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Xianlong Wang

Frank B. Mallory

Clelia W. Mallory

Peter A. Beckmann
Bryn Mawr College, pbeckman@brynmawr.edu

Arnold L. Rheingold

See next page for additional authors

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Authors

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CF_3 Rotation in 3-(Trifluoromethyl)phenanthrene. X-ray Diffraction and ab Initio Electronic Structure Calculations

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Xianlong Wang,[†] Frank B. Mallory,[†] Clelia W. Mallory,[†,‡] Peter A. Beckmann,[§]
Arnold L. Rheingold,[#] and Michelle M. Francl*,[†]

Department of Chemistry and Department of Physics, Bryn Mawr College, 101 North Merion Avenue, Bryn Mawr, Pennsylvania 19010-2899, Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716-2522, and Department of Chemistry, University of California, San Diego, La Jolla, California 92093

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The molecular and crystal structure of 3-(trifluoromethyl)phenanthrene has been determined by X-ray diffraction. The structure of the isolated molecule has been calculated using electronic structure methods at the HF/3-21G, HF/6-31G*, MP2/6-31G* and B3LYP/6-31G* levels. The potential energy surfaces for the rotation of the CF_3 group in both the isolated molecule and cluster models for the crystal were computed using electronic structure methods. The barrier height for CF_3 rotation in the isolated molecule was calculated to be 0.40 kcal mol^{-1} at B3LYP/6-311+G**//B3LYP/6-311+G**. The B3LYP/6-31G* calculated CF_3 rotational barrier in a 13-molecule cluster based on the X-ray data was found to be 2.6 kcal mol^{-1}. The latter is in excellent agreement with experimental results from the NMR relaxation experiments reported in the companion paper (Beckmann, P. A.; Rosenberg, J.; Nordstrom, K.; Mallory, C. W.; Mallory, F. B. *J. Phys. Chem. A* **2006**, *110*, 3947). The computational results on the models for the solid state suggest that the intermolecular interaction between nearest neighbor pairs of CF_3 groups in the crystal accounts for roughly 75% of the barrier to rotation in the solid state. This pair is found to undergo cooperative reorientation. We attribute the CF_3 reorientational disorder in the crystal as observed by X-ray diffraction to the presence of a pair of minima on the potential energy surface and the effects of librational motion.

Introduction

We report the structure of 3-(trifluoromethyl)phenanthrene as determined by X-ray diffraction and ab initio electronic structure calculations. The potential energy surfaces (PES) for the rotation of the CF_3 group in both the isolated molecule and models for the crystal are explored using electronic structure approaches. X-ray diffraction and solid-state NMR relaxometry studies of catacondensed aromatic hydrocarbon derivatives with internal rotational degrees of freedom have provided new insights into the reorientation of methyl and *tert*-butyl groups.[1] The two methods give access to quite different time regimes. The diffraction of X-rays by an electron density distribution occurs on the order of 10^{-19} s, which is much faster than the reorientation motions (on the order of 10^{-10} to 10^{-5} s) and so yields a time average of an ensemble of instantaneous structures. The much longer time scale investigated by nuclear spin relaxation studies is well matched to these intramolecular reorientations.

Ab initio electronic structure calculations are a useful adjunct to these two techniques, as they provide information about the classical potential energy surface for the reorientations. In addition, structural information can be obtained beyond that generally available from X-ray diffraction, including accurate hydrogen positions and improved positions for disordered nuclei. We have computed the classical potential energy surface for the rotation of the CF_3 group in both the isolated molecule and models of the crystal using ab initio electronic structure methods. To our knowledge, this represents the first example in which the effects of neighboring molecules in a single crystal on a barrier to internal rotation are explicitly modeled using a combination of electronic structure theory and results from X-ray diffraction. The approach we have taken is similar to that used by Zimmerman et al.[2] to explore photoreactions in the solid state, in which a subset of the experimentally determined crystal lattice is considered explicitly using quantum mechanical methods. The effective barrier for rotation of the CF_3 group in both the isolated molecule and the cluster models of the solid state can be determined from the computed potential energy surfaces and compared with the “effective activation energy” obtained from solid-state NMR nuclear spin relaxation experiments.

Solid state ^{19}F and ^{1}H spin−lattice relaxation rate measurements in polycrystalline 3-(trifluoromethyl)phenanthrene are reported in the companion paper.[3] The nuclear spin relaxation is complicated by the simultaneous presence of like (F−F) and unlike (F−H) spin−spin interactions. (No H−H spin−spin interactions are modulated by CF_3 rotation.) One interesting result from the solid-state relaxation rate study is a parameter that characterizes the contribution of H−F spin−spin interactions to the ^{1}H and ^{19}F spin−lattice relaxation rates.[3] The structure of the molecule and of the crystal can be used to compute this parameter. The ability of electronic structure calculations to accurately place the hydrogen and fluorine atoms relative to the carbon framework is critical because this parameter depends strongly on both the H−F and F−F distances. C−H distances obtained from X-ray diffraction are known to be too short by more than 0.1 Å. Also, we find we are able to

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[†] Department of Chemistry, Bryn Mawr College.

[‡] Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

[§] Department of Physics, Bryn Mawr College, and Department of Chemistry and Biochemistry, University of Delaware.

[#] Department of Chemistry, University of California, San Diego.

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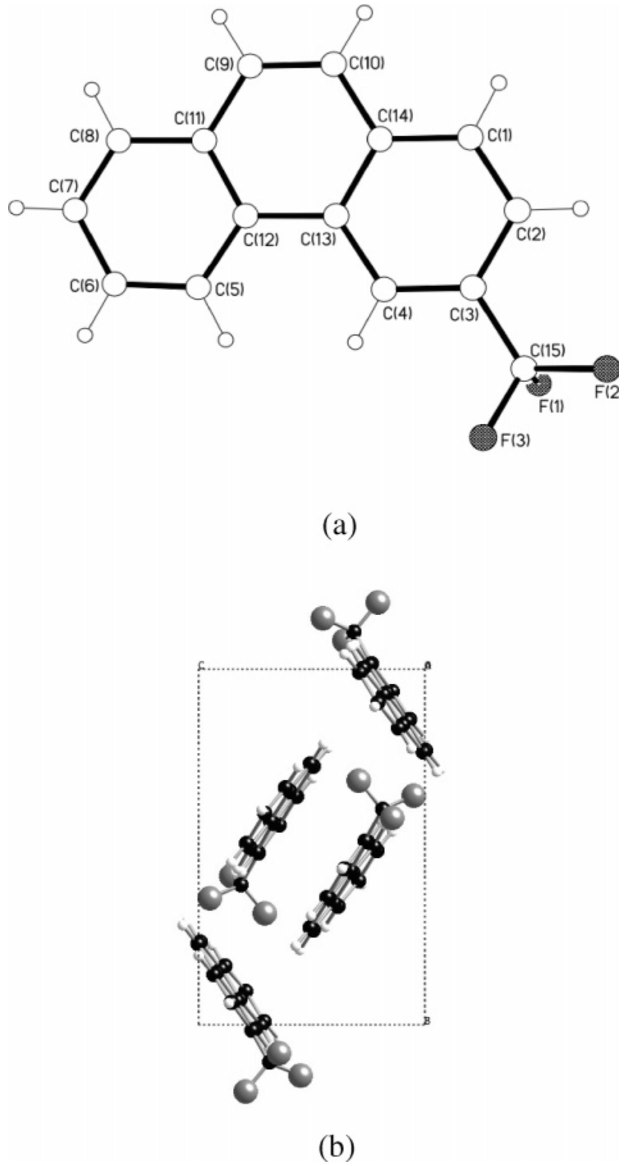

Figure 1. (a) Structure of 3-(trifluoromethyl)phenanthrene and (b) unit cell from single crystal X-ray diffraction. Only the major positions of the fluorines are shown, as discussed in the text. There are four chemically equivalent molecules per unit cell.

use electronic structure calculations to resolve the ambiguities in the fluorine positions determined by X-ray diffraction.

We consider here the relationship between the molecular and crystal structure of 3-(trifluoromethyl)phenanthrene and the dynamics of the CF_3 group motions in the solid.

Methods

Crystallographic Characterization of 3-(Trifluoromethyl)-phenanthrene. The X-ray diffraction structure of 3-(trifluoromethyl)phenanthrene and its numbering scheme are shown in Figure 1; selected structural parameters are collected in Table 1. The complete structure may be found as supplemental information for this paper. Suitable crystals were obtained by recrystallization from methanol.[4] Data were obtained on a four-circle Bruker P4 diffractometer equipped with an APEX CCD detector and an LT2 cryostat from a crystal mounted on a fine glass fiber. The space group ($P2_1/c$) was unambiguously assigned from systematic absences in the diffraction data. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were idealized. Two orientations were seen for the fluorine atoms in the CF_3 group in an 80/20 ratio. Refinement was constrained to maintain unit occupancies for the fluorine atoms. All software was contained in the SMART, SAINT and SHELXTL libraries maintained by Bruker AXS, Madison, WI.

TABLE 1: Comparison of Calculated ab Initio Structures of the Isolated Molecule with X-ray Diffraction Results for 3-(Trifluoromethyl)phenanthrene

parameter[a]	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	B3LYP/ 6-311+G**	X-ray
C1C2	1.360	1.361	1.379	1.375	1.364
C2C3	1.398	1.406	1.409	1.409	1.398
C3C4	1.361	1.365	1.383	1.380	1.375
C4C13	1.407	1.412	1.413	1.412	1.403
C13C12	1.458	1.460	1.452	1.456	1.454
C13C14	1.402	1.402	1.426	1.423	1.418
C12C5	1.408	1.411	1.414	1.413	1.403
C12C11	1.403	1.404	1.426	1.424	1.418
C5C6	1.366	1.367	1.385	1.381	1.376
C6C7	1.400	1.403	1.407	1.406	1.395
C7C8	1.364	1.365	1.382	1.378	1.359
C8C11	1.406	1.409	1.414	1.413	1.409
C11C9	1.438	1.440	1.432	1.433	1.427
C9C10	1.338	1.340	1.364	1.358	1.344
C10C14	1.438	1.439	1.431	1.433	1.432
C14C1	1.409	1.411	1.415	1.415	1.402
C3C15	1.483	1.501	1.495	1.503	1.490
C15F1	1.351	1.323	1.353	1.351	1.316 (1.332)[b]
C15F2	1.354	1.326	1.356	1.357	1.345 (1.315)[b]
C15F3	1.354	1.326	1.356	1.357	1.357 (1.310)[b]
(C3C15F1)	112.1	112.7	112.8	113.0	109.3 (113.5)[b]
(C3C15F2)	112.0	111.5	111.3	111.8	116.0 (111.8)[b]
(C3C15F3)	112.0	111.5	111.3	111.8	111.9 (113.9)[b]
φ (C4C3C15F1)	0.0	0.0	0.0	0.0	89 (70)[b]
φ (C4C3C15F2)	−120.8	−120.6	−120.6	−120.6	−154 (−166)[b]
φ (C4C3C15F3)	120.8	120.6	120.6	120.6	−33 (−48)[b]

[a] See Figure 1 for numbering scheme. Values for parameters are in ångstroms and degrees. [b] Parenthetic values indicate minor positions of fluorines, see text.

Electronic Structure Calculations. All electronic structure calculations were carried out using the Gaussian 03 suite of programs.[5] Models of 3-(trifluoromethyl)phenanthrene in the crystal environment were constructed from the refined single-crystal X-ray structure using code developed in-house. Clusters included all the molecules with any atom falling into a sphere of radius 6.5 Å having its center located at the target sp^3 carbon atom of the trifluoromethyl group (C15). The radius was chosen to include a sufficient number, twelve in this case, of neighboring molecules to reasonably model the local environment for the CF_3 group of interest on the center molecule. Zimmerman and Nesterov find that this first shell around the molecule of interest is the most critical to consider.[6]

Structure optimizations of the isolated molecule were carried out using a variety of theoretical models including HF/3-21G,[7] HF/6-31G*[8] and B3LYP/6-31G*.[9] Calculations on clusters made use of the HF/3-21G and B3LYP/6-31G* models. The small size of the HF/3-21G basis set and its reliability with respect to the calculation of these types of structures allowed rapid and thorough explorations of the potential energy surface for CF_3 rotation in the clusters. The relative computational efficiency of hybrid density functional methods compared to Hartree−Fock approaches, as well as the ability to capture more electron correlation than Hartree−Fock (which lacks a good description of the correlation of electrons with antiparallel spins), makes B3LYP an attractive choice, in particular for the cluster models where short to medium range intermolecular interactions potentially play a significant role. B3LYP has been shown to well-reproduce solid-state experimental structures of simple

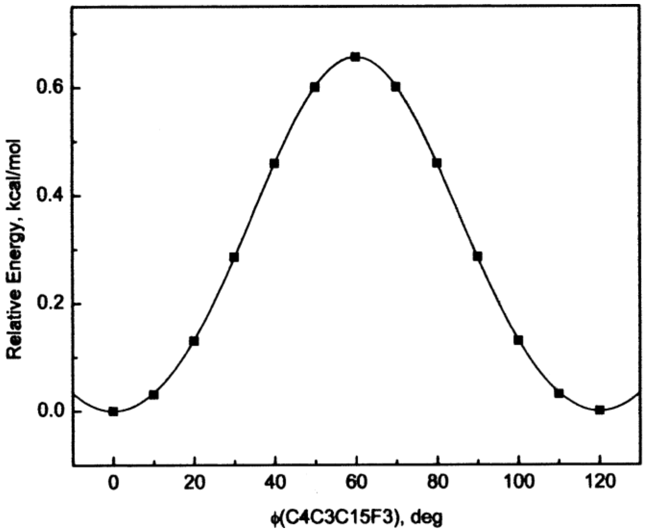

Figure 2. Calculated HF/6-311+G**//HF/6-31G* potential energy surface for CF_3 rotation in isolated 3-(trifluoromethyl)phenanthrene. The smooth curve represents the sinusoidal fit to the computed points.

TABLE 2: Computed CF_3 Rotational Barriers for an Isolated 3-(Trifluoromethyl)phenanthrene Molecule

method	barrier (kcal/mol)
HF/3-21G//HF/3-21G	0.69
HF/6-311+G**//HF/6-31G*	0.66
B3LYP/6-31G*//B3LYP/6-31G*	0.40
B3LYP/6-311+G**//B3LYP/6-311+G**	0.40
MP2/6-31G*//MP2/6-31G*	0.46

catacondensed hydrocarbons, such as anthracene and phenanthrene.[10] This model is capable of accurately locating hydrogen atoms, yielding results in good agreement with those from neutron diffraction.[11]

Relaxed potential energy surfaces (PES) for rotation around the C3−CF_3 axis in the isolated molecule were obtained at the HF/6-311+G**//HF/6-31G* level. Energy calculations on the isolated molecule in the ground and rotational transition states, used to compute barrier heights, were done using the HF/6-311+G**//HF/6-31G*,[12] B3LYP/6-31G*//B3LYP/6-31G*, B3LYP/6-311+G**//B3LYP/6-311+G** and MP2/6-31G*//MP2/6-31G*[13] theoretical models. Barriers were not corrected for zero point energy, as we and others[14] find the corrections to be negligibly small. Likewise, we find that corrections to the rotational barriers for basis set superposition errors (BSSE) are small, and generally insensitive to the orientation of the CF_3 group. Counterpoise corrections[15] to B3LYP calculations for pairs of 3-(trifluoromethyl)phenanthrene molecules suggest that barriers corrected for BSSE are about 10% higher than uncorrected values.

Results and Discussion

Isolated Molecule Structure, Potential Energy Surface and Barrier. The structure of 3-(trifluoromethyl)phenanthrene was calculated at four levels: HF/3-21G, HF/6-31G*, MP2/6-31G* and B3LYP/6-311+G**. Results are shown in Table 1. As expected,[10,11] all four methods reproduce the X-ray diffraction structure well. For the carbon−carbon bond distances, the RMS deviations of the calculated structures from X-ray diffraction results are 0.013, 0.004, 0.010, and 0.005 Å respectively. HF/6-31G* bond lengths are generally shorter than those predicted by B3LYP/6-311+G**. Calculated bond distances in the isolated molecule at both of these levels are all slightly longer than those determined by X-ray diffraction. Meaningful comparisons of C−F bond distances with the X-ray data are more difficult to make due to the observed disorder in the X-ray diffraction experiment, but the mean experimentally determined C−F distance (1.329 Å) is comparable to the mean value predicted by HF/6-31G* (1.325 Å), and somewhat shorter than the B3LYP/6-311+G** mean value (1.355 Å).

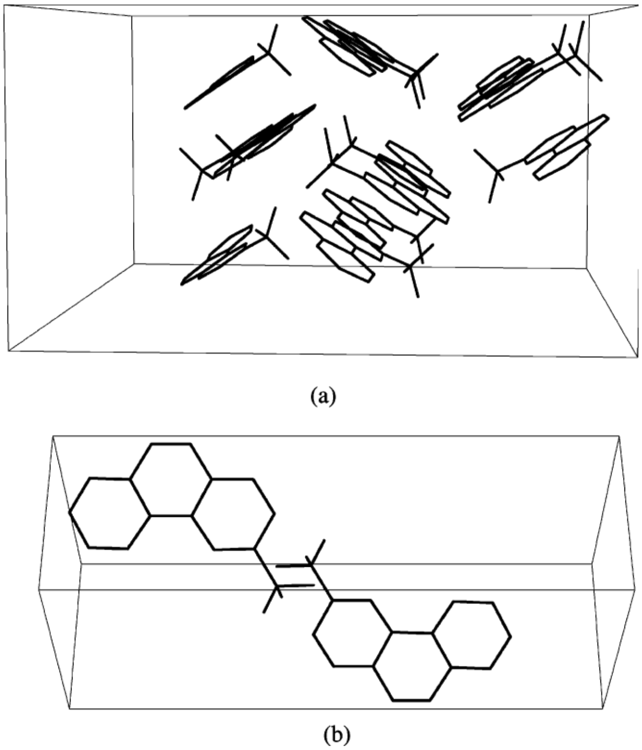

Figure 3. (a) 13-molecule cluster model and (b) relative orientation of the pair of molecules having the closest CF_3 contacts. The boxes are aids to visualization and do not demarcate the unit cell.

A plot of the HF/6-311+G**//HF/6-31G* calculated PES for rotation about the C−C bond in 3-(trifluoromethyl)phenanthrene is shown in Figure 2. The atom numbering scheme is shown in Figure 1. The ground state conformation is found when φ(C4−C3−C15−F3) is 0 ; the transition state for rotation about the C3−C15 bond is found at φ ❩ 60 . Results for both the ground states and transition structures were confirmed as minima and saddle points, respectively, on the PES by normal-mode analyses at the HF/6-31G* level. The rotational barriers for 3-(trifluoromethyl)phenanthrene, defined as the energy difference between the structures having a dihedral angle φ(C4−C3−C15−F3) of 0 and of 60 , at the HF/6-311+G**//HF/6-31G*, B3LYP/6-31G*//B3LYP/6-31G*, B3LYP/6-311+G**//B3LYP/6-311+G** and MP2/6-31G*//MP2/6-31G* levels are given in Table 2. Increasing the size of the basis set does not affect the B3LYP barriers, and they are comparable to those computed at the MP2/6-31G* level. MP2 calculations of small barriers in aromatic systems, such as halogenated phenol derivatives and *o*-fluorotoluene, are likely reliable to within 0.1 kcal mol^{-1}.[16] The insensitivity of the B3LYP calculated barriers to the choice of basis set is not unprecedented.[17,18]

Solid State Structure, Potential Energy Surface and Barrier. To explore the rotation of the CF_3 group in 3-(trifluoromethyl)phenanthrene in the solid state, we constructed a cluster model based on the single crystal X-ray structure, which is shown in Figure 3. The X-ray diffraction results show there is only a single type of molecule in the unit cell, so the local environments of all the CF_3 groups are the same.

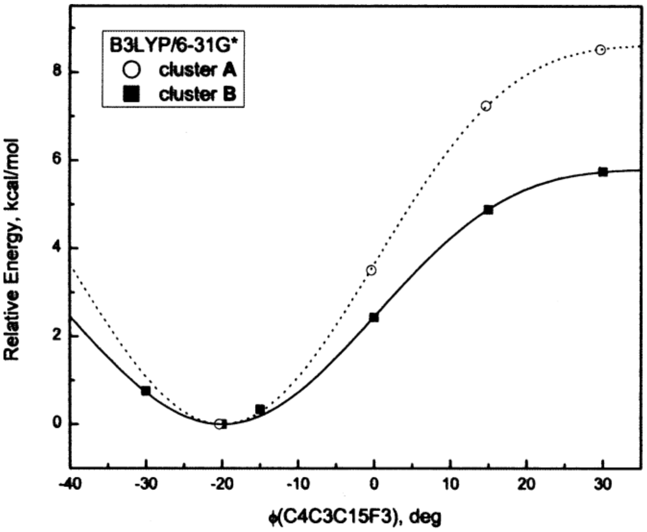

Figure 4. B3LYP/6-31G* potential energy surfaces for rigid CF_3 rotation in the 13-molecule cluster model for 3-(trifluoromethyl)-phenanthrene. The aromatic skeleton structure was fixed at the positions determined in the X-ray crystal structure and the coordinates of all CF_3 groups were optimized at the HF/3-21G level. The smooth curves represent sinusoidal fits to the computed points.

Disorder in the X-ray data precluded the precise location of the CF_3 groups experimentally. Such disorder is characteristic of these kinds of hindered rotors.[19] The positions of the hydrogen atoms were determined by fixing the phenanthrene carbon atom skeleton at the crystallographically determined position and optimizing at the HF/3-21G level. At the same time, we resolved the disorder with respect to the fluorine positions in our model by optimizing the positions of the CF_3 groups. All the C15−F bond lengths were allowed to relax individually, as were the CCF bond angles and related dihedrals. The placements of the CF_3 group relative to the phenanthrene skeletons, i.e., the C15−C3 bond distances, were also optimized to allow as much flexibility in the positions of the fluorines as possible without altering the experimentally determined structure of the phenanthrene skeleton. This cluster model structure is the basis for computation of all the barriers and rotational PES discussed below.

Taking the orientation of the CF_3 group on the central molecule of the 13-molecule cluster described in the preceding paragraph to be representative of the CF_3 groups in the crystal, we replace the CF_3 groups in the 12 neighboring molecules with duplicates of the CF_3 group on the central molecule. An estimate of the barrier to CF_3 rotation in the crystal is obtained by rigidly rotating the CF_3 group on the central molecule. The barrier to rotation for this model (**A**) is calculated to be 7.32 kcal mol^{-1} at HF/3-21G and 8.52 kcal mol^{-1} at the B3LYP/6-31G* level. These estimates are so far in excess of the experimentally determined effective barrier to rotation in the crystal[3] of 2.7 ☾ 0.2 kcal mol^{-1} that we can conclude that such independent rotation does not take place.

We subsequently allowed the cluster to adopt a more realistic structure where the CF_3 groups exhibit a distribution of rotational conformations by permitting the CF_3 groups in the cluster to relax independently of one another. Again, all the parameters related to the CF_3 groups were allowed to vary, including the C3−C15 distances, all C−F distances, the C−C−F angles and the C−C−C−F dihedrals. The resulting "relaxed" cluster (model **B**) has a distribution of C4−C3−C15−F3 dihedrals ranging from −20 to −40 . This is consistent with the disorder observed in the X-ray diffraction structure, where the two CF_3 positions are characterized by C4−C3−C15−F3 dihedral angles of −32 (80% position) and −48 (20% position). We realize that by so severely truncating the infinite crystal, the variations in the computed dihedral angles could result from edge effects. This procedure generates a set of reasonable and energetically accessible rotational states for the CF_3 groups, which we can take as an extremely rough model of a distribution that might be observed in a selected section of the crystal.

To generate a somewhat more realistic PES for the CF_3 rotation, we fixed the parameters of the 12 molecules in the first "shell" at those determined in model **B**. The C4−C3−C15−F3 dihedral of the central molecule was then varied from −60 to +60 in 15 increments (without permitting the structural parameters of the CF_3 group to relax) to compute the potential energy curves shown in Figure 4 for the rigid internal rotation of the CF_3 group on the central molecule of this cluster using the HF/3-21G and B3LYP/6-31G* theoretical models. The critical points of the PES are identical at both levels. The minimum was found to be at the −20 conformation, and the transition state corresponds to +30 .

The computed classical barrier height for model **B** is 4.52 kcal mol^{-1} at HF/3-21G and 5.74 kcal mol^{-1} at the B3LYP/6-31G* level. These estimated barriers are roughly an order of magnitude larger than those for the isolated molecule (0.69 kcal mol^{-1} at HF/3-21G//HF/3-21G and 0.40 kcal mol^{-1} at B3LYP/6-31G*//B3LYP/6-31G*). Qualitatively, the differences between model **B** for the CF_3 rotation in the solid state and the rotation in the isolated molecule are consistent with those determined experimentally for similar systems; for example, the barrier to methyl rotation in 3-fluorotoluene increases by a factor of 10, from 0.05 kcal mol^{-1} for the isolated molecule to 0.5 kcal mol^{-1}in the solid state.[20] Both the HF/3-21G and the B3LYP/6-31G* computed barriers for this model are much higher than the results from NMR relaxometry (2.7 ☾ 0.2 kcal mol^{-1}),[3] again suggesting that independent rotation of the CF_3 groups is a poor model for the motion in these systems even when there is a distribution of orientations in the ground state.

The similarities between the HF/3-21G and B3LYP/6-31G* computed PES for model **B** suggest that we can use HF/3-21G to construct a partially relaxed model (model **C**) for the transition state for rotation of the central CF_3 group. The ground state for model **C** was taken to be that obtained for model **B**. The C4−C3−C15−F3 dihedral angle of the central CF_3 group was fixed at that of the transition state found in model **B** (+30). Parameters associated with the CF_3 groups of the 12 molecules surrounding the CF_3 group of interest were allowed to relax. The C3−C15 distance, the C−F bond lengths, and C−C−F angles of the central CF_3 were allowed to relax as well. The barrier computed for model **C** is 1.95 kcal mol^{-1} at the HF/3-21G level and 2.62 kcal mol^{-1} at B3LYP/6-31G*. The B3LYP/6-31G* value for this partially relaxed barrier is in good agreement with the activation energy of 2.7 ☾ 0.2 kcal mol^{-1} measured by nuclear spin relaxation measurements.[3]

In the model **C** transition state, we note the orientation of the CF_3 group nearest to the central CF_3 group changes significantly relative to the ground state for the model. The distance between the sp^3 carbon atoms of the two groups is 4.154 Å. In the ground state, one C−F bond in this nearest neighbor CF_3 group has a dihedral angle of −28 with respect to its C3−C4 bond. When the central CF_3 group is rotated by 50 to model the transition state, the nearest neighbor CF_3 group responds by increasing its C4−C3−C15−F3 dihedral by 17 , to −45 . The next nearest neighbor in the cluster is 5.405 Å away (defined by the distance between the sp^3 carbon atoms).

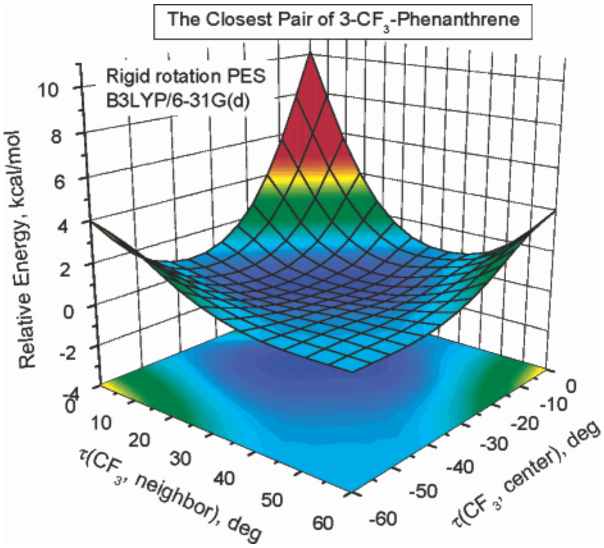

Figure 5. Two-dimensional B3LYP/6-31G* potential energy surface for rigid CF$_3$ rotation in the closest pair of 3-(trifluoromethyl)-phenanthrene, shown in Figure 3b.

No significant change is observed in the structure of this next nearest CF$_3$ group in the transition state, nor are there significant changes in any of the other 10 neighbors in the cluster. This suggests that CF$_3$ rotation involves a "gearing" motion of these two closely packed CF$_3$ groups. To further test this conclusion, the nearest CF$_3$ group was removed from the cluster in model **A** and replaced by a hydrogen substituent at the 3-position of the phenanthrene ring. In the absence of the nearest CF$_3$ group, the rigid rotation barrier for the central CF$_3$ group falls to 2.50 kcal/mol at the B3LYP/6-31G* level, which is a decrease of 6.02 kcal/mol from the barrier in the reference cluster, model **A**.

Resolving the Ambiguity in the X-ray Diffraction Structure. The ability to analyze the NMR spin relaxation data presented in the companion paper[3] depends on an accurate determination of the locations of the hydrogen and fluorine atoms in the crystal structure. The positions of the hydrogens can be easily and directly determined using electronic structure techniques. We can also use these methods to unravel the source of the disorder in the fluorine positions determined by X-ray diffractometry.

As we show above, the intermolecular interaction between the central CF$_3$ group and its closest neighboring CF$_3$ group in the cluster is the dominant factor that determines the equilibrium orientation of the central CF$_3$ group and its rotational barrier. A two-molecule cluster, which comprises the closest pair of molecules in the crystal, was then built to model such an interaction and is shown in Figure 3b.

The PES with respect to the rigid rotations of the two CF$_3$ groups was calculated at the B3LYP/6-31G* level by varying the two CF$_3$ dihedrals independently from 0 to 60 in 10 intervals, and is shown in Figure 5. The two molecules of this pair are connected by an inversion center. Thus, the same conformations of the CF$_3$ groups in the two molecules have the same dihedral angle τ(CF$_3$) but with opposite signs. To be consistent with the labeling in the 13-molecule cluster, the CF$_3$ group with the negative dihedral in the 2-molecule cluster is designated as the center CF$_3$ group and the other one is designated as the closest neighbor, although in this pair model they are completely equivalent.

The PES in Figure 5 is symmetric about the diagonal line, τ(CF$_3$, neighbor) ❩ $-\tau$(CF$_3$, center), as expected because the two molecules are equivalent. There are two equivalent global energy minima in Figure 5. One is the conformation with τ(CF$_3$, center) ❩ −20 and τ(CF$_3$, neighbor) ❩ 30 and the other is the conformation with τ(CF$_3$, center) ❩ −30 and τ(CF$_3$, neighbor) ❩ 20 . This result is in agreement with the optimization results in the 13-molecule cluster, in which the central CF$_3$ group is found at τ(CF$_3$) ❩ −20 and the closest neighbor at τ(CF$_3$) ❩ 28 . Interchange of the orientations of the closest pair in the 13-molecule cluster, produces the second minimum point. The conformations with both the CF$_3$ groups at the same orientation, either −20 /20 or −30 /30 , in the two-molecule cluster are higher in energy by about 0.13 and 0.12 kcal mol^{-1}, respectively, than the energy of the two global minima. There is a saddle point along the diagonal direction close to the −30 / 30 conformation. These results suggest that the strong intermolecular interaction between the closest pair leads the two neighbors to have a slight preference for orientations that are 10 apart. This energetic preference is likely one reason for the disorder of the CF$_3$ groups in the crystal noted in the X-ray data. The conformation with both CF$_3$ groups at 0 , which is the ground state conformation for the isolated molecule, is the global energy maximum point with a relative energy about 10.1 kcal mol^{-1} higher than either of the two global minima.

The two-dimensional PES in Figure 5 not only provides a thermodynamic motive for the appearance of two CF$_3$ orientations in the thermal equilibrium structure of the crystal but also suggests that the rotations of the CF$_3$ groups on the closest pair are coupled. In the partially relaxed rotation of the central CF$_3$ group, the closest neighbor CF$_3$ group was found to reorient by 15 at the rotational transition state of the central CF$_3$ group. From Figure 5, it is clear that the minimum energy path involves the two global energy minima, which can interconvert easily through a saddle point of about 0.12 kcal mol^{-1} height. The coupling between the two groups alleviates the otherwise significant repulsion between the two.

The presence of a second minimum is likely not the only factor underlying the disorder of the fluorine atoms. The harmonic libration of hindered rotors has long been known to lead to disorder in X-ray diffraction structure solutions.[19] Observation of disorder in a structure with groups having internal degrees of rotational freedom can be suggestive of a high barrier toward rotation of the group. This type of disorder is typically manifested as two positions for the "rotating" atoms, spanning roughly the limits of the libration. In fact, estimates for the barrier can be extracted from X-ray data.[21] Cruickshank and Bürgi note that in many cases, the apparent bond lengths will be shortened.[22] Such disorder is evident in the CF$_3$ groups in our structure and suggests that both the presence of additional minima and the relatively high barrier play a role in the apparent disorder observed for the positions of the fluorine atoms.

As Figures 2 and 4 show, the classical PES for the rotation of a CF$_3$ group attached to a phenanthrene framework is well represented by a sinusoidal potential. The energies for the motion can be found by constructing the matrix representation of $\hat{H}$ in the free rotor basis.[23] The lowest energy solutions are well approximated as harmonic librations about the classical minimum energy conformation, with a characteristic librational frequency in this case of approximately 40 cm^{-1} (0.1 kcal mol^{-1}). Assuming a Boltzmann distribution among these states at 213 K (the temperature at which the X-ray diffraction study was carried out), we constructed a probability function for the expected distribution of rotational angles. Statistically, 22.5% of the rotors are expected to be in the ground state, and 17.3% in the first excited state. The first 10 states account for more than 90% of the rotors at this temperature. The quantization of the librational motion gives rise to an inherent uncertainty in the dihedral angles. The classical turning points for the ground state are at approximately ±3 and increase to ±6 by the third excited state, which is significantly populated in the temperature range within which we are working. Ninety percent of rotors have dihedrals within 11 of the minimum.

The difference between the dihedrals of the two locations established for the CF_3 groups in the experimental X-ray diffraction structure is 15 , consistent with the expected thermal distribution described above. The mean C−F bond lengths in the X-ray structure are 0.026 Å shorter than in the B3LYP/6-311+G** theoretical structure, further suggesting that one source of the apparent disorder is the high barrier to rotation of the CF_3 group, and that this will augment the disorder due to the presence of the two minima on the rotational PES.

Computation of the Nuclear Spin Relaxation Parameters. The information obtained by combining the X-ray diffraction data and the ab initio electronic configuration calculations in 3-(trifluoromethyl)phenanthrene, as presented here, is very helpful for severely limiting the number of adjustable parameters used in fitting the ^{19}F and ^{1}H nuclear spin relaxation data.[3] The temperature dependence of the relaxation at two NMR frequencies shows considerable structure, the relaxation rate is inherently biexponential, and the combination of the fact that there is a single motion and that F,,,F and F,,,H vectors are specified by the results of this work results in a very stringent test of dynamical models for the relaxation.

An "effective activation energy" of 2.7 ± 0.2 kcal mol^{-1} is extracted from the relaxation data independently of any other fitted parameters, or indeed, independently of the dynamical model. The value of 2.6 kcal mol^{-1} for the barrier height presented here provides excellent agreement.

CF_3 rotation modulates intramolecular and intermolecular F,,,F and F,,,H spin−spin dipolar interactions and it is the modulation of these interactions that allows an excited nuclear spin system to relax. (No H−H spin−spin interactions are modulated on the NMR time scale by CF_3 rotation in 3-(trifluoromethyl)phenanthrene.) The relaxation is dominated by intramolecular F,,,F interactions that, in this case, are the same as intra-CF_3 interactions. As reviewed in detail in the companion NMR relaxation paper,[3] this dominant contribution to the observed relaxation rate can be calculated with relatively high precision using the information presented here and is not, therefore, an adjustable parameter in fitting the relaxation data.

A detailed fit of the NMR relaxation data provides two additional parameters. One measures the role of intermolecular F,,,F spin−spin interactions that, in this case, are the same as inter-CF_3 dipolar interactions. The relaxation is only weakly dependent on these interactions and the fit of the relaxation data suggests that they provide between 5 and 20% of the relaxation provided by the intramolecular F,,,F spin−spin interactions. Using the fluorine positions given here, a figure of 11% is computed,[3] in good agreement with the experimental value.

Finally, the fit is very sensitive to the modulation of unlike-spin F,,,H spin−spin interactions by CF_3 rotation, and a parameter that specifies the contribution of these interactions can be determined to within 20% by fitting the relaxation data. This parameter can also be calculated from the positional data provided here, although comparing a theoretical and experimental parameter that is a measure of these interactions is more difficult.[3] Overall, this work and the experimental NMR relaxation work[3] taken together provide a very strong test of the model for nuclear spin relaxation.

Conclusions

Ab initio electronic structure calculations on isolated molecules and small cluster models for the crystalline solid state have the potential to provide accurate barriers to intramolecular rotation of substituents in catacondensed hydrocarbons. These calculations also provide an insight into the source of the barrier to reorientation of the CF_3 groups in 3-(trifluoromethyl)-phenanthrene. Our calculations suggest that the coupled reorientation of pairs of CF_3 groups in the crystal is important. We attribute the disorder of the CF_3 groups found by X-ray analysis of crystalline 3-(trifluoromethyl)phenanthrene to the presence of two closely spaced minima on the potential energy surface and to the effects of the librational motion resulting from the high barrier for CF_3 reorientation. The ability of electronic structure methods to locate protons accurately and to resolve the ambiguity in the fluorine positions of CF_3 groups allows computation of key parameters for analyzing solid-state NMR relaxometry data.

Supporting Information Available: Information regarding the X-ray structure, as well as Cartesian coordinates for optimized geometries of isolated 3-(trifluoromethyl)phenanthrene and for the cluster models are available without charge at http://pubs.acs.org.

References and Notes

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(23) The matrix elements in the free rotor basis are $H_{mm} = m^2(\hbar^2/2I_{\mathrm{rotor}})\delta_{mm} + (V_3/2)\delta_{mm} - (V_3/4)\delta_{m\,m+3} - (V_3/4)\delta_{m\,m-3}$, where I_{rotor} is the moment of inertia of the rotating group relative to the axis of rotation and where V_3 is the barrier height for the classical 3-fold hindered rotation described by $V(\varphi) = (V_3/2)(1 - \cos 3\varphi)$. Though the basis is formally infinite, in practice, a finite basis can be employed. We consider here the case for which $I_{\mathrm{rotor}} = 1.491 \times 10^{-45}$ kg m^2 and $V_3 = 2.7$ kcal mol^{-1} with a basis of 1001 functions. See: Flygare, W. H. *Molecular Structure and Dynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1978.