Structure of 9,10-Di(9,9-dioctylfluorenyl)anthracene in the Solid and in Solution

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A new example of magnetic nonequivalence of chemically equivalent atoms is identified from the proton and carbon resonance spectra of 9,10-di(9,9-dioctylfluorenyl)anthracene with the aid of its conformation in the crystalline state. Molecular modeling suggests that it has a similar conformation in solution.

Introduction

After the synthesis of 9,10-di(9,9-dioctylfluorenyl)-anthracene (**I**), following a procedure to be discussed later, a proton magnetic resonance spectrum was obtained in order to get an estimate of the purity. More lines were found than could be explained in a straightforward manner, but the compound appeared to be pure. To explain this apparent contradiction, the compound was investigated by proton and carbon nuclear magnetic resonance in solutions of varying concentration and solvent, by single-crystal X-ray crystallography in the solid, and by the technique of molecular modeling. The combination of these techniques made it possible to explain all the results.

Results and Discussion

The numbering employed for discussion purposes is shown in Figure 1, where for the sake of simplicity, hydrogen atoms have not been included. For purposes of discussion, they will have the same number as the carbon atom to which they are bonded. Some disorder was observed for one of the *n*-octyl chains in the solid state, and this is also reflected in the numbering for the X-ray data, where these atom numbers are followed by the letter A; however, the disorder is ignored for the spectroscopic data. Figure 2 illustrates the conformations and packing in the unit cell of **I**. Once again, hydrogen atoms have been deleted from the figure for the sake of clarity. Several features of this figure will be mentioned because they are significant for the interpretation of results to be discussed later. The anthracene ring system and the fluorene ring systems are planar, and the fluorene ring systems are essentially coplanar but not coplanar with the anthracene ring system. The unit cell contains one molecule and two half molecules. The dihedral angle including carbons 7, 8, 15, and 16 is −107.9(1)° for the single molecule and −91.4(1)° for the corresponding angle
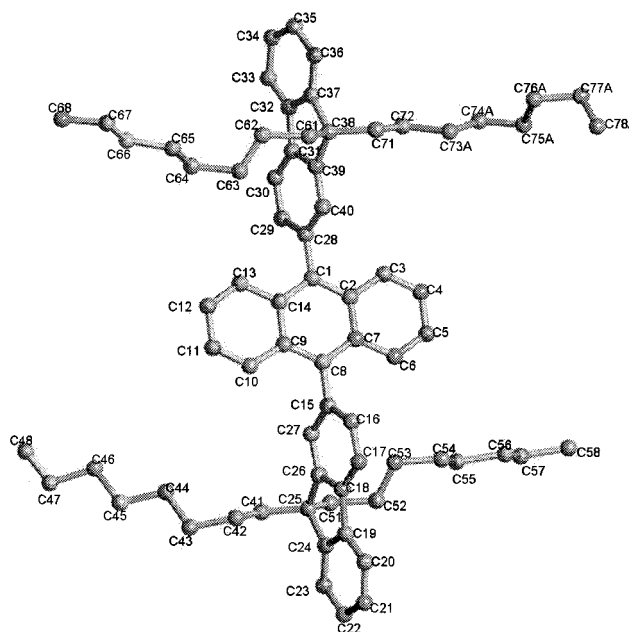

Figure 1. Numbering system used for discussion of **I**.

of the two half molecules. The fluorene rings are oriented such that the *n*-octyl groups face away from each other (trans). The aromatic rings of adjacent molecules are separated by too large a distance for any significant π−π interaction.[1]

Although only a single conformation is observed for the molecules in the solid state, it is possible that the relaxation of packing constraints in solution might allow other conformations to be present. Therefore, a molecular mechanics study was undertaken to determine the potential energy (in kcal/mol) of the molecule as a function of the dihedral angle including carbon atoms 7, 8, 15, and 16. The results are plotted in Figure 3, where the zero of energy is an arbitrary value determined by

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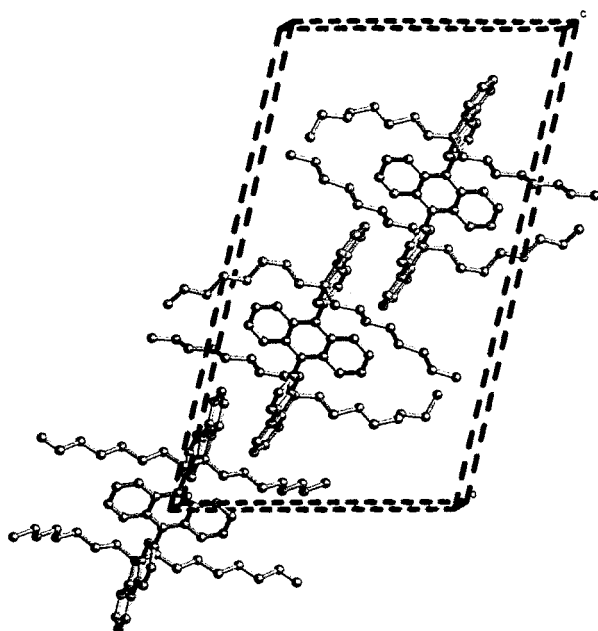(1) Interlayer spacing in graphite is 3.354 Å.

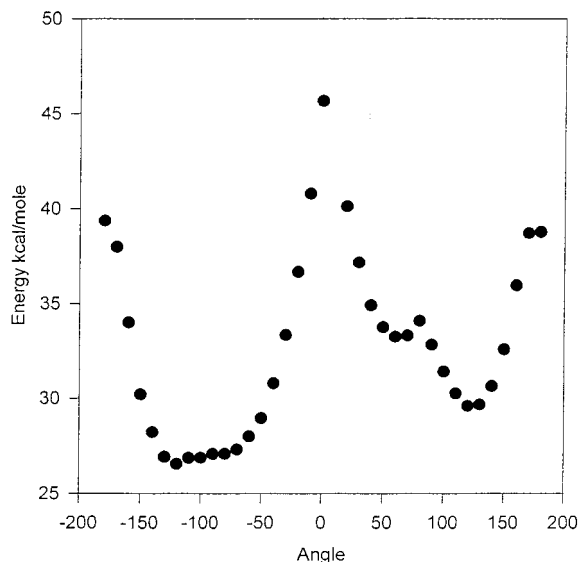**Figure 2.** Arrangement of the molecules of **I** in the unit cell.

Figure 3. Potential energy of **I** as a function of the dihedral angle 7,8,15,16.

Figure 4. Proton resonance spectrum of the aromatic region of a 0.024 M CDCl$_3$ solution of **I**.

the molecular mechanics program. The corresponding opposite dihedral angle including carbon atoms 2, 1, 28, and 29 remained approximately constant at from −41 to −73°. Considerable hysteresis was found in the calculation of energy minima for the various angles, so the 7, 8, 15, and 16 dihedral angle had to be restrained at a random variety of angles and the energy minimized to get the global minimum for any given dihedral angle. A value of 0° for the dihedral angle 7, 8, 15, and 16 corresponds most closely to the cis conformation, while values near 180° correspond to the trans conformation. The energies are not symmetric about 0° for the dihedral angle 7, 8, 15, and 16 because the dihedral angle for 2, 1, 28, and 29 remains in the vicinity of −55°. The very broad minimum about −120° corresponds to the situation where the two fluorene ring systems are coplanar and in the cis conformation. The two minima of 33.269 at 60° and 29.611 at 120° have the two fluorene ring systems
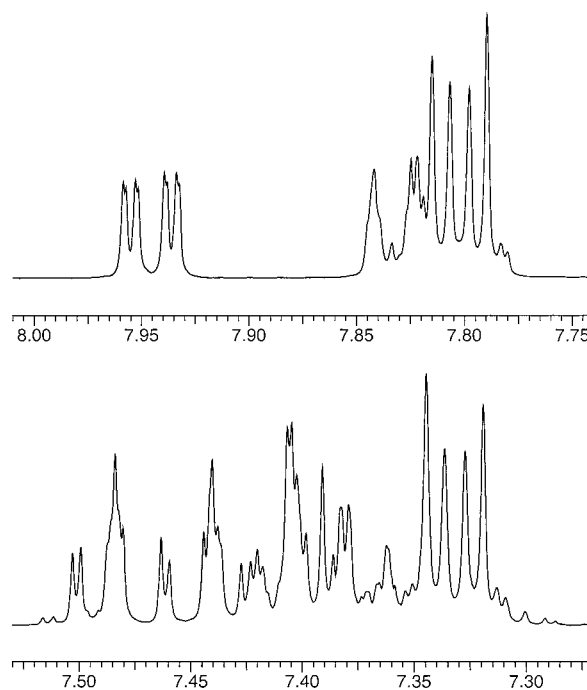
positioned trans. The one at 120° has the fluorene rings coplanar, while the one at 60° has them tilted at opposite angles relative to the anthracene ring system. The difference between the calculated minimum energy conformation for the isolated molecule and that observed for the structure found via X-ray crystallography (29.611) is 3 kcal/mol.

This difference could reasonably arise from two sources. One is the energy requirement for the most efficient packing in the solid as compared with an isolated molecule. The second is the neglect of effects of entropy in the molecular mechanics calculations, which give a potential energy rather than a free energy. Nevertheless, we can conclude from both the X-ray and molecular mechanics results that the most stable conformation in solution is one in which the two fluorene ring systems are coplanar and at an angle of about 120° relative to the plane of the anthracene ring.

The potential energy barrier for rotation between the cis and trans conformations is calculated as 12 kcal/mol. We can conclude that interconversion between cis and trans configurations would be sufficiently rapid on the NMR time scale at room temperature that the very small chemical shifts and sharp lines that are found could not be due to separate cis and trans isomers because only averaged lines would be observed.

The proton resonance spectrum of the aromatic region of a 0.024 molar, degassed solution of **I** in CDCl$_3$ is shown in Figure 4, and the chemical shift assignments and spin couplings are listed in Table 1. These assignments were confirmed, as much as possible, by the internal consistency of spin couplings, by selective decoupling, and by a COSY[2] spectrum. The carbon resonance spectrum of the aromatic region, for the same solution, is shown in Figure 5, and the chemical shift assignments are listed

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Table 1. Proton and Carbon Chemical Shifts (ppm from TMS) and Spin Couplings (Hz) for I in a 0.024 M CDCl₃ Solution, Except as Noted

atoms	chemical shifts	spin couplings	atoms	chemical shifts	spin couplings
C1,C8,C15,C28	137.56		H22,H35 (a)	not resolved	
C2,C7,C9,C14	129.99		H22,H35 (b)	not resolved	
H3,H6, or	7.806 or	$J_{3-4} = 7.0$ or	C22,C35	127.12	
H10,H13	7.799	$J_{10-11} = 7.0$			
H3,H6 or (a)[a]	7.884 or	same as above	H23,H36	not resolved	
H10,H13	7.880				
H3 or (b)[b]	8.121 or	$J_{3-4} = 7.2$ or	H23,H36 (a)	not resolved	
H6 or	8.118 or	$J_{6-5} = 6.8$ or			
H10 or	8.113 or	$J_{10-11} = 6.8$ or			
H13	8.110	$J_{13-12} = 6.8$			
C3,C6,C10,C13	126.99		H23,H36 (b)	not resolved	
H4,H5 or	7.336 or	$J_{4-3} = 7.0$ or	C23,C36 or	122.84	
H11,H12	7.328	$J_{11-10} = 7.0$	C21,C34		
H4,H5 or (a)	7.884 or	same as above	C24,C37	150.87	
H11,H12	7.880				
H4,H5,H11,H12 (b)	not resolved		C25 or	55.29 or	
			C38	55.25	
C4,C5,C11,C12	124.90		C26 or	150.76 or	
			C39	150.75	
H16 or	7.492 or	$J_{16-17} = 7.6, J_{16-27} = 1.6$ or	H27 or	7.484 or	
H29	7.452	$J_{29-30} = 7.6, J_{29-40} = 1.2$	H40	7.441	
H16 or (a)	7.555 or	$J_{16-17} = 7.2, J_{16-27} = 1.6$ or	H27 or (a)	7.562 or	
H29	7.524	$J_{29-30} = 6.0, J_{29-40} = 1.6$	H40	7.516	
H16 or (b)	7.513 or	$J_{16-17} = 7.4, J_{16-27} = 1.4$ or	H27 or (b)	7.548 or	
H29	7.459	$J_{29-30} = 7.4, J_{29-40} = 1.6$	H40	7.483	
C16,C29 or	126.16 or		C27,C40 or	129.78 or	
C27,C40	126.14		C16,C29	129.72	
H17 or	7.949 or	$J_{17-16} = 7.7, J_{17-27} = 0.4$	H41,H51,H61,H71	1.99	
H30	7.943	$J_{30-29} = 7.7, J_{30-40} = 0.4$			
H17,H30 (a)	8.001	$J_{17-16} = 7.2, J_{17-2} = 0.4$	H41,H51,H61,H71 (a)	2.075	
H17 or (b)	7.742 or	$J_{17-16} = 7.4$ or	H41,H51,H61,H71 (b)	2.036	
H30	7.736	$J_{30-29} = 7.4$			
C17,C30	119.56		C41,C51,C61,C71	40.51	
C18,C31	140.44		C42,C52,C62,C72	24.08	
C19 or	140.88 or		C43,C53,C63,C73 or	31.89 or	
C32	140.87		C46,C56,C66,C76	30.14	
H20,H33	7.834	$J_{20-21} = 6.8$	C44,C54,C64,C74 or	29.41 or	
			C45,C55,C65,C75	29.29	
H20,H33 (a)	7.876	$J_{20-21} = 6.8$	H47,H57,H67,H77	1.11	
H20 or (b)	7.724 or	$J_{20-21} = 7.2$ or	H47,H57,H67,H77 (a)	1.244	
H33	7.718	$J_{33-34} = 7.2$			
C20,C33	119.73		H47,H57,H67,H77 (b)	1.168	
H21,H34	not resolved		C47,C57,C67,C77	22.68	
H21,H34 (a)	not resolved		H48,H58,H68,H78	0.805	$J_{48-47} = 7.0$
H21,H34 (b)	not resolved		H48,H58,H68,H78 (a)	0.867	$J_{48-47} = 7.2$
C21,C34 or	126.80		H48,H58,H68,H78 (b)	0.839 and	$J_{48-47} = 6.8$
C23,C36				0.835	
H22,H35	not resolved		C48,C58,C68,C78	14.18	

[a] (a) A 0.10 M CDCl₃ solution. [b] (b) A C₆D₆ solution.

in Table 1. These assignments were made with the aid of DEPT[3] and HETCOR[4] pulse sequences.

The chief feature of interest in these spectra is the doubling of the chemical shift for certain chemically equivalent but magnetically nonequivalent nuclei. The magnetic nonequivalence arises from the fact that the plane of the fluorene rings is not perpendicular to that of the anthracene ring. Therefore, in a given conformation, atoms 2 through 7 will be different from atoms 9 through 14. When the fluorene rings flip to the other corresponding angle, the nonequivalence of the anthracene atoms is reversed but they remain nonequivalent. This is formally similar to the magnetic nonequivalence of the CH2 protons bonded to an adjacent asymmetric carbon atom.[5] For the same reason, the two fluorene ring systems are nonequivalent because when one is closest to one side of the anthracene, the other is closest to the second side, which is not equivalent. The authors are not aware of another example of this asymmetry involving the anthracene ring system.

The carbon chemical shifts seem much less sensitive to this asymmetry than the proton chemical shifts. Thus, H3 and H6 are shifted from H10 and H13 by 0.007 ppm, while there is no discernible splitting of the carbon resonances. The same situation is found for H4,H5 and H11,H12 where the difference is 0.008 ppm without splitting of the corresponding carbon resonances. A similar situation prevails with the first phenyl ring of the fluorene moiety where H16 and H29 are magnetically nonequivalent by 0.040 ppm and H17 and H30 are split by 0.006 ppm while the corresponding carbon atoms are not shifted. This is also observed for H27 and H40 with a chemical shift difference of 0.043 ppm. Splitting of the

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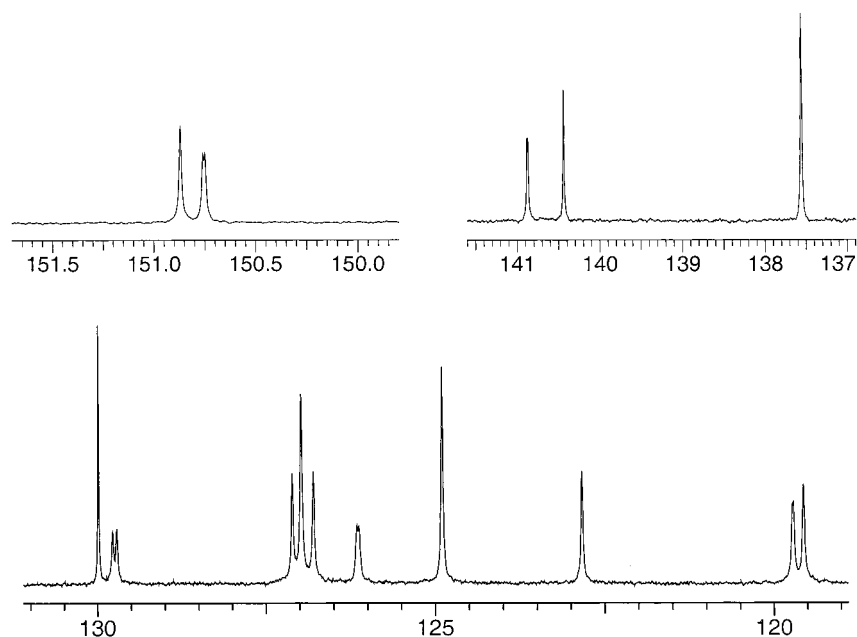
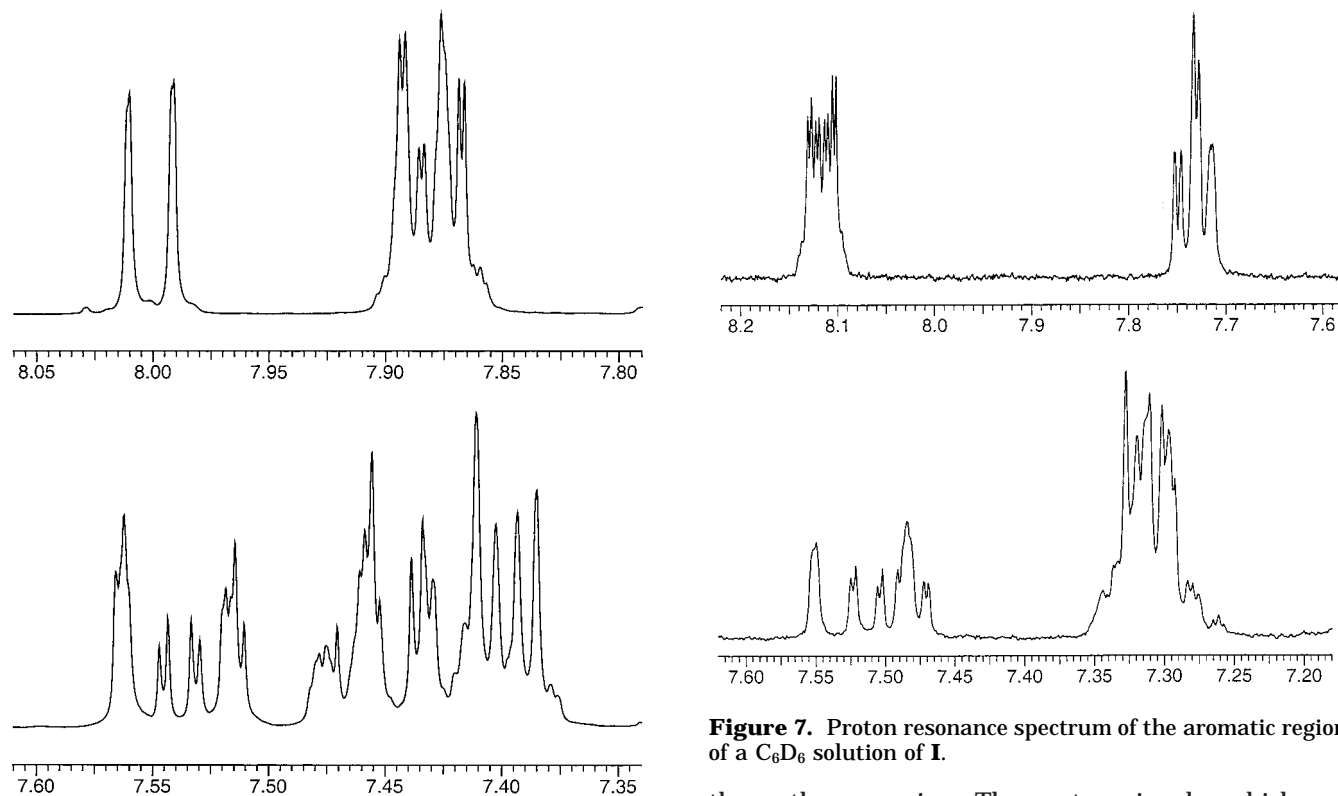**Figure 5.** Carbon resonance spectrum of the aromatic region of a 0.024 M CDCl$_3$ solution of **I**.

Figure 6. Proton resonance spectrum of the aromatic region of a 0.10 M CDCl$_3$ solution of **I**.

Figure 7. Proton resonance spectrum of the aromatic region of a C$_6$D$_6$ solution of **I**.

chemically equivalent C19 and C32 is 0.01 ppm, and the same splitting is found for C26 and C39.

In a 0.10 molar solution of **I**, we have a proton resonance spectrum that appears rather different. It is shown in Figure 6, and the significant proton chemical shifts are also listed in Table 1. The carbon chemical shifts are essentially identical with those of the 0.024 M solution. This is consistent with the observed lack of sensitivity, in the present case, of the carbon chemical shifts to the magnetic nonequivalence of the two sides of

the anthracene ring. The proton signals, which are significantly altered in the 0.10 M solution, are those of H17,H30, which now have the same chemical shift. H3,H6, or H10,H13, are now separated by 0.004 ppm, and for H16,H29, the chemical shift difference is reduced from 0.049 to 0.031 ppm. We postulate that these changes arise from possible overlap of the outer phenyl rings of the fluorene moiety of adjacent molecules. This hypothesis was tested by obtaining the proton resonance spectrum of **I** in deuteriobenzene, which is shown in Figure 7 and partially listed in Table 1. The most significant change is the large downfield shift of H3, H6, H10, and H13. Each of these protons now has a resolvably different chemical shift. This is consistent with solvation of

primarily one of the fluorene ring systems of **I**. There is also an upfield shift of H17,H30, and they are nonequivalent, as in the dilute CDCl₃ solution. H20 and H33 have become magnetically nonequivalent. There are also nonequivalent signals from two of the four CH₃ groups.

It was mentioned that the proton resonance spectra were obtained on degassed and sealed samples. If the samples were not degassed and the solution was exposed to the air, the spectra gradually changed. This change was greatly accelerated if the samples were also exposed to light. It is presumed that the oxide is formed under these conditions.[6] The proton and carbon chemical shifts of the oxide in CDCl₃ solution are normal with no indication of unusual magnetic nonequivalence. Since oxide formation changes the no-longer aromatic anthracene ring into a boat form, hindrance to rotation about the bonds attaching the fluorene moieties is removed.

Experimental Section

Synthesis of I. 2-Bromo-9,9-dioctylfluorene was synthesized from 2-bromofluorene (Aldrich) and 1-bromooctane (Aldrich) in a manner similar to that reported.[7] The product was purified by chromatography with hexane to obtain a colorless oil and was further treated with *n*-butyllithium, triisopropyl borate in ether, and then 2 N HCl to give 9,9-dioctylfluorene-2-boronic acid (**II**) at a total yield of 60%. The Suzuki coupling[8] of **II** and dibromoanthracene (Aldrich) was done in a mixture of toluene and 2 M Na₂CO₃ (3:2, v/v) in the presence of tetrakis-(triphenylphosphine)palladium(0) (2.0 mol % of monomer). The solution was purged with Ar and refluxed with vigorous stirring for 48 h in the dark. **I** was obtained in 92% yield after twice recrystallizing from hexane.

X-ray Diffraction. Although the majority of the crystals were extremely fine, colorless needles, a large rectangular-shaped (0.04 × 0.06 × 0.22 mm) crystal was chosen for single-crystal X-ray diffraction. The data were collected on a Siemens SMART CCD diffractometer using Mo Kα radiation and an ω-scan mode. The unit cell constants at −100 °C were a = 9.080(2) Å, b = 17.153(4) Å, c = 29.692(7) Å, α = 102.27(2)°, β = 95.32(2)°, and γ = 94.85(2)°. The empirical formula for the asymmetric unit (Z = 2) was $C_{109}H_{135}$ with D_c = 1.073 g/cm³ and μ = 0.06 mm⁻¹. No diffraction spots could be observed at 2θ angles greater than 40°. A Wilson plot of the reduced intensities confirmed the absence of meaningful data above this angle. The structure was solved in space group $P\bar{1}$ using the NRCVAX program[9] and refined (on F^2) using the SHELX-TL program with full matrix least squares on all data. One of the *n*-octyl groups (C71−C78) is disordered (each of C73−C78 is disordered over two sites, denoted by A and B, with complementary occupancy). All the ordered, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined in calculated positions. The final residual values R1(wR2) = 0.061(0.1552) for I > $2\sigma(I)$ and 0.1847(0.1802) for all data (6703 unique reflections, 972 parameters).

The molecular modeling was done with the commercial program Hyperchem 4.5.[10] The force field MM⁺, a variant of MM2,[11] was employed. Energy minimization was done with a Polak−Ribiere conjugate gradient procedure. The torsion angle was constrained by putting a high energy barrier to change from the constrained value. These calculations were confirmed for the minimum energy conformation with the program TINKER[12] using the MM3 parameter set[13] and a nonlinear conjugate gradient method.

NMR spectra were obtained with a Varian Unity Inova spectrometer operating at 100 MHz for C¹³, with a sweep width of 25 000 Hz and 60 000 data points, and 400 MHz for H¹, with a sweep width of 6000 Hz and 30 000 data points. Samples (5 mm) were used in a wide bore magnet with the standard programs of the manufacturer.

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