Conformation and Stereodynamics of Decaethylbiphenyl

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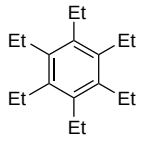
Abstract: The stereochemistry of decaethylbiphenyl (**5**) is analyzed. The potentially low-energy conformers of **5** were generated by formally linking two pentaethylphenyl subunits, and by assuming that no more that one *syn* interaction is present per ring. Molecular mechanics calculations (MM3 program) indicate that the forms "f", "i", "j", and "m" represent the lowest energy conformations. As previously observed for decakis(bromomethyl)biphenyl, the "a" conformation (devoided of any *syn* arrangement of two neighboring ethyl groups) is destabilized by the mutual steric interactions of *ortho* ethyl groups at different rings. Decaethylbiphenyl (**5**) was synthesized by exhaustive ethylation of biphenyl. The compound exists in the crystal in three different conformations ("i", "j", and "m"). Low-temperature ^{13}C NMR data show that the compound exists in $CDCl_2F$ at 149 K in two conformations in a 4:1 ratio, and the major conformer was assigned to the "m" form. Dynamic NMR data indicate that "m" undergoes ethyl rotation with a barrier of $\Delta G_{176}^{\ddagger} = 8.2 \pm 0.1$ kcal mol^{-1}. The interconversion graph of **5** was analyzed, and on the basis of the MM calculations and NMR data, it is concluded that the rotational process followed by NMR involves the stepwise rotation of the *meta* and *para* ethyl groups of "m".

Introduction

Hexaethylbenzene (**1**), the prototype of a multiarmed benzene system, exists in solution and in the solid state in a conformation in which the ethyl groups are perpendicular to the phenyl plane and are arranged in an alternate "up-down" fashion (cf. **2**).[1−4] The relative energy of the different conformers of **1** increases with the number of *syn* interactions, i.e., with pairs of vicinal groups oriented both "up" or both "down".[2b] Empirical force field calculations indicate that the internal rotations of the ethyl groups of **1** and related systems are not correlated but proceed by a stepwise mechanism.[2b] Hexaethylbenzene and its analogs readily form complexes with transition metals (e.g., **3**).[2] Lowering the temperature allows the tripodal rotation of the complexed $Cr(CO)_3$ unit[5,6] to be "frozen" (on the NMR time scale).



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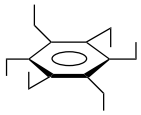

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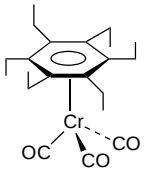

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Although the stereochemistry of polysubstituted benzene systems has been extensively studied, few studies have been conducted on the static and dynamic stereochemistry of decasubstituted biphenyl derivatives.[7,8] These systems are stereochemically more complex than the corresponding polysubstituted phenyl systems due to the presence of the nonplanar biphenyl core and to the larger number of side chains. These structural features result in an increased number of possible conformers and mutual stereoisomerization pathways. We have previously described the preparation of decakis(bromomethyl)biphenyl (**4**) and showed that in the crystal the molecule adopts a conformation in which the "up-down" alternation of the CH_2Br groups is disrupted at the *meta-para* positions of the rings.[8] The presence of a *syn* interaction is each ring is necessary to avoid bromine contacts between *ortho* bromomethyl groups at different rings which will be forced when the conformation is the perfectly alternated "up-down". However, due to the poor solubility of the compound we were unable to determine the solution conformation by ^{13}C NMR at slow exchange conditions. In this paper we analyze the static and dynamic stereochemistry of decasubstituted biphenyls with ten identical side chains of the general form CH_2Y, and describe the preparation, crystal structure, solution conformation, and rotational barrier of the biphenyl analog of **1**, i.e., decaethylbiphenyl (**5**).

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(1) For a review on multiarmed organic compounds see: Menger, F. M. *Top. Curr. Chem.* **1986**, *136*, 1.

(2) (a) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5942. (b) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. (c) Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K.*Organometallics* **1982**, *1*, 448. (d) Blount, J. F.; Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 170. (e) Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 172. (f) Hunter, G.; Weakley, T. J. R.; Mislow, K.; Wong, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 577. (g) Hunter, G.; Weakley, T. J. R.; Weissensteiner, W. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1633.

(3) The related hexa-*n*-propylbenzene is also described in the literature (Hopff, H.; Gati, A. *Helv. Chim. Acta* **1965**, *48*, 509. Hunter, G.; Weakley, T. J. R.; Weissensteiner, W. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1633). The propyl groups undergo fast rotation at room temperature on the NMR time scale (Radcliffe, M. D.; Mislow, K. *J. Org. Chem.* **1984**, *49*, 2058).

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

(8) Zuaretz, N.; Golan, O.; Biali, S. E. *J. Org. Chem.* **1991**, *56*, 2444.

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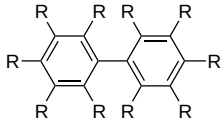
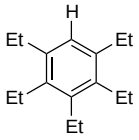


4 R = CH_2Br
5 R = Et



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Results and Discussion

General Considerations. To analyze the static and dynamic stereochemistry of the system, we will assume that in all conformations the biphenyl ring planes are mutually perpendicular and that, in analogy to hexaethylbenzene, all ethyl groups are perpendicular to the plane of the phenyl ring to which they are attached (i.e., all CH_3-CH_2-C-C torsional angles are $\pm 90°$). Under these restrictions, biphenyl **5** should exist in 272 stereoisomeric forms (136 enantiomeric pairs).[9] However, some of these isomers represent high-energy forms due to the presence of several *syn* interactions between vicinal ethyl groups. In the following discussion we will restrict ourselves to the subset of isomers of expected low energy which have at most a single *syn* interaction per ring.

To discuss the static stereochemistry of biphenyl **5**, it is necessary first to generate the possible ideal isomers of expected low energy. For the complete generation of this subset of isomers and the analysis of the possible mutual interconversion routes by rotation of the ethyl substituents, it is convenient to view the biphenyl skeleton as derived from the formal interconnection of two pentaethylphenyl subunits. We will therefore briefly discuss the conformation and interconversion pathways of a pentasubstituted system as exemplified by pentaethylbenzene (**6**).

Conformational Descriptors for Pentaethylbenzene. Assuming that in the minimum energy conformations of **6** all ethyl groups are perpendicular, the system should exist in five different conformations containing at most a single *syn* interaction. Since the *p*-ethyl group destroys the skeletal C_2 axis passing through the *ipso* and *para* carbons, all isomers must belong to either the C_s or C_1 point groups. The five ethyl groups can be labeled in a clockwise fashion by the numbers 1−5. The descriptor of a given conformation can be obtained by orienting the phenyl ring plane normal to the observer (i.e., in the plane of the page) and describing the numbers of the alkyl groups which are pointing to the observer (Figure 1). Since no conformation may belong to the C_2 point group, in all conformers the two aryl faces are symmetry nonequivalent. Two different descriptors exist for each conformation depending on the aryl face, which is oriented toward the observer. The pairs of descriptors for the five possible conformations of **6** are 135 (=24), 35 (=245), 13 (=124), 25 (=235), and 14 (=134) (Figure 1). The pairs 35/13 and 25/14 are enantiomeric while the 135 form is achiral.[10]

(9) In refs 7 and 8 the number of isomers was incorrectly calculated by the configurational matrix method as 132 enantiomeric pairs. In this method (as applied to **5**) a given conformation is represented by a ten-digit one-dimensional configurational matrix. Each of the ten ethyl groups of **5** can be independently oriented "up" (1) or "down" (0), and therefore the total number of possible matrices is 2^{10}. Structures with C_1 symmetry are represented by four different matrices while conformations of C_2 symmetry are represented by two matrices. The calculations in refs 7 and 8 were conducted assuming that there are 2^5 matrices representing isomers of C_2 symmetry. However, since there are *two* dihedral C_2 axes in the biphenyl skeleton, the number of matrices is indeed 2^6, resulting in 32 isomers of C_2 symmetry (16 enantiomeric pairs). The number of isomers of C_1 symmetry is given by $(2^{10} - 2^6)/4 = 240$, i.e., 120 enantiomeric pairs. The total number of enantiomeric pairs is therefore 136. We thank Prof. James H. Brewster (Purdue University) for providing us with an alternate analysis of the number of isomers of **5**.

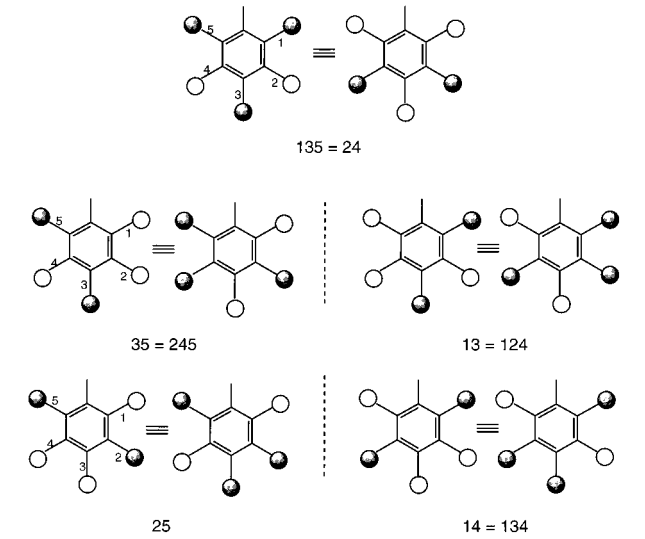

Figure 1. Possible isomers of a $ArEt_5$ system with at most a single *syn* interaction. The CH_2X groups are oriented perpendicular to the phenyl plane ($Me-CH_2-C-C$ torsional angle $\pm 90°$). Ethyl groups pointing to the observer are denoted by a filled sphere, ethyl groups pointing in the opposite direction are denoted by an open sphere. Each isomer is viewed from the two symmetry unequivalent faces of the phenyl ring. The five ethyl groups are numbered (starting from an *ortho* group) in a clockwise fashion; ethyl groups pointing to the observer are included in the descriptor. The pairs 35/13 and 25/14 represent enantiomers.

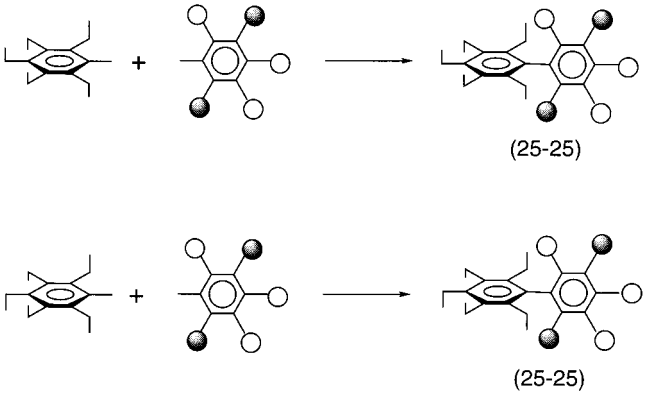

Figure 2. Generation of the low-energy conformations of decaethylbiphenyl by the formal connection of two mutually perpendicular pentaethylphenyl units. Two different orientations are possible, leading to enantiomers or diastereomers. In the case shown two pentaethylphenyl units existing in the 25 arrangement are combined, resulting in two diastereomeric forms.

Generation of the Low-Energy Isomers of Decaethylbiphenyl. The generation of the potential low-energy conformers of **5** can be achieved by combining two pentaethylphenyl subunits having at most a single *syn* interaction each, i.e., with local 135, 35, 13, 25, or 14 arrangements. The descriptors of the conformers of **5** generated by this procedure can be created by indicating the arrangement of groups in each of the two pentaethylphenyl subunits. For example, a "135-35" descriptor (or its equivalent descriptor "35-135") indicates that one pentaethylphenyl subunit has a "135" arrangement while the second subunit has a "35" arrangement. If the two subunits are joined when the two phenyl rings are coplanar, this results in 15 different arrangements: three achiral (135-135, 35-13, 25-14) and twelve chiral (35-135/13-135, 25-135/14-135, 35-25/13-14, 35-14/13-25, 35-35/13-13, and 25-25/14-14). The

(10) In the following discussion a slash (/) will indicate an enantiomeric relationship.

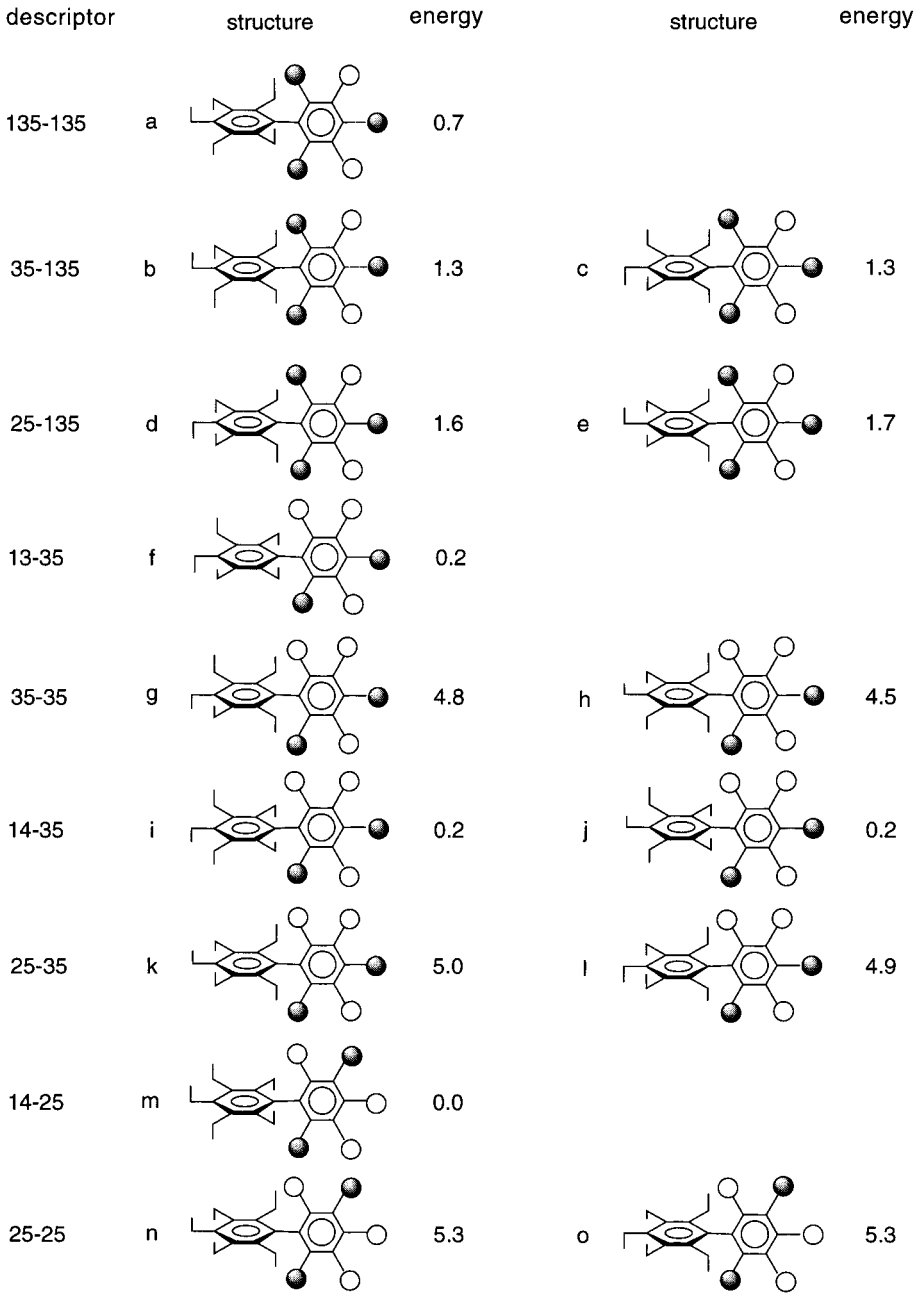

Figure 3. Calculated relative steric energies (MM3 program) of the possible isomers of decaethylbiphenyl having at most a single *syn* interaction per ring

three achiral forms result from combining either two achiral 135 arrangements of the pentaethylphenyl subunits or two enantiomeric arrangements of the two subunits (35/13 and 25/14). These 15 structures correspond to the hypothetical residual isomeric forms[11] that would exist on a time scale in which the rotation around the Ph−Ph bond is fast but the side chain rotations are slow. For a "frozen" conformation in which the two rings are mutually perpendicular (i.e., both Ar−Ar and side chain rotations are slow), the number of stereoisomeric forms increases. Each of the achiral patterns (135-135, 35-13, 25-14) generates two enantiomeric arrangements while each of the chiral patterns generates two diastereomeric arrangements (Figure 2), yielding a total of 15 enantiomeric pairs. Representatives for each of the 15 enantiomeric pairs possessing at most a single *syn* interaction per ring are displayed in Figure 3.[12] The forms "a", "g", "h", "n", and "o" possess ideally C_2 symmetry while the rest of the conformers are asymmetric (C_1 symmetry).

Molecular Mechanics Calculations. The 15 conformers of **5** having at most a single *syn* interaction per ring were calculated with the MM3 program.[13] The calculated relative energies of the forms are collected in Figure 3. As shown in the figure, the lowest energy form is the "m", but three additional forms ("i", "j", and "f") are of very similar energy and lay only 0.2 kcal mol^{-1} above it. As previously observed for **4**, in the low-

(11) Residual stereoisomers can be defined as those subsets of the total set of stereoisomers that can be distinguished under a given time scale. See: Finnocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 8172. Eliel, E. L. *Isr. J. Chem.* **1976**, *15*, 1. Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994, p 55.

(12) Table 5 in ref 8 displays 17 structures with at most one *syn* interaction per ring. However, these do not correspond to 17 diastereomeric structures since two redundant structures were inadvertently introduced. Specifically, the pair of structures located (from the top of the figure) at the fourth position in each column as well as the pair of structures at the eight positions represent enantiomers.

(13) Allinger, N. L. *Molecular Mechanics. Operating Instructions for the MM3 program. 1989 Force Field* (updated 5/6/92). Technical Utilization Corporation.

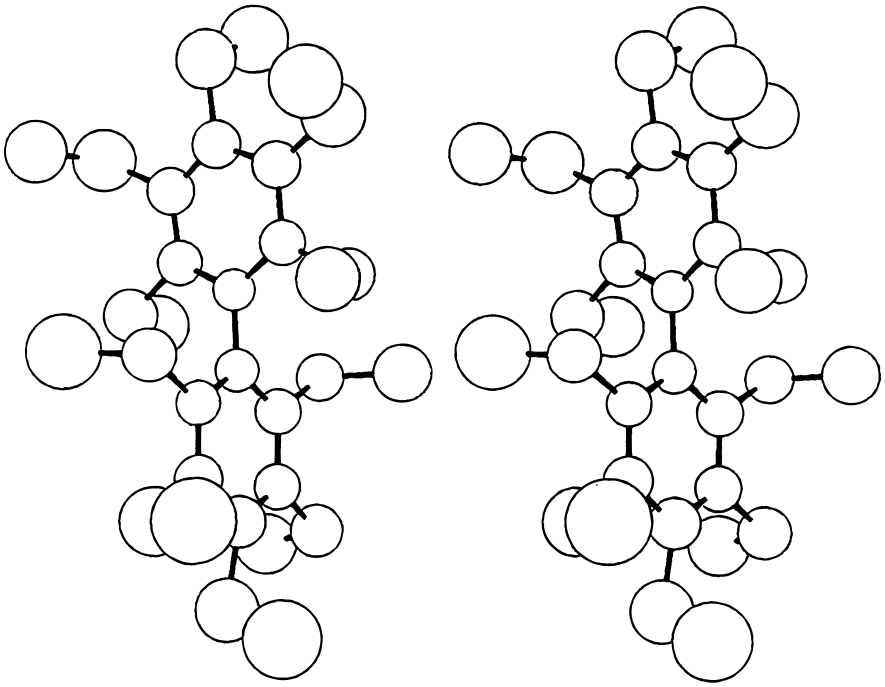

Figure 4. Stereoview of the crystal conformation of **5** (first independent molecule). The molecule adopted the "j" conformation (cf., Figure 3).

Table 1. NMR Data for Decaethylbiphenyl (**5**)

	C[a]	H[a,b]	C (260 K)[c]	C (149 K)[c,d]
ipso-C	139.65		140.52	140.18
o-C	137.05		137.58	137.28, 137.00
m-C	138.36		139.11	139.36,139.29,138.97,138.91
p-C	138.88		139.45	138.66
o-CH_2	25.30	2.24	25.95	26.06, 25.70
m-CH_2	22.26	2.71	22.66	22.50, 22.29
p-CH_2	22.38	2.75	22.89	23.25
o-CH_3	14.69	0.89	14.93	14.69
m-CH_3	16.17	1.16	16.49	18.21, 16.02
p-CH_3	16.56	1.25	16.83	17.36

[a] In $CDCl_3$ at 297 K. [b] $^3J_{HH} = 7.5$ Hz for all ethyl groups. [c] In $CDCl_2F$, see also Figure 8. [d] Peaks for major species; see text.

energy conformations of **5** the "up-down" arrangement of the groups (cf. **2**) is disrupted while the perfectly alternated "up-down" structure ("a") has a higher energy due to the steric interactions between the *ortho* ethyl groups at different rings. In the calculated low-energy forms of **5** a *syn* interaction (involving *meta* and *para* ethyl groups) is present in each ring. According to the calculations, the forms "a", "g", "h", "n", and "o" possess C_2 symmetry.

Synthesis and Room Temperature Solution NMR Spectra of 5. Decaethylbiphenyl was prepared by exhaustive Friedel−Crafts ethylation of biphenyl ($EtCl/AlCl_3$, see Experimental Section). The molecule displays at room temperature in the ^1H NMR spectrum ($CDCl_3$) three ethyl groups in a 2:2:1 ratio. Similarly, three methyl and three methylene signals are observed in the ^{13}C NMR spectra, in addition to the signals of the four different ring carbons (see Table 1). This is consistent with fast Ar−Et rotations, on the NMR time scale. All the signals were assigned unambiguously by 2D-NMR techniques:[14] a COSY spectrum identified methyl and methylene protons on the same ethyl moiety and a CH one-bond correlation spectrum connected these protons to their directly bound carbons. Finally, in a long-range CH correlation spectrum, interactions were found between each ring carbon and the protons of the corresponding ethyl group. In addition, cross peaks were also found between the *ipso* carbon C(1) and the methylene signals at 2.24 ppm, therefore establishing the identity of the latter as corresponding to *ortho* methylene protons. The signal assignment indicates that the *ortho* methyl groups are shifted upfield both in the ^1H and ^{13}C NMR spectra, probably (at least for the protons) due to the shielding effect of the neighboring phenyl ring.

Crystal Structure of Decaethylbiphenyl. A single crystal of **5** was grown from ethanol and submitted to X-ray crystallography.[15] The molecule crystallizes in the chiral space group *P*1 with four independent molecules in the unit cell. Since the structure could be refined only down to a relatively high *R* factor, the obtained fine structural details (e.g., bond lengths) are not very accurate. Notwithstanding the relative *R* value, the conclusions concerning the conformations adopted are trustworthy. Interestingly, the four independent molecules adopt *three* different diastereomeric conformations: "j", "i", and "m", the latter arrangement being adopted by two independent molecules in the unit cell (Figures 4−7). These three structures, with the addition of the "f" form, were predicted by the calculations as the low-energy forms. Interestingly, the calculated lowest energy conformation ("m") is the only one represented twice in the crystal. The related **4** exists in the crystal exclusively in the "m" conformation.[8]

Conformations of 5 in Solution. To determine experimentally the preferred solution conformation of the perethylated biphenyl, **5** was dissolved in $CDCl_2F$[16] and its 150.9-MHz ^{13}C NMR spectra were determined at low temperatures. As shown in Figure 8, below 220 K the ten original lines start broadening, and at 149 K a larger number of peaks are observed. On the basis of their intensities, the signals can be ascribed to two conformers present in a ca. 4:1 ratio.

(a) Major Conformer. A signal pattern consistent with five different ethyl groups was observed for the major species. Interestingly, the methyl signals are the sharpest and best resolved (*vide infra*), and the *meta* pair is the one with the largest

(14) For a review on 2D NMR techniques see: Kessler, H.; Gehrke, M.; Griesinger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.

(15) The authors have deposited atomic coordinates for the structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(16) For the preparation of $CDCl_2F$ see: Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

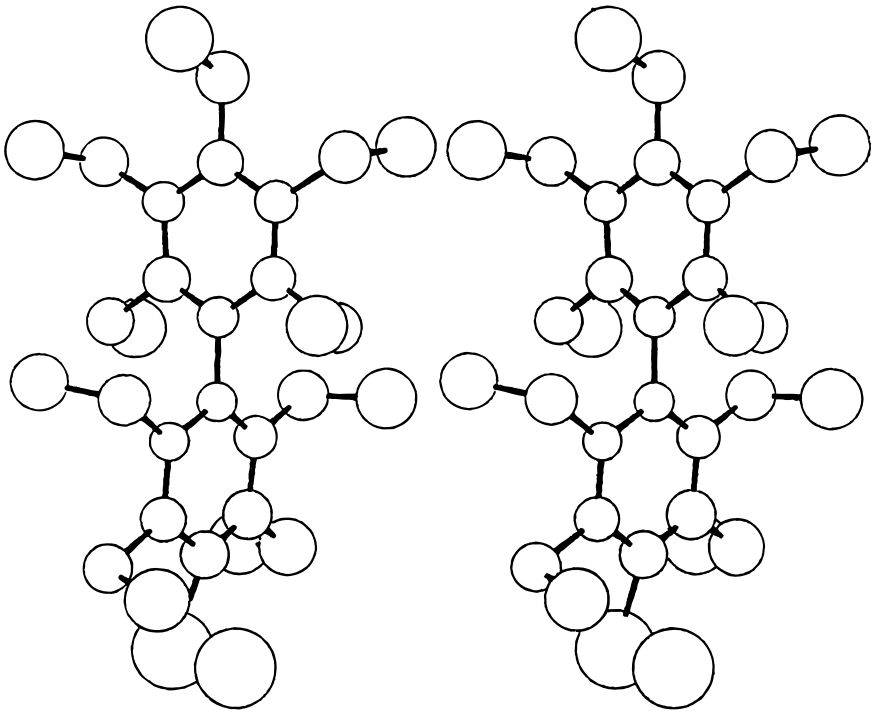

Figure 5. Stereoview of the crystal conformation of **5** (second independent molecule). The conformation adopted is "m".

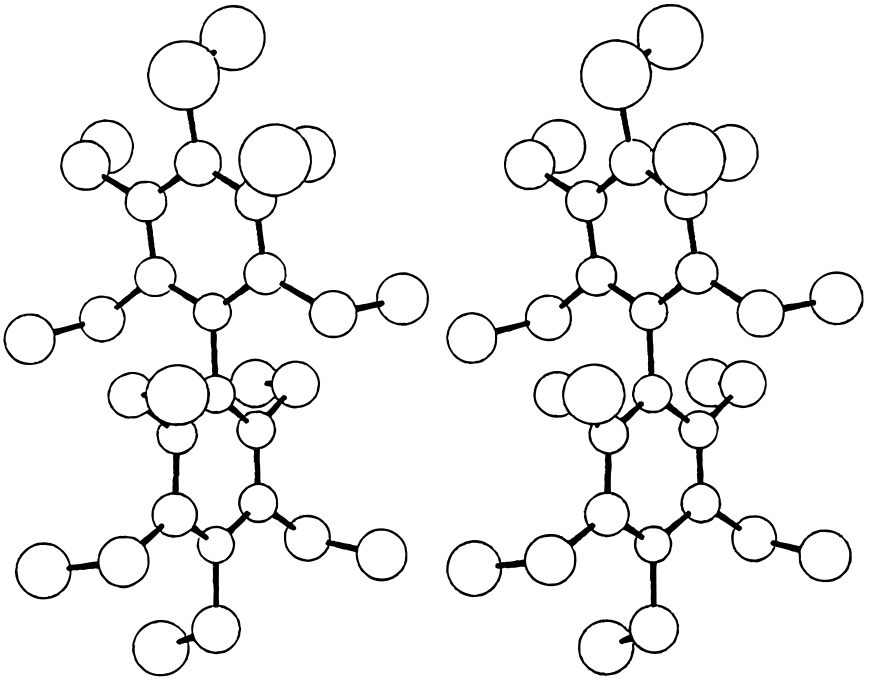

Figure 6. Stereoview of the crystal conformation of **5** (third independent molecule). The conformation adopted is "m".

chemical shift difference ($\Delta\nu = 2.19$ ppm), whereas the *ortho* methyls are accidentally isochronous. This is somewhat surprising since it could be naively expected that the *ortho* methyl groups which are more sterically hindered and are located in steric proximity of a neighboring ring will display the largest chemical shift difference in the "frozen" conformation. However, the relative small chemical shift difference of the *ortho* groups may be the result of the conformation adopted. If the chemical shift of a methyl group reflects mainly its immediate environment, this indicates that in contrast to the *meta* ethyls, all *ortho* ethyls have neighbors in the same relative orientation (*syn* or *anti*). Among the pentaethylphenyl subunits in Figure 1, this only suits those with the 25 and 14 configurations. Combination of two subunits with 25/14 configurations produces conformers "m", "n", and "o". The large differences in their calculated steric energies (Figure 3) strongly suggest that the conformation of the major species in solution is "m". In contrast to conformers "n" and "o" which possess C_2 symmetry, conformer "m" is asymmetric, and in this form pairs of *ortho*, *meta*, and *para* groups at different rings are diastereotopic and should be anisochronous, even if the $\Delta\delta$ might be predicted to be small. While there is no indication of such a splitting for the aliphatic signals, it is very distinctly seen in the signals of the *meta*-ring carbons (at *ca*. 139 ppm) which appear as four lines when some resolution enhancement is applied to the 149 K spectrum (Table 1 and Supporting Information).

Inspection of the conformation "m" helps to rationalize why the four *o*-Me groups are accidentally isochronous in the slow-

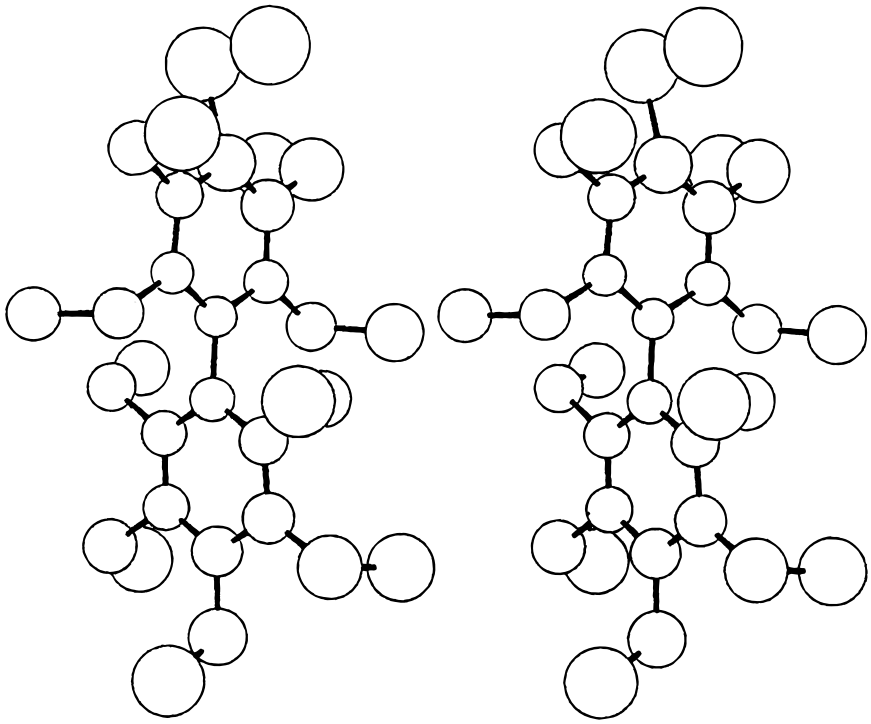

Figure 7. Stereoview of the crystal conformation of **5** (fourth independent molecule). The conformation adopted is the mirror image of the "i" form depicted in Figure 3.

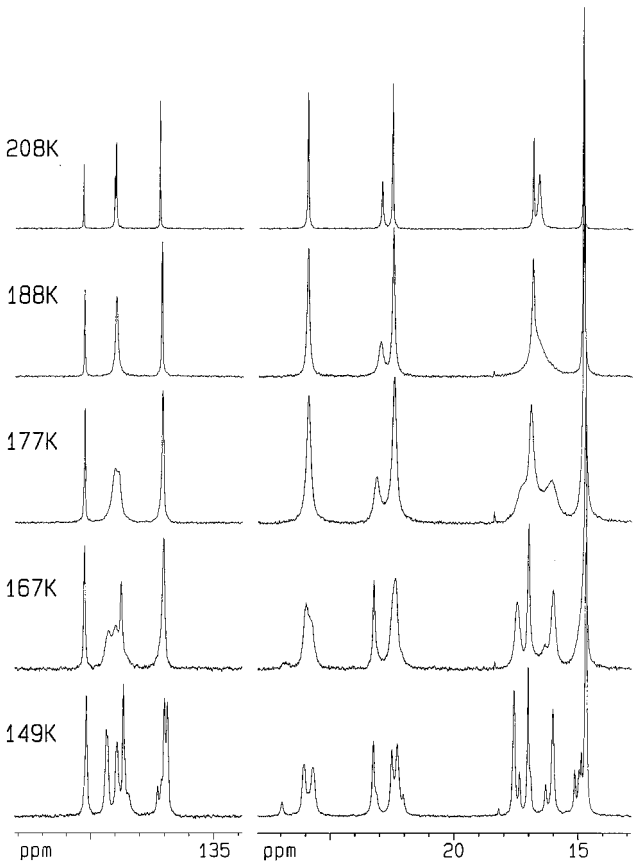

Figure 8. The 150.9-MHz ^{13}C NMR spectra of decaethylbiphenyl (**5**), in $CDCl_2F$, as a function of temperature. The three carbon types appear at 137−141 (ring C), 22−27 (CH_2), and 15−18 ppm (CH_3). The spectra were recorded with an exponential line broadening of 2 Hz.

exchange ^{13}C NMR spectrum while the *m*-Me appear as two well-separated signals. In this conformation the four *ortho* ethyl groups are oriented in a homodirectional arrangement, which disregarding the other substituents possesses S_4 symmetry. Since these groups are surrounded by the *meta* groups which also are oriented in a homodirectional arrangement, the four *ortho* groups should possess very similar chemical shifts. On the other hand, the two *meta* groups in a given ring have opposite orientations (*syn* or *anti*) with regards to their neighboring *para* group, which should result in a large $\Delta\nu$ value of the *meta* groups under slow-exchange conditions as experimentally observed. Interestingly, while this may be fortuitous, the "m" form, the structure with the lowest calculated energy and the major conformer in solution, is the one that appears twice in the crystalline unit cell (*vide supra*).

(b) Minor Conformer. Six signals were observed in the methyl carbon region of the minor conformer at 17.36, 16.91, 16.31, 15.13, 14.96, and 14.87 ppm, of approximately the same intensity. Assuming that these all belong to the same conformer, and that additional signals are hidden by the signals of the major conformer, the diastereotopicity of the ethyl groups suggests that they reside in different environments. For the assignment of this conformer we will assume, as observed for the major conformer, that the chemical shift of every methyl group is mainly sensitive to the conformation of the ring on which it is located, and that the orientation of the substituents in the distal ring has only a minor effect. Among the calculated low-energy forms, the NMR pattern of the minor form can be accounted by the "i", "j", and "f" forms since in these forms pairs of *o*-Me and *m*-Me groups are expected to be anisochronous (for example, the two *o*-Me groups of a given ring of conformer "f" are expected to possess different chemical shifts since one is *syn* while the second is *anti* to their respective vicinal *m*-Et groups). However, one would expect under our experimental conditions only five methyl signals for "f" since the configurations of the two subunits (13 and 35) are enantiomeric (cf. Figure 1) while the "i" and "j" forms should display a larger number of signals. The two latter forms are most likely indistinguishable under our experimental conditions since both possess identical (25-35) arrangements of ethyl groups in the pentaethylphenyl subunits. On the basis of these assumptions, the NMR pattern can be ascribed to either the "i" or "j" forms, or to a mixture of

Table 2. Dynamic NMR Data for Decaethylbiphenyl (**5**)

T (K)[a]	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})[b]
149.1	5	8.0 ± 0.2
166.7	80	8.1 ± 0.1
176.1	270	8.2 ± 0.1
187.5	700	8.4 ± 0.1
208.2	4500	8.6 ± 0.2

[a] Temperatures are believed to be accurate to ±0.5 K. [b] $\Delta H^{\ddagger} = 7 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9 \pm 5$ cal mol^{-1} K^{-1}.

both forms. These forms are present in the crystal structure of **5**. The intensity of the peaks in the ^{13}C NMR spectrum indicates that the minor conformer is some 200 cal mol^{-1} less stable than "m", in agreement with the MM3 calculations.[17]

Rotational Barrier of 5. We performed a full line shape analysis[18] of the ^{13}C NMR spectra in the 149−208 K range for two pairs of coalescing signals: the *meta* methyls and the *ortho* methylenes of the major conformer. Both gave identical rate constants at each temperature; the results are summarized in Table 2. The free energy of activation increased from *ca*. 8.0 to 8.6 kcal mol^{-1} in this temperature range, with a significant negative entropy of activation. This barrier is attributed to a rotational process of the ethyl groups since rotation about the Ar−Ar bond should display a significantly higher barrier.[19] The rotational barrier is ca. 4 kcal mol^{-1} lower than the one observed for **4** (12.5 kcal mol^{-1})[8] which was ascribed to rotation of the bromomethyl groups.

Internal Rotations of Pentaethylbenzene. Before analyzing the dynamic stereochemistry of **5**, it is convenient to analyze first the rotational interconversion graph of pentaethylbenzene, which can be considered as a subunit of **5**. This graph can be constructed by assuming that the rotations of the ethyl groups are noncorrelated (i.e., they proceed in a stepwise fashion) and that the rotational pathway of minimum energy involves only low-energy conformers with at most a single *syn* interaction. The resulting graph is shown in Figure 9, where the vertices represent the different conformations with at most one *syn* interaction, and the edges represent single ethyl rotations. Starting from the 135 conformer, rotation of one of the *ortho* ethyl groups will result in the formation of the 35 (or 13) isomer while the remainder stepwise rotations of the *meta* or *para* groups will result in systems with two *syn* interactions and therefore of high energy. The transformation of the 135 into the 25 (or 14) form requires two steps, while enantiomerization of the 35 and 25 forms requires two and four steps, respectively. Only for the 25/14 pair does rotation of the *para* ethyl group result in homomerization. This is the result of the arrangement of the pairs of *ortho* and *meta* ethyls, which disregarding the *para* ethyl, would be interchangeable by a C_2 axis. Since the two faces of the aryl ring are homotopic in the absence of the *para* group, rotation of this group by 180° results in homomerization.

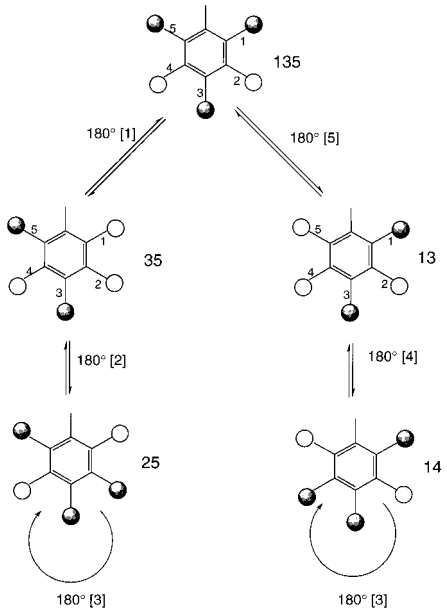

Figure 9. Conformational interconversion of a pentaethylphenyl system by stepwise (uncorrelated) rotations of the ethyl groups. Only conformations with at most one *syn* interaction are considered. The rotating ethyl groups are indicated in square brackets. The pathways 135 → 35 → 25 and 135 → 13 → 14 are enantiomeric.

Interconversion Graph of 5. As in the case of **6**, the rotational interconversion graph of **5** was constructed based on two assumptions: (i) all interconversions proceed by a single ethyl rotation and (ii) the rotational energy pathway does not involve conformers with more than one *syn* interaction per ring. The use of the configurational descriptors of the pentaethylphenyl subunits greatly facilitates the construction of the interconversion graph since rotation of an ethyl group in a given ring may change its configuration according to Figure 9, while the second ring must retain its configuration. The resulting graph has inversion symmetry and is depicted in Figure 10. Enantiomeric conformations are related by the inversion center in the graph. In contrast with **6**, a single *para*-ethyl rotation may never result in homomerization but in diastereomerization. This behavior can be easily rationalized, since in contrast to **6**, the formal removal of a *para* group does not result in a system of C_2 symmetry. On the other hand, rotation of the two *para* groups may result in homomerization. Examination of the graph shows that whereas a single *para*-ethyl group rotation may achieve enantiomerization of conformer "m", at least nine rotational steps are necessary for the enantiomerization of conformer "o".[20]

The energies of the different rotational pathways were calculated by using the "driver" option in the MM3 program and are displayed in Figure 10, where the numbers at the edges of the graph represent steric energies relative to the lowest energy conformation ("m"). The $C_{Me}-C-C_{Ar}-C_{Ar}$ torsional angle of a selected ethyl group was driven by 2° steps from +90° to −90°. In most cases, the clockwise and counterclockwise rotations of the group represent diastereomeric pathways,

(17) The methyl region of the slow-exchange ^{13}C NMR spectrum can be interpreted in a somewhat different fashion under two assumptions: (i) The NMR pattern of a pentaethylphenyl subunit is exclusively a function of the arrangement of its ethyls. If several conformations share identical arrangements of pentaethylphenyl subunits, these subunits are indistinguishable by NMR. Signals should be therefore ascribed to a given arrangement of the subunit (135, 14/25, or 13/35) rather than to a conformation of the biphenyl. (ii) The six low-intensity signals do not correspond to a single conformer. The four high-intensity methyl signals can be assigned to 14 and/or 25 subunit(s) on the basis of chemical shift arguments (see text). These signals have a significantly larger intensity than the rest and therefore it is necessary to assume that in the major conformer both rings adopt 14 and/or 25 conformations. On the basis of the MM3 calculations and the aromatic signal pattern (see text), it can be concluded that the major conformer is the "m" form. By exclusion, the six low-intensity methyl signals should correspond to subunits existing in the 135 and 25/35 configurations. The observed pattern may be the result of the superposition of the spectra of rings with 135, 25, and 35 configurations in the low-energy forms "i", "j", "f", and "a". This interpretation requires fortuitous similar intensities for the six low-intensity "composite" signals.

(18) The line shapes were calculated by using a program based on the equations given by: Sutherland, I. O. in *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Associated Press: London, 1971; Vol. 4, p 80.

(19) Smith, L. I.; Nichols, J. *J. Org. Chem.* **1941**, *6*, 489.

(20) For other examples of enantiomerizations by chiral pathways see: Mislow, K. *Science* **1954**, *120*, 232. Mislow, K.; Bolstad, R. *J. Am. Chem. Soc.* **1955**, *77*, 6712. See also: Mislow, K. *Chemtracts* **1989**, *2*, 155 and references therein.

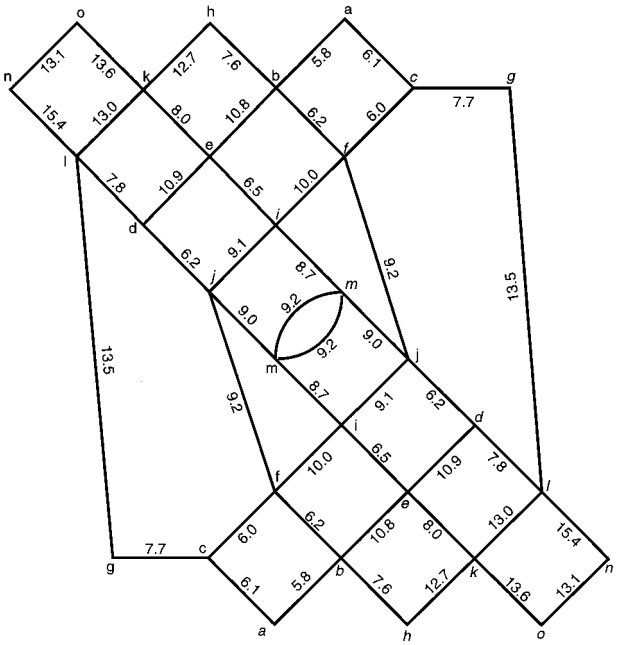

Figure 10. Interconversion graph and calculated (MM3) rotational barriers for **5**. The edges in the graph represent mutual isomerizations by single ethyl rotations. The letters a−o denote the different conformers (cf. Figure 3); enantiomeric structures are denoted by the same letters italicized. Steric energies relative to the lowest energy conformer for the different processes are denoted at the edges of the graph.

and only the calculated energy of the lower energy pathway is shown. In general, rotation of the *ortho*-ethyl groups has a lower barrier (in the 5.8−8.0 kcal mol^{-1} range) than the rotation of the *meta*- or *para*-ethyl groups. The rotational pathway preferred by the *ortho* groups involves their rotation through a transition state in which the methyl group and C_{ipso} are nearly eclipsed.

To characterize the rotational pathway followed in the dynamic NMR experiments it is necessary to identify the minimum energy pathway leading to topomerization of the system. Since according to the NMR data the preferred conformer is 14-25 ("m"), the possible rotational pathways starting from that form must be examined. Inspection of Figure 10 indicates that the minimum energy topomerization pathway may involve a three-step process m → i → j → *m* (which involves rotations of *meta* and *para* groups) with a barrier of 9.1 kcal mol^{-1} or simply a rotation of a *para* group (with a calculated barrier of 9.2 kcal mol^{-1}). Notably, this single rotation results in enantiomerization of the molecule by a chiral pathway.[20] The calculated barrier for this process (9.1−9.2 kcal mol^{-1}) is in satisfactory agreement with the experimental enthalpy of activation ($\Delta H^{\ddagger} = 7 \pm 1$ kcal mol^{-1}).

Experimental Section

X-ray data were measured on a PW1100/20 Philips Four-Circle Computer-Controlled Diffractometer. Mo K α (λ = 0.71069 Å) radiation with a graphite crystal in the incident beam was used. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis. After several cycles of refinements the positions of the hydrogen atoms were calculated and added to the refinement process. All crystallographic computing was done on a VAX 9000 computer using the TEXSAN structure analysis package.

Crystallographic data of 5: $C_{32}H_{50}$, space group P_1, a = 10.142(3) Å, b = 29.464(6) Å, c = 9.723(3) Å, α = 94.84(1)°; β = 91.01(2)°,γ = 83.68(1)°,V = 2877(1) Å^3, z = 4, ρ_{calc} = 1.00 g cm^{-3}, μ(Mo Kα) = 0.52 cm^{-1}, number of unique reflections = 8007, number of reflections with $I \geq 3\sigma_I$ = 4643, R = 0.092, R_w = 0.110.

NMR spectra were recorded on Bruker AM-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz) and DMX-600 (600.1 and 150.9 MHz, respectively) instruments. All chemical shifts are in ppm relative to internal TMS. Resolution enhancements were performed through the multiplication of the FID by a window function prior to Fourier transformation (an ascending exponential causing sharpening of the lines by 8 Hz, followed by a Gaussian centered at 20% of the acquisition window).

Decaethylbiphenyl (5). A solution of 10.7 g of biphenyl and 13 g of $AlCl_3$ in 100 g of EtCl was prepared in a flask equipped with an aqueous NaOH trap, in an ice−salt bath. After the initial vigorous HCl evolution subsided (*ca*. 6 h), the flask was left in a 4 °C cold room for 1 day, then worked up with dilute HCl and ether. ^{1}H NMR of the crude product showed that it was on the average pentaethylated. This material was therefore redissolved in 100 g of EtCl with 7 g of $AlCl_3$ and left in the cold room for 11 days (after 4 days, an additional 20 g of $AlCl_3$ was introduced). After workup, the organic phase (29.6 g of a brown oil) did not contain aromatic hydrogens, as judged by ^{1}H NMR. The crude material was purified by chromatography on a column of picric acid (4%)[21,22] on silica gel (eluent: hexane) followed by recrystallizations from ethanol. Yield (various crops): 13.8 g (46%) of white crystals, mp 103−104 °C. Anal. Calcd for $C_{32}H_{50}$: C, 88.41; H, 11.59. Found: C, 88.35; H, 11.46.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters for **5** and the resolution-enhanced 150.9-MHz ^{13}C NMR spectrum ($CDCl_2F$, 149 K) of the aromatic and methyl region of **5** (9 pages). See any current masthead page for ordering and Internet access instructions.

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