the anthracene from its position above the iron.

In addition to His E7, there are in Hb and Mb Phe CD1 and Val E11 flanking the histidine and presenting a peripheral steric effect to the larger isocyanide ligands. These distal groups introduce steric effects on *n*-butyl and *tert*-butyl isocyanides which are rather similar to that found in **1**.

These results indicate that strong CO-binding hemoproteins such as R-state hemoglobin or isolated hemoglobin chains behave like unhindered model compounds with respect to the binding of small ligands such as CO or O_2[2b,13] and thus do *not* possess the distal face steric strain which has been attributed to them.[3,4] Larger ligands encounter steric effects in all hemoproteins, and small ligands encounter steric effects[17] in the more restricted pockets of Mb[13] and peroxidases.

Comparisons of unhindered model compounds with presumably hindered hemoproteins in the preceding paper suggested that distal side steric effects appear only in the association rates. This conclusion is supported by the observations that the 10^4 reduction in TMIC binding to the 6,6-cyclophane **1** is due to a 10^4 reduction in association rates, and the 700-fold reduction in CO binding comes from a 400-fold decrease in association rates. We propose that the conformational flexibility in the anthracene bridge is a unique feature which allows it to model both the static and dynamic aspects of distal side effects in hemoproteins.

Acknowledgments. This work was supported by National Institutes of Health Grant HL-13581 (T.G.T.).

T. G. Traylor,* D. Campbell, S. Tsuchiya, M. Mitchell
D. V. Stynes[20]
Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

Received March 24, 1980

Enantiomerization Trends in 1,8-Bis(trimethylelement)naphthalenes

Sir:

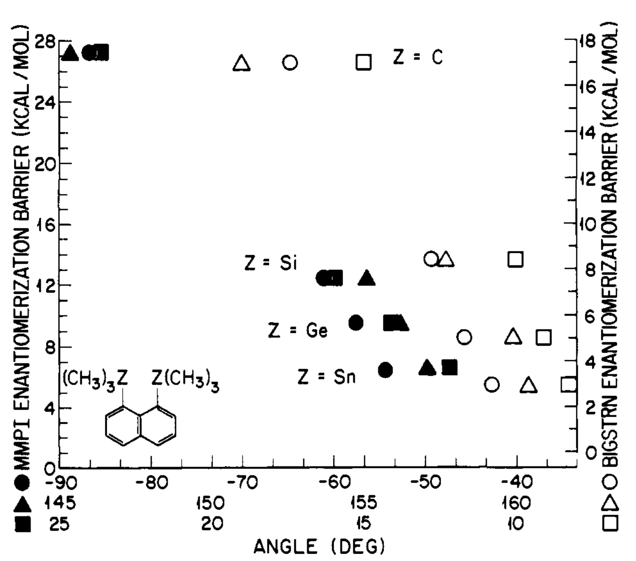
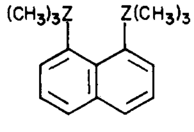
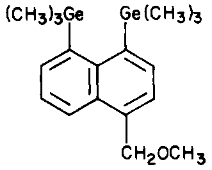


Figure 1. Enantiomerization barriers of 1,8-bis(trimethylelement)-naphthalenes calculated with MMPI (solid symbols, left ordinate) and BIGSTRN (open symbols, right ordinate) as a function of Z1–C1–C8–Z2 (circles), Z1/2–C1/8–C4/5 (triangles), and C1/8–C9–C10–C4/5 (squares).

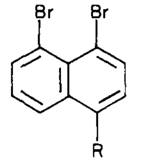
As attested by numerous examples in the literature, close proximity of substituents in the 1,8 (peri) positions of naphthalene often results in out-of-plane deformations, and in a pronounced warping of the molecular skeleton.[1] Particularly striking in this regard are the 1,8-bis(trimethylelement)naphthalenes,[2-10] where repulsion between the peri $(CH_3)_3Z$ (Z = C, Si, Ge, Sn) substituents leads to highly distorted, chiral structures[3,4,9] in which the $(CH_3)_3Z$ groups are displaced to opposite sides of the mean naphthalene plane. However, energy requirements for the interconversion of the enantiomers have thus far remained unknown, though NMR evidence suggests a barrier greater than ca. 24 kcal/mol for 5-benzyl-1,3,8-tri-*tert*-butylnaphthalene.[3] We now report the results of empirical force field (EFF) calculations for 1,8-bis(trimethylelement)naphthalenes **1–4**, which predict a marked dependence of barrier heights on Z, and the experimental determination of an enantiomerization barrier for 1,8-bis(trimethylgermyl)-4-methoxymethylnaphthalene (**5**), which confirms the reliability of values predicted for **3**.



1, Z = C
2, Z = Si
3, Z = Ge
4, Z = Sn



5



6a, R = CH_3
6b, R = CH_2Br
6c, R = CH_2OCH_3

Calculations were performed with the programs BIGSTRN[11] and MMPI,[12] employing previously described approximations.[8,9] Among various reasonable transition state structures explored, the C_s structure in which two of the methyl groups eclipse the naphthalene ring was found to be the lowest in energy for all of the compounds in this series. All structures were optimized with both force fields, the ground states without constraint and the transition states under the constraint of C_s symmetry.

As depicted in Figure 1, the enantiomerization barriers calculated[13] for **1–4** with BIGSTRN and MMPI[14-16] show a direct correlation with the extent of molecular distortion in the ground

---

(1) For a review, cf.: Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567. For recent examples, see: Einspahr, H.; Robert, J.-B.; Marsh, R. E.; Roberts, J. D. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1611. Robert, J.-B.; Sherfinski, J. S.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1152, and references therein. Martin, R. H. *Angew Chem., Int. Ed. Engl.* **1974**, *13*, 649, and references therein. Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *Ibid.* **1976**, *41*, 3603. White, D. N. J.; Carnduff, J.; Guy, M. H. P.; Bovill, M. J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2986. Schweizer, W. B.; Procter, G.; Kaftory, M.; Dunitz, J. D. *Helv. Chim. Acta* **1978**, *61*, 2783. Herbstein, F. H. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1661. Weber, L. D.; Tulinsky, A. *Ibid.* **1980**, *36*, 611, and references therein.

(2) Franck, R. W.; Leser, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 1577; *J. Org. Chem.* **1970**, *35*, 3932.

(3) Anderson, J. E.; Franck, R. W.; Mandella, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 4608.

(4) Handal, J.; White, J. G.; Franck, R. W.; Yuh, Y. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 3345; *Ibid.* **1979**, *101*, 5456.

(5) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *141*, 173.

(6) Wroczynski, R. J.; Baum, M. W.; Kost, D.; Mislow, K.; Vick, S. C.; Seyferth, D. *J. Organomet. Chem.* **1979**, *170*, C29.

(7) Cozzi, F.; Sjöstrand, U.; Mislow, K. *J. Organomet. Chem.* **1979**, *174*, C1.

(8) Hutchings, M. G.; Watt, I. *J. Organomet. Chem.* **1979**, *177*, 329.

(9) Blount, J. F.; Cozzi, F.; Damewood, J. R., Jr.; Iroff, L. D.; Sjöstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99.

(10) Anet, F. A. L.; Donovan, D.; Sjöstrand, U.; Cozzi, F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 1748.

(11) Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168; Andose, J. D. et al. *QCPE* **1978**, *11*, 348. A corrected value of –25.92 kcal/mol was used for the C_{ar}–C_{ar}–C_{ar}–C_{ar} torsion parameter.

(12) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893; Allinger, N. L. et al. *QCPE* **1976**, *11*, 318.

(13) All enantiomerization barriers calculated in this work represent differences in steric energies of ground and transition states.

(14) The activation energy of 18.5 kcal/mol previously calculated[4] with MMPI for the enantiomerization of **1** stands in contrast to the barrier of 27.2 kcal/mol calculated for **1** with MMPI in the present work.[13] The former value was reported[4] as the difference in the enthalpy of formation between ground and transition states. Unfortunately, enthalpies of formation of compounds containing a naphthalene nucleus cannot be calculated by means of the available program,[12] though the procedure for doing so has been outlined in general terms.[15] We are therefore unable to reconcile these two results.[16]

(15) Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.

(16) We are informed that the value of ΔH_f for **1** reported in ref 4 was calculated with a modified version of MMPI (Allinger, N. L.; personal communication).

0002-7863/80/1502-5941$01.00/0

state, as measured by the Z1–C1–C8–Z2, C1/8–C9–C10–C4/5, and Z1/2–C1/8–C4/5 angles.[17] Although the magnitudes of the calculated barriers prove to be force field dependent, the direction of the trend is unambiguous: the barriers decrease in the order **1** ≫ **2** > **3** > **4**, i.e., in the same order as the skeletal deformations in the ground state.[9]

Our calculations indicated that enantiomerization of **2**–**4** takes place on the NMR timescale, in marked contrast to **1**, which should be resolvable. To test this prediction, we undertook a variable temperature NMR study of **5**, a derivative of **3**. The synthesis of this compound was accomplished by the following route.[18] Conversion of 1,8-diamino-4-methylnaphthalene[19] under Sandmeyer conditions[5] gave **6a** (25%), mp 55–57 °C, after column chromatography on silica (hexane). Bromination with purified NBS (1 equiv in refluxing CCl_4, 3 h) to **6b** (mp 111–113 °C) followed by methanolysis (5.0 equiv of $NaOCH_3$ in refluxing methanol, 3 h) yielded **6c** (70%, mp 43–45 °C). Reaction of freshly sublimed **6c** with n-C_4H_9Li (3 equiv, 0 °C, 1 h) followed by addition of trimethylchlorogermane (3 equiv, room temperature, 3 h) afforded **5** as a yellow oil (62%) after column chromatography on silica (ether/petroleum ether). The product was further purified by high-pressure liquid chromatography: ^1H NMR δ ($CDCl_3$) 0.4 (s, 18 H, CH_3Ge), 3.5 (s, 3 H, CH_3O), 4.8 (s, 2 H, CH_2), 7.3–8.0 (m, 5 H, aromatic); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) 3.2 (CH_3Ge), 58.4 (OCH_3), 73.5 (CH_2), 123.9, 124.6, 124.9, 134.6, 135.0 (aromatic CH).

The 396 MHz ^1H NMR spectrum of **5** in a 2:1 mixture of CHF_2Cl/CF_2Cl_2 containing 5% benzene-d_6 features a single line in the methylene region which broadens below ca. −100 °C and gives a clearly resolved AB quartet at −133 °C. The coalescence temperature for the central two lines is −122 °C. The chemical shift difference between the methylene protons at −133 °C is 17 Hz (0.043 ppm), and $|J_{AB}|$ = 10.5 Hz. The rate constant for exchange at −122 °C was calculated[20] to be 30 s^{-1}, and $\Delta G^{\ddagger}$ for enantiomerization of **5** is therefore 7.5 ± 0.1 kcal/mol. It is noteworthy that attempts to observe this dynamic NMR effect at a frequency of 270 MHz failed since only line broadening could be observed.[21]

The value of $\Delta G^{\ddagger}$ found for **5** falls between the barrier heights of 5.0 and 9.5 kcal/mol calculated for **3** (Figure 1). That the presence of the 4-methoxymethyl group in **5** leads to a slight increase in $\Delta G^{\ddagger}$ relative to **3** is suggested by enantiomerization barriers of 6.7 and 11.8 kcal/mol calculated for 1,8-bis(trimethylgermyl)-4-ethylnaphthalene, using BIGSTRN and MMPI, respectively. Calculated and experimentally determined barriers are thus in satisfactory agreement.

The present study demonstrates once again the usefulness of EFF calculations in the prediction of stereodynamic timescale domains, and hence in the selection of appropriate methods and conditions for the measurement of barrier heights.[22]

Acknowledgments. We thank the National Science Foundation (CHE 77-07665 and CHE 78-23858) for support of this work and the Swedish Natural Research Council for a postdoctoral fellowship to one of us (U.S.).

W. Douglas Hounshell*
Department of Chemistry, Wake Forest University
Winston-Salem, North Carolina 27109

Frank A. L. Anet*
Deparment of Chemistry, University of California
Los Angeles, California 90024

Franco Cozzi, James R. Damewood, Jr.
Constance A. Johnson, Ulf Sjöstrand, Kurt Mislow*
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received May 12, 1980

---

(17) The three parameters reflect the pyramidality at the C1/8 center and the twist about the C9–C10 axis.[9] The notation C1/8–C9–C10–C4/5 represents the average of the symmetry-related angles C1–C9–C10–C4 and C8–C9–C10–C5; similarly, Z1/2–C1/8–C4/5 represents the average of Z1–C1–C4 and Z2–C8–C5 (the numbering scheme is as given in ref 9).

(18) All new compounds gave elemental analyses, NMR, and mass spectra consistent with the assigned structures.

(19) Thompson, H. W. *J. Chem. Soc.* **1932**, 2310.

(20) The rate constant at coalescence was calculated by means of a computer program based on the equations for a mutually exchanging AB system: Alexander, S. *J. Chem. Phys.* **1962**, *37*, 967. The line width in the absence of exchange increases as the temperature is lowered and was estimated to be about 3 Hz at −122 °C. The uncertainty in $\Delta G^{\ddagger}$ includes the uncertainty in this line width and in the temperature (±1 °C).

(21) The calculated AB spectrum at 270 MHz has the two inner lines separated by only 5.1 Hz (vs. 9.5 Hz at 396 MHz), and the intensity ratio of inner to outer lines is 5 (vs. 3 at 396 MHz). As a result, the exchange rate constant which leads to coalescence is smaller at 270 MHz than it is at 396 MHz. Since the line width in the absence of exchange increases steadily as the temperature is decreased, it is not surprising that a resolved AB spectrum is not observed at 270 MHz.

(22) For another recent example, see: Hayes, K. S.; Nagumo, M.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2773.

Conformational Variability in Hexaethylbenzene π-Complexes. Crystal and Molecular Structure of Tricarbonyl(hexaethylbenzene)chromium(0) and Dicarbonyl(hexaethylbenzene)(triphenylphosphine)-chromium(0)

Sir:

Although much interest in the stereochemistry of arene transition metal π-complexes has focused on studies of rotational barriers and conformational preferences about the metal–arene bond,[1] little consideration has been given to possible conformational changes in the coordinated arene. We now report evidence for a remarkable change in the conformation adopted by the hexaethylbenzene ligand in $(C_6Et_6)Cr(CO)_3$ (**1**) upon substitution of one of the carbonyl ligands by triphenylphosphine.

Crystals of **1**, grown from heptane solution, are monoclinic, space group $P2_1/n$. Ultraviolet irradiation of a heptane solution of **1** in the presence of an excess of triphenylphosphine yields an orange-yellow precipitate of $(C_6Et_6)Cr(CO)_2PPh_3$ (**2**). Crystals of **2**, grown from benzene/heptane solution, are triclinic, space group $P\bar{1}$. Stereoviews of the X-ray structures of **1** and **2** are shown in Figures 1 and 2.[2]

The ligated hexaethylbenzene in **1** closely resembles the ground state conformation of the free arene (which has D_{3d} symmetry[3]), including the alternation of the ethyl groups above and below the mean plane of the benzene ring.[4,6] In striking contrast, all six ethyl groups in **2** are on the side of the benzene ring remote from the metal; a maverick ethyl group is found on the other side in roughly one third of the molecules, as a disorder in the crystal.

---

(1) See: Albright, T. A.; Hofmann, P.; Hoffman, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546, and references therein.

(2) Crystallographic data for **1**: a = 14.156 (6), b = 16.734 (4), c = 9.103 (3) Å; β = 106.21 (2)°; Z = 4; R = 0.045, R_w = 0.051 for 2417 reflections with $I > 2.5\sigma(I)$. **2**: a = 8.911 (3), b = 9.489 (3), c = 21.665 (7) Å; α = 81.06 (2), β = 80.33 (2), γ = 65.89 (2)°; Z = 2; R = 0.052, R_w = 0.061 for 3877 reflections with $I > 2.5\sigma(I)$. Intensity data were measured on a Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). Reflections were measured for $\theta < 57°$, and data were corrected for absorption. The structures were solved by the heavy atom method and were refined by full matrix least squares, with anisotropic thermal parameters for the heavier atoms and isotropic temperature factors for hydrogen atoms.

(3) Pal, H. K.; Guha, A. C. *Z. Kristallogr.* **1935**, *A92*, 392. Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338.

(4) This result was anticipated by solid-state NMR studies on **1**, which led to an assignment of C_{3v} symmetry.[5]

(5) Maricq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 6902.

(6) In the conformation of the isoelectronic tricarbonyl(hexaethylborazine)chromium(0), the alternation described for **1** is interrupted by one of the N-ethyl groups, presumably as a result of borazine ring puckering in the complex.[7]

(7) Huttner, G.; Krieg, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 512. *Chem. Ber.* **1972**, *105*, 3437.

0002-7863/80/1502-5942$01.00/0