

# FORMATION OF 1- AND 2-METHYLNAPHTHALENE- BIPHENYL EXCIPLEXES FROM VAN DER WAALS COMPLEXES BY VAPOR DEPOSITION ON $\text{Al}_2\text{O}_3$

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## Abstract

The two isomers of methylnaphthalene and biphenyl were individually vapor deposited on a liquid nitrogen cooled crystal of  $\text{Al}_2\text{O}_3$ . Temperature programmed desorption (TPD) experiments were then performed. Spectral signatures of multilayer methylnaphthalene and biphenyl were compared with those that were taken for bilayers in which the methylnaphthalenes were deposited first, and then biphenyl on top. The fluorescence spectra of the bilayer were acquired in real time during the mixing. The evolution of the surface dynamics was determined from the spectral signatures of the individual adsorbates. For 2-methylnaphthalene-biphenyl bilayer, the absence of the characteristic spectra of twisted amorphous biphenyl and in its place, an intense broad and featureless spectrum at 370 nm due to the excimers were good indicators that biphenyl was mostly planar in the amorphous layer, and that the observed fluorescence was predominantly from the exciplex. For the 1-methylnaphthalene-biphenyl bilayer, the initial intensity included not only the twisted conformer of biphenyl, but also the planar biphenyl, as evidenced by the presence of excimer peak centered at 370 nm but at a much lower intensity compared to the 2-methylnaphthalene-biphenyl bilayer. During the TPD, thermally induced mixing of the methylnaphthalene and biphenyl in the bilayer occurred and it facilitated the formation of van der Waals complex through the entire adlayer and the exciplex intensity increased to a maximum before desorption. A plot of the intensity of the 2-methylnaphthalene-biphenyl exciplex as a function of the ratio of the coverages of biphenyl to 2-methylnaphthalene showed the stoichiometry of the exciplex was 1:1, whereas for biphenyl to 1-methylnaphthalene, the stoichiometry was 2:1. An explanation of this difference is proposed. From mass specific TPD data, the van der Waals energies were determined to be approximately 6 and 3  $\text{kJ mol}^{-1}$  for the 2-methylnaphthalene-biphenyl and 1-methylnaphthalene-biphenyl complexes, respectively.

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## Introduction

For some time now, the C-C rotational barrier of ethane has been known to be  $12.029 \text{ kJ mol}^{-1}$  (1-2). The two effects responsible for this barrier are steric repulsion in the eclipsed conformation (3-4) and the hyperconjugation of the staggered conformation (5-6). A similar situation exist for the C-C bond in biphenyl. In vapor deposited biphenyl analysis of the fluorescence spectra of the condensed phase revealed that the planar conformer was approximately  $22 \text{ kJ mol}^{-1}$  more stable than the twisted conformer (7-10).

The examination of spectral profiles of several substituted biphenyls in which the biphenyl framework was planar or twisted allowed the assignment of the conformer of biphenyl from the fluorescence spectra (9-10). In the gas phase the conformer is known to have a dihedral angle at  $45^\circ$  (11). Since vapor deposition of biphenyl on  $\text{Al}_2\text{O}_3$  is done from the gas phase, the  $\lambda_{\text{max}} \sim 320 \text{ nm}$  fluorescence that is observed has been assigned to the twisted conformer. When biphenyl is vapor deposited or annealed at 160 K, the fluorescence red-shifts to  $\lambda_{\text{max}} \sim 340 \text{ nm}$  and this emission has been assigned to the planar conformer (9-10) which is also the conformer in the crystalline state (12). This conformation maximizes the electron delocalization in the phenyl groups (13). When vapor deposited at 138 K on  $\text{Al}_2\text{O}_3$ , the amorphous planar conformer predominate and the  $\lambda_{\text{max}}$  shifts further to the red at  $\sim 370 \text{ nm}$  (10,14) and has been assigned to the biphenyl excimer (9-10,14). Epitaxially biphenyl is known to be sensitive to the surface morphology of the underlayer and the conformer of biphenyl as an overlayer will vary, depending on the nature of this underlayer (15). In a companion study to this one (16), the planar conformer of biphenyl was found to be formed by deposition on  $\text{Al}_2\text{O}_3$  by epitaxy on a naphthalene underlayer. Instead of the expected fluorescence from the naphthalene excimer, the wavelength-resolved

TPD was predominantly from the naphthalene in the naphthalene-biphenyl exciplex with biphenyl presumed to be in the planar conformation (16). The stoichiometry of the exciplex was found to be one molecule of naphthalene per molecule of biphenyl (16). The strength of the van der Waals complex between naphthalene and biphenyl was estimated to be  $5.4 \text{ kJ mol}^{-1}$  from the mass specific TPD since the two molecules in the complex desorbed together (16). In this study, since the two isomers of methylnaphthalene are also known to exhibit excimeric fluorescence (17-18), the van der Waals complexes and the resulting exciplexes of biphenyl with 1- and 2-methylnaphthalene are examined.

## Experimental

Biphenyl and naphthalene were of the highest purity that were commercially available,  $> 99\%$  (Sigma-Aldrich, St. Louis, MO). These compounds were placed in 3 separate sample holders and outgassed and introduced into the ultra-high vacuum chamber with background base pressure of  $1 \times 10^{-9}$  Torr. Deposition onto a single crystal of  $\text{Al}_2\text{O}_3$  (0001) (Crystal Systems, Inc., Salem, MA) was done while using one of 3 precision leak valves. The substrate was suspended on the end of a liquid nitrogen cryostat via copper post on either side of the  $\text{Al}_2\text{O}_3$  with a sapphire spacer for electrical and thermal isolation. In the TPD experiments the  $\text{Al}_2\text{O}_3$  crystal was resistively heated by adjusting the current through a Ta foil. TPD experiments were done by resistively heating the  $\text{Al}_2\text{O}_3$  crystal by adjusting the current through a Ta foil. In addition to the Ta foil, a type K thermocouple was in thermal contact with the  $\text{Al}_2\text{O}_3$  crystal.

Details of the experimental set up have been previously published (15) and only a brief outline is given here. During the TPD, a LabVIEW (National Instruments, Austin, TX) program that

had been written in-house took the real time fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL). The program simultaneously monitored the surface temperature of the  $\text{Al}_2\text{O}_3$  crystal, and through a PID (proportional-integral-derivative) feedback algorithm, linearly ramped the temperature of the  $\text{Al}_2\text{O}_3$  crystal. The program also scanned the residual gas analyzer for the masses of the compounds that had been deposited on the  $\text{Al}_2\text{O}_3$ . Manipulation of the very large numerical array of spectral data as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the wavelength resolved TPD that are shown in Figures 1-5. To ensure a clean surface, the  $\text{Al}_2\text{O}_3$  was heated to 300 K after each run.

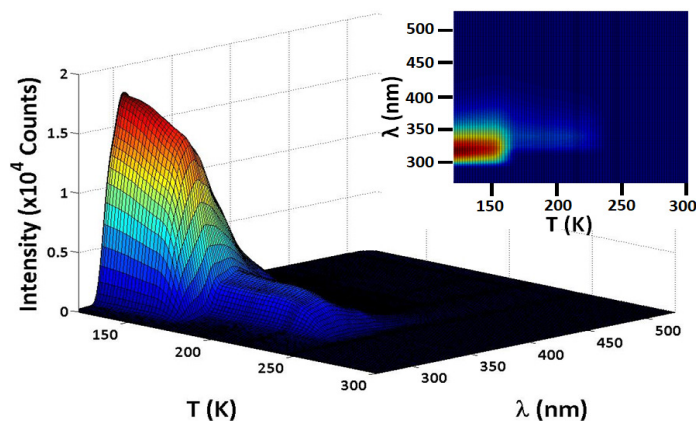
The activation energy for desorption,  $E_a$ , was calculated by Redhead analysis in which a first-order desorption kinetics as described by King was assumed and is based on the mass spectral peak desorption temperature,  $T_p$  (19-21). The uncertainties in the desorption temperatures and the propagated error in the activation energies were  $\pm 2\%$ .

The surface coverages,  $\Theta$ , 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  $\pm 30\%$ , and is described in detail elsewhere (15).

## Results and Discussion

### Biphenyl:

The peak desorption temperature,  $T_p$ , of neat biphenyl was 230 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be  $59.7 \text{ kJ mol}^{-1}$  (19-21). Upon deposition, excitation of neat biphenyl on the  $\text{Al}_2\text{O}_3$  surface with a high-pressure Hg lamp centered at 250 nm caused the amorphous biphenyl to fluoresce with a  $\lambda_{\text{max}}$  of 320 nm. This fluorophore has been assigned to the twisted conformer of biphenyl (9-10). As can be seen from Figure 1, when the surface temperature was linearly ramped, the adlayer underwent a disorder-to-order transition at 160 K, where  $\lambda_{\text{max}}$  red-shifted to 340 nm. This fluorophore has been assigned to the planar conformer of biphenyl (14-15). The reduction in intensity by about 10% occurred because the ordered molecules that became energy carriers for the trap sites

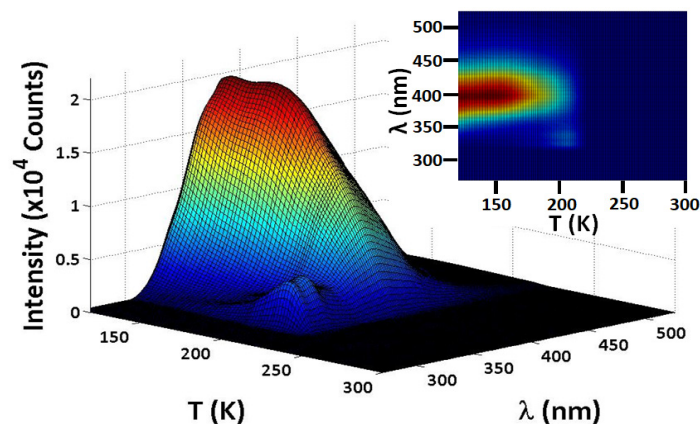


**Figure 1.** Wavelength-resolved TPD of multilayer biphenyl.  $\Theta_{\text{biphenyl}} = 100 \text{ ML}$ . Biphenyl deposited in the twisted conformation with  $\lambda_{\text{max}} \sim 320 \text{ nm}$  that red-shifts to 340 nm subsequent to the disorder-to-order transition. Inset: top view

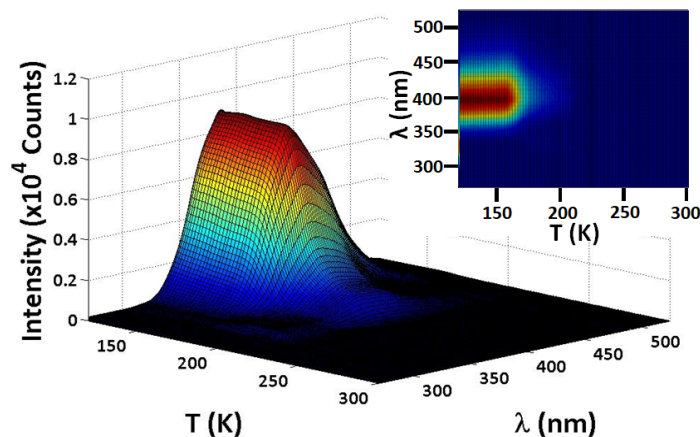
### 1- and 2-methylnaphthalene:

Vapor deposition of aromatic molecules typically results in an adlayer that is morphologically amorphous. Upon optical pumping with light in the ultraviolet, methylnaphthalene molecules form excimers (8). Excimer fluorescence is broad and red-shifted relative to the monomer. When the surface is heated in a TPD experiment, the amorphous adlayer undergoes a disorder-to-order transition, whereupon the fluorescence evolve to the monomer emission. In methylnaphthalenes two resolvable blue-shift peaks at  $\lambda_{\text{max}} \sim 325$  and 336 nm corresponds to  $\sim 50 \text{ kJ mol}^{-1}$  of energy from that of the excimer (17-18).

Figure 2 shows the wavelength-resolved TPD of multilayer 2-methylnaphthalene and in Figure 3 is shown the same for multilayer 1-methylnaphthalene. The fluorescence spectra as a function of temperature were dominated by excimer fluorescence with  $\lambda_{\text{max}} \sim 395 \text{ nm}$ . The peak desorption temperature,  $T_p$ , for 2-methylnaphthalene was 215 K and that for 1-methylnaphthalene was 203.4 K. A first-order desorption kinetics was assumed and  $E_a$  was calculated to be 55.7 and 52.6  $\text{kJ mol}^{-1}$



**Figure 2.** Wavelength-resolved TPD of multilayer 2-methylnaphthalene.  $\Theta_{2\text{-methylnaphthalene}} = 90 \text{ ML}$ . The excimer fluorescence at  $\lambda_{\text{max}} \sim 395 \text{ nm}$  that dominates at deposition, blue-shifts to 325 nm subsequent to the disorder-to-order transition. Inset: top view



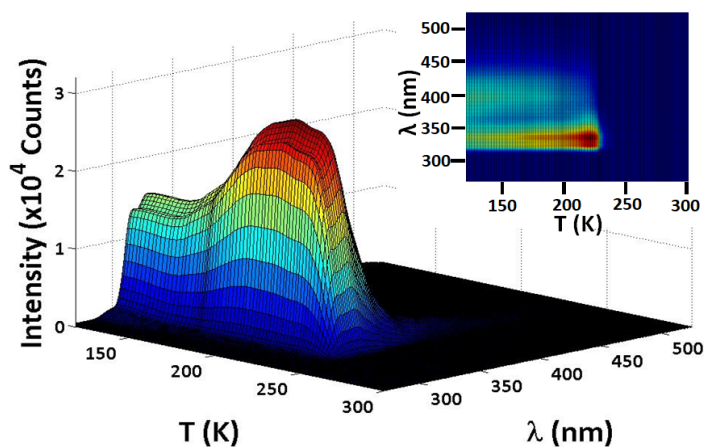
**Figure 3.** Wavelength-resolved TPD of multilayer 1-methylnaphthalene.  $\Theta_{1\text{-methylnaphthalene}} = 88 \text{ ML}$ . The excimer fluorescence at  $\lambda_{\text{max}} \sim 395 \text{ nm}$  that dominates at deposition, blue-shifts to 325 nm subsequent to the disorder-to-order transition. Inset: top view.

for 2-methylnaphthalene and 1-methylnaphthalene, respectively (19-21). Both methylnaphthalene isomers underwent disorder-to-order transition at about 160 K with a new fluorescence  $\lambda_{\max} \sim 325$  nm with an accompanying stronger peak at  $\lambda_{\max} \sim 336$  nm due to the C-H bending motion. These peaks due to the monomer had very low intensities and are difficult to see particularly for 1-methylnaphthalene, see Figures 2 and 3.

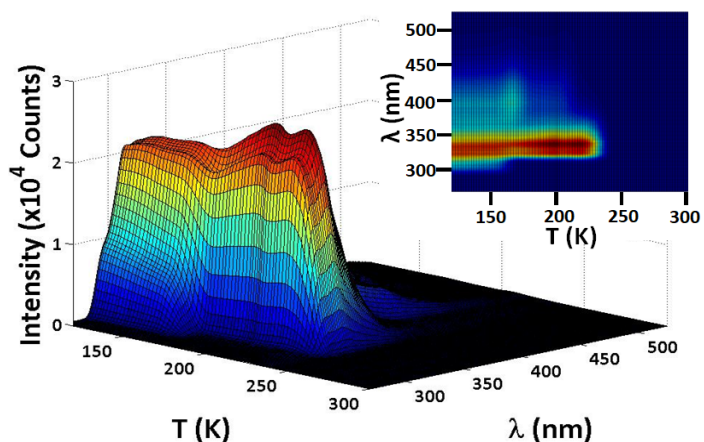
#### Bilayers of 2- and 1-methylnaphthalene and biphenyl:

Shown in Figures 4 and 5 are the wavelength-resolved TPD of the bilayers of 2-methylnaphthalene-biphenyl and 1-methylnaphthalene-biphenyl, respectively. As noted above, the methylnaphthalenes have the lower  $T_p$  and hence, were deposited first. In this way, thermally induced biphenyl mixing of the underlayer will occur as it moves through the biphenyl overlayer. Since the fluorescence spectra of the two adsorbates in the bilayer do not appreciably overlap, the temperature induced surface dynamics of the two molecules can be monitored via the wavelength resolved TPD experiment.

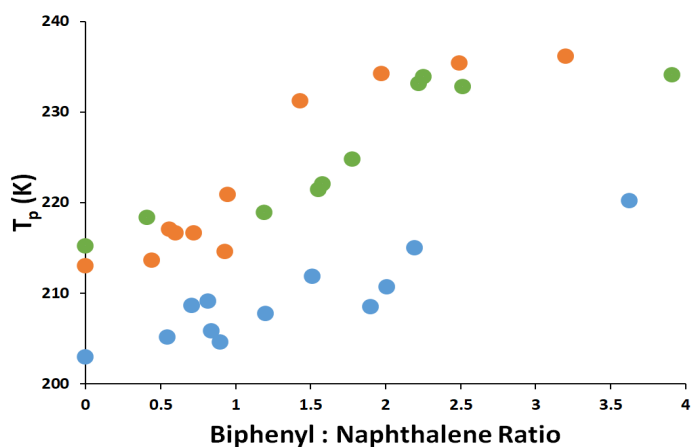
Shown in Figure 6 and 7 are the mass specific TPD data,  $T_p$ 's, for the bilayers of 2-methylnaphthalene-biphenyl and 1-methylnaphthalene-biphenyl. The plots also include mass



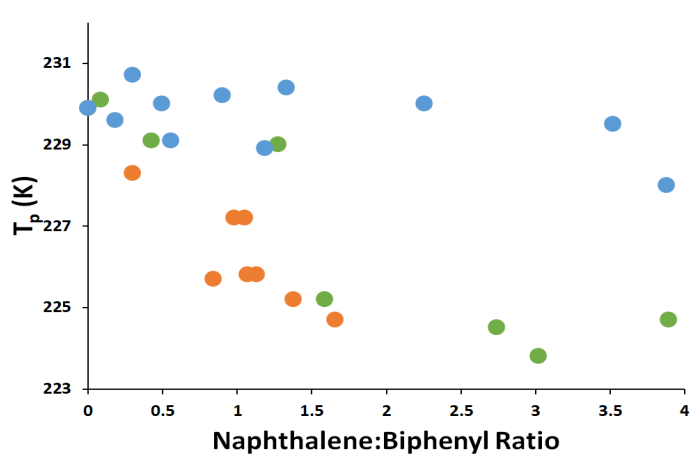
**Figure 4.** Wavelength-resolved TPD of bilayer of 2-methylnaphthalene and biphenyl, for which  $\Theta_{2\text{-methylnaphthalene}} = 88$  ML and  $\Theta_{\text{biphenyl}} = 105$  ML. The fluorescence is that of molecular 2-methylnaphthalene with  $\lambda_{\max} \sim 325$ . Note the absence of the 320 nm emission from the twisted conformer of biphenyl. Inset: top view. The excimers of biphenyl and 2-methylnaphthalene are at 370 and 395 nm, respectively.



**Figure 5.** Wavelength-resolved TPD of bilayer of 1-methylnaphthalene and biphenyl, for which  $\Theta_{1\text{-methylnaphthalene}} = 110$  ML and  $\Theta_{\text{biphenyl}} = 130$  ML. The fluorescence is that of molecular 1-methylnaphthalene with  $\lambda_{\max} \sim 325$ . Note the presence of the 320 nm emission from the twisted conformer of biphenyl. Inset: top view. The excimers of biphenyl and 1-methylnaphthalene are at 370 and 395 nm, respectively.



**Figure 6.** Increase in  $T_p$ 's for naphthalene, 2-methylnaphthalene and 1-methylnaphthalene for bilayers of naphthalene-biphenyl, 2-methylnaphthalene-biphenyl and 1-methylnaphthalene-biphenyl, respectively, from mass specific TPD as a function of biphenyl to naphthalene or methylnaphthalene ratio of coverages (ML ML<sup>-1</sup>).  $T_p$ 's for naphthalene (orange) with  $\Theta_{\text{naphthalene}} = 146 \pm 15$  ML,  $T_p$ 's for 2-methylnaphthalene (green) with  $\Theta_{2\text{-methylnaphthalene}} = 110 \pm 15$  ML and  $T_p$ 's for 1-methylnaphthalene (blue) with  $\Theta_{1\text{-methylnaphthalene}} = 106 \pm 13$  ML.



**Figure 7.** Decrease in  $T_p$ 's for biphenyl for bilayers of naphthalene-biphenyl, 2-methylnaphthalene-biphenyl and 1-methylnaphthalene-biphenyl, respectively, from mass specific TPD as a function of naphthalene or methylnaphthalene to biphenyl ratio of coverages (ML ML<sup>-1</sup>).  $T_p$ 's for biphenyl (orange) with  $\Theta_{\text{biphenyl}} = 120 \pm 9$  ML in naphthalene-biphenyl bilayer,  $T_p$ 's for biphenyl (green) with  $\Theta_{\text{biphenyl}} = 120 \pm 9$  ML in 2-methyl naphthalene-biphenyl bilayer and  $T_p$ 's for biphenyl (blue) with  $\Theta_{\text{biphenyl}} = 110 \pm 7$  ML in 1-methylnaphthalene-biphenyl bilayer.

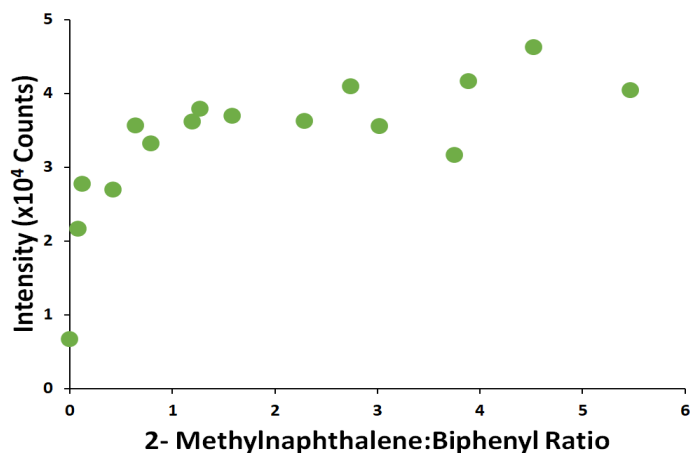
**Table 1.**  $\Delta T_p$  (K) from Figs. 6 and 7 for adsorbates (bold) in bilayers. Signs are relative to  $T_p$  of the multilayer. Calculated  $\Delta E_a$ 's are the approximate van der Waals energies.

	$\Delta T_p$ (K)	$\Delta E_a$ (kJ mol <sup>-1</sup> )
<b>Naphthalene with Biphenyl</b>	$-21 \pm 2$	$-5.5 \pm 0.6$
<b>2-Methylnaphthalene with Biphenyl</b>	$-16 \pm 2$	$-4.3 \pm 0.6$
<b>1-Methylnaphthalene with Biphenyl</b>	$-10 \pm 6$	$-2.6 \pm 1.5$
<b>Biphenyl with Naphthalene</b>	$3 \pm 2$	$0.7 \pm 0.6$
<b>Biphenyl with 2-Methylnaphthalene</b>	$5.4 \pm 0.7$	$1.4 \pm 0.2$
<b>Biphenyl with 1-Methylnaphthalene</b>	$0.9 \pm 1.2$	$0.2 \pm 0.3$

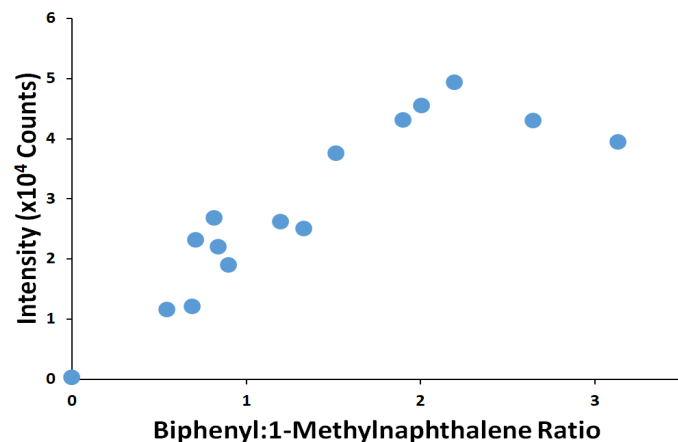


specific TPD data for naphthalene-biphenyl bilayer for comparative purposes. The coverages for each of the species in the respective bilayers are given in the figures. In Figure 6 are plotted the  $T_p$ 's of naphthalene, 2- and 1-methylnaphthalenes as a function of the ratio of biphenyl to (2- and 1-methyl)naphthalene in  $ML\ ML^{-1}$ . In these experiments the naphthalene, 2- and 1-methylnaphthalene were kept constant while the biphenyl coverage was varied. What is apparent from these plots is the degree to which the  $T_p$ 's are affected by the presence of biphenyl. The presence of biphenyl causes the naphthalenes to desorb at the higher  $T_p$ 's presumably due to van der Waals interaction. On the other hand, biphenyl is also affected by the presence of the naphthalenes as seen in Figure 7. In this figure are plotted the  $T_p$ 's of biphenyl as a function of the ML ratio of 2- and 1-methylnaphthalene and naphthalene,  $ML\ ML^{-1}$ . What these plots show are the lowering of the  $T_p$ 's of biphenyl due to the presence of the naphthalenes. As was apparent in the previous Figures 6, naphthalene and 2-methylnaphthalene are much more affected by biphenyl than 1-methylnaphthalene. Also as seen in Figure 7, 1-methylnaphthalene does not affect the  $T_p$ 's of biphenyl as much as naphthalene and 2-methylnaphthalene do.

Since the activation energies for desorption,  $E_a$ 's, can be calcu-



**Figure 8.** Intensity of the exciplex (2-methylnaphthalene peak at 336 nm) as a function of the ratio of 2-methylnaphthalene to biphenyl coverages ( $ML\ ML^{-1}$ ).  $\Theta_{\text{biphenyl}}$  was held constant at  $130 \pm 16\ ML$ .



**Figure 9.** Intensity of the exciplex (1-methylnaphthalene peak at 336 nm) as a function of the ratio biphenyl to 2-methylnaphthalene coverages ( $ML\ ML^{-1}$ ).  $\Theta_{\text{1-methylnaphthalene}}$  was held constant at  $99 \pm 14\ ML$ .

lated from  $T_p$  (16-18), the difference in the multilayer  $T_p$  and the maximum  $T_p$  that result due to the van der Waals interaction are summarized in Table 1. As is clearly evident, the interaction energies are the largest for naphthalene-biphenyl and 2-methylnaphthalene-biphenyl bilayers, while 1-methylnaphthalene-biphenyl has the smallest van der Waals energy. The energies of 5-6  $\text{kJ mol}^{-1}$  are consistent with experimentally obtained van der Waals energies for complexes of such molecules as naphthalene-2-methoxynaphthalene (5.6  $\text{kJ mol}^{-1}$ ) (22) and perylene-naphthalene (4.2  $\text{kJ mol}^{-1}$ ) (23). A possible explanation as to why 1-methylnaphthalene-biphenyl complex has the lowest van der Waals energy can be shown by manipulating molecular models of the two isomers of methylnaphthalene and biphenyl in the planar conformation. This exercise indicates that the 2-methylnaphthalene's structure is such that a planar biphenyl can be accommodated in the eclipsed geometry more readily than the 1-methylnaphthalene because of the location of the steric hindrance from the methyl group. This model is supported by the observation of the twisted conformer of biphenyl at deposition temperature with  $\lambda_{\text{max}} \sim 320\ \text{nm}$  for the 1-methylnaphthalene-biphenyl bilayer. Conversely, there is a much smaller intensity at  $\lambda_{\text{max}} \sim 370\ \text{nm}$  from the planar conformer of biphenyl (Figure 5). The same twisted conformer of biphenyl is not observed for 2-methylnaphthalene-biphenyl bilayer at  $\lambda_{\text{max}} \sim 320\ \text{nm}$  (Figure 4) with a much more pronounced intensity at  $\lambda_{\text{max}} \sim 370\ \text{nm}$ , just as was observed for the naphthalene-biphenyl bilayer at deposition (16).

In order to determine the molecular ratio of the exciplex, the fluorescence intensity of the exciplex was plotted as functions of the ML ratios of molecules that comprise the bilayer. Figure 8 shows the fluorescence intensity of the exciplex at 336 nm (the more intense of the pair) as a function of the 2-methylnaphthalene to biphenyl ( $ML\ ML^{-1}$ ) ratio in which the  $\Theta_{\text{biphenyl}}$  was held constant. Here, the slope of the plot clearly levels off at a  $ML\ ML^{-1}$  ratio of about 1:1. In Figure 9, the exciplex fluorescence intensity as a function of the biphenyl to 1-methylnaphthalene shows a slope that levels at about 2:1. This makes sense in that the methyl group in 1-methylnaphthalene causes a hindrance sterically to the formation of a exciplex so that on the average, only 50% of the 1-methylnaphthalene complexes for every biphenyl molecule and epitaxy occurs only to this limited extent. Another possible explanation is that the 1-methylnaphthalene-biphenyl exciplex forms with two biphenyl molecules in the twisted conformation.

In summary, 2-methylnaphthalene form van der Waals complex with biphenyl with interaction energy comparable to naphthalene-biphenyl complex, about 6  $\text{kJ mol}^{-1}$ . The energy for 1-methylnaphthalene-biphenyl complex is about half as strong, and biphenyl forms a complex with half of the 1-methylnaphthalene or with 2 biphenyl molecules in the twisted conformer for every 1-methylnaphthalene.

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