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Polyethylated Triptycene Derivatives

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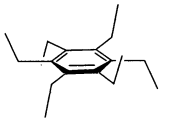
Abstract: The octaethyl triptycenes **7** and **8** were synthesized by Diels−Alder reaction of the octaethylanthracene **4** with the corresponding benzynes. Low-temperature NMR spectra of **7** and **8** are consistent with the presence of the fully alternated conformation "**a**" of C_2 symmetry. However, in the determined crystal structures, the compounds adopt a higher energy conformation with a pair of vicinal ethyls oriented in the same direction.

The ethyl substituent is the simplest alkyl group of nonconical symmetry. Systems possessing several ethyl groups attached to a central frame are of interest since they can be viewed as multiarmed organic compounds.[1,2] The most thoroughly studied compound of this class is hexaethylbenzene (**1**). As shown by Mislow and coworkers, in the lowest energy conformation of **1** the ethyl groups are perpendicular to the aryl plane and are arranged in a fully alternated up−down fashion.[3] In this arrangement, the three ethyls at the 1, 3, and 5 positions are oriented toward the same face of the aromatic ring (the three remaining ethyls are oriented toward the opposite face). This segregation of the ethyl groups has been utilized for the design of molecular hosts in which the three groups attached to the 1, 3, and 5 positions of a hexasubstituted benzene are oriented toward the same face of the aromatic ring in a convergent fashion.[4] In systems possessing two polyethylaryl subunits in steric proximity, the fully alternated arrangement of the arms may be perturbed to minimize repulsive steric interactions between ethyls attached to different aryl groups.



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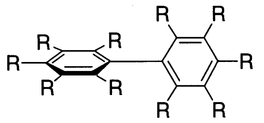
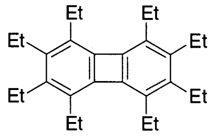


2 R = Et

We have previously described the preferred conformation and rotational barriers of compounds containing two polyethylated rings arranged in a perpendicular (e.g., **2**) or nearly coplanar fashion (**3**−**6**).[5] In this paper, we describe the preparation, the crystal structures, and rotational barriers of two polyethylated triptycene derivatives (**7** and **8**) with two tetraethylphenylene rings arranged in a V-shaped disposition.[6,7]



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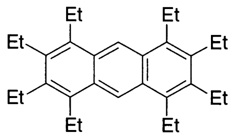

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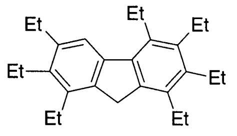

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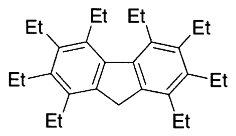

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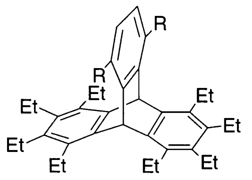

7 R = H
8 R = Me

Preparation of the Systems. The two triptycene derivatives **7** and **8** were prepared by Diels−Alder

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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. Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: Chichester, 1994; Chapter 10. See also: Metzger, J. V.; Chanon, M. C.; Roussel, C. M. *Rev. Heteroatom Chem.* **1997**, *16*, 1.

(3) (a) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. (b) Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 448. (c) Weissensteiner, W.; Gutierrez, A.; Radcliffe, M. D.; Siegel, J.; Siegel, M. D.; Tuohey, P. J.; Mislow, K. *J. Org. Chem.* **1985**, *50*, 5822. (d) 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. (e) For a recent paper on the stereodynamics of substituted benzenes structurally related to **1**, see: Kilway, K. V.; Siegel, J. S. *Tetrahedron* **2001**, *57*, 3615.

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(5) (a) Marks, V.; Gottlieb, H. E.; Biali, S. E. *J. Am. Chem. Soc.* **1997**, *119*, 9672. (b) Gottlieb, H. E.; Ben-Ari, C.; Hassner, A.; Marks, V. *Tetrahedron* **1999**, *55*, 4003. (c) Taha, M.; Marks, V.; Gottlieb, H. E., Biali, S. E. *J. Org. Chem.* **2000**, *65*, 8621. (d) Marks, V.; Gottlieb, H. E.; Melman, A.; Byk, G.; Cohen, S.; Biali, S. E. *J. Org. Chem*, **2001**, *66*, 6711.

(6) Very recently, the synthesis and molecular structure of dodecaphenyltriptycene has been reported (Lu, J.; Zhang, J.; Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 8035). For studies on additional polyphenyl organic compounds, see, for example: Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 741. Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1996**, *61*, 6748. Tong, L.; Lau, H.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 6000.

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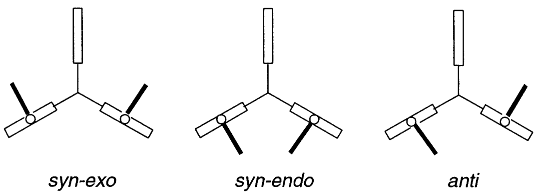
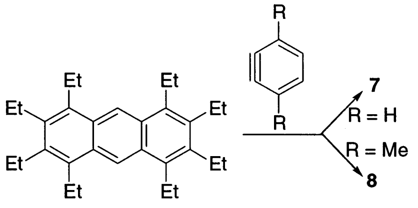
CHART 1



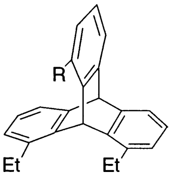
cycloaddition of benzyne or 3,6-dimethylbenzyne to 1,2,3,4,5,6,7,8-octaethylanthracene **4**,[5d,8] respectively (eq 1).



(1)

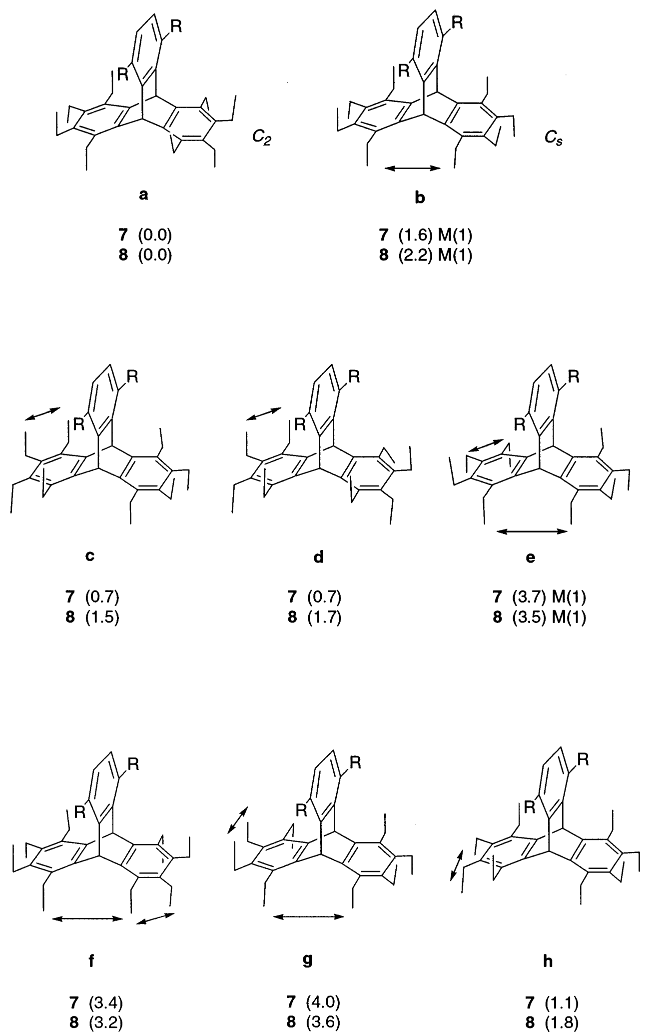
4

Static Stereochemistry of 7. Eight diastereomeric conformations are possible for the parent **1** which differ in the “up” or “down” arrangement of the ethyl groups.[3a] Molecular mechanics calculations performed on **1** have indicated that the relative steric energy of the conformers increases with the number of “syn” interactions, i.e., with the number of pairs of ortho ethyl groups pointing to the same face of the aromatic ring.[3a]



9 R = H
10 R = Me

To estimate the stereochemical consequences of the V-shaped disposition of the rings in **7** and **8** and the presence of methyl substituents in the latter compound on the preferred conformation of the ethyl groups, two simpler model systems were initially calculated (MM3 program): the diethyltriptycenes **9** and **10**. The two faces of a given ethylated ring of **9** and **10** are symmetry nonequivalent and assuming that in the lowest energy arrangements the ethyls are arranged in a perpendicular fashion, two achiral (syn-exo and syn-endo) and a chiral conformation (anti) are possible (Chart 1). If the two substituted rings were sterically isolated from each other (as observed for the parent **4**) it could be expected that the three conformations would possess similar energies. MM3 calculations performed on the model compound **9** indicate that the syn-endo arrangement (of C_s symmetry) corresponds to a saddle point lying 1.4 and 1.2 kcal mol^{-1} above the syn-exo and anti arrangements, respectively. For **10**, the syn-endo conformation of C_s symmetry is also a high-energy form, but the energy gaps relative to the syn-exo and anti forms are reduced to 0.9 and 0.6 kcal mol^{-1}. On the basis of these calculations it can be concluded that a syn-endo arrangement is intrinsically repulsive. The smaller energy gaps calculated for **10** are probably due to the repulsive interaction between the methyl and the proximal ethyl group(s) in the syn-exo and anti conformations.



a — **7** (0.0); **8** (0.0)
b — **7** (1.6) M(1); **8** (2.2) M(1)
c — **7** (0.7); **8** (1.5)
d — **7** (0.7); **8** (1.7)
e — **7** (3.7) M(1); **8** (3.5) M(1)
f — **7** (3.4); **8** (3.2)
g — **7** (4.0); **8** (3.6)
h — **7** (1.1); **8** (1.8)

FIGURE 1. Calculated (MM3) steric energies of selected conformers of **7** and **8**. Numbers in parentheses are energies relative to the lowest energy conformer. Double-headed arrows denote syn interactions between pairs of vicinal ethyls on the same ring or syn-endo interactions (cf. Chart 1). According to the calculations, conformations **b** and **e** of both **7** and **8** correspond to saddle points (one imaginary frequency).

Two conformations of **7** and **8** are possible in which the ethyls in each ring are arranged in a perfectly alternated up−down fashion (conformations **a** and **b**, Figure 1). MM3 calculations indicate that the C_2 form (**a**) is of lower energy. The C_s form is a saddle point in the potential energy surface that in **7** and **8** lies 1.6 and 2.2 kcal mol^{-1} above form **a**, respectively. The higher energy of form **b** can be rationalized, since in this conformation one syn-endo arrangement is present, whereas no such destabilizing arrangement is present in **a**.

Conformations possessing a pair of *o*-ethyl groups oriented in the same direction were also included in this study (forms **c**−**h**, Figure 1). Conformations **e**, **f**, and **g**

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(8) Takahishi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154.

(that in addition to the syn arrangement between a pair of *o*-ethyls possess also a syn-endo interaction) were substantially less stable, lying 3−4 kcal mol^{-1} above conformation **a**. Conformations **c**, **d**, and **h** on the other hand were only 0.69−1.13 (for **7**) and 1.47−1.75 (for **8**) kcal mol^{-1} less stable than **a**.[9]

NMR Spectra of 7 and 8. Triptycenes **7** and **8** displayed in the NMR spectra at room temperature a signal pattern consistent with fast ethyl rotations on the NMR time scale and with structures of dynamic C_{2v} symmetry. In both compounds, the methylene protons displayed in the ^{1}H NMR spectrum a signal pattern characteristic of the AB subspectrum of a ABX_3 system. As a result of the substitution pattern of the triptycene skeleton (only two rings are identically substituted), there is a single molecular mirror plane present that does not bisect any of the methylene groups, and these protons are diastereotopic even if the rotations of the side chains are fast on the NMR time scale.

Spectra consistent with slow ethyl rotation (on the NMR time scale) were observed in the ^{13}C NMR spectra at low temperatures (151 MHz, $T = 150$ K for **7**, 180 K for **8**). Under these conditions, four signals each were observed for the CH_2 and CH_3 groups of the ethyls, six signals for the aromatic carbons of the ethylated rings, but only a single bridgehead carbon signal (in the case of **8**, also a single methyl signal) and three aromatic signals for the nonethylated ring. Precluding accidental isochrony, these low-temperature spectra are consistent with a preferred conformation of either C_2 or C_s symmetry (with the C_2 axis or symmetry plane bisecting or perpendicular to the nonethylated ring, respectively). On the basis of the MM3 calculations, we assign the major conformer detected in solution to form "**a**" (Figure 1), that for both **7** and **8** was calculated as the conformer of lowest steric energy.

In the case of **7**, in addition to the major conformer, small signals were detected in the low temperature spectra. These signals were particularly visible near the 134 ppm region and are ascribed to low populated conformers of **7** (most likely, forms **c**, **d**, and **h**). For **8**, lowering the temperature resulted, in addition to the peak duplication described in the previous paragraph, in spectral changes (broadening of specific peaks and re-sharpening without a noticeable decoalescence) normally associated with the exchange with a "hidden partner".[10] This spectral behavior is obtained when the dynamic process mutually exchanges between two or more species involved in a strongly biased conformational equilibrium.[10] As in the case of **7**, we ascribe the low populated conformer(s) indirectly detected by the changes in the line shape to conformers **c**, **d**, **h**, their lower population in **8** (as compared to **7**) in agreement with the calculated energy gaps.

The rotational barriers of the ethyl groups of **7** and **8** were estimated from the temperature dependent ^{13}C NMR spectra. Because of the presence of minor conformers (vide supra), we could not perform exact line shape analyses; however, we estimate ethyl rotational barriers of 9.3 and 9.7 kcal mol^{-1} for **7** and for **8**, respectively. These barriers are similar to the ones previously measured for **3** and **4**.

Crystal Structures of 7 and 8. Although solution NMR data and/or calculations indicated that the lowest energy conformation of **3**, **5** and **6** is the fully alternated up−down form, the conformations adopted in the crystal possessed one or two syn arrangements between pair of ortho or peri ethyl groups.[5c,d] The adoption of the higher energy conformation was rationalized in terms of packing forces: for example, in the case of the crystal structure of **5**, the presence of three ethyl groups pointing to the same face of the aromatic ring rendered the opposite face more exposed, thus enabling a more dense packing of the molecules in the crystal.[5d]

To determine the crystal conformations of **7** and **8**, single crystals of the compounds were grown from acetonitrile and submitted to X-ray crystallography. Both derivatives adopted in the crystal the same conformation (**h**) possessing a syn arrangement between a pair of *o*-ethyl groups. As observed previously with other polyethyl systems, the crystal conformation is not the lowest in energy. Apparently conformations with a single syn interaction are adopted since they are energetically accessible (they lie less than 2 kcal mol^{-1} above the lowest energy conformer) and they allow for a more dense packing of the molecules in the crystal.

Experimental Section

NMR Spectroscopy. $CDCl_2F$ was prepared according to the literature.[11] Probe temperatures were measured with a calibrated digital thermometer.

Calculations. MM3(94) calculations were performed using the Alchemy 2000 program.[12,13] All stationary points were characterized as minima or saddle points by the number of imaginary frequencies in the frequency matrix.

Crystallography. Cu Kα ($\lambda = 1.541\,78$ Å) or Mo Kα ($\lambda = 0.710\,69$ Å) 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 7:** $C_{36}H_{46}$, space group P-1, $a = 10.444(2)$ Å, $b = 14.810(2)$ Å, $c = 9.779(1)$ Å, $\alpha = 98.69(2)°$, $\beta = 92.62(3)°$, $\gamma = 73.11(2)°$, $V = 1430.7(7)$ Å^3, $z = 2$, $\rho_{calc} = 1.11$ g cm^{-3}, μ(Mo Kα) = 0.62 cm^{-1}, no. of unique reflections = 4583, no. of reflections with $I \geq 3\ \sigma_I = 3095$, $R = 0.060$, $R_w = 0.086$. **Crystal data for 8**: $C_{38}H_{50}$, space group P-1, $a = 10.350(4)$ Å, $b = 16.650(5)$ Å, $c = 9.89(1)$ Å, $\alpha = 93.38(5)°$, $\beta = 112.04(6)°$; $\gamma = 77.05(3)°$; $V = 1539(2)$ Å^3, $z = 2$, $\rho_{calc} = 1.09$ g cm^{-3}, μ(Cu Kα) = 4.48 cm^{-1}, no. of unique reflections = 4564, no. of reflections with $I \geq 3\ \sigma_I = 3904$, $R = 0.053$, $R_w = 0.099$.

1,2,3,4,5,6,7,8-Octaethyltriptycene (7). A 0.5 g sample of 1,2,3,4,5,6,7,8-octaethylanthracene **4**[5d,8] (1.24 mmol) was dissolved in 3.75 mL of 1,2-dichloroethane, and to the solution were added benzediazonium-2-carboxylate hydrochloride[14] (0.35 g, 1.9 mmol) and propylene oxide (0.3 mL). The mixture was refluxed

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(9) Following the suggestions of one reviewer, we conducted fully optimized B3LYP/6-31G(d) calculations of conformers **a** and **h** of triptycene **7**. According to the DFT calculations the fully alternated conformation **a** is 1.0 kcal mol^{-1} lower in energy than conformation **h**, in full agreement with the MM3 calculations.

(10) 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. Biali, S. E.; Böhmer, V.; Cohen, S.; Ferguson, G.; Grüttner, C.; Grynszpan, F.; Paulus, E. F.; Thondorf, I.; Vogt, W. *J. Am. Chem. Soc.* **1996**, *118*, 12938.

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

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

(13) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(14) Adams, R.; Johnson, J. R.; Wilcox, C. F., Jr. *Laboratory Experiments in Organic Chemistry*, 6th ed., Macmillan: London 1970; p. 452.

for 1 h, and the solvents were evaporated. The residue was recrystallized from ethanol yielding 0.24 g (40%) of **7**, mp 209 °C. CI MS *m*/*z*: 479.1 (MH^+). ^1H NMR (600 MHz, $CDCl_3$, rt): δ 7.33, 6.93 (AA′BB′ pattern, 2H each), 5.90 (s, 2H), 2.98 and 2.88 (ABq of q, $J_{gem} = 14$ Hz, $J_{vic} = 7$ Hz, 4H each), 2.58 and 2.54 (ABq of q, $J_{gem} = 14$ Hz, $J_{vic} = 7$ Hz, 4H each), 1.26 (t, $J = 7$ Hz, 12H), 1.09 (t, $J = 7$ Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, rt): δ 147.32, 141.57, 135.88, 134.14, 124.80, 123.01, 47.39 22.37, 22.23, 16.23, 15.96 ppm.

Preparation of 1,2,3,4,5,6,7,8-Octaethyl-13,16-dimethyltriptycene (8). To a solution of **4** (0.21 g, 0.52 mmol) dissolved in 1.4 mL of 1,2-dichloroethane were added 3,6-dimethylbenzediazonium-2-carboxylate hydrochloride (0.11 g, 0.67 mmol, prepared from 3,6-dimethyl anthranilic acid,[15] according to the procedure in ref 14) and propylene oxide (0.12 mL). The mixture was refluxed for 7 days, and the solvent was evaporated affording (based on NMR analysis) a 1:1 mixture of the reactant and product (**8**). Flash chromatography (silica, eluent: petroleum ether 40−60 °C) afforded **4** (0.09 g) and **8** (0.11 g, 67% based upon the recovered reactant), mp 232 °C (recrystallized from ethanol). CI MS *m*/*z*: 507.4 (MH^+). ^1H NMR (600 MHz, $CDCl_3$, rt): δ 6.74 (s, 2H), 6.20 (s, 2H), 2.99 and 2.88 (ABq of q, $J_{gem} = 14$ Hz, $J_{vic} = 7$ Hz, 4H each), 2.63 and 2.58 (ABq of q, $J_{gem} = 14$ Hz, $J_{vic} = 7$ Hz, 4H each), 2.52 (s, 6H) 1.22 (t, $J = 7$ Hz, 12H), 1.10 (t, $J = 7$ Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, rt): δ 144.85, 141.95, 136.88, 134.93, 129.28, 126.85, 43.87, 22.68, 22.37, 18.85, 16.99, 16.24 ppm.

Acknowledgment. We thank Dr. Shmuel Cohen for the crystal structure determinations and the USA−Israel Binational Science Foundation for support of this work.

Supporting Information Available: ^1H and ^{13}C NMR spectra and assignments, final calculated (MM3) coordinates of conformations **a**−**h**, ORTEP drawings of the crystal conformations of **7** and **8** and crystallographic data (cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

JO026206V

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[15] Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195.