

and its oxygen atom substituents were located in the *E* map prepared from the phase set with the highest figure of merit. The positions of these three atoms were refined, with isotropic temperature factors, by full-matrix least-squares (based on *F*) to give values of the standard agreement factors where the weights, *w*, were initially assigned as unity.

$$R = \sum(|F_o| - |F_c|) / \sum|F_o| = 52.0\%$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 57.6\%$$

The function minimized in the least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ . A difference Fourier calculation next revealed the positions for all remaining non-hydrogen atoms. Refinement of these positions with isotropic temperature factors yielded the residuals *R* and *R<sub>w</sub>*, 10.5% and 11.4%, respectively. Further refinement of all non-hydrogen atoms with anisotropic librational parameters afforded the residuals *R* = 7.1% and *R<sub>w</sub>* = 14.4% where the weights are now defined as  $w = 1/\sigma(R_o)^2$  with  $\sigma(F_o)^2$  given by the expression  $[(\sigma(I)^2 + (pF_o)^2)]^{1/2}$  and  $p = 0.05$ . A difference Fourier map next revealed the positions of all 16 hydrogen atoms. All hydrogen atoms were assigned isotropic thermal parameters (4.0) which remained fixed during the remainder of the structure refinement. Least-squares treatment of the 15 non-hydrogen atoms (anisotropic librational parameters) along with the 16 hydrogen atom positions gave residuals *R* = 3.9% and *R<sub>w</sub>* = 7.8%. At this stage of the refinement three reflections with asymmetric backgrounds and five strong reflections suspected of counter flooding were rejected. Of the remaining 3120 reflections, 2790 reflections ( $I > 3\sigma(I)$ ) were used in the final least-squares treatment. After a statistical analysis of the weighting scheme the ignorance factor, *p*, was reset to 0.02. The final least-squares refinement (184 variables, 2790 observations) converged to *R* = 3.6% and *R<sub>w</sub>* = 5.6% with no parameter shifting by more than 0.05 times its estimated standard deviation in the final cycle. Examination of values *F<sub>o</sub>* and *F<sub>c</sub>* for several low order reflections showed no evidence of secondary extinction effects. The goodness of fit was 3.651. A final difference Fourier calculation was featureless showing only one significant peak (0.4 eÅ<sup>-3</sup>) near the sulfur atom. A plot of the function minimized vs.  $\sin \theta\lambda^{-1}$  showed no significant trends. Values of the neutral atom scattering factors were taken from the "International Tables for

X-Ray Crystallography". Effects of anomalous dispersion for all atoms were included with values of *f'* and *f''* taken from the "International Tables". Hydrogen atoms scattering factors were those of Stewart, Davidson, and Simpson. All programs used for structure solution and refinement were from the Enraf-Nonius Structure Determination Package.

**Single-Crystal X-ray Structure Determination of 7.** Crystals suitable for X-ray diffraction were grown from ethyl acetate/hexane. The crystal were monoclinic space group *P*2<sub>1</sub>/*n*, with *a* = 6.643 (1) Å, *b* = 22.695 (5) Å, *c* = 7.449 (2) Å,  $\beta$  = 99.99 (2)°, and *d<sub>c</sub>* = 1.383 g cm<sup>-3</sup> for *Z* = 4 (C<sub>11</sub>H<sub>18</sub>O<sub>3</sub>S, *M<sub>r</sub>*, 230.33). The crystal used for data collection was a colorless, transparent block measuring 0.40 × 0.35 × 0.35 mm. Excluding standards a total of 3564 measurements were obtained and the data analyzed as previously described. A plot of standard intensities showed a significant decay in the crystal during data collection, the maximum loss in intensity was 6.7%. The data were corrected for this decay. After rejection of 91 systematically absent reflections and averaging Friedel pairs, 3225 unique observations remained of which 2374 with  $I > 3\sigma(I)$  were used in the subsequent least-squares treatments. In the final cycle of refinement, 15 non-hydrogen atoms (anisotropic), 18 hydrogen atoms (isotropic), 209 variable, 2374 observations, converged to *R* = 3.6% and *R<sub>w</sub>* = 4.9% with no parameter shifting by more than 0.01 times its estimated standard deviation. The goodness of fit was 1.323. A final difference Fourier synthesis was featureless. A plot of the function minimized vs.  $\sin \theta\lambda^{-1}$  showed no significant trends.

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**Supplementary Material Available:** Tables of positional parameters and their esd's for **3b** and **7** (22 pages). Ordering information is given on any current masthead page.

## Conformations and Internal Mobility of Side Chains in Heterosubstituted Hexaalkylbenzenes. Isopropyl/Ethyl and Isopropyl/Cyclopropyl Systems

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Variable-temperature NMR spectra of hexaalkylbenzenes containing both isopropyl and ethyl or cyclopropyl groups, in conjunction with empirical force-field calculations, have shown that the alkyl groups in these heterosubstituted benzenes retain the conformation they individually adopt in the homosubstituted analogues: isopropyl groups maintain a bisected conformation, whereas ethyl or cyclopropyl groups adopt a perpendicular one. Two site-exchange processes have been observed in heterosubstituted benzenes containing vicinal isopropyl groups: a low-energy process, which leads to fast rotation of all alkyl groups *except* for the isopropyl groups, and a high-energy process that corresponds to the unfreezing of the gear-locked isopropyl groups. The magnitude of the barriers for both processes has been determined for 1,2-diethyl- and 1,2-dicyclopropyl-3,4,5,6-tetraisopropylbenzene and for 1,2-diisopropyl-3,4,5,6-tetracyclopropylbenzene.

Homosubstituted hexaalkylbenzenes of the type C<sub>6</sub>-(Cab<sub>2</sub>)<sub>6</sub> are found to follow two conformational patterns, conveniently characterized by the values of the a-C-C<sub>ar</sub>-C<sub>ar</sub> torsion angles ( $\theta$ ) as *perpendicular* ( $\theta = 90 \pm 30^\circ$ ) or *eclipsed* ( $\theta = 0 \pm 30^\circ$ ); the latter is also called *bisected* with reference to the bCb angles (Figure 1).<sup>2</sup> In the perpen-

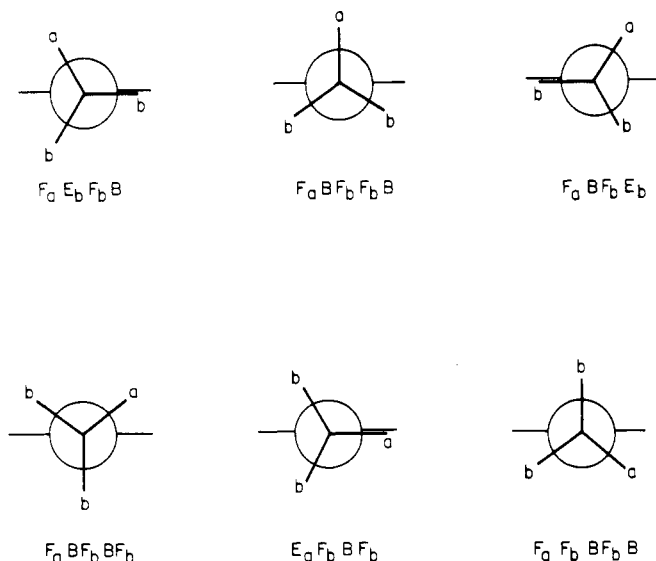
dicular conformation, exemplified by hexaethylbenzene (1)<sup>3</sup> and hexacyclopropylbenzene (2),<sup>4</sup> the Cab<sub>2</sub> groups are arranged so that the a's (atoms or groups) extend alternately above and below the plane of the benzene ring, and

(2) The descriptors in Figure 1 are adapted from the analogous scheme for ethane skeletons. See: Hounshell, W. D.; Dougherty, D. A.; Mislow, K. J. *Am. Chem. Soc.* **1978**, *100*, 3149.

(3) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. J. *Am. Chem. Soc.* **1981**, *103*, 6073.

(4) Bar, I.; Bernstein, J.; Christensen, A. *Tetrahedron* **1977**, *33*, 3177.

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**Figure 1.** Newman projections of  $Cab_2$  groups in alkylbenzenes. The projections indicate the range of values for the torsion angle  $\theta$  ( $a-C-C_{ar}-C_{ar}$ ) in the perpendicular conformation (top row,  $\theta = 90 \pm 30^\circ$ ) and eclipsed (or bisected) conformation (bottom row,  $\theta = 0 \pm 30^\circ$ ). Descriptors:<sup>2</sup> F = front, B = back, E = eclipsed.

the molecular conformation has approximate  $D_{3d}$  symmetry.<sup>5</sup> The bisected conformation is exemplified by hexaisopropylbenzene (3). In this molecule the isopropyl groups form a tightly interlocking tongue-and-groove arrangement that results in a structure with  $C_{6h}$  symmetry.<sup>6,7,8</sup> This statically gear-meshed conformation is extraordinarily rigid, with an isopropyl group rotation barrier of  $\geq 22$  kcal mol<sup>-1</sup>,<sup>8</sup> by comparison, for example, the calculated ethyl group rotation barrier in hexaethylbenzene is only 11.8 kcal mol<sup>-1</sup>.<sup>3</sup>

No hexaalkylbenzenes are known which contain isopropyl groups along with other  $Cab_2$  alkyl groups. The present work compares the static and dynamic stereochemistry of such systems with that of the homosubstituted analogs. We investigated two heterosubstituted systems,  $C_6(i-Pr)_n(Et)_{6-n}$  (isopropyl/ethyl) and  $C_6(i-Pr)_n(c-Pr)_{6-n}$  (isopropyl/cyclopropyl), and limited our experimental study to five substitution patterns:<sup>9</sup> one isomer of  $R_2R_4'$  and  $R_4R_2'$  in each system, plus one isomer of  $R_3R_3'$  in the isopropyl/cyclopropyl system (compounds 4–8 in Scheme I). These and additional structures were also studied by use of the empirical force-field method.

## Results and Discussion

**Synthesis.** The homosubstituted analogues (1, 2, and 3) were all prepared by transition-metal-catalyzed trimerization of the corresponding dialkylacetylenes.<sup>10</sup> The

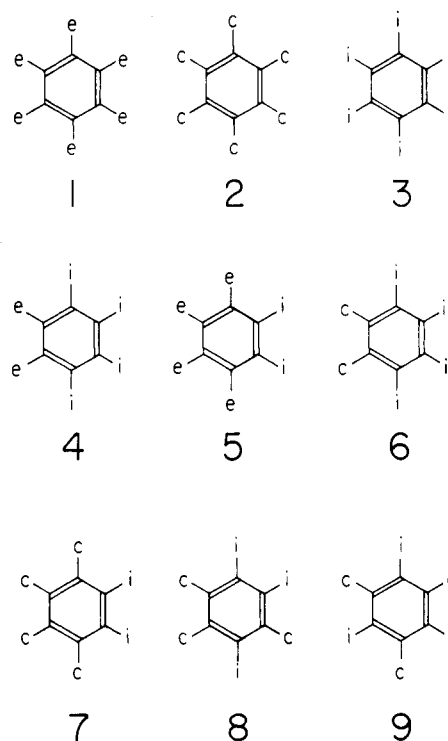
(5) The same conformation is adopted by  $C_6(CH_2X)_6$  derivatives such as hexakis(bromomethyl)benzene (Marsau, M. P. *Acta Crystallogr.* 1965, 18, 851) and MacNicol's hexahosts (MacNicol, D. D. In "Inclusion Compounds"; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 2, Chapter 5). However, as shown in the case of 1,  $\pi$ -complexation may lead to nonalternating conformations. See ref 3, and also: Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* 1982, 1, 448. Blount, J. F.; Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* 1984, 170.  
(6) (a) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* 1964, 86, 4729. (b) Bollinger, J. M. Ph.D. Dissertation, University of Pittsburgh, 1965.  
(7) Hopff, H. *Chimia* 1964, 18, 140. Hopff, H.; Gati, A. *Helv. Chim. Acta* 1965, 48, 509.

(8) Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* 1983, 105, 7763. Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *Ibid.*, in press.

(9) Eleven combinations are possible with two different alkyl groups:  $1 \times R_2R_4' + 3 \times R_4R_2' + 3 \times R_3R_3' + 3 \times R_3R_3' + 1 \times RR_5'$ .

(10) For reviews on the oligomerization of acetylenes, see: Bird, C. W. "Transition Metal Intermediates in Organic Synthesis"; Logos Press: London, 1967; Chapter 1. Yur'eva, L. P. *Russ. Chem. Rev. (Engl. Transl.)* 1974, 43, 48.

## Scheme I<sup>a</sup>



<sup>a</sup> e = ethyl; c = cyclopropyl; i = isopropyl.

same approach was employed in the synthesis of the heterosubstituted benzenes. Thus, cotrimerization of 3-hexyne and diisopropylacetylene in the presence of  $Hg[Co(CO)_4]_2$  yielded a mixture from which 1,2-diethyl-3,4,5,6-tetraisopropylbenzene (4) and 1,2-diisopropyl-3,4,5,6-tetraethylbenzene (5) could be isolated by HPLC. Similarly, 1,2-dicyclopropyl-3,4,5,6-tetraisopropylbenzene (6) and 1,2-diisopropyl-3,4,5,6-tetracyclopropylbenzene (7) were isolated from the mixture obtained by cotrimerizing dicyclopropylacetylene and diisopropylacetylene.<sup>11</sup>

Cotrimerization of symmetrically substituted acetylenes with  $Hg[Co(CO)_4]_2$  is capable of yielding only hexaalkylbenzenes in which like alkyl groups are arranged contiguously, as in 4–7; cyclotrimerization of an unsymmetrically substituted acetylene is required to produce a heterosubstituted benzene in which there is some alternation

(11) In an attempt to circumvent the need for separating cotrimerization mixtures, an alternative synthetic route was briefly explored. The Diels-Alder reaction of tetraisopropylcyclopentadiene with 3-hexyne and dicyclopropylacetylene should, in principle, yield 4 and 6 directly. An improved synthesis of this dienone, which had previously been obtained in 2% yield as one of the byproducts in the synthesis of 3,<sup>6</sup> was achieved by preparation of the tricarbonyliron complex<sup>12</sup> followed by decomplexation with trimethylamine oxide. However, although the dienone reacts with dimethyl acetylenedicarboxylate under mild conditions to give dimethyl 3,4,5,6-tetraisopropylbenzene-1,2-dicarboxylate, no 4 was obtained by reaction with 3-hexyne.<sup>14,15</sup> This approach was therefore abandoned.

(12) The synthesis of this complex was patterned after the reported synthesis of tricarbonyl(tetracyclopropylcyclopentadiene)iron by reaction of dicyclopropylacetylene with  $Fe_3(CO)_{12}$ .<sup>13</sup>

(13) (a) Usieli, V.; Victor, R.; Sarel, S. *Tetrahedron Lett.* 1976, 2705. (b) Victor, R.; Usieli, V.; Sarel, S. *J. Organomet. Chem.* 1977, 129, 387.

(14) More strenuous conditions are required for less reactive dienophiles. Thus, 1,2-diethyl-3,4,5,6-tetraphenylbenzene is formed by heating 3-hexyne with tetraphenylcyclopentadienone at 220 °C (Hübel, W.; Hoogzand, C. *Chem. Ber.* 1960, 93, 103). Under similar conditions, no trace of 4 was formed from 3-hexyne and tetraisopropylcyclopentadienone, while the latter suffered extensive decomposition.

(15) [4 + 2] cycloadditions are promoted by high pressures (Dauben, W. G.; Krabbenhoft, H. O. *J. Org. Chem.* 1977, 42, 282). However, no trace of 4 was formed when a mixture of 3-hexyne and the dienone was heated at 100 °C under a pressure of 6000 atm for 17 h. We thank Y. Okamoto, Polytechnic Institute of New York, for carrying out this experiment.

of the six substituents around the ring periphery. Trimerization of cyclopropylisopropylacetylene did indeed yield a mixture of 1,2,4-tricyclopropyl-3,5,6-triisopropylbenzene (8) and 1,3,5-tricyclopropyl-2,4,6-triisopropylbenzene (9). However, we were able to recover only 8 from this mixture.

**Side-Chain Conformations.** In mixed alkylbenzenes such as 4–9 there exists an intriguing possibility for conformational adaptation, i.e., for the imposition of a perpendicular conformation on isopropyl groups by ethyl or cyclopropyl groups in the same molecule, or, conversely, the imposition of a bisected conformation on ethyl or cyclopropyl groups by isopropyl groups in the same molecule. Alternatively, each group maintains its conformational integrity and behaves in the heterosubstituted system exactly as it does in the corresponding homosubstituted compound.

In the isopropyl/ethyl compounds 4 and 5, a structure in which all six alkyl groups adopt an alternating up-down conformation belongs to  $C_2$ . Such a structure is immediately ruled out by the room-temperature  $^{13}\text{C}$  NMR spectra, which feature six signals in the aromatic region of each compound. On the other hand, the spectra are compatible with a ground-state structure of  $C_s$  symmetry, in which all six alkyl groups adopt a bisected conformation, with adjacent isopropyls in a gear-meshed arrangement, or with time-average  $C_s$  symmetry, i.e., with rapid internal rotation of ethyl—but not isopropyl—groups on the NMR timescale. The latter alternative is supported by variable temperature NMR studies (see below), which show that ethyl group rotation is frozen out at low temperatures. Empirical force-field (EFF) calculations<sup>16</sup> provide corroborative evidence for a ground-state conformation of 4 in which the four isopropyl groups are gear-meshed as in 3, with  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}-\text{C}-\text{H}$  torsion angles deviating negligibly ( $< 10^\circ$ ) from  $0^\circ$ , while the two ethyl groups are arranged in trans fashion, with  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}-\text{C}-\text{H}$  torsion angles ca.  $105^\circ$ . It may be safely assumed that the alkyl groups in 5 are similarly disposed. We thus conclude that there is no evidence for conformational adaptation in these systems.

Conformational adaptation should be abetted in the isopropyl/cyclopropyl system by the electronic stabilization resulting from overlap of the cyclopropane ring orbitals and the benzene  $\pi$  orbitals. Such overlap is at a maximum in the bisected conformation, in which the cyclopropyl methine hydrogen lies in the benzene ring plane.<sup>20</sup> Accordingly, it might be expected that the two cyclopropyl groups in 6 would align themselves in the

manner of the isopropyl groups so as to yield a ground-state conformation of  $C_s$  symmetry in which all six methine hydrogens lie in the benzene plane. The room-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 6 show the nonequivalence of all six alkyl groups and the pairwise equivalences of the methyls and methylenes in each group. These observations are consistent with the picture developed above—but equally so with time-average  $C_s$  symmetry, i.e., with rapid internal rotation of cyclopropyl—but not isopropyl—groups on the NMR timescale. As in the case of 4 and 5, this last alternative is supported by variable-temperature NMR studies (see below) which show that cyclopropyl group rotation in 6 is frozen out at low temperatures. Thus, in complete analogy with 4, the four isopropyl groups in 6 are gear-meshed while the two cyclopropyl groups are arranged in trans perpendicular fashion. As in the case of 2, where, contrary to expectations,<sup>13a</sup> the cyclopropyl groups adopt a perpendicular conformation,<sup>4</sup> the electronic stabilization that might be gained in a bisected conformation is evidently insufficient to compensate for the destabilization that would result from steric repulsion by adjacent alkyl groups. The ground-state structure calculated for 6 by the EFF method also corresponds to the conformation described above.<sup>21</sup>

The room-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 7 provide a radically different picture: only one methyl and methylene group is in evidence, indicative of a structure with time-average  $C_{2v}$  symmetry in which all six alkyl groups undergo rapid internal rotation on the NMR timescale. This conclusion is supported by variable-temperature NMR studies (see below). EFF calculations indicate that the two isopropyl groups in the ground state of 7 are gear-meshed, while the four cyclopropyl groups are arranged in an alternating up-down fashion, with  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}-\text{C}-\text{H}$  torsion angles close to  $90^\circ$ .

The room-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 8 are compatible with the highest symmetry attainable,  $C_s$ . That this is a time-average symmetry is shown by variable-temperature NMR studies (see below) as well as by EFF calculations. According to these calculations, the ground-state adopts one of three asymmetric conformations differing by at most 1 kcal mol<sup>-1</sup> from one another; in all three the cyclopropyl groups are arranged in alternating up-down fashion and the isopropyl methine hydrogens are in the eclipsed conformation, with  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}-\text{C}-\text{H}$  torsion angles ranging from 9 to  $26^\circ$ .

In summary, variable-temperature NMR studies, in conjunction with EFF calculations, provide compelling evidence that conformational adaptation plays no significant role in the determination of ground-state structures

(16) Input geometries were based on standard bond lengths and bond angles. These structures were then optimized<sup>17</sup> by the program BIGSTRN-3<sup>18</sup> using the MM2 force field.<sup>19</sup> Final structures were characterized as minima by the absence of negative eigenvalues in the matrix of analytical second derivatives.

(17) Geometry optimizations were routinely begun with the variable-metric method and concluded with the full-matrix Newton-Raphson method; analytical second derivatives were used at both stages. The final convergence criteria for the Newton-Raphson stage were as follows: rms gradient less than  $10^{-6}$  kcal mol<sup>-1</sup> Å<sup>-1</sup> and rms atom movement less than  $10^{-6}$  Å.

(18) Nachbar, R. B., Jr.; Mislow, K., to be submitted to *QCPE*. A listing is available from the authors upon request.

(19) Allinger, N. L.; Yuh, Y. H. *QCPE* 1980, 13, 395. Two modifications for  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}$  bonds were  $l^\circ = 1.3937$  Å and  $k_s = 8.0667$  mdy Å<sup>-1</sup>. See also: Osawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* 1981, 103, 7475.

(20) According to semiempirical MO calculations, cyclopropylbenzene adopts a bisected ground-state conformation in which the planes of the two rings are orthogonal. See: Collet, G.; Leroy, G. *J. Chim. Phys.* 1974, 71, 1033. Sorriso, S.; Stefani, F.; Semprini, E.; Flamini, A. *J. Chem. Soc., Perkin Trans. 2* 1976, 374. See also: Parr, W. J. E.; Schaefer, T. *J. Am. Chem. Soc.* 1977, 99, 1033. Electron diffraction data for cyclopropylbenzene (Vilkov, L. V.; Sadova, N. I. *Dokl. Akad. Nauk SSSR* 1965, 162, 565) and a microwave study of *p*-cyclopropylbenzaldehyde (True, N. S.; Bohn, R. K.; Chieffalo, A.; Radhakrishnan, J. *J. Phys. Chem.* 1983, 87, 4628) leads to the same conclusion.

(21) The  $\text{C}-\text{C}_{\text{ar}}$  cyclopropane parameters needed for these calculations (1 stretch, 1 dipole, 3 bend, 9 torsion) were assumed to be the same as the corresponding  $\text{C}_{\text{alk}}-\text{C}_{\text{ar}}$  parameters furnished in the MM2 force field.<sup>19</sup> In its applications to the present study, this modified force field gave decidedly mixed results. On the one hand, agreement between the calculated structure ( $D_{3d}$ ) and the X-ray structure (site symmetry  $m$ )<sup>4</sup> of 2 was generally satisfactory: C-C bond lengths differed by 0.01 Å or less, except for  $\text{C}_{\text{ar}}-\text{C}$  (0.017 Å), C-C-C bond angles differed by 0.2° or less, except for  $\text{C}_{\text{ar}}-\text{C}-\text{C}$  ( $2.9^\circ$ ), and the calculated  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}-\text{C}-\text{C}$  torsion angle ( $55.6^\circ$ ) was in good agreement with the observed value of  $53.9^\circ$ . On the other hand, the calculated ground-state structure of cyclopropylbenzene was found to be perpendicular and to lie 1.9 kcal mol<sup>-1</sup> below the bisected conformation: complete neglect of orbital overlap in the parametrization of the force field thus leads to a reversal in the relative energies of the two conformations.<sup>20</sup> Because steric effects predominate in the crowded environment of the hexaalkylbenzenes, EFF calculations may therefore be taken as reasonably reliable indicators of ground-state conformations in isopropylcyclopropyl systems such as 6–9. However, such calculations cannot be used to gauge the relative energies of structures with different (perpendicular vs. bisected) cyclopropyl conformations, and their use in modeling dynamic processes involving cyclopropyl group rotation is therefore inadmissible.

Table I. Internal Rotation Barriers in Heterosubstituted Hexaalkylbenzenes

compd	process <sup>a</sup>	solvent	temp range, °C	nuclei observed in signal coalescence <sup>b</sup>	$\Delta G^\ddagger$ , kcal mol <sup>-1</sup> (temp, K)	method <sup>c</sup>
4	LE	C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub>	-90/50	<i>CH<sub>2</sub>CH<sub>3</sub></i>	11.9 ± 0.3 (253)	GH
	HE	C <sub>6</sub> D <sub>6</sub>	27/81	<i>CH<sub>2</sub>CH<sub>3</sub></i>	17.2 ± 0.3 (330)	LS
5	HE	C <sub>6</sub> D <sub>6</sub>	25/77	<i>CH<sub>2</sub>CH<sub>3</sub></i>	17.2 ± 0.3 (321)	GH
				<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	16.6 ± 0.3 (320)	LS
				<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	16.8 ± 0.3 (321)	GH
6	LE	CD <sub>2</sub> Cl <sub>2</sub>	-80/25	<i>CH(CH<sub>2</sub>)<sub>2</sub></i>	10.9 ± 0.5 (217)	GH
	HE	C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub>	40/100	<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	17.4 ± 0.3 (298)	LS
7	LE	CD <sub>2</sub> Cl <sub>2</sub> /CS <sub>2</sub> (1:1)	-100/-60	<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	17.7 ± 0.5 (348)	GH
				<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	9.9 ± 0.5 (203)	LS
	HE	CDCl <sub>3</sub>	-53/47	<i>CH(CH<sub>2</sub>)<sub>2</sub></i>	9.9 ± 0.5 (205)	GH
				<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	12.7 ± 0.3 (298)	LS
				<i>CH(CH<sub>3</sub>)<sub>2</sub></i>	12.1 ± 0.5 (260)	GH

<sup>a</sup> LE = low energy. HE = high energy. <sup>b</sup> Italicized. <sup>c</sup> LS = line-shape analysis. GH = Gutowsky-Holm approximation at the coalescence temperature.

in heterosubstituted C<sub>6</sub>(Cab)<sub>6</sub> hydrocarbons. Thus, isopropyl groups maintain a bisected arrangement,<sup>22</sup> whereas ethyl or cyclopropyl groups adopt a perpendicular conformation. Furthermore, vicinal isopropyl groups prefer a gear-meshed arrangement, as previously demonstrated for a variety of five-membered ring heterocycles<sup>23</sup> and other analogous systems,<sup>24</sup> while vicinal ethyl or cyclopropyl groups prefer a trans up-down arrangement. The generality of these conclusions is confirmed by additional EFF calculations on a variety of structures in the isopropyl/cyclopropyl system. Thus, in the ground state of 1-isopropyl-2,3,4,5,6-pentacyclopropylbenzene, the five cyclopropyl groups assume the alternating up-down conformation, with C<sub>ar</sub>-C<sub>ar</sub>-C-H torsion angles close to 90°, while the methine C-H bond deviates from the benzene plane by only 15°. In the ground state of 1-cyclopropyl-2,3,4,5,6-pentaisopropylbenzene, the C<sub>ar</sub>-C<sub>ar</sub>-C-H torsion angles are 89° for the cyclopropyl group and 19°, -10°, -1°, 4°, and 2° for the 2-, 3-, 4-, 5-, and 6-isopropyl groups, respectively. Finally, the ground state of 9 has C<sub>3</sub> symmetry, with C<sub>ar</sub>-C<sub>ar</sub>-C-H torsion angles of 88° and 15° for the cyclopropyl and isopropyl groups, respectively.

**Internal Mobility of Side Chains.** As noted above, rotation of ethyl or cyclopropyl groups is frozen out at low temperatures. In the case of 4, slowing the rotation of the ethyl groups lowers the effective molecular symmetry from C<sub>s</sub> to C<sub>1</sub>. As a result, isopropyl methyl and ethyl methylene protons, which are enantiotopic on the NMR time scale at room temperature, become diastereotopic at low temperatures. The spectrum becomes correspondingly more complex: disregarding accidental isochronies, the number of isopropyl methyl resonances doubles and the signals of the ethyl groups conform to an ABC<sub>3</sub> pattern. Similar observations are made for 6: at low temperatures, the number of isopropyl methyl and cyclopropyl methylene carbon resonances doubles, in accord with the desymmetrization from C<sub>s</sub> to C<sub>1</sub> that accompanies the freezing out of cyclopropyl group rotation. In both cases, the four isopropyl groups maintain their gear-meshed positions.

At elevated temperatures, a second process is observed in 4 and 6 which corresponds to internal rotation of the

isopropyl groups. This process increases the time-average symmetry from C<sub>s</sub> to C<sub>2v</sub>. As a result, the ethyl and cyclopropyl groups in 4 and 6, which are diastereotopic on the NMR timescale at room temperature, become homotopic at elevated temperatures; likewise, the two pairs of diastereotopic isopropyl groups in each molecule become homotopic. This high-energy process is observable in the pairwise collapse of the ethyl, cyclopropyl, and isopropyl NMR signals.

Barriers for the low-energy (LE) and high-energy (HE) processes are listed in Table I and are remarkably similar for both 4 and 6: 11–12 kcal mol<sup>-1</sup> for the LE and 17 kcal mol<sup>-1</sup> for the HE process. In the case of 4, the mechanism of the LE process quite possibly involves the intermediacy of an isomer in which the ethyl groups bear a cis relationship, and which is calculated<sup>16</sup> to lie only 1.6 kcal mol<sup>-1</sup> above the trans ground state. An analogous mechanism was previously found for the enantiomerization of 1,2-dineopentyl-3,4,5,6-tetramethylbenzene.<sup>25</sup>

By analogy with the mechanism of homomerization (automerization) established for 3,<sup>8</sup> it may be assumed that the mechanism of the HE process in 4 and 6 involves stepwise rotation of the four isopropyl groups.<sup>26</sup> Figure 2 depicts ten torsion isomers of 4 under conditions of rapid ethyl group rotation, the calculated relative energies for the trans isomer, the reaction graph for their interconversion, and a likely homomerization pathway for the HE process. As seen by inspection of Figure 2, and as previously noted in the case of 3,<sup>8</sup> the relative energies of the torsion isomers of 4 are a function of the number and types of unfavorable nonbonded interactions between adjacent non-gearing isopropyl groups. It may be assumed, by analogy with 3,<sup>8</sup> that homomerization proceeds by way of the lowest energy intermediates, i.e., via the pathway a → b → c → b → a.

As noted above, in 7 rotation of all six alkyl groups is rapid at room temperature on the NMR timescale. Lowering the temperature to -50 °C slows rotation of the isopropyl—but not cyclopropyl—groups, with a concomitant lowering of the time-average symmetry from C<sub>2v</sub> to C<sub>s</sub>. Consequently, the two pairs of homotopic cyclopropyl groups and the two homotopic isopropyl groups all become diastereotopic, as seen, for example, in the resonance doubling of the isopropyl methyl and methine proton NMR signals in CD<sub>2</sub>Cl<sub>2</sub>/CS<sub>2</sub> (1:1). Below -50 °C the iso-

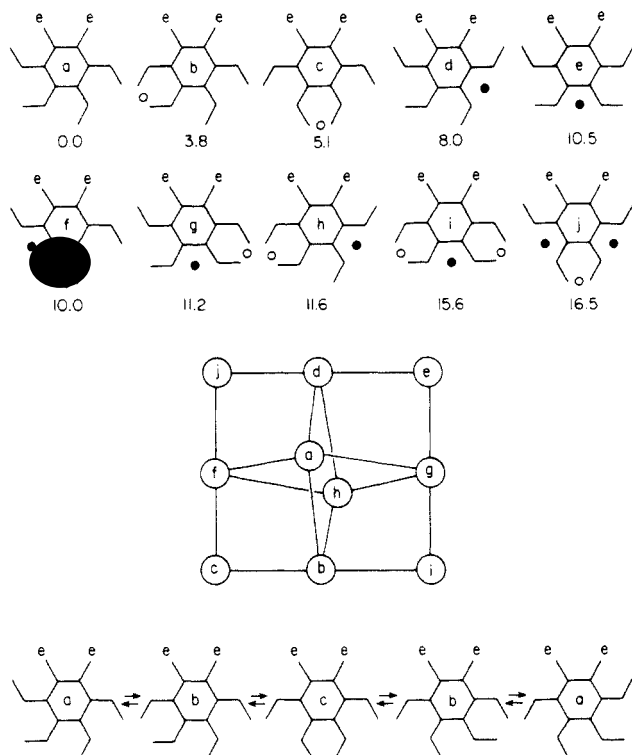
(22) According to EFF calculations,<sup>16</sup> isopropylbenzene adopts a ground-state conformation in which the methine hydrogen lies in the benzene plane. Electron diffraction data for isopropylbenzene (Vilkov, L. V.; Sadova, N. I.; Mochalov, S. S. *Dokl. Akad. Nauk SSSR* 1968, 179, 896) and a microwave study of para-substituted isopropylbenzenes (True, N. S.; Farag, M. S.; Bohn, R. K.; MacGregor, M. A.; Radhakrishnan, J. *J. Phys. Chem.* 1983, 87, 4622) lead to the same conclusion.

(23) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* 1985, 18, 80 and references therein.

(24) Static gearing has been observed in vicinal dichloromethyl groups. See: Mark, V.; Pattison, V. A. *Chem. Commun.* 1971, 553. Hutton, H. M.; Hiebert, W. E.; Mark, V. *Can. J. Chem.* 1978, 56, 1261.

(25) Iverson, D. J.; Mislou, K. *Organometallics* 1982, 1, 3 and references therein.

(26) It has previously been shown that stepwise rotation is the preferred mode of motion in other systems with vicinal isopropyl groups.<sup>23</sup> There is no evidence in support of the claim<sup>24</sup> that conformational processes in *o*-bis(dichloromethyl)benzenes involve correlated rotation (cogwheeling or dynamic gearing).



**Figure 2.** Top: schematic representation of ten torsion isomers of 1,2-diethyl-3,4,5,6-tetraisopropylbenzene (**4**) under conditions of rapid ethyl group rotation. Isomers are identified by the descriptors a–j. Relative energies are calculated for the trans isomer by the EFF method<sup>16</sup> and are in kcal mol<sup>-1</sup>. Symbols around the ring periphery are: e = ethyl group; <math>\langle</math> = disposition of the in-plane isopropyl C–H bond vector; <math>\circ</math> = interaction of two isopropyl methine hydrogens; <math>\bullet</math> = interaction of four isopropyl methyls. Center: reaction graph showing the interconversion of the ten torsion isomers of **4** by a mechanism involving the rotation of one isopropyl group at a time. Each such process is represented by one of the 16 edges of the graph. Bottom: a likely homomerization pathway for the HE process in **4**.

propyl methyl signals split again, and at  $-100$  °C four methyl doublets are observed. This is consistent with a process in which the rotation of all six groups is slow and the symmetry is lowered from  $C_s$  to  $C_1$ : under these conditions the enantiotopic isopropyl methyl and cyclopropyl methylene groups become diastereotopic.

Whereas the barrier for the LE process in **7**, 9.9 kcal mol<sup>-1</sup>, is only slightly lower than comparable barriers in **4** and **6** (Table I), the barrier for the HE process, 12.7 kcal mol<sup>-1</sup>, is substantially lower than the corresponding barriers in **4** and **6** (Table I). Considering that there is only a 0.6 kcal mol<sup>-1</sup> difference in barrier heights for the HE processes in **4** and **5** (Table I), the magnitude of the corresponding difference in barrier heights for **6** and **7**, 4.7 kcal mol<sup>-1</sup> (Table I), is also surprising.

The room-temperature <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **8** shows three different sets of isopropyl and cyclopropyl signals, but at  $-90$  °C the <sup>13</sup>C spectrum shows six isopropyl methyl and three isopropyl methine carbons. This observation is compatible with a lowering of symmetry from  $C_s$  to  $C_1$ . However, it was also observed that lowering the temperature sharpened two and broadened one of the three isopropyl methine proton resonances; this may be indicative of an exchange process involving another asymmetric isomer. As shown by the EFF calculations (see above), several such isomers may be present in comparable quantities.

In summary, the variable-temperature NMR studies reveal the operation of two processes. In the first, or LE, process, the asymmetric ground-state structures are con-

verted into nonrigid structures with time-average  $C_s$  symmetry; in the case of **9** this implies a change from  $C_3$  to  $C_{3h}$ . If the molecule contains adjacent isopropyl groups, a second, or HE, process occurs at higher temperatures, corresponding to the unfreezing of the gear-locked isopropyl groups; given the appropriate substitution pattern, as in **4–7**, this corresponds to a change from time-average  $C_s$  to time-average  $C_{2v}$  symmetry.

It remains to be pointed out that even in **4** and **6**, molecules that contain four contiguous isopropyl groups, the HE process requires less than 18 kcal mol<sup>-1</sup>. This is in contrast to the  $\geq 22$  kcal mol<sup>-1</sup> barrier observed for **3**.<sup>8</sup> Evidently, all six isopropyl groups are needed for the “cooperative nonbonded repulsions”<sup>6</sup> that place **3** in its unique position among hexaalkylbenzenes.

## Experimental Section

Solution 250.13-MHz <sup>1</sup>H and 62.83-MHz <sup>13</sup>C NMR spectra were recorded at ambient temperature on a Bruker WM-250 spectrometer. <sup>1</sup>H NMR spectra were also obtained on a JEOL FX-90Q spectrometer, with tetramethylsilane as an internal reference. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. Mass spectra were measured on an AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. High-performance liquid chromatography was done on a Waters Associates Prep LC/System 500 instrument using prepak 500 silica columns. Melting points were recorded on a Thomas Hoover melting point apparatus and are corrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**Tricarbonyl(tetraisopropylcyclopentadienone)iron.** A mixture of diisopropylacetylene<sup>6,27</sup> (1 g, 9.1 mmol) and Fe<sub>3</sub>(CO)<sub>12</sub> (ca. 1 g, 2 mmol) was heated in a sealed tube under argon at 176 °C for 2 h. The reaction product was extracted with chloroform. After removal of solvent, the residue (0.8 g) was chromatographed (preparative TLC, heptane/ether eluent) to give 0.34 g (19%) of the title compound: mp 112–115 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.36, 1.43 (dd, 24 H, CH<sub>3</sub>), 2.38, 2.94 (doublet of septets, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  20.98, 23.80, 24.18, 24.78, 25.75, 25.97 (CH(CH<sub>3</sub>)<sub>2</sub>), 91.36, 110.05 (ring carbons), 171.10, 209.72 (ketonic and metal carbonyl carbons); IR (CCl<sub>4</sub>) 1635 cm<sup>-1</sup> (ketonic carbonyl), 1950, 1980, 2000, 2050 cm<sup>-1</sup> (metal carbonyl).

Anal. Calcd for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>Fe: C, 61.87; H, 7.27; Fe, 14.38. Found: C, 62.69; H, 7.43; Fe, 14.51.

Reaction of the tricarbonyliron complex with dimethylamine oxide according to the general decomplexation procedure<sup>12</sup> gave tetraisopropylcyclopentadienone in 71% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.14, 1.21 (dd, 24 H,  $J = 7.0, 7.0$  Hz, CH<sub>3</sub>), 2.82 (overlapping septets); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  1.13, 1.22 (dd, 24 H, CH<sub>3</sub>), 2.77, 2.78 (doublet of septets, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>) (for CCl<sub>4</sub> ref 6b reports doublets centered at  $\delta$  1.13 and 1.21 and a multiplet at 3.24); IR (CCl<sub>4</sub>) 1695 cm<sup>-1</sup> (lit.<sup>6b</sup> 1696 cm<sup>-1</sup>).

**Dimethyl 3,4,5,6-Tetraisopropylbenzene-1,2-dicarboxylate.** A solution of tetraisopropylcyclopentadienone (0.10 g, 0.4 mmol) and dimethyl acetylenedicarboxylate (0.40 g, 2.8 mmol) in 5 mL of benzene was heated at reflux for 24 h. Evaporation of the solvent followed by trituration with methanol yielded white crystals (0.10 g, 67%), mp 147–148 °C after recrystallization from methanol: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.35 (overlapping doublets, 24 H,  $J = 7.25$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.05 (m, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.70 (m, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.82 (s, 6 H, COOCH<sub>3</sub>); mass spectrum (high resolution),  $m/e$  331.2257  $\pm$  0.0033 (331.2273 calcd for C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>). Anal. Calcd for C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>: C, 72.92; H, 9.39. Found: C, 73.40; H, 9.57.

**Cotrimerization of Diisopropylacetylene and 3-Hexyne.** A mixture of diisopropylacetylene<sup>6,27</sup> (6.0 g, 54.5 mmol), 3-hexyne (2.2 g, 26.8 mmol), and Hg[Co(CO)<sub>4</sub>]<sub>2</sub><sup>28</sup> (1.0 g, 1.83 mmol) was refluxed under an atmosphere of argon for 24 h. After an ad-

(27) See also: Courtneidge, J. L.; Davies, A. G.; Luszytky, E.; Luszytky, J. *J. Chem. Soc., Perkin Trans. 2* 1984, 155. For a more convenient synthesis of this acetylene, see ref 8, and also: Nicholas, K. M.; Siegel, J., *J. Am. Chem. Soc.* 1985, 107, 4999.

(28) Dighe, S. V.; Orchin, M. *Inorg. Chem.* 1962, 1, 965.

ditional 48 h of heating (bath temperature 110–120 °C), the unreacted acetylenes were removed by distillation and the residue was extracted with hexane. Evaporation of the extracts left a residue (6.0 g) which was chromatographed on silica gel, using hexane as eluent. The main fraction of the eluate ( $R_f$  0.6–0.8) consisted of a pale yellow solid which was washed with methanol to yield white crystals (3.5 g, 52%) of the cotrimerization mixture. The mixture was separated by HPLC, using hexane as eluent, into the two components described below.

**1,2-Diethyl-3,4,5,6-tetraisopropylbenzene (4)** has mp 148–150 °C after recrystallization from acetone:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.16, 1.21 (dt, 6 H,  $J = 7.46, 7.30$  Hz,  $\text{CH}_2\text{CH}_3$ ), 1.38, 1.39 (dd, 24 H,  $J = 7.28, 7.32$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 2.71, 2.80 (dq, 4 H,  $J = 7.47, 7.30$  Hz,  $\text{CH}_2\text{CH}_3$ ), 3.56–3.74 (m, 4 H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  16.02, 17.04 ( $\text{CH}_2\text{CH}_3$ ), 27.81, 28.13, 28.56, 28.73 ( $\text{CH}(\text{CH}_3)_2$ ), 22.49, 22.80, 22.98 (br) ( $\text{CH}_2\text{CH}_3$ ), 139.52, 140.05, 142.44, 143.34, 143.99, 144.20 (aromatic carbons); mass spectrum (high resolution),  $m/e$  302.2967  $\pm$  0.003 (302.2973 calcd for  $\text{C}_{22}\text{H}_{38}$ ).  
Anal. Calcd for  $\text{C}_{22}\text{H}_{38}$ : C, 87.42; H, 12.58. Found: C, 87.31; H, 12.11.

**1,2-Diisopropyl-3,4,5,6-tetraethylbenzene (5)** has mp 85–86 °C after recrystallization from methanol:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.15 (overlapping multiplets, 12 H,  $\text{CH}_2\text{CH}_3$ ), 1.38 (overlapping doublets, 12 H,  $\text{CH}(\text{CH}_3)_2$ ), 2.84 (q, 2 H,  $J = 7.22$  Hz,  $\text{CH}_2\text{CH}_3$ ), 2.65 (m, 6 H,  $\text{CH}_2\text{CH}_3$ ), 3.56, 3.70 (doublet of septets, 2 H,  $J = 7.35$  Hz,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  15.82, 15.82, 16.02, 17.15 ( $\text{CH}_2\text{CH}_3$ ), 21.50, 22.27, 22.90, 23.06,<sup>29</sup> 23.60 ( $\text{CH}_2\text{CH}_3$  and  $\text{CH}(\text{CH}_3)_2$ ), 28.79, 28.95 ( $\text{CH}(\text{CH}_3)_2$ ), 137.84, 137.95, 139.52, 140.15, 142.00, 143.02 (aromatic carbons); mass spectrum (high resolution),  $m/e$  274.2664  $\pm$  0.003 (274.2660 calcd for  $\text{C}_{20}\text{H}_{34}$ ).  
Anal. Calcd for  $\text{C}_{20}\text{H}_{34}$ : C, 87.59; H, 12.41. Found: C, 88.00; H, 11.91.

**Cotrimerization of Diisopropylacetylene and Dicyclopopylacetylene.** A mixture of diisopropylacetylene<sup>6,27</sup> (0.88 g, 8 mmol), dicyclopopylacetylene<sup>30</sup> (0.42 g, 4 mmol), and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ <sup>28</sup> (ca. 0.1 g) was heated at 120 °C under an atmosphere of nitrogen for 6 days. The reaction mixture was extracted with hexane and flash-chromatographed (silica). The first, yellowish band contained 0.30 g of the four possible trimerization products. This material was crystallized from cyclohexane to remove **2**, and the remaining mixture was separated by HPLC, using hexane as eluent, into the two components described below.

**1,2-Dicyclopopyl-3,4,5,6-tetraisopropylbenzene (6)** has mp 156–157 °C after recrystallization from methanol and acetone:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  0.42, 0.57, 1.01<sup>29</sup> (tm, 8 H,  $\text{CH}(\text{CH}_2)_2$ ), 1.32, 1.33,<sup>29</sup> 1.44 (td, 24,  $J = 7.37, 7.25, 7.21$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.92, 2.06 (dm, 2 H,  $\text{CH}(\text{CH}_2)_2$ ), 3.64,<sup>29</sup> 3.66, 4.34 (triplet of septets, 4 H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  10.91, 12.83 ( $\text{CH}(\text{CH}_2)_2$ ), 16.03, 17.75 ( $\text{CH}(\text{CH}_2)_2$ ), 22.88, 22.91, 23.23, 23.31 ( $\text{CH}(\text{CH}_3)_2$ ), 28.41,

28.83, 29.10, 30.13 ( $\text{CH}(\text{CH}_3)_2$ ), 143.53,<sup>29</sup> 143.75, 144.51, 145.51, 147.36 (aromatic carbons); mass spectrum (high resolution),  $m/e$  326.2962  $\pm$  0.003 (326.2973 calcd for  $\text{C}_{24}\text{H}_{38}$ ).

Anal. Calcd for  $\text{C}_{24}\text{H}_{38}$ : C, 88.27; H, 11.73. Found: C, 88.22; H, 11.83.

**1,2-Diisopropyl-3,4,5,6-tetracyclopopylbenzene (7)** has mp 121.5–122 °C after crystallization from methanol and acetone:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  0.41, 0.65, 1.03<sup>29</sup> (tm, 16 H,  $\text{CH}(\text{CH}_2)_2$ ), 1.41 (d, 12 H,  $J = 7.28$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.91, 2.05 (dm, 4 H,  $\text{CH}(\text{CH}_2)_2$ ), 4.01 (bm, 2 H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_2$ ) 10.49, 11.45 ( $\text{CH}(\text{CH}_2)_2$ ), 15.77, 17.49 ( $\text{CH}(\text{CH}_2)_2$ ), 23.04 ( $\text{CH}(\text{CH}_3)_2$ ), 29.96 ( $\text{CH}(\text{CH}_3)_2$ ), 141.76, 145.39, 145.93 (aromatic carbons); mass spectrum (high resolution),  $m/e$  322.2649  $\pm$  0.003 (322.2660 calcd for  $\text{C}_{24}\text{H}_{34}$ ).

Anal. Calcd for  $\text{C}_{24}\text{H}_{34}$ : C, 89.37; H, 10.63. Found: C, 88.98; H, 10.85.

**1,2,4-Tricyclopopyl-3,5,6-triisopropylbenzene (8).** Cyclopopylisopropylacetylene<sup>31</sup> (1.0 g, 9.3 mmol) was heated with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ <sup>28</sup> (0.1 g) for 48 h at 120 °C under an atmosphere of argon. The reaction mixture was diluted with hexane (20 mL), and the resulting suspension was filtered through a short silica column. There was thus obtained 0.24 g of a viscous, yellow oil which was separated by HPLC, using hexane as eluent. The main fraction, white crystals (0.20 g), was identified (GC-MS) as a 4:1 mixture of **8** and **9**. Recrystallization from acetone afforded 73 mg of **8**, mp 83–84 °C:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  0.47, 1.03 (dm, 12 H,  $\text{CH}(\text{CH}_2)_2$ ), 1.35, 1.45, 1.47 (td, 18 H,  $J = 7.31, 7.23, 7.29$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.88, 2.00, 2.12 (tm, 3 H,  $\text{CH}(\text{CH}_2)_2$ ), 3.71, 4.26, 4.40 (triplet of septets, 3 H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  11.23, 12.30, 12.44 ( $\text{CH}(\text{CH}_2)_2$ ), 15.00, 16.52, 16.57 ( $\text{CH}(\text{CH}_2)_2$ ), 22.36, 22.94, 23.36 ( $\text{CH}(\text{CH}_3)_2$ ), 29.69, 30.08, 30.71 ( $\text{CH}(\text{CH}_3)_2$ ), 142.30, 143.95, 145.55, 145.61,<sup>29</sup> 147.65 (aromatic carbons); mass spectrum (high resolution),  $m/e$  324.2793  $\pm$  0.003 (324.2817 calcd for  $\text{C}_{24}\text{H}_{36}$ ).

Anal. Calcd for  $\text{C}_{24}\text{H}_{36}$ : C, 88.82; H, 11.18. Found: C, 88.86; H, 11.23.

**Variable-Temperature NMR Measurements.** Variable-temperature  $^1\text{H NMR}$  spectra for **4** and **5** were recorded at 90 MHz on a JEOL FX-90Q spectrometer. For **7** and **8**, variable-temperature  $^1\text{H}$  and  $^{13}\text{C NMR}$  spectra were recorded at 250.13 and 62.83 MHz on a Bruker WM 250 spectrometer (5 mm o.d. sample tubes). Temperatures are considered accurate to  $\pm 2$  °C. Free energies of activation are listed in Table I and were calculated by use of the Gutowsky–Holm coalescence expression<sup>32</sup> or by line-shape analysis using the program DNMR3.<sup>33</sup> Solvent signals were used for the measurement of internal line-width parameters.

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