STRUCTURE OF BIPHENYL IN VACUUM DEPOSITED ADLAYER ON Al$_2$O$_3$

Marissa K. Condie*, Zackery E. Moreau* and A.M. Nishimura[†]

Department of Chemistry, Westmont College, Santa Barbara, CA 93108

Abstract

A molecular adlayer of biphenyl was vapor deposited onto a single crystal of cryogenically cooled Al$_2$O$_3$. Vapor deposition amorphously prepares the biphenyl adlayer in which biphenyl is in the twisted conformation. At 165 K, biphenyl undergoes disorder-to-order transition to a solid crystal in which the biphenyl is planar and less radiative. The lower fluorescence intensity is thought to be due to more efficient non-radiative energy transfer.

Introduction

Biphenyl is structurally unique because of the steric hindrance of the proximal ortho-hydrogens. The movement of electrons in the two phenyl rings can be modulated by adjusting the torsional angle by different substituent groups in the phenyl rings (1). The torsional angle has been the subject of many theoretical studies, with predicted dihedral angles from 35.5°-41.1° (2,3). A planar conformer has also been postulated to be the stable due to potential π-conjugation and σ-σ* hyperconjugation. (4,5). The crystallographic analysis by Trotter indicated that the crystal is monoclinic with 2 molecules per unit cell and that the biphenyl is planar (6). Hargeaves and Rizvi postulated that no conjugation exists between the rings with C-C bond length of 1.506 Å and that intermolecular forces were involved in forcing the rings to be planar.(7) Charbonneau reported that in a solid crystal. biphenyl exhibited large librational modes (8). Brock suggested that the solid state favors nearly planar biphenyl because of packing efficiency (9). He further stated that the conformer of biphenyl was easily changed and that it was especially sensitive to its environment (9).

Spectroscopically E.C. Lim's study showed that the ground state of biphenyl was planar as was the excited state. The 0,0 band in *n*-heptane at 77 K was 299.6 nm, with a strong progression band at 305.5 nm. The 5.9 nm progression was assigned to a torsional mode (10). Others have stated that the torsional angle was 20-40° in the ground state, 0-20° in the excited and a distribution of conformers gave different spectra (11). In a later paper, Fujii reported that biphenyl was twisted in the ground state and planar in the excited state (12,13) In Friedrich's study of the gas phase, the dihedral angle was determined to be 45° due to the competition between the steric hindrance of the ortho-hydrogens and the π-electrons that can delocalize if the phenyl groups were co-planar (14).

In vacuum deposited biphenyl on Al$_2$O$_3$, biphenyl undergoes a disorder-to-order transition at about 165 K. Subsequent to the transition, the fluorescence of multilayer biphenyl red-shifts and decreases to about 15% of the initial intensity. This is due to the enhanced non-radiative energy transfer that occurs in the ordered phase.(15,16) It was previously found that when alkanes and cycloalkanes were passed through the ordered phase of biphenyl, the intensity of the fluorescence increased due to the formation of additional defect sites in the ordered biphenyl. (15,16) If a biphenyl adlayer were deposited and annealed at temperatures higher than the transition temperature, additional deposition would result in the added biphenyl becoming ordered (17). However the nature of biphenyl before and after the transition was unknown. In this study, we report the conformational change in biphenyl on Al$_2$O$_3$ by spectroscopic examination of biphenyl analogs that are constrained to be planar or twisted.

Experimental

Biphenyl, 2-methylbiphenyl, 2,2'-dimethylbiphenyl, fluorene, and 9,10-dihydrophenanthrene were of the highest purity that were commercially available, typically > 99% (Sigma-Aldrich, St. Louis, MO). These compounds were placed in separate sample holders and vapor deposition was accomplished with adjustable precision leak valves. Details of the experimental set up have been previously published (15-17) and a brief summary is given here. The ultra-high vacuum chamber had a background hydrogen base pressure of 1 x 10^{-9} Torr. A single crystal of Al$_2$O$_3$ (0001) (Crystal Systems, Inc., Salem, MA) was suspended on the lower end of a liquid nitrogen cryostat via copper post on either side of the Al$_2$O$_3$ with a sapphire spacer for electrical and thermal isolation. Resistive heating of the Al$_2$O$_3$ was done by sending current through a thin tantalum foil that was in thermal contact with the substrate. A type-K (chromel/alumel) thermocouple (Omega, Norwalk, CT) that was also in thermal contact with the Al$_2$O$_3$ monitored the temperature. Process control during the temperature programmed desorption (TPD) experiment was accomplished by a program written in LabVIEW (National Instruments, Austin, TX) that incorporated a PID (proportional-integral-derivative) feedback algorithm that linearly increments the temperature of the Al$_2$O$_3$ crystal.

During the TPD experiment, the LabVIEW program also took the fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) in real time every 300 ms. Finally, the LabVIEW program scanned the residual gas analyzer for the masses of the compounds that were deposited onto the Al$_2$O$_3$. Manipulation of the array of spectra as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the wavelength resolved TPD that are shown in the figures. To ensure a clean surface, the Al$_2$O$_3$ was heated to 300 K after each run to desorb any residual sample. Temperature ramps to higher temperatures did not indicate any other adsorbates.

The activation energy for desorption, E$_a$, was calculated by

Redhead analysis in which a first-order desorption kinetics as described by King was assumed and is based on the mass spectral peak desorption temperature, T_p (18-20). The uncertainties in the desorption temperatures and the propagated error in the activation energies were ± 2%.

The surface coverages, Θ, in monolayers (ML) were calculated by calibrating the integrated mass spectral peaks to an optical interference experiment. The interference experiment yielded accurate rate of deposition with coverage error of ± 30%, and is described in detail elsewhere (21).

Results and Discussion

From the peak desorption temperature of biphenyl on Al_2O_3, T_p the activation energy for desorption, E_a,were calculated and are given in Table 1. In Figure 1 the spectral profile for biphenyl is shown. The $\lambda_{max} \sim 319$ peak dominates the spectrum initially, followed by about a 15% decrease in intensity and a spectral red-shift to $\lambda_{max} \sim 345$ nm at 165 K, the disorder-to-order transition. Fine structure has been assigned by Lim *et al*. to torsional modes (10). Since this vibrational peak consistently has a very strong intensity, it will be used as a reference (italicized in Table 1).

In order to determine the relative stabilities of the two forms of biphenyl, the biphenyl adlayer was heated to an annealing temperature of 170 K, 5 K higher than the disorder-to-order transition for 20 s. This procedure ensures that the adlayer had undergone the transition. (See Figure 2, left side). Apart from the species that fluoresce at 345 nm, the absence of changes in the spectrum taken after the anneal (Figure 2, right side) indicates that this fluorophore is more stable than that observed at deposition. In other words, the conformer that emits at this wavelength is more stable.

In an attempt to assign the conformers that were involved in the fluorescence at these two wavelengths, 319 nm at deposition and 345 nm the thermally stable ordered fluorophore, biphenyl derivatives that had structurally constrained dihedral angles were examined. Four molecules were chosen, two molecules that are known to be non-planar and two that were almost or totally planar. The criteria were that the substituent groups had to be the simplest possible so that they would minimally affect the electronic energies: 2-methylbiphenyl and 2,2'-dimethylbiphenyl were chosen for the non-planar analogs of biphenyl and 9,10-dihydrophenanthrene and fluorene for the planar biphenyl.
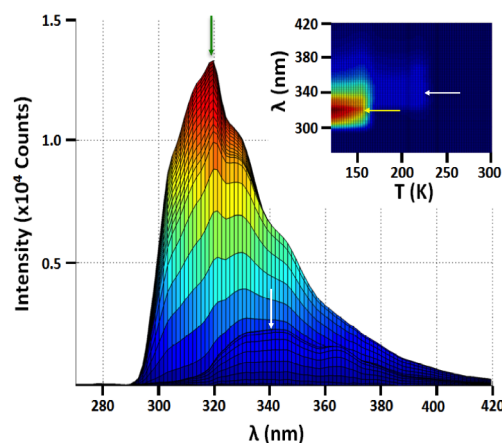

Figure 1. TPD optics, biphenyl multilayer, Θ_biphenyl ~96 ML. The green arrow refers to the peak fluorescence at 319 nm, attributed to the biphenyl twisted conformation. The white arrows refer to the fluorescence at 345 nm, planar monomer (trap). Inset: top view (wavelength versus temperature) yellow arrow points to 319 nm twisted conformer and white arrow points to the 345 nm planar conformer
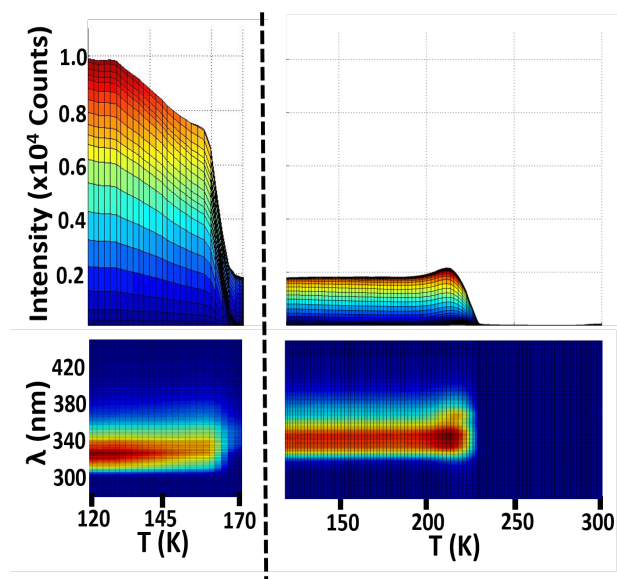

Figure 2. Top left intensity versus temperature plot of an biphenyl adlayer of Θ_biphenyl ~89 ML being heated to the annealing temperature of 170 K, and bottom left is the top view. Top right is the intensity versus temperature plot after annealing at 170 K and the bottom right plot is the top view.

Table 1 Peak desorption temperature (T_p, K), activation energy for desorption (E_a,kJ/mol), λ_{twist} and λ_{planar} for biphenyl and biphenyl analogues in nm. (intensities: vw=very weak, w=weak, m=medium, s=strong) Wavelengths that correlate are in italics.

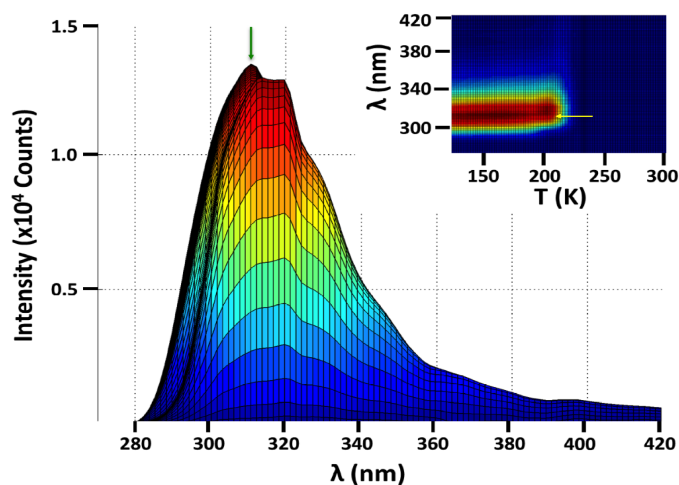|	Biphenyl	2-methylbiphenyl	2,2'-dimethylbiphenyl	9,10-dihydrophenanthrene	fluorene
T_p (K)	227	219	233	237	244
E_a (kJ/mol)	58.9	56.9	60.5	61.5	63.4
λ_{twist} (nm)	304(w), 310(w), *319(s)*	310(s), *320(s)*	*304(s)*, 310(w), 319(w)		
λ_{planar} (nm)	*331(m)*, *345(m)*			336(vw), *349(s)*	330(w), *340(s)*

Figure 3. Wavelength-resolved TPD of multilayer 2-methylbiphenyl, $\Theta_{2\text{-methylbiphenyl}}$ ~150 ML. Due to the rotational barrier the conformer is non-planarGreen arrow points to the 310 nm peak. Due to the rotational barrier, the conformer is non-planar. Inset: top view. Yellow arrow points to the 310 nm peak.
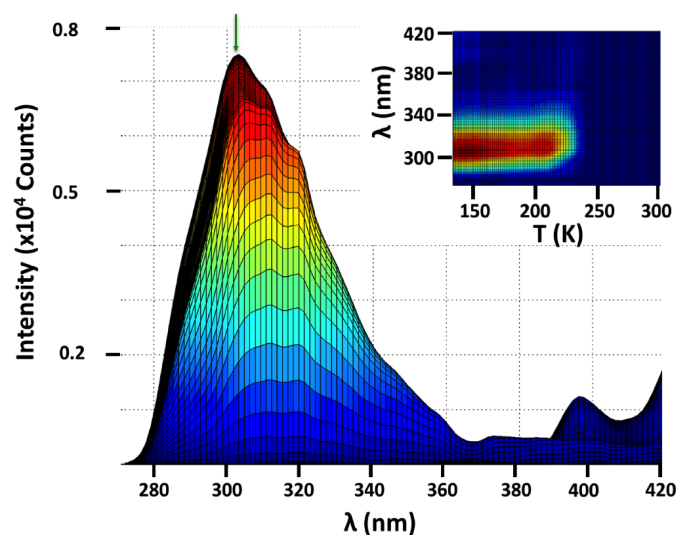

Figure 5. Wavelength-resolved TPD of multilayer 9,10-dihydrophenanthrene, with $\Theta_{9,10\text{-dihydrophenanthrene}}$ ~90 ML. Green arrow points to the fluorescence at 349 nm peak. The molecule is constrained to be almost planar. Inset: top view. White arrow points to the 349 nm peak.

Figure 4. Wavelength-resolved TPD of multilayer 2,2'-dimethylbiphenyl, with $\Theta_{2,2'\text{-dimethylbiphenyl}}$ ~126 ML. Due to the rotational barrier, the conformer is non-planar. Green arrow points to the 304 nm peak. Inset: top view.

Figure 6. Wavelength-resolved TPD of multilayer fluorene with Θ_{fluorene} ~ 99 ML. Green arrow points to the 340 nm peak. The spectrum is that of a planar fluorene molecule. Inset: top view. White arrow points to the 340 peak.

The T_p and E_a of these molecules are given in Table 1, along with the wavelengths λ_{max} of the (0,1) torsional mode as assigned by Lim *et al.*(10). The two non-planar biphenyl molecules, 2-methylbiphenyl and 2,2'-dimethylbiphenyl were deposited and the wavelength-resolved TPD recorded in Figures 3 and 4, respectively. As can be seen the fluorescence showed λ_{max} that remains relatively constant throughout the entire TPD experiment. From Table 1, the intense 310 nm peak for 2-methylbiphenyl and the 304 nm peak for 2,2'-dimethylbiphenyl correspond well with the intense 319 nm biphenyl fluorescence. Since both 2-methylbiphenyl and 2,2'-dimethylbiphenyl are twisted, the 319 nm biphenyl peak is assigned to the twisted conformer.
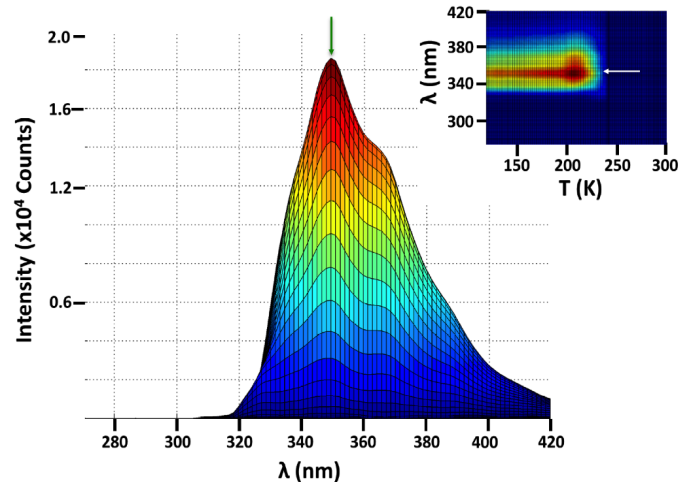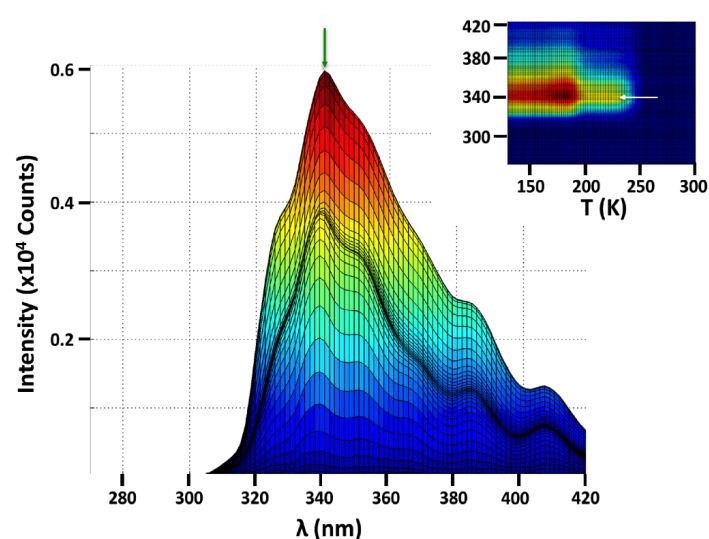
9,10-Dihydrophenanthrene is slightly twisted out of plane and the dihedral angle has been reported to be $18 \pm 1°$ from crystallographic analysis (22). Fluorene is definitely planar (23,24). As can be seen from Figures 5 and 6, the 349 nm peak for 9,10-dihydrophenanthrene and the 340 nm peak for fluorene correspond well with the 331/345 nm peak progression in biphenyl. Hence the progression can be reasonably assigned to a planar conformer.

Conclusion

For biphenyl the gas phase deposition on Al_2O_3 results in an amorphous disordered form that favor the twisted conformation. During the TPD experiment, thermal energy of ~1.4 kJ/mol is suf-

ficient to overcome the activation energy for the adlayer to become ordered. The ordered form that is thermally more stable than the amorphous phase is similar to the crystalline biphenyl in which the biphenyl molecules are planar. In this ordered form the fluorescence intensity is diminished with roughly 85% of the biphenyl molecules non-radiatively transferring energy to defect sites.

References

1. M. Gomez-Gallego, M. Martin-Ortiz, M.A. Sierra, *Eur. J. Org. Chem.* **2011**, 6502-6506.
2. J. Poater, M. Solà and F.M. Bickelhaupt, *Chem. Eur. J.* **2006**, 12, 2889-2895.
3. K. Eskandari and C. Van Alsenoy, *J. Computational Chemistry*, **2014**, 35, 1883-1889.
4. J. Jia, H.S. Wu, Z. Chen and Y. Mo, *Eur. J. Org. Chem.*, **2013**, 611-616.
5. L.F. Pacios, *Struct. Chem.*, **2007**, 18, 785-795.
6. J. Trotter, *Acta Cryst.* **1961**, 14, 1135-1140.
7. A. Hargreaves and S.H. Rizvi, *Acta Cryst.* **1962**, 15, 365-373.
8. G.P. Charbonneau and Y. Delugeard, *Acta Cryst.* **1977**, B33, 1586-1588.
9. C.P. Brock and R.P. Minton, *J. Am. Chem. Soc.*, **1989**, 111, 4586-4593.
10. E.C. Lim and Y.H. Li, *J. Chem. Phys.*, **1970**, 52, 12, 6416-6422.
11. T. Fujii, S. Suzuki and S. Komatsu, *Chem. Phys. Lett.*, **1978**, 57,2, 175-178.
12. H. Cailleau, J.L. Baudour, J. Meinnel, A. Dworkin, F. Moussa, C.M.E. Zeyen, *Faraday Disc. Chem. Soc.*, **1980**, 7-18.
13. T. Fujii, S. Komatsu and S. Suzuki, *Chem. Soc. Japan*, **1982**, 55, 2516-2520
14. G. Friedrich. *J. Phys. Chem. A*, **2002**, 106, 3823-3827.
15. B.D. Fonda, J.B. Cleek, K.A. Martin and A.M. Nishimura, *JUCR*, **2017**, 16, 3, 85-88.
16. J.B. Cleek, B.D. Fonda, K.A. Martin and A.M. Nishimura, *JUCR*, **2017,** 16,4, 110-114.
17. B.D. Fonda, Z.I. Shih, J.J. Wong, L.G. Foltz, K.A. Martin and A.M. Nishimura, *JUCR* **2018**, 2, 32-35.
18. P.A. Redhead. *Vacuum*, **1962**, 12, 203-211.
19. F.M. Lord and J.S. Kittelberger. *Surf. Sci.*, **1974**, 43, 173-182.
20. D.A. King. *Surf. Sci.,* **1975***, 47, 384-402.
21. C.L. Binkley, T.C. Judkins, N.C. Freyschalg, K.A. Martin and A.M. Nishimura, *Surf. Sci.* **2009**, 603, 2207-2209.
22. D. Li, H. Yu, T. Yu, H. Liang, T. Liu, *Acta Crystallographica Section E.* **2012**, 68, 607.
23. M. Maus, W. Rettig, *Chemical Physics* **1997**, 218, 151-162.
24. J. Tan, Q. Wang, Y. Liu, Y. Zeng, Q. Ding, R. Wu, Y. Liu, X. Xiang, *Journal of Macromolecular Science Part A: Pure and Applied Chemistry*, **2018**, 55, 75-84.