 g mol $^{-1}$, space group $P2_1/c$, $a = 10.276(4) \text{ \AA}$, $b = 11.125(5) \text{ \AA}$, $c = 11.385(4) \text{ \AA}$, $\beta = 112.97(3)$; $V = 1198(1) \text{ \AA}^3$, $z = 2$, $\rho_{\text{calc}} = 1.04 \text{ g cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 4.25 \text{ cm}^{-1}$, no. of unique reflections = 2377, no. of reflections with $I \geq 3 \sigma_I = 1931$, $R = 0.046$, $R_w = 0.051$.

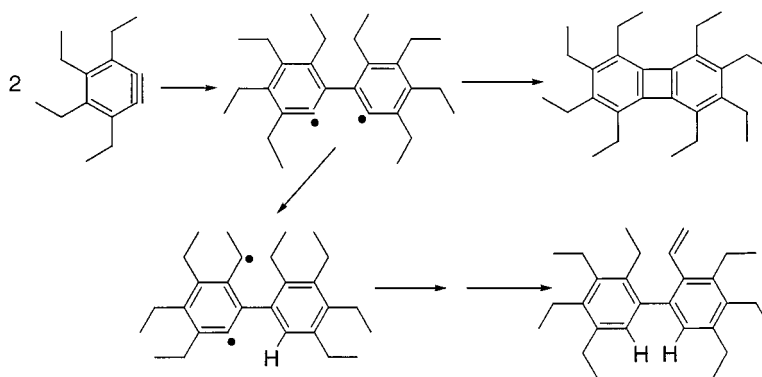
1,2,3,4-tetraethylbenzene (**7**) was prepared according to the literature,^{11a,b} but using EtBr instead of EtCl in the alkylation step. 1,2-Dibromo-3,4,5,6-tetraethylbenzene (**8**) was prepared by bromination of **7** according to the literature procedure,¹² mp 73 °C (lit.¹² 76–77 °C).

1,2,3,4,5,6,7,8-octaethylbiphenylene (3). 1,2-Dibromo-3,4,5,6-tetraethylbenzene (1000 mg, 2.87 mmol) was dissolved in 10 mL of dry THF. The magnetically stirred solution was cooled to 0 °C and under an inert atmosphere 3 mL BuLi (1.6 M in hexane, 4.8 mmol) was slowly dropped over a period of 10 min. The mixture was stirred for 24 h at room temperature. After quenching with 6 mL water, the phases were separated,

(29) Alchemy 2000. Tripos Inc., St. Louis, MO 63144.

(30) *Gaussian 98, Revision A.8*, 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

Scheme 8



the aqueous phase was extracted with ether, and the combined organic phases were dried and evaporated. The residue was recrystallized twice from dichloromethane/methanol yielding yellow crystals of **3**, (17 mg, 3%) mp 197 °C. HR MS found: m/z 376.3127 (M^+), calcd m/z 376.3130

The major product of the reaction was purified by chromatography (silica, eluent: petroleum ether 40–60 °C). This oily product was characterized as 2,3,4,5,3',4',5'-heptaethyl-2'-vinylbiphenyl **9** (150 mg, 28%). EI MS m/z 376 (M^+). δ ^1H NMR (600 MHz, CDCl_3 , rt) δ 6.93 (1H, s, Ar-H), 6.79 (1H, s, Ar-H), 6.53 (1H, dd, 18, 12 Hz, $\text{H}_2\text{C}=\text{CH}$), 5.04 (1H, dd, 12, 2 Hz, $\text{HC}(\text{H})=\text{CH}$), 4.82 (1H, dd, 18, 2 Hz, $\text{HC}(\text{H})=\text{CH}$), 2.77–2.58 (12H, m, CH_3CH_2), 2.47 (1H, dq, 14, 7 Hz, CH_3CH_2), 2.27 (1H, dq, 14, 7 Hz, CH_3CH_2), 1.22, 1.21, 1.20, 1.19, 1.17, 1.16, 0.91- (each 3H, t, 7 Hz, CH_3CH_2). ^{13}C NMR (151 MHz, CDCl_3 , rt) δ 140.24, 140.02, 139.67, 139.67, 139.58, 138.53, 138.20, 138.01, 137.27, 134.21 (C_{Ar}), 135.26 ($\text{H}_2\text{C}=\text{CH}$), 128.43, 128.47 (HC_{Ar}), 118.50 ($\text{H}_2\text{C}=\text{CH}$), 25.68, 25.46, 23.12, 22.88, 22.04, 21.86, 21.76 (CH_3CH_2), 16.06, 15.70, 15.63, 15.57, 15.56, 15.52, 15.40 (CH_3CH_2).

Attempt to Prepare 1,2,3,4,1',2',3',4'-Octaethylbiphenyl (11). To a solution of 6.25 mL of BuLi (1.6 M in hexane) in 10 mL of dry THF at -78 °C was added during 5 min under an inert atmosphere 0.5 g of 1,2-dibromo-3,4,5,6-tetraethylbenzene. The mixture was stirred at -78 °C for 1 h and then slowly allowed to reach rt. After quenching with 10 mL water, the organic phase was separated, dried, and evaporated, yielding 0.13 g crude product, which according to GC MS consisted of a mixture of **12** and **7**.

Acknowledgment. We thank Dr. Shmuel Cohen for the crystal structure determination and the Israel Science Foundation for support of this work.

Supporting Information Available: Crystallographic tables of **3**. ^1H NMR spectra of **3** and **9** and assignment of the ^1H and ^{13}C NMR signals of **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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