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The quenching of isopropyl group rotation in van der Waals molecular solids

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X-ray diffraction experiments are employed to determine the molecular and crystal structure of 3-isopropylchrysene. Based on this structure, electronic structure calculations are employed to calculate methyl group and isopropyl group rotational barriers in a central molecule of a ten-molecule cluster. The two slightly inequivalent methyl group barriers are found to be 12 and 15 kJ mol^{-1} and the isopropyl group barrier is found to be about 240 kJ mol^{-1}, meaning that isopropyl group rotation is completely quenched in the solid state. For comparison, electronic structure calculations are also performed in the isolated molecule, determining both the structure and the rotational barriers, which are determined to be 15 kJ mol^{-1} for both the isopropyl group and the two equivalent methyl groups. These calculations are compared with, and are consistent with, previously published NMR ^{1}H spin-lattice relaxation experiments where it was found that the barrier for methyl group rotation was 11 ± 1 kJ mol^{-1} and that the barrier for isopropyl group rotation was infinite on the solid state NMR time scale. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2884344]

INTRODUCTION

In a large class of planar aromatic compounds, the rotational barrier for methyl group rotation in ethyl[1–9] and isopropyl[1,7,10–12] groups tends to be dominated by *intramolecular* interactions in both the isolated molecule[6–9] and in the crystal.[1–5,10–12] The barriers for ethyl and isopropyl group rotations in these compounds, however, are much larger in the crystal than in the isolated molecule because these groups lack rotational symmetry. As such, the interactions that determine the rotational barrier are dominated by *intermolecular* interactions. Ethyl and isopropyl group rotational barriers in isolated molecules similar to that studied here[6–9] are in the $1-8$ kJ mol^{-1} range, but in the solid state they are effectively infinite.[1–5,10–12] In the solid state, rotational barriers in the $5-50$ kJ mol^{-1} range can be determined by observing the temperature and the nuclear magnetic resonance (NMR) frequency dependence of ^{1}H spin-lattice relaxation rates. Previously published experiments with solid 3-isopropylchrysene[1] were fitted with a model that suggested that the methyl groups rotated in a barrier of 11 ± 1 kJ mol^{-1}. This same study (along with others[10–12]) suggested that the isopropyl groups were motionless on the NMR time scale, indicating, in this case, that the barrier for isopropyl group rotation was

much greater than 50 kJ mol^{-1}. We have now determined the molecular and crystal structure of 3-isopropylchrysene, and we have performed electronic structure calculations in both the isolated molecule and in a cluster of ten molecules based on the x-ray structure. We are able to confirm the results of the earlier NMR relaxation experiments and determine, unambiguously, that isopropyl group rotation is completely quenched in the solid state.

EXPERIMENTAL AND COMPUTATIONAL METHODS

The synthesis of 3-isopropylchrysene is presented elsewhere.[1] Colorless, rod-shaped crystals were grown by the controlled diffusion of acetonitrile into a toluene solution. Tetragonal $I4$, $a = 21.1099(3)$, $c = 6.6425(2)$ Å, $V = 2960.08(11)$ Å^3, $Z = 8$, and $T = 100$ K. Of 10,501 reflections collected with a Bruker Kappa APEXII diffractometer using Cu $K\alpha$ radiation, 2668 were unique ($R_{int} = 0.0159$). $R1 = 0.0253$ and $wR2 = 0.0690$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (see Ref. 13).

Electronic structure calculations were carried out using the GAUSSIAN 03 suite of programs.[14] The orientations of the isopropyl and methyl groups were varied, and a two-dimensional potential energy surface was computed. The isopropyl and methyl group barriers were then computed from the energy difference between the top and the bottom of the

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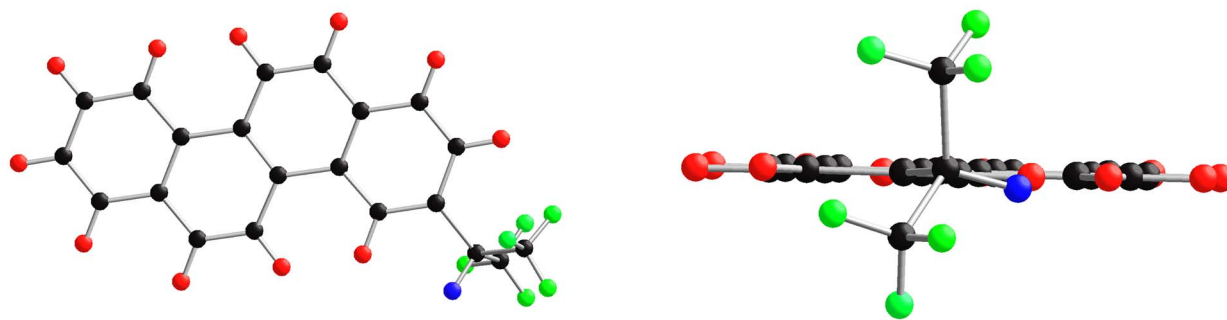
    128, 124502-1

FIG. 1. (Color online) The molecule 3-isopropylchrysene in a plane perpendicular to the aromatic plane and in the aromatic plane. The structure is that found in the crystal. The positions of the carbon atoms (black) are determined by x-ray diffraction and the positions of the hydrogen atoms are determined by electronic structure calculations. Aromatic hydrogen atoms are in red online and gray in print, isopropyl methyl group hydrogen atoms are in green online and gray in print, and the single isopropyl group hydrogen atom is in blue online and black in print.

potential energy surface. For comparison purposes, methyl and isopropyl group rotational barriers were computed both in the isolated molecule and in the solid state. For the isolated molecule, for each fixed methyl group and isopropyl group orientation, all bond angles and bond lengths were allowed to relax to compute the energy. Geometry optimizations of isolated molecules were carried out using the HF/6-31G*//HF/6-31G* theoretical model.[15] Single point energy calculations were done at the HF/6-311 +G**//HF/6-31G* level.[16]

Models of 3-isopropylchrysene in the crystal environment were constructed from the refined single crystal x-ray structure using the MATHEMATICA code DIRACCRYSTAL.[17] Clusters included all the molecules with any atom falling within a sphere of radius 0.71 nm having its center located at the target CH carbon atom of the isopropyl group. The radius was chosen to include a sufficient number, 10 in this case, of neighboring molecules to model the local environment for the isopropyl group of interest on the center molecule. The C–H bond lengths were allowed to relax individually in the cluster with the carbon atoms fixed at the crystallographically determined positions. The partial geometry optimizations of clusters were conducted at the HF/3-21G//HF/3-21G level, while single point energy calculations were done using B3LYP/6-31G*. The effect of the basis set size and the choice of the theory level for the computational results in clusters have been discussed previously.[18] The basis set superposition error was not corrected for calculations on clusters, as it has been shown to have a minor effect for the purpose of calculating rotation barriers.[18]

RESULTS

In the isolated molecule, the ground-state orientation of the isopropyl group as determined by the electronic structure calculation has a dihedral angle of 0° between the CH bond on the central carbon of the isopropyl group and the plane of the carbon skeleton of the chrysene ring system. The ground-state orientation for the methyl groups is the usual staggered conformation. The barrier heights of the isopropyl group and the two methyl groups are almost the same, 15 kJ mol^{-1}.

Figure 1 shows the structure of the individual molecule in the crystal with carbon atom positions determined by the

x-ray diffraction experiments and proton positions determined by the electronic structure calculations. Figure 2 shows the crystal structure. All molecules are equivalent. In the crystal (Fig. 1), the CH bond on the central carbon of the isopropyl group has a dihedral angle of 15° relative to the plane of the carbon skeleton of the chrysene ring system, and the two CC bonds to the methyl groups have dihedral angles of 48° and 76° relative to that plane. The isopropyl barrier is about 240 kJ mol^{-1}, and the two methyl barriers are 12 and 15 kJ mol^{-1}, computed at the B3LYP/6-31G* level.

DISCUSSION

In 3-isopropylchrysene, the NMR relaxation experiments in the solid state were interpreted in terms of a barrier of 11 ± 1 kJ mol^{-1} for the methyl groups and an infinite barrier for the isopropyl group.[1] Similar results have been found for other ethyl[1–5] and isopropyl[10–12] compounds in the solid state. In the NMR relaxation experiments, the relaxation rate $R=Af(\omega,T)$, where the function $f(\omega,T)$ is an appropriately normalized function of NMR frequency $\omega/2\pi$ and temperature T.[2,10] The constant A depends on geometrical factors of the various alkyl groups and *both* on the number of hydrogen atoms involved in the motion and on whether or not methyl group rotation is superimposed on ethyl or isopropyl group rotation. It is on the basis of the fitted parameter A that one concludes with some degree of confidence that ethyl and isopropyl group reorientations are completely quenched or, equivalently, have an infinite barrier. Infinite barrier here means that no ethyl or isopropyl group motion has been observed in the solid state on the NMR time scale, which is equivalent to a barrier of >50 kJ mol^{-1}.

The electronic structure calculations in 3-isopropylchrysene indicate that the methyl groups are in slightly different environments in the crystal (Figs. 1 and 2) with barriers of 12 and 15 kJ mol^{-1}. Whereas the calculations determine the difference between the bottom and the top of the barrier, the NMR measurements determine an effective barrier that depends on the details of the potential energy surface and on the size of the barrier. NMR barriers are generally found to be 10%–20% lower than the "real" barriers for barriers in the 10 kJ mol^{-1} range.[19,20] As such, the agreement here is good. The more important result, though, is that the
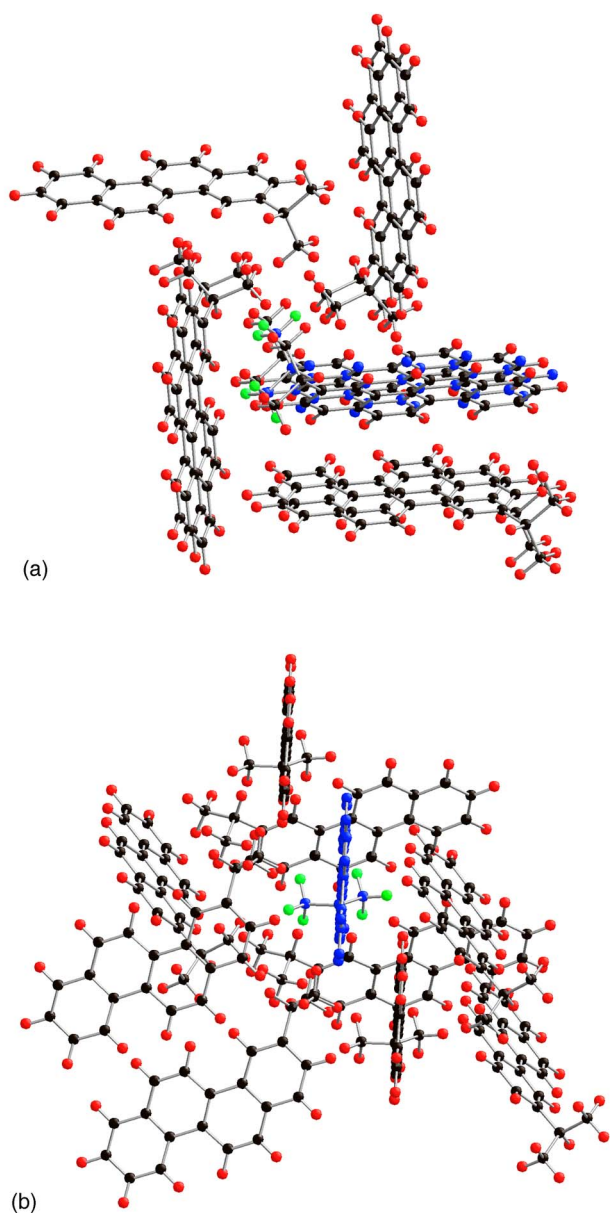
(a)

(b)

FIG. 2. (Color online) The cluster of ten 3-isopropylchrysene molecules used in the electronic structure calculations. The positions of carbon atoms are determined by x-ray diffraction, and the positions of hydrogen atoms are determined by electronic structure calculations. All molecules are equivalent. The six methyl group protons on the central molecule are colored green online and gray in print. All other atoms on the central molecule are colored blue online and black in print. In the surrounding nine molecules, carbon atoms are colored black (online and print) and hydrogen atoms are colored red online and gray in print. The view in (a) is a rotation of 10° about the *x* axis and 10° about the *y* axis from the 001 plane. The view in (b) is in the plane of the chrysene backbone of the central molecule.

calculations in 3-isopropylchrysene indicate that the isopropyl group rotation is completely quenched in the solid state. The "infinite" barrier observed by NMR is indeed consistent with the 200+ kJ mol^{-1} barrier determined by the electronic structure calculations. Given the *quantitative* similarity between the relaxation rate results in 3-isopropylchrysene[1] and other isopropyl[10–12] and ethyl[1–5] compounds in the solid

state, we conclude that the quenching of isopropyl and ethyl group rotations is quite general.

CONCLUSIONS

Nuclear spin relaxation rate experiments determine barriers for methyl group rotation in a large class of ethyl and isopropyl substituted compounds. These experiments are modeled by quantitative models that suggest that ethyl and isopropyl rotations do not occur on the NMR time scale; the motion is completely quenched. Electronic structure calculations can compute these barriers so long as the molecular and crystal structures have been determined, either by x-ray diffraction or neutron scattering. The methyl group barriers in crystalline 3-isopropylchrysene, as determined by the calculations and the NMR experiments, are completely consistent, as is the fact that the isopropyl group rotation in the solid state is completely quenched, even though the barrier for that motion in the isolated molecule is approximately the same as the barrier for methyl group rotation. The NMR relaxation experiments, then, are completely consistent with the electronic structure calculations, and this gives one more confidence in using these calculations to investigate the relationship between the various intramolecular and intermolecular interactions in the solid state where the barriers involved are relatively small.

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