

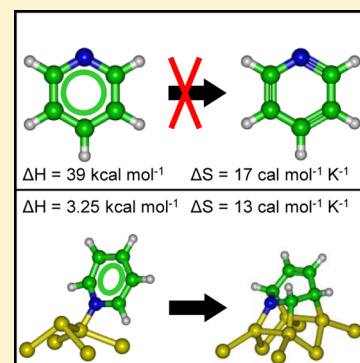
Entropy, the Silent Killer of Aromaticity of Adsorbed Pyridine on Si(100) and Ge(100)

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ABSTRACT: This paper studies the chemical attachment of pyridine on two semiconductor surfaces, Si(100) and Ge(100), at low coverages. We use thermodynamic arguments to show that the aromaticity of pyridine is preserved in both cases at low temperatures. At high temperatures, a transition toward nonaromatic structures—tetrapod structure for Si(100) and dipod structure for Ge(100)—occurs without cleavage of C–H bonds. We show that this transition can be explained by the tiny entropy increase associated with the disappearance of aromaticity.



INTRODUCTION

Goal of the Present Paper. Organic functionalization of semiconductor surfaces, particularly Si(100) and Ge(100), has sparked a number of studies.¹ An essential feature of these surfaces is buckling,^{2,3} which leads to the transfer of a fraction of one electron from the down to the up atom in the dimer. In other words, down and up atoms behave as Lewis acids and bases, respectively. Let us mention three studies showing the importance of buckling in the field of adsorbed organic molecules.

- The cycloaddition of acrylonitrile on Si(100)⁴ may result in three different configurations. Because of its dipolar structure, which matches the Si dimer, the enthalpy of the cumulene configuration is more negative than its unfavorable geometry would predict.
- Purine molecules have been shown⁵ to adsorb on Ge(100) via double dative bonding, with both ring nitrogen atoms donating charge to two Ge down atoms.
- The dative attachment of pyridine on Si(100) and on Ge(100) and therefore the preservation of aromaticity is made possible by the existence of an atom of the dimer acting as a Lewis acid. More generally, the properties resulting from this dative bonding are discussed in two recent extensive studies dealing with the chemical binding and the reactivity of five- and six-membered aromatic molecules.^{6,7}

As pointed out by Naumkin et al.,⁸ pyridine has an interesting feature that permits a reversible adsorption as a function of temperature and composition: not only does the adsorbed molecule retain its aromaticity, but also cleavage of

C–H bonds does not occur during the adsorption process, unlike other molecules, such as 3-pyrroline.⁹

The present study, based on a thermodynamic analysis using both density functional theory (DFT) calculations and available experimental data, is devoted to the study of the temperature dependence of aromaticity of adsorbed pyridine on Si(100) and Ge(100).

We shall also briefly discuss potential applications of adsorbed pyridine in the field of molecular scale electronics.^{10–14} Examples of such devices have been published quite recently: electroluminescence of a polythiophene molecular wire¹⁵ and spin crossover induced by a number of external stimuli.¹⁶

We have used the Vienna ab initio simulation package (VASP),^{17,18} which is a DFT code solving the Kohn–Sham equations¹⁹ in a plane-waves basis set. More details can be found in a review by Hafner,²⁰ with an emphasis on the reaction of organic molecules on solid surfaces. We have made essentially the same technical choices in this study as in our earlier study,²¹ regarding the adsorption of pyridine on Si(100). We have made no van der Waals corrections.

Outline. Our study of the chemical attachment of gaseous aromatic rings on a semiconductor surface is organized as follows: First, we examine the change of thermodynamic properties associated with the virtual transition from a nonaromatic (Kekule-like) structure to an aromatic structure in the gas phase. This transition is associated with a large

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Table 1. Aromaticity Contribution to Enthalpy (H_{arom}) and Entropy (S_{arom}) for Benzene and Some Heterocyclic Molecules

aromatic molecule	formula	aromaticity		refs
		enthalpy (kcal mol ⁻¹)	entropy cal mol ⁻¹ K ⁻¹	
benzene	C ₆ H ₆	−36	−15	24, 26–30
pyridine	C ₅ NH ₅	−39	−17	31–35
furan	C ₄ H ₄ O	−14.5	−4	36, 37
thiophene	C ₄ H ₄ S	−14.6	−3	38
pyrrole	C ₄ H ₅ N	−26.4	−5	39–41

Table 2. Dative Bonded Pyridine on Si(100) and Ge(100)^a

	adsorption energy (kcal mol ⁻¹)	lattice deformation (kcal mol ⁻¹)	molecule deformation (kcal mol ⁻¹)	bond energy (kcal mol ⁻¹)
Si–N	−29.7	5.53	0.92	−36.2
Ge–N	−21.9	2.77	0.69	−25.4

^aAccording to refs 4, 21, and 45, the net adsorption energy is the sum of three contributions arising from the lattice deformation, the molecule deformation, and the surface–molecule bond formation. A unit cell with eight Si surface atoms and one molecule has been used.

decrease in enthalpy, which is a well-established result, but also with a tiny decrease in entropy.

Second, we examine the differences between dative and covalent bonds in adsorbed pyridine because binding via a dative bond of pyridine is the only attachment which preserves aromaticity. We show that the dative attachment is the more stable structure at low temperature despite its unique weak bond because aromaticity contributes a large reduction in enthalpy. On the other hand, the tiny decrease in entropy is able to compensate for that reduction in enthalpy at high temperatures, thus leading to the disappearance of aromaticity.

Third, we study the specific cases of adsorption on Si(100) and Ge(100) in more detail.

Finally, we briefly outline some implications in the development of molecular electronics.

■ ENTROPY AND AROMATICITY

Gas Phase. The quantitative study of the thermodynamic quantities associated with aromaticity requires defining a reference state. The simplest choice is a Kekule structure,^{22,23} which was used by Kistiakowsky.²⁴ While several studies devoted to enthalpy have been published over the last 80 years, the aromaticity contribution to entropy has been largely ignored. The only qualitative estimation we are aware of is that of Franklin,²⁵ who noted that electronic excited levels are too high to be thermally populated and that therefore the electronic entropy is zero. Franklin stated that changes in bond distances, force constants, and symmetry give small and negative contribution to the entropy of aromatic compounds. Let us define the quantities

$$H_{\text{arom}} = H_{\text{experiment}} - H_{\text{Kekule}} \quad (1)$$

and

$$S_{\text{arom}} = S_{\text{experiment}} - S_{\text{Kekule}} \quad (2)$$

where $H_{\text{experiment}}$ and $S_{\text{experiment}}$ denote the enthalpy and entropy deduced from thermodynamical measurements, respectively, extending the calculations used for pyridine in our earlier paper.²¹ We report results for several other molecules in Table 1. As expected, aromaticity contributes a large decrease in enthalpy, but a quite small decrease in entropy, confirming the predictions of Franklin.

Adsorbed Pyridine at Low Temperatures: The Dative Configuration. We use the nomenclature of Tao et al.⁴² to describe the various bonding modes. In this section, we discuss

properties of the dative configuration (mode XII), which is the only adsorption mode that preserves the aromaticity of pyridine.²¹ This structure has been reported as being the more stable at 0 K for adsorption on both Si(100)^{21,43} and Ge(100).⁴⁴

Comparison between Bond Energies in Attachments with Si and Ge. Following a procedure described elsewhere,^{4,21,45} we evaluated Si–N and Ge–N dative bond energies from calculated adsorption energies of pyridine on Si(100) and Ge(100). These values are reported in Table 2 using a unit cell with eight Si surface atoms and one adsorbed molecule.

The values reported in Table 2 are in line with the general trend noted by Kachian et al.⁴⁶ Dative bonds with Si(100)-(2×1) are stronger than those with Ge(100)-(2×1) because of the slightly larger electron affinity for Si. It is noteworthy that the difference in bond energies is still larger between covalent bond energies, as can be seen in Table 3.

Table 3. Covalent and Dative Bond Energies and Lengths

			Si–N	Ge–N
bond energies (kcal mol ⁻¹)	covalent dative	from refs 47–49	−85	−61
		this study (from Table 2)	−36.2	−25.4
bond length (Å)	covalent dative	from ref 50	1.82	1.91
		this study	1.92	2.11

The comparison of the properties of dative Si(Ge)–N bonds (energy and lengths) reported in Table 3 with the ones of corresponding covalent bonds is consistent with the IUPAC definition⁵¹, which states that the dative bond is not just an ordinary covalent bond, but has some distinct features: significant polarity, lesser strength, and greater length. In the remainder of this paper, we shall use the terms nondative and covalent interchangeably.

■ THERMODYNAMICS OF ADSORPTION OF PYRIDINE ON Si(100) AND ON Ge(100)

Overview. In order to understand the behavior of pyridine adsorbed on Si(100) or Ge(100) as temperature varies, the quantities of interest are the enthalpy and entropy differences between the dative configuration and the covalent configuration

of lowest enthalpy chosen as reference (tetrapod for adsorption on Si(100)²¹ and dipod for adsorption on Ge(100)⁴⁴).

Equations 1 and 2 have to be replaced by eqs 3 and 4:

$$H_{\text{arom}} = H_{\text{experiment}} - H_{\text{nonaromatic}} \quad (3)$$

and

$$S_{\text{arom}} = S_{\text{experiment}} - S_{\text{nonaromatic}} \quad (4)$$

Now let us compare the thermodynamic properties of dative configurations with those of covalent configurations. All published studies^{42–44,52} have concluded that the dative configuration is not present at high temperatures for adsorption on Si(100) and on Ge(100). The purpose of this section is to examine how the calculated thermodynamic properties are able to explain the disappearance of dative configuration, and therefore of aromaticity.

Adsorption on Si(100). Overview. The structure of adsorbed structures has been shown to be a function of both the temperature and the coverage.⁵³ Therefore, it may be thought that a separate study of both the enthalpy and of the entropy should provide valuable information. Such studies are discussed in the next two paragraphs.

Enthalpy. The results of available plane waves DFT calculations gathered in Table 4 show that the difference of

Table 4. Adsorption Enthalpy Difference (Dative – Tetrapod)^a

	W.K.H. Ng et al. ⁴³	Coustel et al. ²¹	Kim and Cho ⁴⁴
coverage	1	1 2	2
enthalpy difference (kcal mol ^{−1})	−1.0	−5.5 −2.0	+1.0

^aIn this table, the coverage has been defined as the number of molecules adsorbed on eight dimers.

adsorption enthalpies between dative and tetrapod structures shown in Figure 1 is quite small. An important feature is the

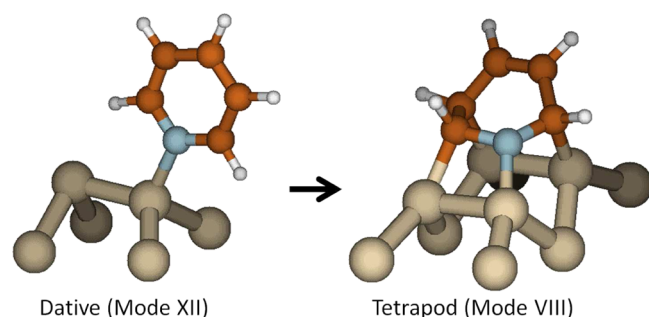


Figure 1. Dative and tetrapod structures (modes XII and VIII).

existence of repulsive interactions between dative structures due to steric repulsion,²¹ a consequence of which is the large values of the adsorption enthalpy difference (dative – tetrapod) on Si(100) for high coverage. To have a reliable estimation of the adsorption enthalpy difference (dative – tetrapod), we average the values of W.K.H. Ng et al. and those of the present study at low coverage (2 pyridine molecules adsorbed on eight dimers), yielding the value $-3.25 \text{ kcal mol}^{-1} \text{ K}^{-1}$.

Entropy. Let us evaluate the entropy difference between the dative and tetrapod configurations for adsorption on Si(100) by combining the XPS results of Tao et al.⁴² and our DFT calculations. According to Tao et al.⁴² and Miwa et al.,⁵⁴ the

dative configuration is predominant at low temperatures (180 K). An increase in temperature leads to a gradual increase of covalent configuration population at the expense of the dative population, both of them being equal at 250 K. Assuming that the surface equilibrium is reached, the entropic and enthalpic contributions to the free-energy difference between these two configurations cancel each other at that temperature. Thus, S_{arom} should be equal to $-3250/250 = -13 \text{ cal mol}^{-1} \text{ K}^{-1}$, to be compared to the value of $-17 \text{ cal mol}^{-1} \text{ K}^{-1}$ obtained in Table 1. This difference is easily understood: The essential change between eqs 1 and 2 on the one hand and 3 and 4 on the other is that the reference state is the Kekule configuration in the first case and the tetrapod configuration in the second. The dative configuration is loosely bound to the Si(100) surface. Therefore, the entropy of the gaseous pyridine and of the dative configuration are roughly equal. Compared to the Kekule structure, the mode VIII has a more rigid structure because of its tetrapod attachment, leading to a decrease of entropy. This predicts that the aromaticity effect should be more important for adsorption of pyridine on Si(100) than for gaseous pyridine.

Adsorption on Ge(100). For this system, as already indicated, the covalent structure of minimum enthalpy is a dipod, shown in Figure 2

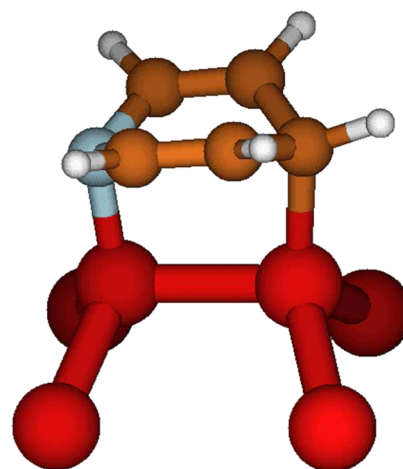


Figure 2. Butterfly structure (dipod).

The results of our calculations for pyridine adsorbed on Ge(100) are reported in Table 5. They are very similar to those of Kim and Cho.

Table 5. DFT Determinations of Adsorption Enthalpies of Pyridine on Ge(100) Surface for Medium Coverage (One Adsorbed Molecule for Four Dimers)

	Kim and Cho (kcal mol ^{−1})	this study (kcal mol ^{−1})
dative	−22	−21.9
dipod	+6.2	+6.2
tetrapod	+14.5	+13.9

Let us assume that the order of magnitude of the small entropy effect is $-15 \text{ cal mol}^{-1} \text{ K}^{-1}$, intermediate between those of modes VIII and XII for adsorption on Si(100), for the system germanium–pyridine, which has only two tethered atoms instead of four.

The small entropy difference is not able to destroy aromaticity at room temperature against the large difference

between the adsorption enthalpies of the dative and the butterfly configurations. This is in agreement with the observation of dative configurations even at room temperatures for low coverage,⁵² whereas dipod structures are found for large exposures.

POTENTIAL APPLICATIONS

Importantly, these systems fulfill two important requirements for the use of adsorbed molecules in molecular electronics: selective functionalization⁵⁵ and conservation of the aromatic ring allowing charge transfer between the molecular Π electron system and the Si=Si or Ge=Ge surface dimers.⁹ A simple reversible molecular switch that would use temperature as an easy-to-control external constraint could be feasible, thanks to the conjunction of three favorable features:

- (1) As detailed above, dative configurations which preserve the aromaticity of adsorbed molecules are stable at low temperatures, but not at high temperatures.
- (2) Experimental studies show that the conversion from a dative bond to a tetrapod configuration is easy.⁴²
- (3) Grafted aromatic rings whose electron delocalization is extended to surface dimers is expected to present an increased electrical conductivity compared to that of nonaromatic grafting mode.⁵⁶

SUMMARY AND CONCLUSIONS

The results of our calculations are summarized in Figure 3. The contributions of aromaticity to the free energy of five gaseous

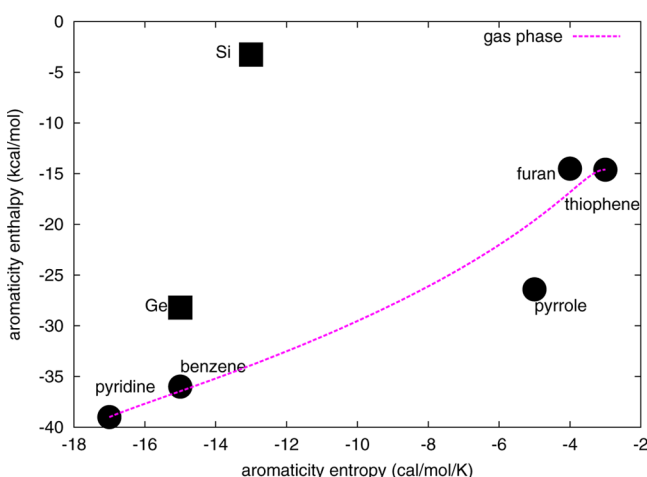


Figure 3. Correlation between H_{arom} and S_{arom} . Data corresponding to adsorbed pyridine (black squares) on Si(100) and on Ge(100) are significantly above the smooth line fitting the data for the gas phase (black circles), which means that entropy is expected to cause the disappearance of aromaticity at low temperatures for pyridine adsorbed on Si(100) but not at all for gaseous molecules.

molecules have been determined by reference to a virtual Kekule structure. For these five molecules, both contributions are negative. It is clear that the tiny entropy reduction is unable to reverse the sign of the free energy difference at any reasonable temperature.

On the other hand, aromaticity is easily lost in the case of adsorbed pyridine on Si(100) because the negativity of the enthalpy difference is less pronounced, while the entropy differences are only slightly smaller than those observed for the gas phase. Thus, a temperature transition from an aromatic

structure to a nonaromatic structure becomes possible. For low coverages, we get a transition temperature equal to 250 K for adsorption on Si(100). This figure is expected to vary significantly as a function of the coverage, or equivalently, of the chemical potential of pyridine. Interestingly, it is not uncommon for such small values of entropy differences to be able to reverse the structure of the adsorbed molecule. For instance, Kim et al.⁵⁷ studied benzene adsorbed on Si(100), using van der Waals energy-corrected functional theory as well as the exact exchange with electron correlation in the random-phase approximation and showed that the energy of the tight bridge structure is 4.186 kcal mol⁻¹ smaller than that of the butterfly structure, but with an entropy smaller by only 23 cal K⁻¹ mol⁻¹. The two effects cancel each other at 182 K.

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Notes

The authors declare no competing financial interest.

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