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Single-crystal X-ray diffraction, isolated-molecule and cluster electronic structure calculations, and scanning electron microscopy in an organic solid: Models for intramolecular motion in 4,4'-dimethoxybiphenyl

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This paper brings together field emission scanning electron microscopy, single-crystal X-ray diffraction, and ab initio electronic structure calculations in both an isolated molecule and a cluster of 7 whole and 14 half molecules of 4,4'-dimethoxybiphenyl to investigate coupled methyl group rotation (over a barrier) and methoxy group libration (meaning a rotation from the ground state *not* all the way to the transition state and back again). The structure of the isolated molecule, determined by the electronic structure calculations, is compared with the structure of the molecule found in the crystal. As the methyl group rotates from its ground state to its transition state, the methoxy group rotates 30$^{\mathrm{O}}$ in the isolated molecule and 16$^{\mathrm{O}}$ in the cluster. The calculated barriers for this coupled methyl group rotation and methoxy group libration in the isolated molecule and in the crystal are 12.8 kJ mol^{-1} and 10.3 kJ mol^{-1} respectively, suggesting that intermolecular interactions in the crystal *lower* the barrier. These barriers are compared with the value of 11.5 ± 0.5 kJ mol^{-1} obtained from solid state ^{1}H spin-lattice relaxation measurements [P. A. Beckmann and E. Schneider, *J. Chem. Phys.* **2012**, *136*, 054508, 1-9.]

Introduction

Small methyl-substituted organic molecules in the solid state are good systems for investigating (1) the relationship between methyl group rotation and molecular and crystal structure[1-12] and (2) for developing models for intramolecular motion.[7, 11, 13-16] They are also good test cases for comparing calculated and measured barriers to intramolecular motion.[17-22] In this paper we bring together single crystal X-ray crystallography, isolated molecule and molecular cluster ab initio electronic structure calculations, and field emission scanning electron microscopy with 4,4'-dimethoxybiphenyl (Figures 1 and 2). This allows us to relate the properties describing methyl group rotation and methoxy group libration to the structure on both the microscopic and macroscopic scales. By "methyl group rotation", we mean a rotation from a ground state to a transition state followed by a return to the ground state either by rotating in the same direction or by rotating in the opposite direction. By "methoxy group libration", we mean a rotation from the ground state only part way to the transition state followed by a reversal of the rotation back to the ground state. We compare the calculated barrier for this coupled methyl group rotation and methoxy group libration in the isolated molecule with the calculated barrier in the cluster, and the latter with the barrier determined from solid state nuclear magnetic resonance (NMR) ^{1}H spin-lattice relaxation experiments reported elsewhere.[23] The calculations assume that methyl group rotation corresponds to classical rotation or hopping over a barrier and that tunnelling plays no role. This is appropriate for methyl group rotation above approximately 80 K as discussed elsewhere.[23] The X-ray structure was determined at 113 K and this is high enough, at least for this compound, to interpret methyl group rotation as a semi-classical thermally hopping process.[23]

The covalent bonding in small organic molecules like 4,4'-dimethoxybiphenyl is much stronger than the intermolecular van der Waals interactions that predominantly determine the packing pattern of the solid. The differences in molecular structure in the isolated molecule and in the crystal in these van der Waals solids are often very small except for some conformational changes that show the competition between intermolecular interactions and intramolecular interactions in the solid state, particularly intramolecular non-bonded interactions. As an example, the inter-ring angle of biphenyl and its derivatives varies in the gas, liquid, and solid phases. The rotational dynamics around the linkage bond have been well studied both experimentally and theoretically.[24-33] The parameters that characterize methyl group rotation and other similar motions can be studied in bulk samples using solid state NMR relaxation techniques[23] and interpreted in terms of small intermolecular perturbations to parameters determined from intramolecular interactions alone by electronic structure calculations.[34] Using electronic structure calculations and the X-ray data together, we show that even though there is a change in conformation for 4,4'-dimethoxybiphenyl in going from the isolated molecule to the crystalline state, this change involves only the relative orientation of the two benzene rings (Figure 1) and the "half molecule" (or 4-methoxyphenyl group), has almost the same conformation in the crystal as it has in the isolated molecule. In addition to methyl group rotation (over the barrier) in 4,4'-dimethoxybiphenyl, the two phenyl groups can rotate with respect to one another and each methoxy group can rotate with respect to its benzene ring. Electronic structure calculations provide insights into these rotational motions and allow a comparison of the various interactions found in the isolated molecule with those found in a cluster of molecules built from the X-ray diffraction determination of the crystal structure.[4, 34, 35] Field emission scanning electron microscopy[36] is used to help determine the sizes of the crystallites used in the NMR relaxation experiments.[23]

Results

Single-crystal X-ray diffraction

The crystal structure of 4,4'-dimethoxybiphenyl at 113 K is shown in Figure 2. Although there are 4 molecules per unit cell ($Z = 4$), they are all chemically equivalent. All methyl, methoxy and 4-methoxyphenyl groups are chemically equivalent. That is, the asymmetric unit is half a molecule ($Z' = 1/2$). Figures 1 (b) and (c) show a single molecule taken from the crystal structure in Figure 2 [(a) and (b)]. The X-ray crystallographic measurements show the magnitudes of thermal ellipsoids are small and nearly identical for all oxygen and ring carbon atoms. This suggests that the rotations of the phenyl groups are frozen in the crystal, in agreement with the electronic structure calculations presented below. The out-of-plane elongation of the methoxy carbon atom [see Figure 1 (b)] is consistent with the calculated methoxy group libration, also discussed below.

Field emission scanning electron microscopy

Figure 3 shows field emission scanning electron microscopy[36] images of (a small part of) the same polycrystalline sample of 4,4'-dimethoxybiphenyl used in the solid state NMR relaxation experiments.[23] An important question in interpreting solid state NMR relaxation results is whether or not a significant number of methyl groups see a barrier different from that characterized by the perfect crystalline environment. The crystallites appear to be flat plates with two dimensions in the range 50 – 150 μm [Figure 3(a)]. In addition, the plate thicknesses appear to be remarkably uniform [Figure 3(b)], characterized by sizes of 10 – 20 μm. However, it is not clear that these are single crystals. They may be much thinner stacked crystals or if they are 10 – 20 μm thick crystals, they might have faults between the layers.

Electronic structure calculations in the isolated molecule

In a manner described in the Experimental Methods section, potential energies were calculated for $0^{\circ} < \alpha < 180^{\circ}$, $0^{\circ} < \delta < 180^{\circ}$, and $0^{\circ} < \gamma < 180^{\circ}$. The angle α (H-Cm-O-C4) is the dihedral angle for the methyl group with the Cm-O bond being the rotation axis. The carbon atom numbering scheme is defined in Figure 1 (c). The angles α, δ, and γ are also indicated in Figure 1(c). The angle δ (Cm-O-C4-C5) is the dihedral angle for the methoxy group with the O-C4 bond being the rotation axis. The angle γ (C6-C1-C1'-C2') is the rotational dihedral angle for the 4-methoxyphenyl group (with the C1-C1' bond being the rotation axis). In the ground state of the isolated molecule, the two benzene rings make an angle of approximately $\gamma = 40^{\circ}$ with respect to each other [Figure 1(a)]. Forcing the two rings to be coplanar (as found in the solid state) ($\gamma = 0^{\circ}$) raises the energy by 8.0 kJ mol^{-1}. In the ground state, the two methoxy groups have $\delta = 0^{\circ}$ and the methyl group is oriented with $\alpha = 60^{\circ}$. Except for the 40° relative orientation of the two benzene rings, the calculated conformation for the isolated molecule is very close to the X-ray single-crystal diffraction structure as indicated in Table 1. That is, the ground state conformation of each 4-methoxyphenyl group (one-half the molecule) is essentially the same in the isolated molecule as it is in the molecule in the crystal. The root mean square deviation between the calculated C-C and C-O bond lengths in the isolated molecule and the experimental bond lengths in the crystal is approximately 1.2 pm while all the bond angles are essentially the same (see Table 1).

Considering the methyl group rotation about the Cm-O bond, the barrier height is V_{isolated} = 12.8 kJ mol^{-1}. The barrier has an approximate 3-fold rotational symmetry (i.e., not 6-fold or higher). The methyl group rotates by -73° from the $\alpha = 60^{\circ}$ ground state or $+47^{\circ}$ from the $\alpha = -60^{\circ}$ ground state to reach the transition state ($\alpha = -13^{\circ}$). In the methyl group rotational transition state, one of the methyl group hydrogen atoms gets too close to the neighboring aromatic hydrogen atom at the 5 position. The steric hindrance results in the rotation of the whole methoxy group out of the benzene ring plane by 30° from $\delta = 0^{\circ}$ to $\delta = 30^{\circ}$. When $\alpha = -13^{\circ}$ and $\delta = 30^{\circ}$, the close contact between a methyl group hydrogen and the ring hydrogen on C5 then becomes 203.0 pm. This coupled rotation is indicated in Figure 4.

The rotational transition state of the methoxy group corresponds to $\delta = 90^{\circ}$. The barrier is 12.3 kJ mol^{-1}. The rotation does not cause any change in α for the methyl group or any change in γ for the other 4-methoxyphenyl group. This means that the energies as a function of δ are independent of α and γ so long as α and γ are near their ground state values.

The orientation of the methoxy groups has little effect on the rotational potential energy surface of the 4-methoxyphenyl groups, which leads to three rotational transition states of similar energy for the 4-methoxyphenyl groups, whose ground state corresponds to $\gamma = 40^{\circ}$. In the first transition state, the two phenyl rings are perpendicular to each other ($\gamma = 90^{\circ}$) and the energy is 8.33 kJ mol^{-1} higher than that of the ground state. In the other two transition states, the two phenyl rings are coplanar ($\gamma = 0^{\circ}$) and the two methoxy groups are trans or cis to each other. The latter two transition states are very close in energy. One gives a phenyl-phenyl rotational barrier height of 7.99 kJ mol^{-1} and the other gives a barrier height of 8.04 kJ mol^{-1}. The barrier heights for phenyl-phenyl rotation are consistent with the computational results and the experimental measurements in biphenyls of other research groups.[24-30]

Electronic structure calculations in the cluster

As outlined in the Experimental Methods section, a cluster of 7 whole and 14 half molecules was constructed from the structure determined by the X-ray diffraction at a temperature of 113 K. This cluster is shown in Figure 2 (c). As also outlined in the Experimental Methods section, three levels (models) of calculations were performed. Comparing the results from the three models is instructive. In the *rigid rotation model* (the first of the three models used) atom positions were not permitted to relax when atomic groups on the central molecule were rotated. The barrier height for the methyl group (α: $60^{\circ} \rightarrow 0^{\circ}$) is 19.4 kJ mol^{-1}. The transition state occurs at $\alpha = 0^{\circ}$. But for the methoxy group and the benzene ring, the barriers are very high, 2.1 MJ mol^{-1} for the benzene ring

(γ: $0^{\mathrm{O}} \rightarrow 90^{\mathrm{O}}$), and 0.77 MJ mol^{-1} for the methoxy group (δ: $3^{\mathrm{O}} \rightarrow 90^{\mathrm{O}}$). This means that these rotations over their barriers will be completely quenched in the crystal.

In the *partially relaxed model I* (the second of the three models used), in which only the atoms in the methoxy group and the hydrogen atoms on the same molecule as the rotations are occurring [i.e. the central one in Figure 2 (c)] are allowed to optimize, the barrier height becomes 10.5 kJ mol^{-1} for methyl group rotation (α: $60^{\mathrm{O}} \rightarrow 0^{\mathrm{O}}$). The greatest structural change different from the situation encountered in the isolated molecule is that the methoxy group reorients by approximately 16^{O} (δ: $3^{\mathrm{O}} \rightarrow 19^{\mathrm{O}}$) in the transition state, rather than the 30^{O} (δ: $0^{\mathrm{O}} \rightarrow 30^{\mathrm{O}}$) found in the isolated molecule. This says that a significant methoxy group libration takes place as the methyl group rotates through its rotational transition state. This coupled rotation-libration reduces the barrier by 8.9 kJ mol^{-1} from 19.4 kJ mol^{-1} found in the *rigid rotation model* to 10.5 kJ mol^{-1}.

In the *partially relaxed model II* (the third and final model), in addition to the structural relaxation of the methoxy group and the hydrogen atoms in the central molecule of the cluster, structural relaxation of the benzene ring to which the methoxy group is attached and all the other methoxy groups and hydrogen atoms in the cluster is also allowed. Thus both the intramolecular rotational coupling of methyl and methoxy groups *and* the possible additional intermolecular rotational coupling among methyl or methoxy groups involving neighboring molecules could be investigated. The calculated methyl barrier is changed from 10.5 kJ mol^{-1} in the *partially relaxed model I* to 10.3 kJ mol^{-1}, a small difference. In this model, the phenyl ring shows very slight twisting with respect to the other phenyl ring in the transition state. The methyl and methoxy groups in the neighboring molecules show no appreciable structural change when the methyl group in the central molecule rotates from its ground state to its transition state (accompanied by its parent methoxy group libration). This means that there are no significant intermolecular rotational couplings.

Conclusions and Summary

There are many examples in the literature where activation energies for methyl group rotation have been measured using solid state nuclear magnetic resonance (NMR) relaxation techniques. Although these measurements involve a large class of small methyl-substituted organic molecules like methyl-, ethyl-, isopropyl-, and *t*-butyl-substituted benzenes, naphthalenes, anthracenes, and phenanthrenes,[1, 3-7, 11, 16, 20, 34-35, 37-46] only recently has a compound with a methoxy group been investigated.[23] The observed NMR activation energy E_{NMR} for methyl group rotation in all these systems is in the 3 - 20 kJ mol^{-1} range. By "methyl group rotation", we mean a rotation from a ground state to a transition state followed by a return to the ground state either by rotating in the same direction or by rotating in the opposite direction. Electronic structure calculations are now able to calculate these relatively small barriers in clusters of molecules with considerable accuracy.[4, 34, 35] Here we use a central molecule surrounded by 7 whole and 14 half-molecules of 4,4'-dimethoxybiphenyl. This totals more than 300 atoms involving many intermolecular van der Waals interactions as well as intramolecular covalently bonded interactions. Non-hydrogen atoms are fixed in the positions determined by X-ray crystallography, though the positions of some carbon and oxygen atoms are allowed to relax in determining the energy of the rotational transition states. Hydrogen atom positions are determined by the electronic structure calculations (in all states) since the X-ray experiments position the hydrogen atoms with C-H bond lengths that are too short.[47, 48] For example, the X-ray positioning of the H atoms in 4,4'-dimethoxybiphenyl gives the methyl C-H bonds as 98.1 pm whereas the calculations give these bond lengths as 107.6, 108.0, and 108.1 pm, a difference of approximately 10 pm, consistent with previous studies.[47, 48] The X-ray positions the ring H atoms such that all the ring C-H bonds are 94.9 pm. The calculated distances vary between 106.7 and 107.0 pm so here the difference is approximately 12 pm. The shortening could be as large as 3 pm for C-H bond lengths in methyl groups in neutron diffraction measurements at room temperature due to thermal vibrations.[47]

A major result of this work is that the electronic structure calculations suggest that one cannot really speak of only a "methyl group barrier" in molecules like 4,4'-dimethoxybiphenyl. It is necessary to consider methyl group rotation plus methoxy group libration. Allowing the methoxy group to go from a ground state to a transition state results in a very high barrier, even allowing the methyl rotation axis and the position of all neighboring atoms to find their lowest energy positions. This motion is completely quenched in the crystalline environment.

If everything is kept rigid in a suitable cluster of molecules, the barrier for methyl group rotation over the barrier in 4,4'-dimethoxybiphenyl is calculated to be 19.4 kJ mol^{-1}. In this case, the methoxy group is not permitted to rotate from its ground state. If the positions of the atoms in the targeted methoxy group are allowed to relax (including a rotation of the methoxy group), this calculated barrier reduces to 10.5 kJ mol^{-1} and if additional atom positions in the home molecule and neighboring molecules are allowed to relax a further 0.2 kJ mol^{-1} decrease is obtained. This significant reduction from the rigid model to the partially relaxed models says that it is important to allow atom positions in the vicinity of the dynamical process of interest to vary in the calculation but more distant atom positions are less important. This 10.5 kJ mol^{-1} barrier then becomes the barrier for methyl group rotation plus methoxy group libration. Indeed, this agrees with one's general understanding of the intramolecular and intermolecular interactions involved. Allowing additional atoms in neighboring molecules to relax does show, however, that there are no coupled motions involving methyl or methoxy groups on different molecules. Previous studies also suggest the computation methodology is accurate enough to study methyl group rotation in van der Waals crystals.[4, 34, 35] Thus, we report the barrier for methyl group rotation to be V_{crystal} = 10.3 kJ mol^{-1}. Determining a computational uncertainty for this value is a difficult problem and the best approach at this time is to compare this value with experimental results.

^{1}H NMR nuclear spin relaxation experiments in polycrystalline 4,4'-dimethoxybiphenyl provide an activation energy of E_{NMR} = 11.5 ± 0.5 kJ mol^{-1} that is reasonably independent of the details of the fitting model.[23] The assumptions are that the statistics for methyl group "hops" from one ground state configuration to another are given by Poisson statistics and that the mean time between hops is modeled with an Arrhenius Equation.[23] This is one parameter that solid state NMR relaxation measurements can provide with some confidence. This value is in reasonable agreement with the value of V_{crystal} = 10.3

kJ mol^{-1} determined here from the electronic structure calculations, even though E_{NMR} and V_{crystal} are not the same parameter and relating them is a complicated problem in and of itself.[49,50] The parameter determined by the electronic structure calculation is very clear; it is a barrier height. $V_{\mathrm{crystal}}\, f(\theta)$, where $f(\theta)$ is an appropriately normalized angular function (approximately $\cos 3\theta$ for methyl group rotation in the present case) for some rotation angle θ, is the *potential function* one would use in Schrödinger's equation. E_{NMR} on the other hand is a Canonical Ensemble average of energy differences involving many possible transitions from quantum states whose energies are near the bottom of the potential well to quantum states whose energies are above the top of the potential well. Many factors come into play. The theoretical studies relating E_{NMR} and V_{crystal}[49,50] only involve methyl group rotation not methyl group rotation plus methoxy group libration.

A comparison between values of V_{crystal} and E_{NMR} as defined here has been made for eight methyl-substituted phenanthrenes and naphthalenes.[34] The differences $V_{\mathrm{crystal}} - E_{\mathrm{NMR}}$ for barriers in the 5 – 12 kJ mol^{-1} range were found to vary from +3 kJ mol^{-1} to –0.8 kJ mol^{-1}. For 4,4'-dimethoxybiphenyl, this difference is $V_{\mathrm{crystal}} - E_{\mathrm{NMR}} = -1.2$ kJ mol^{-1}. This negative value is larger than any of the eight methyl-substituted systems studied in reference 34 but that study involved methyl groups bonded directly to an aromatic ring, not via an oxygen atom as is the case for 4,4'-dimethoxybiphenyl. We are investigating this further in other methoxy substituted compounds.

Considering only the electronic structure calculations, the $V_{\mathrm{crystal}} = 10.3$ kJ mol^{-1} barrier for methyl group rotation plus methoxy group libration in 4,4'-dimethoxybiphenyl in the solid state is *less* than the barrier $V_{\mathrm{isolated}} = 12.8$ kJ mol^{-1} for this coupled motion in the isolated molecule. Comparison with the electronic structure calculations in the several methyl-substituted phenanthrenes and naphthalenes[34] shows that the barrier height in the central molecule in the cluster V_{crystal} is the same as or very slightly larger than the barrier calculated in the isolated molecule V_{isolated}. An intermolecular steric interaction can either increase or decrease the barrier for methyl group rotation, depending on whether the destabilizing steric crowding of that methyl group against an adjacent molecule in the cluster is more severe in the transition state or more severe in the ground state for that rotation.[51] It might be that a cooperative methyl group rotation and methoxy group libration, as opposed to methyl group rotation alone, will generally result in a lower barrier in the crystalline state than in the isolated molecule. Again, we are investigating this further in other methoxy substituted compounds.

The final comment concerning the relationship between structure and methyl-methoxy motion is that the orientation between the two phenyl groups in 4,4'-dimethoxybiphenyl doesn't matter. Previous studies[1, 3-7, 11, 16, 34, 35, 37-39] have involved only alkyl-substituted "rigid" molecules, meaning rigid on the NMR time scale which is approximately 10^{-12} to 10^{-5} s for the relaxation experiments reported elsewhere[23]. In an isolated molecule of 4,4'-dimethoxybiphenyl, the two phenyl rings are oriented at 40^{O} and in the solid state this angle is 0^{O}; the backbone of the molecule is planar. Although this increases the energy associated with intramolecular interactions by approximately 8 kJ mol^{-1}, presumably the energy associated with intermolecular interactions are decreased by more than that. In the isolated molecule the barrier for rotation of the phenyl group is approximately 17 kJ mol^{-1} but in the solid it is sufficiently large as to prohibit phenyl group rotation over a barrier as might be expected from inspection of the crystal structure. However, the coupled methyl-methoxy group motion is completely insensitive to this phenyl-phenyl angle. This is an important result and it means that we need only consider "half-molecules" in this discussion. Indeed, the asymmetric unit in the crystal structure is half a molecule.

NMR says nothing about "motion" in the classical sense. For methyl group rotation at high temperatures where tunneling plays no role,[23] it simply provides statistics concerning the hopping of the triangle of hydrogen atoms from one minimum in the potential to another. It is a purely statistical model in which the concept of continuous position as a function of time has no place. The triangle of hydrogen atoms "sits" in an equilibrium configuration and once in a while reorients to an "identical" position. The time for the transition is zero (on the NMR time scale). The hops are instantaneous. This is why comparing the parameters obtained from an analysis of NMR relaxation experiments with parameters obtained from electronic structure calculations is so interesting. For sure, the ab initio electronic structure calculations begin by calculating an energy from Schrödinger's equation but then this energy is provided as a function of position, in this case an angle or angles for some rotation(s). So, electronic structure calculations of rotational barriers and solid state NMR relaxation rate parameters like activation energies provide two completely different stories about the same physical reality.

Experimental Methods

The sample of 4,4'-dimethoxybiphenyl

The compound 4,4'-dimethoxybiphenyl was purchased from Sigma Aldrich. The quoted purity of the purchased sample was 99%. Two samples were produced. The first was recrystallized from 95% ethanol and the second was recrystallized from slow evaporation of a diethyl ether solution. The former was used for the scanning electron microscopy experiments and *both* were used in the X-ray diffraction experiments.

Single-crystal X-ray diffraction

A single crystal of 4,4'-dimethoxybiphenyl was mounted using Paratone oil onto a glass fiber and cooled to the data collection temperature of 113 ± 1 K. Crystals from both samples were used and there were no differences in the two structures. We report the conditions here for the single crystal produced by slow evaporation of a diethyl ether solution. The intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated MoKα radiation ($\lambda = 71.073$ pm). The strategies for the data collections were determined using COLLECT software[52] and data were scaled and reduced using DENZO-SMN.[53] Of 4646 reflections collected over $\theta = 3.25^{\circ} - 25.36^{\circ}$, 1003 were unique ($R_{\mathrm{int}} = 0.0442$). Unit cell parameters were refined over all reflection data and yielded $a = 0.72829(6)$ nm, $b = 0.61450(6)$ nm, $c = 2.4622(3)$ nm, $\alpha = \beta = \gamma = 90^{\circ}$, $V = 1.1025(2)$ nm^3. The space group (*Pbca*) was unambiguously assigned from systematic absences in the diffraction data. The positions of all non-hydrogen atoms were located using direct methods with SHELXS-97[54] and refined by full-matrix least-squares with SHELXL-97,[55] refining on F^2. The program X-seed[56] was used as a graphical interface. In the difference Fourier map, the highest residual electron density peak (0.187

e Å^{-3}) was found at 0.29 Å from one of the methoxy methyl hydrogens and the deepest hole (-0.205 e Å^{-3}) at 0.77 Å from the O atom. There is no indication of disorder. All non-hydrogen atoms were refined anisotropically. The data were insufficient to accurately determine the positions of the hydrogen atoms. As such, the hydrogen atoms were placed geometrically with C–H distances of 95 pm or 98 pm and were assigned U_{iso} = 1.2 or 1.5 x U_{eq} of the parent carbon for the aromatic hydrogens and methyl group hydrogens respectively. The structure was refined successfully with a final R_1 = 0.0390 and wR_2 = 0.0801. The structure of the molecule in the solid state is shown in Figure 1 (b) and (c) and the crystal structure is shown in Figure 2 (a) and (b).

Field emission scanning electron microscopy

Field emission scanning electron microscopy[36] was performed using a FEI Quanta 600FEG Scanning Electron Microscope. Loose crystalline material was "sprinkled" on graphite conductive adhesive on a cantilevered platform with a 45^{O} slant which allowed for different views. By sprinkling the sample we were able to achieve a variety of orientations for the sample which was composed of flat crystallites, thus allowing a determination of the smallest dimension because many were imbedded in an edge-on orientation. The sample is not a good electrically conducting material. To achieve a high resolution image, the specimen must be conductive and well grounded to prevent the accumulation of static electric charge at the surface.[36] Therefore, the sample was thoroughly degassed and then sputtered with approximately 5 nm of gold/palladium (for 20 s at 1 kV and 0.1 mbar) using a Cressington magnetron sputter coater. Images are shown in Figure 3.

Electronic structure calculations in the isolated molecule

All electronic structure calculations were carried out using the Gaussian03 suite of programs.[57] The geometry of an isolated 4,4'-dimethoxybiphenyl molecule was taken from the X-ray crystallographic structure of the compound (see Table 1) and subsequently optimized at the B3LYP/6-311+G** level.[58-63] Potential energy surfaces for the rotation of the methyl groups, the methoxy groups, and the 4-methoxyphenyl groups were done at the B3LYP/6-311+G**//B3LYP/6-311+G** level.[64] Calculations were performed for 15^{O} steps in α, δ and γ and all other structural parameters were allowed to be optimized. This calculation scheme has been shown to be a good compromise between the accuracy and speed in studying the internal rotation problem.[35] The rotational ground state and the rotational transition state identified by this scheme were indistinguishable from those obtained by directly locating the minimum and first-degree saddle points.[34, 35] Figure 1(a) shows the optimized ground state structure of the isolated molecule with the parameters as indicated in Table 1. In addition, a two-dimensional potential energy surface as a function of α and δ in the isolated molecule was calculated at the B3LYP/6-311+G**//B3LYP/6-311+G** level and is shown in Figure 4. Rotational barriers were taken to be the difference between the calculated energy in the ground state and the calculated energy in the transition state for the methyl group, the methoxy group, and the 4-methoxyphenyl group.

Electronic structure calculations in a cluster

A cluster for simulating the crystal packing environment for 4,4'-dimethoxybiphenyl, shown in Figure 2(c), was constructed from the single-crystal X-ray diffraction data. The cluster is made up of 7 complete molecules and 14 half-molecules. For the 14 half-molecules, the other half of the molecule (another 4-methoxyphenyl group) is replaced by a hydrogen atom to complete the valency. Thus, these are 4-methoxyphenyl molecules. The cluster fixes all C and O atoms at the positions determined from the X-ray structure (for the ground state) but the H positions are determined by the electronic structure calculation at the B3LYP/6-31G level. Potential energy surface calculations were performed on the central molecule in Figure 2(c). Prior experience[4, 34, 35] has shown that adding additional molecules to this cluster will not appreciably change the results. The basis set superposition error, which has been shown to be not significant for the calculation of rotational barriers,[35] was not corrected due to the computational cost. Another method of performing these calculations is to use periodic boundary conditions. It is not immediately clear how many unit cells would be required to avoid artificial dynamical couplings. On the other hand, the cluster model is valid in simulating the local environment in molecular crystals. Previous comparison studies by research groups other than our own have shown that for many applications, small cluster models reproduced the results from periodic models very well.[65-68]

We performed three groups (or models) of calculations, all at the B3LYP/6-31G level.[69-70] In the *rigid rotation model*, calculations were made for 15^{O} steps in α ($0^{\mathrm{O}} < \alpha < 180^{\mathrm{O}}$) and δ ($0^{\mathrm{O}} < \delta < 180^{\mathrm{O}}$). But for the calculations where γ is varied ($0^{\mathrm{O}} < \gamma < 180^{\mathrm{O}}$), the methoxy group and the other 4-methoxyphenyl group were fixed. That is, we investigated the rigid rotational potential energy surface of the benzene ring only on the central molecule.

The rotational ground and transition states of the methyl group identified from these calculations were subject to two additional calculations. In the *partial relaxation model I*, only the positions of the atoms in the parent methoxy group containing the methyl group of interest and the positions of the hydrogen atoms on the central molecule were optimized. In the *partial relaxation model II*, the positions of the atoms in the benzene ring to which the methoxy group is attached and all the other methoxy groups and hydrogens in the cluster were additionally optimized. Similar calculation schemes have been employed to study the rotation of methyl groups in the crystals of five methyl-substituted phenanthrenes and three methyl-substituted naphthalenes.[34] The rotational barriers were taken to be the difference between the calculated energy in the ground state and the calculated energy in the transition state for methyl group rotation, methoxy group rotation, and 4-methoxyphenyl group rotation.

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Supplementary Information

Crystallographic data for 4,4'-dimethoxybiphenyl have been deposited with the Cambridge Crystallographic Data Centre with CCDC number 604799 and reference code JEHDEG. The data can be obtained free of charge via ww.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Table 1. Comparison of parameters for the calculated isolated molecule structure and the X-ray crystallographic structure of the 4,4'-dimethoxybiphenyl molecule.

Parameters[a,b]	Calc	X-ray
Bond Lengths (pm)		
C1-C1^{I}	148.3	149.6(4)
C1-C2	140.6	140.0(3)
C2-C3	138.6	137.9(3)
C3-C4	140.0	138.6(3)
C4-C5	139.6	137.8(3)
C5-C6	139.6	138.7(3)
C6-C1	139.8	139.2(3)
C4-O	136.6	137.9(2)
O-Cm	142.0	143.2(2)
RMSD[c]	1.2	
Bond Angles (^{O})		
C2-C1-C1^{I}	121.3	121.7(2)
O-C4-C5	124.7	125.0(2)
Cm-O-C4	118.5	117.2(2)
Bond Dihedral Angles (^{O})		
C6-C1-C1^{I}-C2^{I}	39.8	0.0
Cm-O-C4-C5	0.0	2.9(3)

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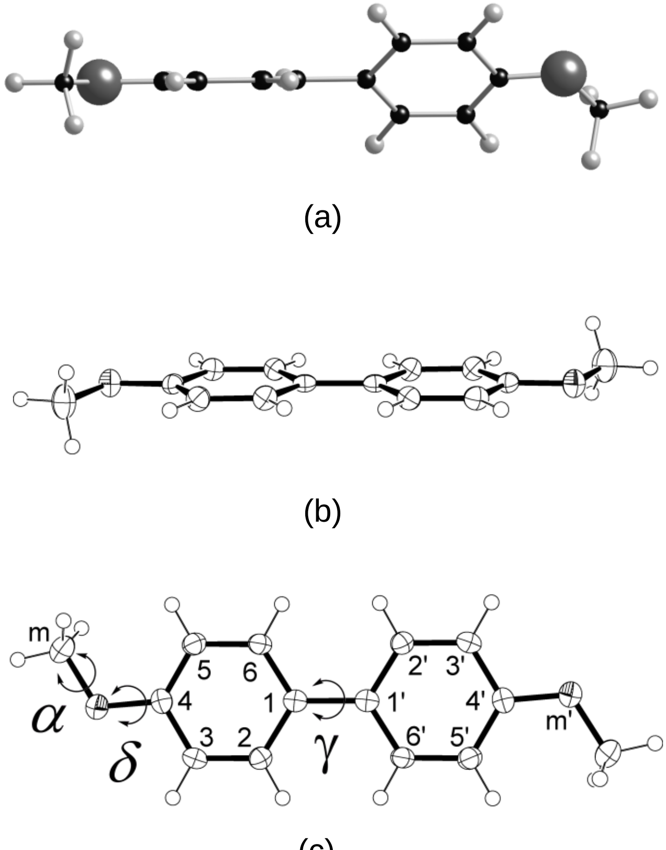
[a] Since the two 4-methoxyphenyl groups are equivalent in both the calculated (isolated molecule) and experimental structures, only the parameters of one part of the molecule or between the two parts are given.

[b] Atom labeling is indicated in Fig. 1.

[c] Root mean square deviation between the calculated values in the isolated molecule and the X-ray values in the crystal.



(a)

(b)

(c)

Figure 1. The molecular structure of 4,4'-dimethoxybiphenyl. **(a)** The conformation of the isolated molecule as determined by electronic structure calculations. The two phenyl rings are at an angle of approximately 40°. Small black spheres are carbon atoms, small light grey spheres are hydrogen atoms, and large dark grey spheres are oxygen atoms. **(b)** and **(c)** The molecular structure (Ortep diagrams) in the solid state [see Figure 2 (a) and (b)] as determined by X-ray diffraction, showing two projections differing by a rotation of approximately 90° about a horizontal axis. The numbering scheme for the carbon atoms is shown in (c) as are the angles α, δ, and γ. Hydrogen atoms are placed in idealized positions.

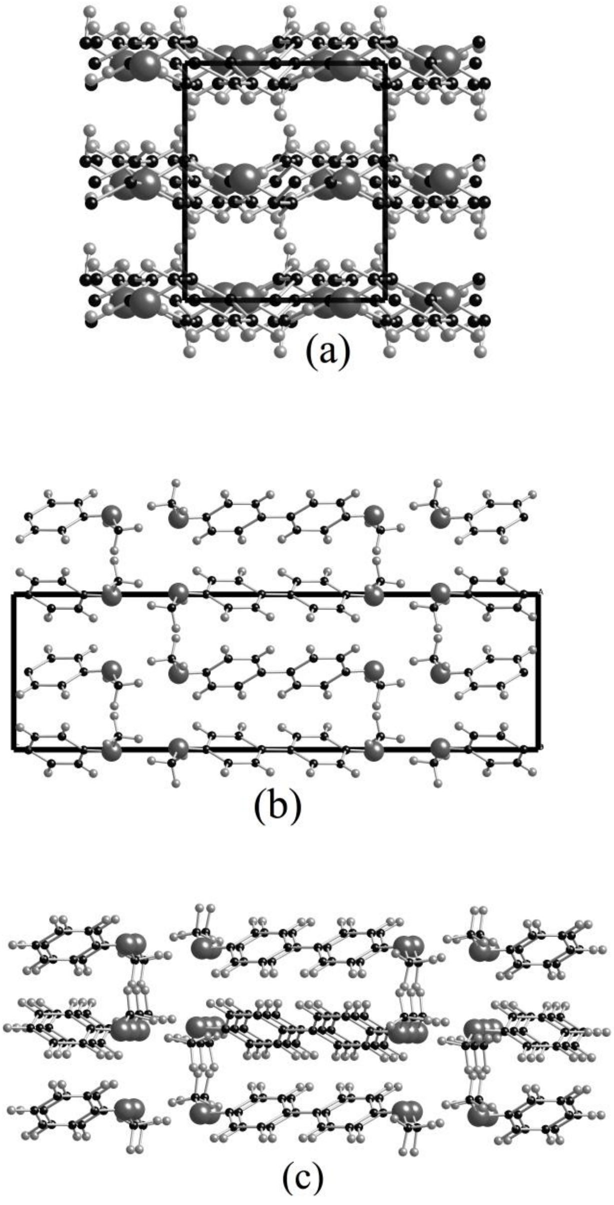
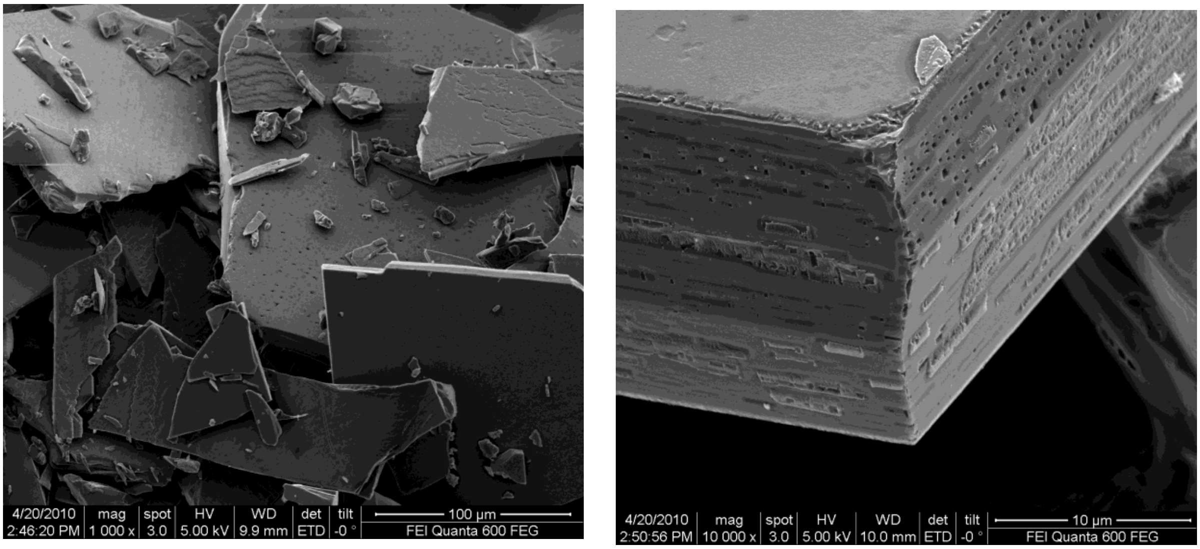


Figure 2. The crystal structure of 4,4'-dimethoxybiphenyl. Carbon atoms are small black spheres, hydrogen atoms are small light grey spheres, and oxygen atoms are large dark grey spheres. **(a)** The 001 plane showing 1.6 unit cells in the *x*-direction (vertical) and 2.0 unit cells in the *y*-direction (horizontal). **(b)** the 010 plane showing 1.0 unit cells in the *z*-direction (horizontal) and 2.1 unit cells in the *x*-direction (vertical). All atom positions in (a) and (b), where the unit cell is indicated, are determined from the single-crystal X-ray diffraction experiments. **(c)** The cluster used in the electronic structure calculations. The view is similar to (b) but rotated by 4 degrees about the vertical (*x*) axis to show all 21 complete or part molecules used in the calculation. There are three full molecules in the center, three half-molecules to both the left and the right of center, two full molecules at both the top and bottom center, and two half-molecules in each of the four corners. Methyl, methoxy, and 4-methoxyphenyl group rotational barrier calculations are performed on the central molecule. Note that for the half-molecules, the missing half is replaced by a hydrogen atom. Oxygen and carbon atom positions are taken from the X-ray diffraction structure but hydrogen atom positions are determined from the electronic structure calculations.



(a) (b)

Figure 3. Field emission scanning electron microscopy images of the 4,4'-dimethoxybiphenyl polycrystalline sample showing **(a)** a typical 297 X 273 μm section and **(b)** a 30 X 27 μm section of a crystallite edge.

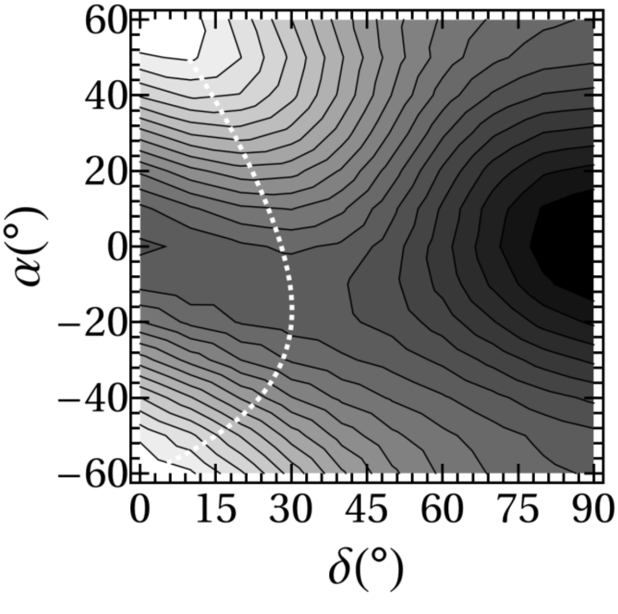


Figure 4. A potential energy contour map as a function of methyl group dihedral angle α (H-Cm-O-C4) and methoxy group dihedral angle δ (Cm-O-C4-C5) in an isolated molecule of 4,4'□dimethoxybiphenyl. The energy is zero in the upper and lower left-hand corners and the contour lines are separated by 0.94 kJ mol^{-1}. The white dashed line traces the coupled methyl group rotation and methoxy group libration. When the methyl group is in its ground state ($\alpha = \pm 60^{\circ}$), $\delta = 0^{\circ}$ corresponds to the lowest energy. When the methyl group is in its transition state ($\alpha = -13^{\circ}$), $\delta = 30^{\circ}$. Note that the contour plot does not have reflection symmetry about the $\alpha = 0^{\circ}$ line.