Crystal Structure and Rotational Barrier of Octakis(bromomethyl)naphthalene

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Received August 22, 2002

Abstract: Octakis(bromomethyl)naphthalene (**4**) adopts in the crystal a chiral conformation with a helical central naphthalene core and the bromomethyl groups disposed in an alternate up−down "in" arrangement. According to MM3 calculations, this conformation is less stable than the corresponding all alternated "out" form, while B3LYP/LANL2DZ calculations suggest the opposite stability order. The topomerization barrier (16.0 kcal mol^{-1}) is ascribed to an enantiomerization process requiring 180° rotation of all the bromomethyl groups and reversal of the helical sense of the naphthalene core.

Two of the simplest substituents of stereochemical interest are the bromomethyl and ethyl groups.[1−3] When attached to an aromatic ring, ethyl and bromomethyl groups prefer a perpendicular (i.e., with Br−CH$_2$−C$_{Ar}$−C$_{Ar}$ torsional angles equal to ca. ±90°) arrangement over a coplanar one. Both hexaethylbenzene (**1**)[2] and hexakis(bromomethyl)benzene (**2**)[3] adopt conformations with the side chains oriented perpendicularly to the central ring and arranged in an alternate up−down fashion.

The sterically overcrowded octamethylnaphthalene (**3**) and its organometallic derivatives have been the subject of numerous studies.[4] X-ray crystallography indicates that the naphthalene core of **3** is nonplanar and adopts a helical conformation of D_2 symmetry. This helical conformation is adopted to alleviate the steric interactions between the methyl groups at the peri positions.

3 R = H
4 R = Br

5
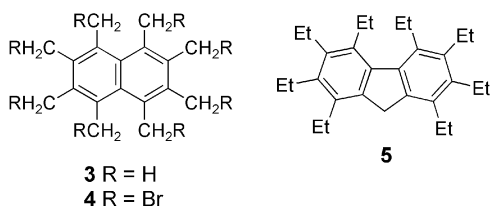
Octakis(bromomethyl)naphthalene **4** is a multiarmed organic compound possessing a polysubstituted central

naphthalene core.[5,6] Naphthalene **4** was prepared by Hart and co-workers in 1977 by electrophilic bromination of octamethylnaphthalene (**3**).[5] The published ^{1}H NMR data of **4** (two broad methylene signals in CDCl$_3$ at 41 °C, two sharp singlets in tetrachloroethylene at 100 °C) suggested restricted rotation of the bromomethyl groups on the NMR time scale at room temperature.[5] In this paper, we report the conformation, crystal structure, and rotational barrier of the crowded multiarmed naphthalene **4**.

"In" and "Out" Forms. By analogy to **3**, it could be expected that the central naphthalene core of **4** should adopt a chiral helical conformation. As recently described for the octaethylfluorene **5**[7] (which possess a helical central core), two diastereomeric fully alternated up−down forms are possible for **4**. This can be rationalized by viewing those conformations as resulting from the superposition of two independent stereogenic elements: the two enantiomeric fully alternated up−down patterns of the bromomethyl groups and the two enantiomeric helical conformations (helicities) of the central naphthalene core. This superposition yields two diastereomeric forms (Figure 1), denoted "in" and "out". MM3 calculations have indicated that in **5** the "out" arrangement is of lower energy.

X-ray Crystallography. A single crystal of **4** was grown from ethanol and submitted to X-ray crystallography. The molecule possesses crystallographic D_2 symmetry with the bromomethyl groups at the peri positions adopting the "in" conformation (Figure 2). The bromine atoms connected to C5 were disordered between two adjacent positions (Br2 and Br2′) with 50% occupancy each. The naphthalene core is helical, and its degree of twist can be characterized by the C1−C3−C3*−C1* torsional angle (20.4°), which is similar to the value obtained in the crystal structure of octamethylnaphthalene (21.3°).[4c]

Calculations. The relative steric energies of the fully alternated "in" and "out" conformers of **4** were initially estimated using MM3 calculations.[9,10] The MM3 calcula-

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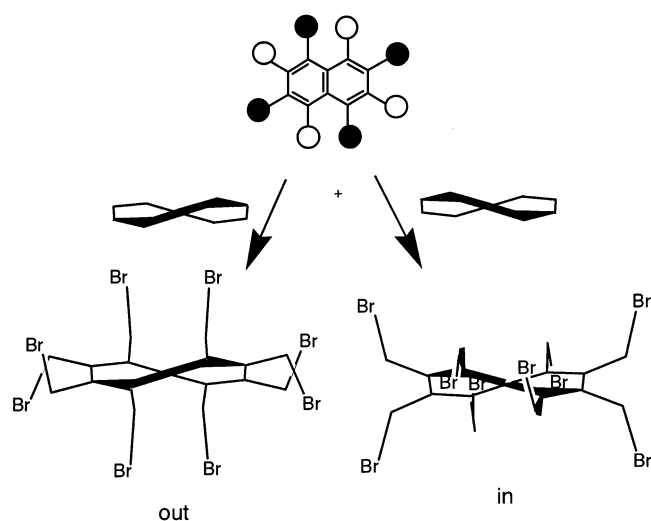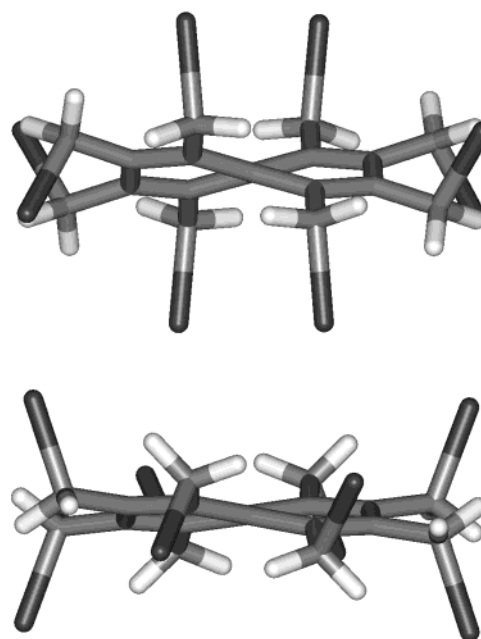
FIGURE 1. Superposition of a chiral, fully alternated, up–down pattern of bromomethyl groups with the two possible helicities of the naphthalene core giving two diastereomeric forms with fully alternated up–down disposition of the bromomethyl groups.
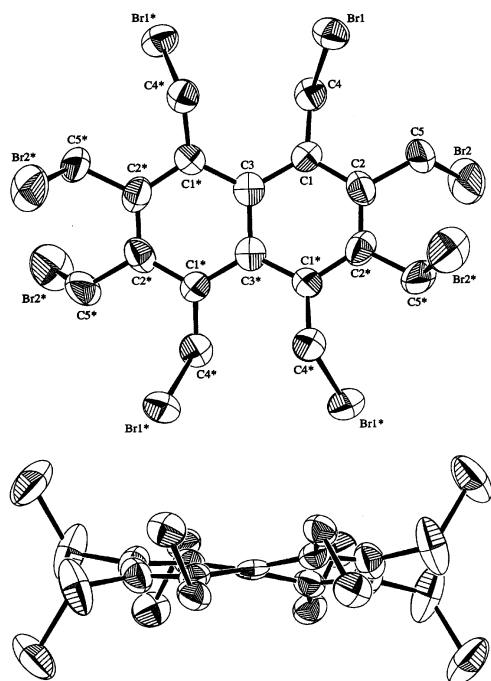
FIGURE 2. Top and side view of the X-ray structure of octakis(bromomethyl)naphthalene (**4**). The crystal conformation corresponds to the "in" fully alternated up–down form. Only one of the two positions of the disordered bromine atoms attached to C5 is shown.

tions predict that the "in" form (present in the crystal of **4**) is 4.6 kcal mol^{-1} less stable than the D_2 "out" form. The lowest energy conformation of a multiarmed molecule may not be the one preferred in a crystal, as observed, for example, for **5**.[7] However, the calculated energy gap is too large to be surmounted by packing

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FIGURE 3. Calculated (B3LYP/LANL2DZ) "out" (top) and "in" (bottom) forms of **4**.

forces. To get a better estimate of the relative stabilities of both forms and the mutual energy gap, we conducted hybrid density functional calculations using effective core potential for the bromine atoms at the B3LYP/LANL2DZ theoretical level. The calculations predict that the central skeleton is more twisted in the "out" form than in the "in" form (Figure 3). According to the calculations, the fully alternated "in" form is 6.3 kcal mol^{-1} more stable than the "out" form. In general, the structural parameters of the naphthalene core of the calculated "in" structure are in very good agreement with the crystal structure, in contrast to the MM3 calculations that overestimated the distortion of the naphthalene core. For example, the value of the endocyclic dihedral angles C(1)–C(3)–C(3*)–C(1*) found in the crystal (20.3°) was calculated as 18.6° by the B3LYP/LANL2DZ method, but the MM3 method predicted a substantially larger value of 31.7°.
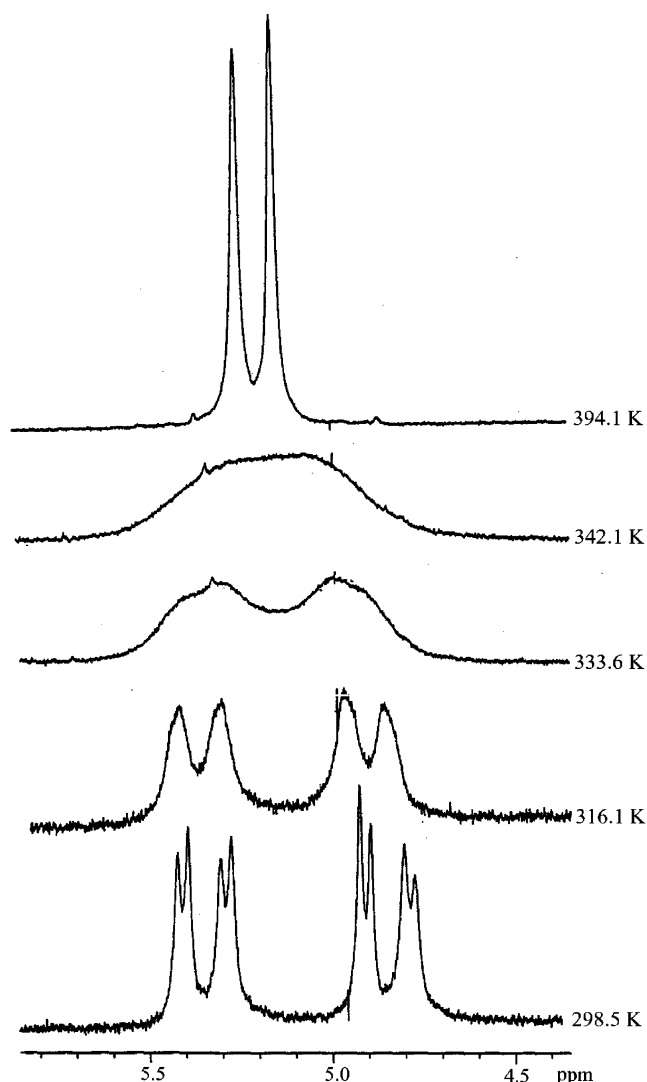
Dynamic NMR Studies. Hart and co-workers reported that the 100-MHz ^{1}H NMR spectrum of **4** in CDCl$_3$ at 41 °C displayed two broad singlets at 4.90 and 5.17 ppm.[5] The 400-MHz ^{1}H NMR spectrum of naphthalene **4** (in CDCl$_2$CDCl$_2$) displays at room temperature two pairs of doublets for the methylene protons (Figure 4), in agreement with a frozen conformation on the NMR time scale, while the ^{13}C NMR spectrum displays two aliphatic and three aromatic signals. On the basis of the signal pattern and the B3LYP/LANL2DZ calculations, we assign the solution conformation to the fully alternated "in" form of D_2 symmetry.

Upon raising the temperature of a sample of **4** in CDCl$_2$CDCl$_2$, the two pairs of methylene signals broadened and coalesced at an identical temperature (340 K, cf. Figure 4).[11] Total line shape simulation of the ^{1}H NMR

(11) Pairs of signals corresponding to protons connected to the same methylene group were identified by a COSY spectrum. The signals in the ^{1}H and ^{13}C NMR spectra were assigned by a combination of 2D techniques (HMBC, HSQC).

FIGURE 4. 400-MHz ^{1}H NMR spectrum of **4** (in CDCl$_2$CDCl$_2$) at different temperatures.

potential energy surface scan (PES) was employed, where the scanned parameter was the dihedral angle of one of the naphthalenic rings. Although the energy rise is modest (2.6 kcal mol^{-1} to planarize the ring from the optimized dihedral angle of $-18.6°$, and 7.3 kcal mol^{-1} to 18.6°) no minimum was detected. The second naphthalenic ring does not follow the changes in the first ring (for example, when the scanned dihedral angle is 0°, the respective dihedral angle in the second ring is changed only to 13.4°). Thus, the PES was continued to a dihedral angle of 37.2° ($\Delta E = 10.9$ kcal mol^{-1}) and then back to 18.6°, to explore the possibility that the mechanism involved overtwisting and back-twisting to a different geometry. The calculations show that this is not a preferred pathway.

Is the planar system a real intermediate or a transition state in the enantiomerization process? To answer this question, planar **4** was optimized and underwent analytical second-derivative calculations. The results show that the planar form is a minimum lying only 3.8 kcal mol^{-1} above the "in" form, but with a very small lowest frequency (4.3 cm^{-1}). At a lower theoretical level (HF/LANL2DZ), the planar **4** is a transition state with an imaginary frequency of -8.0 cm^{-1}.

The 180° rotation around the α- and β-bromomethyl groups was studied in the optimized and planar **4**. For both cases, the rotational barrier around the bonds is larger in planar **4** (by ca. 1–5 kcal mol^{-1}) than in the helical **4**. The rotational barriers around the α- and β-bromomethyls are 19.5 kcal mol^{-1} (18.5 kcal mol^{-1}, ZPE corrected, Br–CH$_2$–C(1)–C(9) $= -48.2°$) and 20.0 kcal mol^{-1} (19.2 kcal mol^{-1}, ZPE corrected, Br–CH$_2$–C(2)–C(3) $= -4.1°$), respectively. The groups neighboring the rotating bromomethyl undergo a librational motion (up to ca. 30° from their angle in the "in" form), but on completion of the rotation they return to their initial conformation. From the computational studies it may be concluded that most likely the enantiomerization mechanism involves independent rather than correlated rotations of the bromomethyls and inversion of the naphthalenic system.

Experimental Section

Octakis(bromomethyl)naphthalene was prepared by electrophilic bromination of octamethylnaphthalene[4b] according to the procedure of Hart:[5] ^{1}H NMR (400 MHz, CDCl$_2$CDCl$_2$, rt) δ 5.40 (C$_\beta$CH$_2$Br), 5.29 (C$_\alpha$CH$_2$Br), 4.90 (C$_\beta$CH$_2$Br), 4.78 (C$_\alpha$CH$_2$Br) ppm [(d, $J = 11.3$ Hz, 2H) × 4]; ^{13}C NMR (100 MHz, CDCl$_3$, rt) δ 139.5 (C$_\beta$), 138.0 (C3), 135.7 (C$_\alpha$), 31.6 (C$_\alpha$CH$_2$Br), 25.7 (C$_\beta$CH$_2$Br) ppm.

Calculations. MM3(94) calculations were performed using the Alchemy 2000 program.[10] All stationary points were char-

spectrum of the methylene protons in the 298–380 K temperature range afforded a topomerization barrier of 16.0 ± 0.2 kcal mol^{-1}.[12]

Mechanistic Aspects. As discussed previously for **5**,[7] rotation of all the side chains of **4** by 180° does not lead to topomerization of pairs of protons within a given methylene group but transforms the "in" into the "out" form and vice versa. Topomerization of the methylene protons requires an additional process involving reversal of the helical sense of the naphthalene core. On this basis, the topomerization barrier measured is ascribed to an enantiomerization process involving both nearly 180° rotations of all the bromomethyl groups and helicity reversal of the central core. There are few possibilities for the enantiomerization mechanism, and theory was used in order to get more insight and information. One possibility is twisting of the naphthalenic skeleton to convert the "in" form to the "out" form and then rotation of the bromomethyl groups. To test this possibility, a

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acterized as minima by the absence of imaginary frequencies in the frequency matrix. Ab initio and DFT calculations were conducted using the Gaussian 98[13] package of programs. All the structures were fully optimized and analytical frequencies calculations were performed on the minima and transition state to ensure $N_{imag} = 0$ and 1, respectively.

Crystallography. The X-ray diffraction data were measured with an ENRAF-NONIUS CAD-4 computer-controlled diffractometer. Cu Kα ($\lambda = 1.54178$ 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 **4**: $C_{18}H_{16}Br_8$, space group *Fddd*, $a = 16.768(6)$ Å, $b = 22.719(9)$ Å, $c = 12.017(3)$ Å, $V = 4578(2)$ Å^3, $Z = 8$, $\rho_{calc} = 2.53$ g cm^{-3}, μ(Cu Kα) = 167.94 cm^{-1}, number of unique reflections = 1136, number of reflections with $I \geq 3\sigma_I = 828$, $R = 0.065$, $R_w = 0.083$.

Supporting Information Available: Final calculated coordinates for selected conformations of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026343S