Absorption energetics and simulation of STM images for fluorobenzene on the Cu(110) surface

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A crystalline linear combination of atomic orbitals approximation (LCAO) has been used at the density functional theory (DFT) level to study the adsorption of fluorobenzene on the Cu(110) surface. Adsorption energetics have been modelled and scanning tunneling microscope (STM) images have been generated for the preferred adsorption geometry using the Tersoff and Hamann method. An adsorption energy of -93.4 kJ mol^{-1} is calculated, with the fluorobenzene molecule occupying a bridging site between the rows of surface copper atoms and an adsorption height of approximately 2 Å. Relaxation effects involving a tilt of the hydrogen and fluorine atoms away from the surface are accounted for in the calculations. Our predicted energetics compare favourably with experimental binding energies determined from temperature programmed desorption (TPD). The simulated STM images are compared with recent theoretical STM images of benzene.

Keywords: Ab initio quantum chemical methods and calculations, Density functional calculations, Scanning tunneling microscopy, Physical adsorption, Copper, Aromatics.

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INTRODUCTION

In recent years interest has developed in the possibility of using STM to identify and discriminate between molecules adsorbed in mixtures on surfaces. Such an ability has extensive applications in the study of co-adsorbed molecules, including adsorption characterisation [1,2] and the observation of surface-catalysed reactions [3-5]. Strong interest is also generated by the possibility of using STM to determine the sequence of nucleic bases in deoxyribonucleic acid (DNA), a practice common in biotechnology, medical science, and forensic science [6-8]. The discrimination of adsorbed molecules by STM is also central to many fields of nanotechnology such as molecular electronics and biosensors [9]. Development in these areas relies upon two factors; firstly, sufficient resolution is required in the experimental images to allow for discrimination of subtle differences, and secondly the interpretation of STM images must allow these differences to be well understood. While there are constant improvements in the former, the latter requires theoretical support and there are currently a number of competing models commonly used to guide interpretation. Furthermore, theoretical methods ideally need to be able to predict adsorption geometries and provide a useable description of the tunnelling process on an equal footing. It is towards this end that considerable research effort is currently directed.

In this paper we present a first principles investigation of the adsorption energetics and prediction of the preferred adsorption site and geometry of fluorobenzene on Cu(110). From this STM images are calculated using the Tersoff-Hamann approximation [10]. While this methodology, in principle, provides a complete description of the density of states of the adsorbate-substrate system and predicts the preferred geometry, it does not implicitly describe the tunnelling process itself.

However, the utility of the Tersoff-Hamann method is well-documented and it is commonly used for image simulation.

Mono-fluorobenzene is chosen as the absorbed species since is differs from benzene only by substitution of a single functional group. A number of studies of benzene absorption on Cu(110) already exist including our own [11], and hence fluorobenzene provides a good test the effects of functional group substitution on STM images. The fluorine atom is smaller than the hydrogen atom and hence may conventionally be expected to appear smaller in STM images than the hydrogen atom. However, the electronic density of states will be greater in the region of the atom and we may in fact expect the fluorine to be highly prominent in STM images of fluorobenzene.

The adsorption of fluorobenzene onto metallic surfaces has been the focus of little previous research. Very little is therefore known about the adsorption characteristics of the system, including the adsorption site. Nakazawa and Somorjai [12] performed extensive studies on substituted benzene adsorbed on gold foil. They report a similar Temperature Programmed Desorption (TPD) spectrum for fluorobenzene as they obtain for benzene adsorbed on the gold surface. However, analysis of this TPD spectra reveals a slightly lower heat of desorption of 70 kJ mol^{-1} compared to the value obtained for benzene of 76 kJ mol^{-1}. Nakazawa and Somorjai suggest that these results indicate that the adsorption of fluorobenzene onto the gold surface occurs through the same mechanism as that of benzene. Specifically, the adsorption bond forms primarily between the central benzene ring of the fluorobenzene molecule, while the fluorine atom has little effect. In addition, this adsorption mechanism and the similarity of the TPD spectra suggest a similar

orientation of the fluorobenzene molecule on the surface, with the plane of the molecule parallel to the surface.

In a study by Hallmark and Chiang [13], the STM image of fluorobenzene adsorbed on the Pt(111) surface was calculated using extended Hückel cluster calculations. No explanation is provided for the choice of adsorption site in this calculation, although the orientation is identical to the three-fold hollow site observed in the adsorption of benzene on the Rh(111) surface. The plane of the benzene ring is parallel to the surface in this orientation. The STM image calculated in this study shows a reduction in the local density of states at the position of the fluorine atom and in the region of the ring system associated with it. The authors indicate that these results are unexpected, as an increase may be predicted in the local density of states due to the electronegative nature of the fluorine atom. No further explanation of the results is provided however and no experimental STM studies are available for comparison.

CALCULATION METHOD

The commercially available CRYSTAL98 package [14] was employed for all calculations. The package approximates true wavefunctions through an expansion of crystalline orbitals as a linear combination of atomic orbitals. Calculations were performed at the density functional level of theory using Dirac-Slater exchange [15] and Vosko-Wilk-Nusair [16] correlation. Default conversion tolerances for the program were used throughout. Numerical integration was performed using 34 symmetry irreducible k points, while 130 symmetry irreducible k points were used in evaluating the density matrix. This k-space sampling is sufficient to ensure convergence of the calculated properties of a clean copper slab [11]. The calculations were performed using a serial compilation of the CRYSTAL98 code [14] on the Linux Beowulf cluster

maintained by the South Australian Partnership for Advanced Computing. These calculations are therefore well within the realm of desktop computing.

An 86-4111(41D)G all-electron copper basis set developed by Doll and Harrison [17] was modified to incorporate a Hay and Wadt small core (HAYWSC) pseudopotential in order to improve the computational time. The use of small core pseudopotentials is supported by previous studies in which similar pseudo-potentials were found not to significantly affect the predicted surface geometry of rutile [18]. The copper surface was modelled using a semi-infinite periodic slab consisting of 4 atomic layers. This has previously been shown to provide an adequate model of the Cu(110) surface for ab initio studies of adsorption [11]. A 4 layer slab represents a good compromise between sufficiently converged properties and computational expense and ensures that through slab interactions between the absorbed molecules is relatively small. No account is taken of surface relaxation of the Cu either before or after adsorption. Such effects are expected to be relatively small, and experimental STM images support the view that there is little surface reconstruction, although relaxation of the interlayer spacing near the surface may still play a small role. Changes in the interlayer spacing for metallic surfaces are typically of the order of a few percent, and subsequent changes in our calculated absorption energies are below the uncertainties introduced by other effects, particularly basis set superposition errors. Hence the error introduced in our calculations by neglecting this effect is relatively small.

Previous studies suggest that fluorobenzene adsorbs parallel to the Cu(110) surface through essentially the same mechanism as benzene. The H-flip conformation described by Pettersson and co-workers [19,20] provides an accurate representation of the adsorption conformation of benzene on the Cu(110) surface [11] and hence it serves as a

useful first approximation for the adsorption of fluorobenzene. In addition, it is assumed that adsorption of fluorobenzene occurs at sites of maximum symmetry. Four possible adsorption sites for fluorobenzene on the Cu(110) surface have therefore been investigated. At each of these sites, fluorobenzene may adsorb to the surface in four different orientations. A total of sixteen possible adsorption orientations are therefore used, as presented in Fig. 1a.

The fluorobenzene molecule was described using 6-21G* all-electron basis sets. Prior to all adsorption calculations, the bond lengths of gas-phase fluorobenzene were optimised with respect to the total energy. The predicted C-C and C-H bond lengths deviated from those of benzene by less than 1%. It is therefore reasonable to use the C-C and C-H bond lengths described by Pettersson and co-workers [19,20] for adsorption of benzene on Cu(110) in the adsorption calculations. The C-F bond length was also optimised for the adsorption calculation and agreed with experimental results to within 2%. It is expected that the relaxed geometries of benzene and fluorobenzene on Cu(110) should be similar. Hence, to account for relaxation of fluorobenzene on absorption, we start with the optimised H-flip geometry of benzene absorbed on Cu(110) reported by Pettersson and co-workers[19, 20], and then optimise the C-F bond angle relative to the substrate. A supercell of the Cu(110) slab was employed in order to allow a separation of approximately 5 Å . This is sufficient to ensure that intermolecular effects are negligible. Calculations were performed in which fluorobenzene was positioned above a Cu(110) 4-layered slab in each of the proposed orientations and the optimum adsorption height was determined in terms of total system energy. The adsorbed molecule was modelled in symmetry-equivalent positions on opposite sides of the slab in order to maximise the symmetry of the system. Subsequent calculations of the binding energy of adsorbed fluorobenzene in

each of the orientations at the optimum adsorption heights revealed the preferred adsorption orientation of fluorobenzene on the Cu(110) surface. The binding energy calculations were performed using the counterpoise method to account for basis set superposition errors. This method provides only an estimate of BSSE and in some cases has been shown to be inadequate for unbalanced and / or extended basis sets [21] giving energy corrections that shift in the wrong direction. However, we have already shown that it has a dramatic effect on absorption energies for benzene on Cu(110) calculated under similar conditions [11] and in this and the present case consistently produces energy changes in the correct direction. Moreover, absorption energies calculated for benzene which include BSSE are in far better agreement with experiment than the uncorrected values. The effect of the C-F bond angle was then quantified by optimising this angle with respect to energy.

Adsorption chemistry was investigated using electron density difference plots and total electronic charge variations. Electron density difference plots for the optimised geometries were generated by subtracting electron density maps of isolated fluorobenzene and copper from an electron density plot of the combined surface-adsorbate system. Simulated STM images of preferred orientations were calculated using CRYSTAL98 [14] through the method described by Tersoff and Hamann [10]. A discussion of the merits and limitations of this model is given elsewhere [11,22,23].

RESULTS AND DISCUSSION

A. Prediction of the optimum absorption geometry and energy

Predicted values for the adsorption height and binding energy for each of our proposed adsorption sites are presented in Table 1. The adsorption energies, although generally smaller, typically follow a similar pattern to those calculated in a previous

study for benzene adsorbed on the Cu(110) surface [11]. The results fall into two broad groups. Adsorption at sites 2 and 3 results in the molecule being either unbound or only weakly bound, while adsorbed molecules in sites and 1 and 4 are relatively strongly bound. Adsorption sites 2 and 3 position the fluorobenzene molecule directly on top of the row of surface Cu atoms, whereas in sites 1 and 4 it is positioned between the rows. As would typically be expected, these results indicate that adsorption of fluorobenzene in bridging positions between the rows of copper surface atoms is preferred over adsorption on top of the surface rows. Adsorption energies for the four favoured sites vary by approximately 35 kJ mol^{-1}. The largest adsorption energy was calculated for orientation 4ax, in which the molecule adopts a bridging position between surface layer rows centred on the surface layer atoms. An adsorption energy of –89 kJ mol^{-1} was calculated for adsorption in this orientation. This orientation is identical to the optimum adsorption orientation found for benzene on the Cu(110) surface [11] suggesting that the fluorine substituent results in little change in the adsorption mechanism as suggested by the TPD results of Nakazawa and Somorjai [12]. No experimental evidence is available for direct comparison in order to confirm this adsorption site.

The adsorption energy was found to be relatively insensitive to the C-F bond angle for angles between approximately -3˚ to +7˚, where a positive angle indicates a tilt away from the surface. This provides further evidence that the fluorine substituent has only minor effects on the adsorption chemistry of fluorobenzene. With greater deviations of the C-F angle away from the plane of the carbon ring, the energy of the system increases markedly, indicating an increasingly unfavourable conformation. Analysis of a second order polynomial fitted to the calculated data indicates that the optimum C-F bond angle is +3.13˚, indicating a slight tilt away from the surface.

This is expected, as both hydrogen and fluorine are electron withdrawing substituents. It is therefore reasonable to expect the fluorine to adopt a similar tilt away from the surface as the hydrogen atoms which are bound to the other carbon atoms. The optimisation of the C-F bond angle resulted in a relatively small variation in the adsorption bond strength, with a final adsorption energy of -93.4 kJ mol^{-1}. This represents a significantly stronger interaction than the value of 70 kJ mol^{-1} obtained through experimental TPD by Nakazawa and Somorjai [12]. However, the inert gold surface used by these authors is expected to result in a weaker adsorption interaction. Our calculated adsorption energy is therefore reasonable.

B. Adsorption Chemistry

Electron density difference maps have been calculated for the preferred adsorption geometry in order to investigate the bond formed between fluorobenzene and the Cu(110) surface.

An examination of figure 2a reveals electron density increases between the fluorobenzene ring and copper surface around the 4 carbon atoms in close proximity to the surface copper atoms. The other two carbon atoms which lie between the surface Cu rows show a small decrease in electron density. The electronic redistribution in this plane is essentially identical to that observed for benzene adsorbed on the Cu(110) surface [11].

Charge redistribution due to bonding between the benzene ring and surface is also evident in figure 2b. Here the density difference is plotted in a plane perpendicular to the surface through the two carbon atoms closest to the surface Cu rows. Electron density about the positions of the 2 carbon atoms appears to have been pulled into the region between these atoms and the copper surface, while small

decreases in electron density may be observed at the positions of the surface layer copper atoms. Once again, the variation is identical in the case of benzene adsorbed on the Cu(110) surface [11].

For a perpendicular plane through the two carbon atoms sitting between the copper surface rows (figure 2c), the redistribution of density is smaller and occurs between the carbon atoms themselves rather than toward the copper substrate. Change of electron density in the second layer of Cu atoms is also evident in this plot. Two layers of atoms from the substrate participate in the bonding process when benzene adsorbs. This is perhaps not surprising given the delocalised nature of the electrons in the metallic copper substrate and demonstrates why (at least) 4 layer slabs are necessary to describe the adsorption process. A comparison with the density difference map of benzene on the Cu(110) surface reveals identical variations [11].

These density difference diagrams suggest that adsorption of fluorobenzene occurs via essentially the same mechanism as benzene on the Cu(110) surface. Adsorption occurs primarily through those carbon atoms which are in close proximity to surface layer copper atoms. The impact of the fluorine substituent is minimal, although the weaker adsorption bond observed for fluorobenzene indicates that some effect does occur.

The effect of the fluorine substituent on the adsorption chemistry may be investigated further by examining the variations in the total electronic charges of the atoms of the molecule and surface. These charges may be calculated using Mulliken population analysis [24,25]. A summary of the calculated total electronic charges is shown in table 2, in which the atoms of the molecule and the surface are referred to as they are numbered in figure 1b. Errors in these calculated charges are expected to be less than 0.002 fundamental charge units. Gains in electronic charge on the carbon

atoms which are closest to surface layer copper atoms are observed, with a corresponding loss in charge from the other carbon atoms. The same result was observed for benzene absorption. However, some significant differences are evident which occur as a result of the presence of the fluorine substituent. The fluorine atom itself loses a small amount of charge during adsorption. As a result of the fluorine substituent, we observe a greater loss of charge from the *ipso* carbon atom (atom 8) than we do for the same atom in benzene. A greater loss of charge is also observed on the *para* carbon atom (atom 5), although the difference is not as significant. These variations also affect the changes in electronic charge on the *ortho* (atoms 14 and 16) and *meta* (atoms 13 and 15) carbon atoms. A greater gain in electronic charge may be observed on the *meta* carbons (13 & 15) than is observed in the case of benzene, while less electronic charge is gained by the *ortho* carbon atoms (14 & 16).

At the surface, significant losses of electronic charge occurs from those surface layer copper atoms which are in close proximity to carbon atoms. Hence, we observe large negative variations at copper atoms 2 and 11. These variations are essentially identical to those observed in the adsorption of benzene. Smaller losses of electronic charge are observed on the second layer copper atoms (6 & 7). It is interesting to note that the loss of electronic charge from the second layer copper atom (7) closest to the fluorine substituent is much less than in the case of benzene adsorption. Similarly, those surface layer copper atoms (18 & 20) which are not close to carbon atoms but which are close to the fluorine substituent gain significantly more charge than in the case of benzene adsorption. This is in contrast to the surface layer copper atoms (17 & 19) at the opposite end of the molecule, for which the gain in charge is very similar to variations observed in the case of benzene adsorption.

Bonding in this system is conventionally described in terms of the DCD model of adsorption proposed by Dewar [26], Chatt and Duncanson [27] where electrons are donated from the molecular π-orbitals into the metal and back-donated from the metal to the antibonding orbitals of benzene. The decrease in electronic charge of the surface layer copper atoms which are in close proximity to carbon atoms of the adsorbed molecule is evidence of electronic back-donation. The corresponding increase in electronic charge in the associated carbon atoms provides further evidence of this back-donation. This charge transfer may also be observed as the increase of charge density on the carbon atoms seen in the electron density difference plots. However, the observation of a larger gain in electronic charge on the surface layer copper atoms close to the fluorine substituent and a smaller gain of electronic charge on the *ortho* carbon atoms (14 & 16) indicates a reduced level of back-donation occurring in the region of the molecule to which the fluorine substituent is bound. This effectively allows the adsorption interaction to be dominated by the opposite side of the molecule, where an increase is observed in the intensity of the charge variations. The lower adsorption energies observed for fluorobenzene than for benzene indicates that the increased adsorption interaction away from the fluorine substituent is unable to compensate for the decrease in interaction in the region of the fluorine atom.

C. Simulated STM Images

A theoretical STM image of fluorobenzene in the H-flip geometry adsorbed on the Cu(110) surface in the preferred orientation, orientation 4ax, is presented in figure 3. A bias voltage of 40 mV between surface and tip and a tip height of 2.5 Å was simulated. This conditions are consistent with those implemented in experimental STM studies of benzene on the Cu(110) surface by Doering *et al.* [28,29] The image

reveals a slightly lower level of electron density at the positions of those carbon atoms which lie in close proximity to surface layer copper atoms. Comparison of the calculated STM image of fluorobenzene with a theoretical STM image of benzene calculated under identical conditions reveals very few significant differences. In order to facilitate a comparison of the two images, a difference plot was produced by subtracting the image of fluorobenzene from the image of benzene. The resulting plot is shown in figure 4. Regions of intensity at the positions of the *ispo* and *para* carbon atoms and in the region between the *ortho* and *meta* carbon atoms indicate that the STM image of fluorobenzene is less intense in these regions than the STM image of benzene. In contrast, the depressions in the difference plot at the positions of the *ortho* and *meta* carbon atoms indicate that these regions show greater intensity in the STM image of fluorobenzene. Clearly, the presence of the fluorine substituent does result in some subtle variation of the STM image. However, the magnitude of these variations is quite small and would require excellent resolution in the STM experiment in order to differentiate these two molecules co-adsorbed on the Cu(110) surface.

CONCLUSION

Overall the results presented in this paper demonstrate the utility of the CRYSTAL98 software package and modest computing resources as providing an effective method for predicting STM images. STM images have been simulated within the Tersoff-Hamann approximation [10] from a fully self-consistent calculation of the density of states of fluorobenzene absorbed on the Cu(110) surface using CRYSTAL98. This is a relatively straightforward approach which we have

implemented on extremely modest hardware, and the present work demonstrates the utility of this approach.

Fully *ab initio* calculations of the adsorption of fluorobenzene molecules onto the Cu(110) surface using a periodic linear combination of atomic orbitals approximation using DFT methods have been reported. Fluorobenzene coverage is well below single monolayer so that adsorbate-adsorbate interactions are negligible. This approach describes the substrate surface reliably by modelling it as an essentially infinite slab in two dimensions, compared with cluster calculations where a small section of the surface is modelled. It has the attraction that the preferred absorption site and geometry together with the absorption energies can be predicted using modest computing resources. The preferred adsorption site and adsorption energy has been calculated the STM image of this system has been simulated under conditions consistent with experiment. However, it must be noted that our method does not take account of tip-surface interactions in simulation of the STM images.

A adsorption energy of -93.4 kJ mol^{-1} is predicted. A previous experimental TPD study of fluorobenzene on gold reports a desorption energy of 70 kJ mol^{-1} [12]. Considering the inert nature of the gold surface, our adsorption energy represents a reasonable value of the stronger interaction expected with the Cu(110) surface. The preferred adsorption site is a bridging position with the benzene ring centred with respect to the surface layer atoms. In their experimental STM images of benzene on the Cu(110) surface Doering and co-workers [29] reach the same conclusion. An examination of density difference plots and total electronic charge variations indicates that adsorption occurs through the DCD model of adsorption proposed by Dewar [26], Chatt and Duncanson [27].

The predicted differences between the STM images of benzene and fluorobenzene adsorbed on the Cu(110) surface essentially consist of variations in image intensity rather than topographical variations. These differences are subtle and suggest that extremely good resolution would be required in order to discriminate between these two molecules co-absorbed onto Cu(110) using STM.

Future work could, ideally, focus on confirming the relaxed absorption conformation through full geometry optimisations. This requires significant computational resources and in any case it is unlikely to change the present conclusions. The single largest source of uncertainty in our calculations is most likely the estimate of basis set superposition errors. In addition, the effects of various other functional groups on the adsorption chemistry and STM images of benzene derivatives should be investigated. Once again, the study of larger functional groups requiring the optimisation of a number of degrees of freedom will only become possible with significantly larger computational resources or more efficient optimisation procedures.

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Figure 1a. Positions of the sixteen proposed possible adsorption orientations of fluorobenzene on the Cu (110) surface. Grey disks represent upper layer Cu atoms, while open circles represent second layer Cu atoms. **b.** Detail of the favoured adsorption orientation. The individual atoms are labelled in order to facilitate an analysis of changes in the atomic charges due to adsorption. Note that atoms 6 and 7 are second-layer copper atoms which are partially obscured by carbon atoms of fluorobenzene.

Figure 2. Density difference plots of fluorobenzene adsorbed in orientation 4ax on a 4-layer Cu(110) surface calculated using the DFT level of theory. Arrows on diagrams indicate the orientation of the plane. **a.** Midway between the benzene ring and surface Cu atoms parallel to the surface. **b.** Perpendicular to the surface through the C atoms positioned above the row of surface Cu atoms. **c.** Perpendicular to the surface through the two C atoms positioned between the rows of surface Cu atoms.

Figure 3. Theoretical STM image of fluorobenzene adsorbed on the Cu(110) surface in orientation 4ax. The image was obtained using conditions designed to simulate a 40mV negative bias on the sample, as in the work of Doering *et al.* [28,29] A tip height of 2.5 Å and a scanning area of 7 Å by 7 Å was simulated.

Figure 4. Difference plot produced by subtracting the theoretical STM image of fluorobenzene from the theoretical STM image of benzene.

TABLE 1. Comparison of adsorption energies and adsorption heights of fluorobenzene in the H-flip conformation proposed by Pettersson et al. [19] on the Cu(110) surface. Adsorption energies are calculated at the DFT level of theory using a C-F bond angle of 0°. A 4 layer copper slab is implemented. Adsorption height refers to the height of the carbon ring above the surface layer Cu atoms.

Orientation	Adsorption Energy (kJ mol^{-1})	Adsorption Height (Å)
1ax	-65.2	2.050
1ay	-64.2	2.062
1bx	-86.9	2.064
1by	-56.5	2.123
2ax	17.3	2.093
2ay	31.4	2.090
2bx	28.5	2.260
2by	22.0	2.131
3ax	-21.3	2.092
3ay	-4.2	2.110
3bx	-2.9	2.152
3by	-20.8	2.128
4ax	-89.7	2.014
4ay	-54.2	2.040
4bx	-63.5	2.090
4by	-73.6	2.105

TABLE 2. A summary of the changes in atomic charges in fluorobenzene and the Cu(110) surface which occur due to adsorption. Labels refer to the atom labels shown in figure 5. For comparison, relevant changes in electronic charges in benzene and the Cu(110) surface are included in parentheses.

Copper

Atom No.	Isolated Charge	Adsorbed Charge	Variation	% Variation
2	18.909	18.849	-0.060 (-0.057)	-0.317 (-0.301)
6	19.091	19.061	-0.030 (-0.031)	-0.157 (-0.162)
7	19.091	19.082	-0.009 (-0.025)	-0.047 (-0.131)
11	18.909	18.855	-0.054 (-0.050)	-0.286 (-0.264)
17	18.909	18.928	0.019 (0.016)	0.100 (0.085)
18	18.909	18.949	0.040 (0.021)	0.212 (0.111)
19	18.909	18.934	0.025 (0.023)	0.132 (0.122)
20	18.909	18.953	0.044 (0.024)	0.233 (0.127)

Fluorobenzene

Atom No.	Isolated Charge	Adsorbed Charge	Variation	% Variation
F9	9.246	9.221	-0.025	-0.270
C5	6.179	6.075	-0.104 (-0.092)	-1.683 (-1.495)
C8	5.588	5.480	-0.108 (-0.087)	-1.933 (-1.414)
C13	6.129	6.268	0.139 (0.128)	2.268 (2.080)
C14	6.268	6.379	0.111 (0.128)	1.771 (2.080)
C15	6.129	6.265	0.136 (0.123)	2.291 (1.999)
C16	6.268	6.380	0.112 (0.130)	1.787 (2.113)
H1	0.848	0.843	-0.005 (-0.005)	-0.590 (-0.592)
H3	0.826	0.823	-0.003 (-0.007)	-0.363 (-0.828)
H4	0.846	0.848	0.002 (0.002)	0.236 (0.235)
H10	0.848	0.843	-0.005 (-0.006)	-0.590 (-0.710)
H12	0.826	0.823	-0.003 (-0.006)	-0.363 (-0.710)