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RESEARCH ARTICLE

An Experimental and Computational Study of the Valence Photoelectron Spectra of Halogenated Pyrimidines

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The electronic structures of pyrimidine and a selection of its halogen substituted derivatives have been investigated using ultraviolet photoelectron spectroscopy and *ab initio* quantum chemical methods. Assignments are proposed for all of the features in the PES spectra by comparison with the vertical ionisation energies of the molecular orbitals calculated using the partial third order quasiparticle approximation as applied to electron propagator theory and a corrected density functional method based on the B3LYP functional. The shifts of the outermost five molecular orbitals of the pyrimidine ring structure in the halogen substituted derivatives with respect to the binding energies of the equivalent orbitals in the parent pyrimidine molecule are discussed as a function of the identity and ring position of the halogen atom.

Keywords: Photoelectron spectra; Halogenated pyrimidines; Substituent effects; Density functional theory; Electron propagator theory.

1. Introduction

Pyrimidines are an important class of organic molecules mainly due to the fact that the pyrimidine ring forms the base structure of three nucleic acids, i.e. uracil, cytosine and thymine. Furthermore, halogenated pyrimidine bases have found applications as radiosensitisers in radiotherapy where, for example, it has been discovered more than 40 years ago that 5-bromodeoxyuridine (an analogue of thymidine) radiosensitises cells [1, 2]. A deep understanding of valence photoelectron spectra of the halogenated pyrimidines will help a greater understanding of the electronic structure of the halogenated bases. In addition, a study of the valence shell structure of a molecule provides the basis for further studies on the fragmentation of such molecules following both valence shell and inner shell ionisation.

This work is part of an overall investigation of the valence and inner shell electronic structure and electronic spectra of this class of molecules undertaken by probing them with laboratory sources [3] and synchrotron radiation. In particular, results of the present work constitute the basis to interpret the resonant Auger structure produced after innershell excitation.

The photoelectron spectrum (PES) of pyrimidine and some of its derivatives have been studied in the past [4, 5], however to the best of our knowledge no work has

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been published on the effect of the halogen substitution of the pyrimidine ring on the valence photoelectron spectrum of the molecule. In particular the valence PES of pyrimidine has been analysed in detail in the work of Holland *et al.* [4]. This group has also performed a systematic experimental and computational study of the halobenzenes [6, 7], halothiophenes [8–10] and, most recently, the halouracils [11]. In this work we concentrate on the substituent effects of the halogen atoms on the pyrimidine parent molecule as a function of ring position and halogen character. The analysis of experimental valence photoelectron spectra are supported by a detailed computational analysis of the orbitals energies and ionisation potentials.

2. Experimental Section

The photoelectron spectra were measured using a resonance noble gas discharge lamp operated on the He I line at 21.22 eV in combination with a home-built hemispherical analyser (mean radius = 60 mm). The He I radiation was transported to the interaction region by means of a capillary tube where it intersected the gas flow at an angle of 90° . The kinetic energy of the photoelectrons emitted into an acceptance angle of $\pm 5^\circ$ oriented at 90° with respect to the direction of propagation of the radiation was measured.

Energy calibration of the spectra was achieved by adding a small amount of Argon to the gas flow and the resulting photoelectron peaks at 15.759 eV and 15.937 eV, corresponding to the $3p^{-1} {}^2P_{3/2} \text{Ar}^+ \leftarrow \text{Ar} ({}^1S_0)$ and $3p^{-1} {}^2P_{1/2} \text{Ar}^+ \leftarrow \text{Ar} ({}^1S_0)$ transitions, were then used to correct the energy scale of the molecular photoelectrons. The photoelectron spectra were also corrected for the non-linear transmission of the analyser by measurement of the known spectra of benzene [12, 13] and methyl oxirane [14]. The transmission function of our apparatus was extracted by comparing the intensities of the peaks of the literature spectra with the raw intensities of the equivalent spectra recorded using the electron spectrometer used in this work. The different collection angle: magic angle in the case of the reference spectra and 90° in the case of the electron spectrometer used here was also taken into account by using the β parameter for each peak. All spectra were measured at a resolution of 160 meV (FWHM) as determined from the width of the above Argon photoelectron peaks. Furthermore, the low binding energy region of each molecule (typically 9.5 to 13.5 eV) were scanned at the higher resolution of 75 meV (FWHM). The peak positions were determined using standard peak fitting procedures.

Finally, all compounds were purchased from Sigma Aldrich and used without further purification (see Figure 1). The compounds were introduced into the interaction region *via* a leak valve where the room temperature vapour pressures of the samples were sufficient to provide a high enough gas density in the interaction region to allow the electron spectra to be recorded.

3. Computational Details

All *ab initio* calculations were performed using the Gaussian03 package of programs [15] where the geometries were optimised at the B3LYP density functional level of theory [16–18] using the split valence plus polarisation basis set 6-311++G(d,p) [19]. These geometries, the resulting vibrational frequencies and total energies can be found in the supporting information section of this article. Subsequently a number of methods were employed to calculate the vertical ionisation energies of the molecules using these geometries in order to achieve a reliable interpretation of their photoelectron spectra. The three computational methods

employed to calculate the vertical ionisation energies were: 1) Hartree Fock together with Koopmans' Theory, [20] 2) Partial third order (P3) quasiparticle approximation as applied to electron propagator theory (implemented by Ortiz *et al.* [21] in the Gaussian suite of programs) and 3) SCF molecular orbital energies of the Kohn-Sham orbitals calculated at the B3LYP/6-311++G(d,p) level of theory and corrected for the vertical ionisation energy by calculating the energy of the cation in the ground state neutral geometry, i.e. essentially the equivalent of Koopmans' theorem for DFT calculations [22] (discussed in more detail below). Furthermore, the effects of the basis set on the P3 calculation were investigated by performing the calculations on all molecules using the following basis sets: 6-311G(2df,2p) and cc-pVTZ [19, 23] while in addition P3 calculation with the 6-311G(2df,2p) basis augmented by the SDD basis set on the heavy halogen atom were performed on the bromine containing molecules.

4. Results and Discussion

4.1. Pyrimidine

In order to be able to discuss the effect of the substituents on the electronic structure of the halogenated pyrimidines it is first necessary to briefly re-examine the photoelectron spectrum of the parent molecule: pyrimidine. To this end the He I PES of pyrimidine has been measured and is presented in Figure 2 and the results of the *ab initio* calculations on this molecule are summarised and compared to the experimental peaks in Table 1.

At the Hartree-Fock (HF) level of theory the ground state valence orbital configuration of pyrimidine in C_{2v} symmetry is

$$\begin{aligned} \text{inner valence: } & (1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(4a_1)^2 \\ \text{outer valence: } & (3b_2)^2(5a_1)^2(4b_2)^2(6a_1)^2(1b_1)^2(7a_1)^2 \\ & (1a_2)^2(5b_2)^2(2b_1)^2 \end{aligned}$$

where the orbitals of a_1 and b_2 symmetry correspond to σ orbitals while those of a_2 and b_1 symmetry correspond to π type orbitals. In particular for the outermost 5 molecular orbitals (MOs) we adopt the notation of Lotermoser *et al.* [5] in which the $5b_2$ and $7a_1$ orbitals are denoted as n_{N-} and n_{N+} , respectively, and the $2b_1$, $1a_2$ and $1b_1$ orbitals are denoted as π_3 , π_2 and π_1 orbitals. These HF molecular orbitals are shown in Figure 3 where it can be seen that the three π orbitals are localised above and below the pyrimidine ring while the n_{N-} and n_{N+} orbitals are principally the nitrogen lone pairs where the + and - symbols indicate symmetric and antisymmetric combinations. The influence of electronegative halogen substituents on the composition and binding energy of these orbitals will be discussed in detail in the following subsection.

The first intriguing point to note from the *ab initio* calculations lies in the change of the energy ordering of the orbitals on passing from the Hartree-Fock/Koopmans' theorem to the higher level methods involving electron propagator theory (EPT) and the modified density functional theory (DFT) method. These changes, which have already been noted in the past [4, 5], include the inversion of the ordering of the HOMO and HOMO-1 as well as the inversion of the HOMO-2 and HOMO-3 (see Table 1). This is mainly due to the fact that the energy of the π_3 and π_2 orbitals change very little while the energy of the n_{N-} and n_{N+} orbitals are reduced by > 1.5 eV on passing to the higher level theories. These changes are due to a greater effect of electron correlation and final state orbital relaxation on the n_{N-}

and n_{N+} orbitals with respect to the π_3 and π_2 orbitals as these effects are not taken into account at the HF level of theory.

The DFT method also determines the correct energy ordering of the orbitals as determined by an examination of the symmetry of the Kohn Sham orbitals. Furthermore, the absolute energies of the orbitals can be corrected by the following procedure: 1) single point calculation of the energy of the cation at the neutral state optimised geometry (-264.39394 Hartree) 2) comparison of this value to the energy of the neutral state (-264.03967 Hartree) and thus extraction of the vertical ionisation energy of the HOMO (9.64 eV) 3) Use of the difference between the calculated binding energy of the HOMO orbital and the above value as a correction for all MO energies. This method leads to very good agreement with the experimental values of the binding energies as can be seen from Table 1 and the work of Lotermoser *et al.* [5]

The effect of the basis set was also briefly examined. In contrast to the work of Potts *et al.* [4] no large difference in the basis set effect was observed when comparing the nitrogen lone pair orbitals and the π orbitals. Those authors pointed out that the nitrogen lone pair orbitals might be sensitive to the approximation scheme being used. This is supported by the fact that the approximation scheme used in this work [21] is different with respect to Potts *et al.* [24] thus explaining the difference basis set effect in the two calculations. Indeed the P3/6-311G(2df,2p) and P3/cc-pVTZ give very similar results with the difference in ionisation energy calculated using these two basis sets not exceeding 0.07 eV for any orbital. It should be noted in the tables comparing the *ab initio* calculations with the experimental results that the pole strengths are shown only for the P3/cc-pVTZ calculation as they do not vary significantly with basis set.

The P3 and B3LYP computational methods give similar results when compared to the experimental ionisation energies with both methods predicting the same energy ordering of the molecular orbitals. A numerical comparison of the two computational methods show that the P3/6-311G(2df,2p) calculation results in a rms deviation of the calculated ionisation energies from the experimental ones for the 4 outermost orbitals of 0.08 eV while the B3LYP method gives an rms deviation for these orbitals of 0.13 eV. When considering the complete energy range (excluding the bands under the broad feature in the range 13-15 eV) the rms deviation of the P3/6-311G(2df,2p) method increases to 0.26 eV while that of the B3LYP calculation increases to 0.19 eV. This is due to the larger error of the P3 method in the inner valence region especially for ionisation energies > 17 eV. Although the P3 method is a higher level method (and therefore should be more reliable) than the B3LYP based method we will present the results of both methods for all molecules for comparative purposes.

4.2. Mono Halogenated Pyrimidines

When a halogen substituent is added to the aromatic ring of pyrimidine the electronic structure of the molecule changes quite significantly. First of all two new orbitals which correspond to the p orbitals of the halogen atom are added to the outer valence orbital manifold. The orientation of these orbitals can be parallel $n_{||}$ or perpendicular $n_{\perp}$ to the ring as shown in Figure 4. In addition, the added electronegative substituent can perturb the π_3 , π_2 , π_1 , n_{N-} and n_{N+} orbitals in the pyrimidine ring with respect to the parent molecule either by the inductive (I) or resonant (R) effect. The changes in the electronic structure of the monohalogenated pyrimidines studied in this work is illustrated by a correlation diagram (see Figure 5) where the evolution of the binding energies of the various π and σ

orbitals are shown at the B3LYP/6-311++G(d,p) level of theory. However, before proceeding to a detailed discussion of the interplay of the above mentioned effects we will first give a brief description of the individual PES for each molecule.

4.2.1. 2-bromopyrimidine

The first significant change in the PES with respect to the pyrimidine parent is the shift of the lowest band to higher ionisation energy by 0.2 eV (see Figure 6). The comparison with the *ab initio* calculations leads to some uncertainties in the assignment of the identity of the HOMO and HOMO-1. While the B3LYP based method suggests that these orbitals are the n_{N_-} and π_3 orbitals, the P3 method implies that they are the π_3 and $n_{||}$ orbitals. This uncertainty can be resolved by examining the next band in the spectrum at 10.83 eV. This is a much sharper band with respect to the other features in the spectrum and indeed on passing to the higher resolution scan (see the upper part of Fig. 6) this band becomes narrower while the other bands do not and so appears to be limited by the resolution of the electron spectrometer. It has been noted in the literature [25] that sharp narrow bands in the PES of halogenated aromatic systems correspond to ionisation from strongly localised non-bonding orbitals as one would expect from the Franck Condon principle. In this energy region the best candidate for such an orbital is the $n_{||}$ orbital which is strongly localised on the bromine atom. In order to definitively resolve the difficulty in assigning this band, photoelectron spectra in this kinetic energy range have been recorded following ionisation of this molecule at different excitation energies using synchrotron radiation at the GasPhase photoemission beamline at Elettra. This experiment was motivated by the work of Potts *et al.* [9] who observed a reduction in the relative intensities of the photoelectron lines due to the ionisation of bromine lone pair orbitals in the bromothiophenes at energies in the region of the Cooper minimum due to the Br 4p subshell around 70 eV. The comparison of the photoelectron spectra of the 2-bromopyrimidine excited following ionisation at 30 eV and 70 eV showed a drastic reduction ($>$ factor of 2) in the relative intensity of the photoelectron line at an ionisation energy of 10.83 eV when the molecule is ionised with a photon energy of 70 eV. This confirms that this peak is due to ionisation of the lone pair of the Br atom. These results suggest that the B3LYP calculation gives the correct HOMO/HOMO-1 assignment although the ordering from an experimental point of view remains unclear. In order to test the possibility that the basis set used for the P3 calculation do not describe sufficiently the Br atom, the calculation has been repeated with the 6-311G(2df,2p) augmented by the SDD (Stuttgart/Dresden effective core potential) [26] basis set for the heavy halogen atom. The results, which are shown in Table 2 show that although the ionisation energies of the molecular orbitals with large electron density on the halogen atom do shift by a larger amount than those with little density on the halogen atom the energy ordering of the orbitals remain the same in the two calculations.

It should be noted that the largest difference between the P3/6-311G(2df,2p) and the B3LYP calculations resides in the ionisation energy, E_i , of the n_{N_-} orbital ($\Delta = 0.91$ eV) while the two methods give a similar result for the E_i of the $n_{||}$ orbital. Comparing to the experiment we find that both methods underestimate the E_i of the $n_{||}$ by ~ 0.5 eV while the P3 method overestimates the E_i of the n_{N_-} orbital and the B3LYP underestimates the same quantity. Therefore, although the B3LYP does correctly predict the $n_{||}$ to be the HOMO-2 while the P3 method does not the overall quality of the two results in comparison with the experiment are similar.

The next part of the spectrum is again quite different from the corresponding energy range of the 2-bromopyrimidine spectrum and a broad structured band

centered at 11.89 eV is observed. Comparison with the results of both the B3LYP and P3 calculations leads to the conclusion that the three MOs contributing to this band are the n_{N+}, π_2 and $n_{\perp}$ orbitals, however, considering how close they are in energy to each other a definitive assignment of the energy ordering is difficult.

The absolute error of the *ab initio* calculations increases on going to higher binding energy orbitals. This is to be expected due to the increase of the contribution of shake-up satellite peaks and many-electron effects [4]. However, the deviations appear to be quite uniform and therefore it is still possible to at least discuss the principal contributions to these peaks. Three distinct bands are observed in the energy range from 13.5 eV to 16.5 eV with the intensity of the central band appearing to be larger than the other two. Both sets of calculations suggest that the first peak is due to ionisation of an inner σ orbital, while the second contains contributions from ionisation of both the π_1 and σ orbital and finally the last of these series is due to ionisation of a single σ orbital.

4.2.2. 5-bromopyrimidine

The lowest energy band in the PES of 5-bromopyrimidine (see Figure 7) occurs at the same energy as the corresponding band in the PES of 5-bromopyrimidine and again consists of contributions from both the HOMO and the HOMO-1. Comparison with the *ab initio* calculations suggests that this band consists of contributions due to ionization of both the HOMO and the HOMO-1 (π_3 and n_{N-} MOs). This is in contrast to the parent pyrimidine molecule where the binding energies of these two orbitals differed by 0.8 eV. Both the P3 and the B3LYP computational methods predict a stabilisation of the n_{N-} orbital and a destabilisation of the π_3 orbital. However, while the B3LYP based method predicts the ordering to be $BE(n_{N-}) < BE(\pi_3)$ the P3 method predicts the opposite although the energy differences are small in both cases (0.15 and 0.21 eV, respectively). From an experimental point of view however (even at the higher resolution scan - FWHM $\approx$ 75 meV) it is not possible to separate the two contributions but the relative intensity of the band is consistent with contributions from ionization of two MOs under this band. Again the comparison of the next highest electronic system with the *ab initio* calculations suggest that it is the result of contributions from the ionisation of no less than three different MOs ($n_{\parallel}$, n_{N+} and π_2) and furthermore the two computational methods used are in agreement on the ordering of the MOs. Also in this case the experimental intensity of the band is in agreement with this conclusion. The next band (at 12.34 eV) is well separated and corresponds to the $n_{\perp}$ MO.

As in the case of the 2-bromopyrimidine the PES of 5-bromopyrimidine were recorded with photon energies of 30 and 70 eV at the GasPhase beamline at Elettra. Comparing these spectra reveals a reduction in the relative intensity of the band at 12.34 eV when passing from the spectra produced using photons at 30 eV with respect to that recorded following ionisation with a photon energy of 70 eV. This is consistent with the assignment arising from the both computational methods indicating that this band is due to ionisation of the $n_{\perp}$ MO which is principally located on the Br atom. The decrease in intensity of the central part of the band located at 11.42 eV when comparing the PESs recorded at 30 and 70 eV respectively suggest that the ionisation of the $n_{\parallel}$ contributes to the central part of this band and not to the lower energy shoulder as the comparison with both computational methods would suggest.

The inner binding energy region (13 - 18 eV) of the spectrum is also quite different from the corresponding region of the 2-bromopyrimidine molecule. The broad band

between the ionisation energies 14 and 16 eV consists of contributions from the ionisation of four MOs which are the three σ orbitals and the most highly bound π orbital, π_1 . The last band in the spectrum of the 5-bromopyrimidine appears to be less intense and broader than the corresponding feature in the 2-bromopyrimidine spectrum. Again by comparison to the calculations one can see that this is most likely due to the close matching of the ionisation energies of two σ orbitals in the case of the 2-bromopyrimidine (see Table 2) while the corresponding orbitals in 5-bromopyrimidine are separated by 0.25 eV (see Table 3).

4.2.3. 2-chloropyrimidine

The PES of 2-chloropyrimidine is shown in Figure 8 and the experimental band energies are compared to the *ab initio* calculations in Table 4. Here the P3 calculations are presented only for the cc-pVTZ and 6-311G(2df,2p) basis sets as the ionisation energies do not change with the SDD basis set for the lighter halogen atom chlorine. In this case on the lower energy side of the lowest energy band it is possible to see a partially resolved shoulder due to the ionisation of the HOMO. Both the P3 and B3LYP *ab initio* methods agree that the ordering of the HOMO and the HOMO-1 is $\text{BE}(n_{N_-}) < \text{BE}(\pi_3)$ although the splitting in the case of the B3LYP method (0.29 eV) is more consistent with the observed experimental splitting than the case of the P3 calculation (0.11 eV). The next part of the spectrum would appear to be quite similar to that of 5-bromopyrimidine in that it consists of a broad peak with contributions from 3 MOs (partially resolved in the higher resolution scan) the identity of which are predicted by both *ab initio* methods used here to be the $n_{||}$, n_{N_+} and π_2 orbitals although the ordering of the latter two is unclear. Finally, a low intensity band appears at higher energy (12.40 eV) and is due to ionisation of the $n_{\perp}$ orbital. The second half of the PES on the other hand is more similar to that of 2-bromopyrimidine and indeed the order of the MOs is predicted to be identical to that molecule by the *ab initio* calculations.

4.2.4. Substituent effects in the monohalogenated pyrimidines

We begin this section with a discussion of the effects of the halogen atom on the energies of the π orbitals. As mentioned above, the halogen atom acts on the electronic structure of the pyrimidine derivatives *via* two main mechanisms: the inductive effect (I) and the resonance effect (R). The energy changes induced by these effects on the π orbitals localised on the pyrimidine ring are often antagonistic. The I effect is due to the electronegativity of the halogen substituent which withdraws electron density from the ring thus reducing the electron repulsion within the π orbitals hence increasing their binding energies. The R effect, on the other hand, is due to conjugation between the lone pair orbitals of the halogen atom and the π orbitals of the ring. The effect on the energy of the π orbital depends on the type of conjugation. For example, in the case of the π_3 orbital the interaction of the electron density in the out of plane p orbitals of the halogen atom with the π electrons on the pyrimidine ring leads to a nodal/anti-bonding plane along the C-X bond. This in turn leads to a destabilisation of the π_3 orbital (decrease in binding energy). In order to be able to perform a quantitative discussion on the resonance effects we have performed a Mulliken population analysis on each of the Hartree-Fock MOs (see Table 5). In this table the contributions of all orbitals on each atom is summed in order to give the overall contribution of each atom to the electron density to the individual molecular orbitals.

The net effect on the π_3 orbitals in all of the molecules is a destabilisation with the effect being more pronounced in the case of the bromopyrimidines with respect to the chloropyrimidine (see Figure 5). As described above the I effect stabilises the π_3 orbital while the R effect destabilises it. Since the net effect is a destabilisation

it is clear that the R effect dominates in this case. The relative magnitude of the destabilisation ($\text{Br} > \text{Cl}$) can be rationalised by an inspection of the population analysis (see Table 5) for these orbitals which shows that chlorine contributes 31.9% to the electron density of the π_3 orbital in 2-chloropyrimidine while Br contributes 47.6% and 50.1% to the corresponding orbitals in 5-bromo and 2-bromopyrimidine, respectively. This explains why the π_3 orbital is more destabilised in the bromine substituted molecules.

The π_2 orbital shows the opposite effect in that it is stabilised by the addition of the halogen atoms in all cases. This observation can again be explained by consulting the population analysis where it can be seen that the halogen atoms contribute zero to the electron density of these orbitals which means that the R effect has no influence on the energy of these orbitals. This is due to nodal plane perpendicular to the ring and passing through C1 and C5. Therefore, only the I effect operates in this case and as expected (due to the relative electronegativities) the effect is larger in the case of chlorine than for bromine.

The last π orbital, π_1 , is also stabilised but in this case both the inductive and the resonance effects stabilise the orbital as the $n_{\perp}$ conjugates in a bonding fashion with the π_1 orbital on the pyrimidine ring thus further stabilising this orbital.

The energy of the lone pair orbitals on the nitrogen atoms (n_{N+} and n_{N-}) are also changed by the presence of the halogen atom. Indeed, the n_{N+} orbitals are changed in a very similar way to the π_2 orbitals suggesting that the principal effect operating is the inductive effect, i.e. withdrawal of electron density from the lone pair thus stabilising the MO and furthermore the effect is larger for chlorine than for bromine. The energy dependence of the n_{N-} orbital is more complicated because in addition to the I effect there is a through space resonance effect between the $n_{\parallel}$ and the antisymmetric lone pair orbitals of the nitrogen atoms resulting in further stabilisation of the n_{N-} orbital. In the case of 5-bromopyrimidine the bromine atom is on the opposite side of the molecule with respect to the nitrogen lone pairs and thus the resonance effect is no longer possible.

The lone pairs on the halogen atoms ($n_{\parallel}$ and $n_{\perp}$) are destabilised by the inductive effect (increased electron density on the halogen atoms due to the electron withdrawing effects decreases the binding energy of these orbitals) and hence the average binding energy of these orbitals, $\langle n \rangle = n_{\parallel} + n_{\perp}$, is lower than in the isolated atoms (see Figure 5). However, the resonance effects further modify the energies of these orbitals. In the case of the $n_{\perp}$ the resonance effect leads to some π bonding character along the C-X bond leading to a stabilisation of this orbital. In contrast, the $n_{\parallel}$ in which the lone pair orbital lies in the plane of the pyrimidine ring interacts with the σ orbitals of the pyrimidine ring. In all cases this leads to destabilisation of this orbital. For the 2-bromopyrimidine this effect is particularly marked due to the nodal planes which arise between the lobes of the bromine lone pair and the electron density on the nitrogen lone pairs. Indeed this effect is complementary to that described for the n_{N-} in the previous paragraph.

4.3. Dihalogenated Pyrimidines: 5-bromo-2-chloropyrimidine

The He I PES of 5-bromo-2-chloropyrimidine is shown in Figure 9 while the band energies are compared to the *ab initio* calculation results in Table 6. The first band (lowest ionisation energy) again consists of contribution from ionisation of both the HOMO and the HOMO-1 and the two higher level sets of *ab initio* calculations agree that these are the π_3 and n_{N-} orbitals, respectively. The second peak at 11.9 eV consists of contributions from five different MOs among which are the π_2 orbital, three lone pair orbitals on the chlorine and bromine atoms and the n_{N+}

orbital although the two sets of calculations predicts quite different relative energy ordering. The relative intensity of this band is in agreement with the contribution of five MOs. A small band at 13.1 eV is due to ionisation of the $n_{\perp}$ (Br/Cl) orbital. The more tightly bound region from 14.0 - 17.5 eV contains two broad structured band, the first of which contains contributions from the ionisation of 4 MOs while the second is due to ionisation of 2 MOs. All of these MOs (apart from the π_1 orbital) are of σ character.

4.3.1. Substituent effects

The first noticeable substituent effect is that this molecule has the lowest IP of all of the molecules examined. This is due to the change of the binding energy of the π_3 orbital which is destabilised by the resonance effect with the substituted halogen atoms. It appears that this effect is additive because in the 5-bromopyrimidine molecule the experimentally observed shift of this orbital with respect to the parent pyrimidine molecule is $\Delta = -0.60$ eV while the equivalent shift in the 2-chloropyrimidine molecule is $\Delta = -0.38$ eV : the sum of these value is quite close to the shift in the 5-bromo-2-chloropyrimidine molecule, i.e. $\Delta = -0.85$ eV. Indeed, due to this resonance effect the π_3 becomes the HOMO in this molecule.

The $n_{N_{-}}$ orbital is stabilised by the inductive effect of the halogen atoms by 0.15 eV and becomes the HOMO-1. In this case it is difficult to conclude whether the effects are additive or not because the size of the shifts are comparable to the width of the peaks in the PES. However, it is consistent that the shift is very similar to the case of the 2-chloropyrimidine molecule ($\Delta = 0.11$ eV) as the chlorine substituent is likely to be dominant due to its proximity to the nitrogen lone pairs.

Both the π_2 and $n_{N_{+}}$ orbitals are stabilised by the presence of the halogen atoms however as the electrons produced by the ionisation of these two MOs appear in the PES of the 5-bromo-2-chloropyrimidine molecule under a broad peak centered at 11.6 eV it is difficult to discuss from an experimental point of view the shifts of these orbitals with respect to the parent molecule.

The more surprising aspect of the substituent effects in the dihalogen species is the effect on the non-bonding orbitals on the halogen atoms themselves. While in the case of the mono-halogenated pyrimidines the addition of the halogen atom adds three MOs to the valence manifold (one of which lies in the inner valence shell, the other two being the $n_{\parallel}$ and $n_{\perp}$ orbitals), the substitution with two halogen atoms leads to the addition of six new MOs in the valence shell. By analogy to the monohalogenated species the four of these which lie in the outer valence shell would be expected to be two $n_{\parallel}$ orbitals and two $n_{\perp}$ orbitals with one of each on the chlorine and bromine atom. This is exactly what happens for the $n_{\parallel}$ orbitals where two quite distinct orbitals are attributable to the $n_{\parallel}$ (Cl) and the $n_{\parallel}$ (Br) orbitals. A Mulliken population analysis on the HF/6-311++G(d,p) orbitals revealed that the chlorine atom contributes 38.3% to the $n_{\parallel}$ (Cl) while the bromine atoms contributes 53.9% to the $n_{\parallel}$ (Br) orbitals. The binding energies of these are predicted to be very close by the *ab initio* calculations and on comparison with the experimental PES they are suggested to lie on the low energy side of the broad peak centered at 11.6 eV. These orbitals are close in energy in spite of the fact that the binding energy in the isolated atom is much higher for the chlorine atoms because the $n_{\parallel}$ (Cl) orbital experiences additional destabilisation with respect to the $n_{\parallel}$ (Br) due to its proximity to the nitrogen lone pairs.

The situation of the $n_{\perp}$ orbitals is slightly more complicated. Upon performing a Mulliken population analysis on the first of these orbitals (lowest binding energy) it was found that it contains almost equal contributions from the chlorine (46.2%) and bromine (45.5%). In this orbital there is little or no binding along the C-X bond and therefore the orbitals is not stabilised by the resonance effect and thus has a

binding energy similar to that of the $n_{\parallel}$ orbitals. The other $n_{\perp}$ orbital also contains comparable contributions from the chlorine (47.0%) and bromine (26.9%) atoms but in this case there is significant π bonding along the C-X bonds and indeed the energy of this orbital is strongly stabilised by the resonance effect (binding energy = 13.03 eV).

5. Conclusions

The valence shell photoelectron spectra of gas phase 5-bromopyrimidine, 2-bromopyrimidine, 2-chloropyrimidine and 5-bromo-2-chloropyrimidine have been recorded following excitation with He I radiation. The computational methods were tested by comparison to the known assignment of the pyrimidine PES. Assignments are then proposed for all features in these PES by comparison to the vertical ionisation energies calculated by three different *ab initio* methods and in the cases of the 2-bromopyrimidine and 5-bromopyrimidine by comparing the relative intensities of the PES recorded with photon energies of 30 and 70 eV (the latter of which corresponds to the Cooper minimum of the Bromine atom. This experiment allowed a definitive assignment of the bands due to ionisation of molecular orbitals dominated by bromine lone pairs. Comparison of the B3LYP based method and the P3 method with these results showed similar quality results for the two methods which is surprising considering the lower level of the B3LYP calculations. It should also be noted that the remaining uncertainties in the assignments of the bands of the halogenated pyrimidines presented in this work (principally due to overlapping bands) may be resolved by future measurements on the angular distributions of the photoelectrons.

The substituent effects on the π and σ orbitals of the pyrimidine ring have been discussed as a function of the identity and position of the halogen atom. The shifts of the binding energies of these orbitals can be accounted for by a combination of the inductive and resonance effects of the halogen atoms of the ring orbitals.

Furthermore, the results presented in this work will provide the basis in order to permit an in depth interpretation of future experiments on the electron-ion coincidence studies on these molecules following either resonant inner shell excitation or valence shell ionisation. The fact that a knowledge of the valence shell electronic structure of a molecule is necessary to interpret electron-ion coincidence studies on that molecule is demonstrated by the recent work on pyrimidine [27, 28].

6. Acknowledgments

The authors are grateful for the technical help provided by Dr. Ettore Fainelli and Marcello Mastropietro. The authors would also like to thank the High Performance Computing center at CINECA for computing time awarded via the Progetto Supercalcolo Convenzione CINECA-INFN-CNR.

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Figure 1. Schematic representation of the pyrimidine molecule and its halogen substituted derivatives investigated in this work. Structure 1 also indicates the numbering of the ring atoms employed.

FIGURES

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Figure 2. He I photoelectron spectrum of pyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p) method. The asterisk marks a peak due to ionisation of water molecules in the sample.

Figure 3. Hartree Fock molecular orbitals of pyrimidine together with the notation adopted in this work.

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Figure 4. Hartree Fock molecular orbitals of the halogen atom lone pairs (in 2-chloropyrimidine) together with the notation adopted in this work.

FIGURES

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Figure 6. He I photoelectron spectrum of 2-bromopyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p)/SDD method. The inset represents a high resolution scan of the ionisation energy region 9 - 12.5 eV.

Figure 7. He I photoelectron spectrum of 5-bromopyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) is due to the P3/6-311G(2df,2p)/SDD method. The inset represents a high resolution scan of the ionisation energy region 9 - 13 eV.

FIGURES

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Figure 8. He I photoelectron spectrum of 2-chloropyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p) method. The inset represents a high resolution scan of the ionisation energy region 9 - 13 eV.

Figure 9. He I photoelectron spectrum of 5-bromo-2-chloropyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p)/SDD method. The inset represents a high resolution scan of the ionisation energy region 9 - 14 eV.

Exp.	Orb.	MO	HF cc-pVTZ	P3(PS) cc-pVTZ	P3 6-311G(2df,2p)	B3LYP
9.73	$5b_2$	n_{N-}	11.29	9.90 (0.89)	9.84	9.64
10.53	$2b_1$	π_3	10.26	10.60 (0.89)	10.56	10.59
11.20 sh	$7a_1$	n_{N+}	12.88	11.37 (0.88)	11.31	10.96
11.40	$1a_2$	π_2	11.48	11.48 (0.88)	11.44	11.40
13.95	$1b_1$	π_1	15.68	14.38 (0.81)	14.34	13.94
	$6a_1$	σ	15.95	14.49 (0.87)	14.43	14.18
14.40	$5a_1$	σ	16.19	14.69 (0.88)	14.63	14.35
15.95	$3b_2$	σ	17.71	16.10 (0.86)	16.04	15.52
16.95	$4a_1$	σ	19.07	17.31 (0.85)	17.26	16.78
17.45	$3a_1$	σ	20.09	18.10 (0.84)	18.06	17.38

Table 1. Experimental band energies taken from the He I PES of pyrimidine together with the assignments of each band. sh indicates a shoulder in experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. The results of the HF and P3 calculations are reported for two different basis sets: cc-pVTZ and 6-311G(2df,2p). The pole strengths of the P3 calculations are presented in brackets after P3 ionisation energies for the cc-pVTZ basis set. All energies are in eV.

Orbital	MO	Exp.	HF cc-pVTZ	P3 (PS) cc-pVTZ	P3 6-311G(2df,2p)	P3 6-311G(2df,2p) SDD	B3LYP
$5b_2$	n_{N-}	9.93	11.97	10.61 (0.88)	10.56	10.58	9.67
$3b_1$	π_3		10.12	10.09 (0.89)	10.05	10.08	9.78
$6b_2$	$n_{ }$	10.83	11.19	10.27 (0.90)	10.19	10.27	10.34
$8a_1$	n_{N+}	11.24sh	12.97	11.76 (0.88)	11.70	11.73	11.19
$2b_1$	$n_{\perp}$	11.63	12.16	11.65 (0.89)	11.59	11.66	11.40
$1a_2$	π_2	11.89	11.99	11.85 (0.87)	11.81	11.81	11.59
$7a_1$	σ	13.73	15.49	14.10 (0.87)	14.05	14.08	13.67
$4b_2$	σ	14.48	16.66	15.04 (0.87)	15.00	15.00	14.34
$1b_1$	π_1		16.52	15.03 (0.80)	15.00	15.00	14.78
$6a_1$	σ	15.58	19.74	16.01 (0.86)	15.96	15.97	15.26
$3b_2$	σ	17.08	17.62	17.84 (0.84)	17.80	17.80	17.11
$5a_1$	σ		19.85	17.88 (0.84)	17.83	17.84	17.12

Table 2. Experimental band energies derived from the He I PES of 2-bromopyrimidine together with the assignments of each band. sh indicates a shoulder in the experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

Orbital	MO	Exp.	HF cc-pVTZ	P3 (PS) cc-pVTZ	P3 6-311G(2df,2p)	P3 6-311G(2df,2p) SDD	B3LYP
$6b_2$	n_{N-}	9.93	11.45	10.26 (0.89)	10.19	10.22	9.87
$3b_1$	π_3		9.97	10.05 (0.89)	10.00	10.04	10.02
$5b_2$	$n_{ }$	11.13sh	12.19	11.12 (0.89)	11.06	11.13	11.05
$8a_1$	n_{N+}	11.42	13.05	11.71 (0.88)	11.65	11.67	11.27
$1a_2$	π_2	11.42	11.92	11.81 (0.87)	11.78	11.78	11.72
$2b_1$	$n_{\perp}$	12.34	12.90	12.24 (0.88)	12.18	12.24	12.09
$7a_1$	σ	14.02sh	16.10	14.70 (0.86)	14.63	14.67	14.21
$4b_2$	σ	14.60	16.51	15.14 (0.87)	15.16	15.16	14.63
$1b_1$	π_1	15.22sh	16.28	14.82 (0.80)	14.79	14.79	14.77
$6a_1$	σ		16.79	15.20 (0.87)	15.10	15.10	14.86
$3b_2$	σ	17.1sh	19.77	17.88 (0.84)	17.84	17.84	17.32
$5a_1$	σ	17.3	20.42	18.38 (0.84)	18.33	18.34	17.58

Table 3. Experimental band energies derived from the He I PES of 5-bromopyrimidine together with the assignments of each band. sh indicates a shoulder in the experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

Orbital	MO	Exp.	HF cc-pVTZ	P3 (PS) cc-pVTZ	P3 6-311G(2df,2p)	B3LYP
$6b_2$	n_{N-}	9.84	11.77	10.26 (0.88)	10.22	10.11
$3b_1$	π_3	10.15	10.28	10.37 (0.89)	10.40	10.40
$5b_2$	$n_{ }$	11.38	12.62	11.55 (0.89)	11.54	11.32
$8a_1$	n_{N+}	11.61	13.41	11.94 (0.88)	11.90	11.69
$1a_2$	π_2	11.80	11.99	11.86 (0.87)	11.84	11.90
$2b_1$	$n_{\perp}$	12.40	13.15	12.29 (0.88)	12.27	12.21
$7a_1$	σ	14.2 sh	16.02	14.68 (0.87)	14.66	14.40
$4b_2$	σ	14.5	16.66	15.07 (0.87)	15.04	14.66
$1b_1$	π_1	14.9 sh	16.65	15.17 (0.81)	15.16	15.20
$6a_1$	σ	15.8	17.75	16.16 (0.86)	16.13	15.74
$3b_2$	σ	17.3	19.78	17.91 (0.85)	17.88	17.47
$5a_1$	σ		19.94	17.99 (0.84)	17.97	17.51

Table 4. Experimental band energies derived from the He I PES of 2-chloropyrimidine together with the assignments of each band. sh indicates a shoulder in the experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

	π_3	n_{N-}	π_2	n_{N+}	$n_{ }$	$n_{\perp}$
Pyrimidine						
N1	7.7	33.4	32.9	28.8		
C2	22.2	5.2	0.4	8.2		
N3	7.7	33.4	32.9	28.8		
C4	9.7	8.1	16.9	6.9		
C5	42.9	7.1	0.1	13.4		
C6	9.7	8.4	16.9	6.9		
5-bromopyrimidine						
N1	3.2	13.4	32.4	25.7	11.8	3.9
C2	11.4	1.8	0.4	7.9	2.1	6.6
N3	3.2	13.4	32.4	25.7	11.8	3.9
C4	6.4	17.8	17.3	5.6	7.3	0.4
C5	21.9	7.9	0.1	11.2	5.3	11.0
C6	6.4	17.8	17.3	5.6	7.3	0.4
Br	47.6	26.3	0.0	14.4	52.7	73.9
2-bromopyrimidine						
N1	6.0	27.6	33.7	20.7	10.8	0.1
C2	9.7	7.4	0.4	14.7	1.7	6.3
N3	6.0	27.6	33.7	20.7	10.8	0.1
C4	3.6	6.5	16.0	5.5	5.0	5.1
C5	21.0	5.7	0.1	12.3	1.4	12.6
C6	3.6	6.5	16.0	5.5	5.0	5.1
Br	50.1	14.1	0.0	18.7	64.6	70.7
2-chloropyrimidine						
N1	7.1	29.0	33.8	24.0	11.4	0.5
C2	14.0	4.1	0.5	11.6	10.6	2.0
N3	7.1	29.0	33.8	24.0	11.4	0.5
C4	5.5	9.7	15.9	5.7	2.6	3.7
C5	28.9	5.5	0.1	15.4	1.8	6.7
C6	5.5	9.7	15.9	5.7	2.6	3.7
Cl	31.9	9.6	0.0	11.0	58.7	82.9

Table 5. Mulliken population analysis on the MOs of pyrimidine, 5-bromopyrimidine, 2-bromopyrimidine and 2-chloropyrimidine (sum of contributions of all AOs belonging to the same atom to the electron density of a given MO expressed as a percentage of the total electron density on that MO).

Orbital	MO	Exp.	HF cc-pVTZ	P3 (PS) cc-pVTZ	P3 6-311G(2df,2p)	P3 6-311G(2df,2p) SDD	B3LYP
$4b_1$	π_3	9.68	10.04	10.01 (0.89)	9.99	10.02	9.66
$7b_2$	n_{N_-}	9.88	11.75	10.58 (0.89)	10.54	10.58	9.85
$6b_2$	$n_{ }(\text{Br})$	11.47 sh	12.49	11.31 (0.89)	11.23	11.32	10.93
$5b_2$	$n_{ }(\text{Cl})$		12.90	11.76 (0.89)	11.76	11.76	11.06
$3b_1$	$n_{\perp}(\text{Br/Cl})$		12.57	11.71 (0.89)	11.67	11.72	11.12
$9a_1$	n_{N_+}	11.6	13.53	12.22 (0.88)	12.18	12.20	11.52
$1a_2$	π_2	11.85	12.39	12.16 (0.86)	12.14	12.14	11.75
$2b_1$	$n_{\perp}(\text{Br/Cl})$	13.03	13.95	13.07 (0.88)	13.05	13.07	12.52
$8a_1$	σ	14.20	16.49	14.81 (0.86)	15.28	15.31	14.18
$4b_2$	σ	14.64	17.21	15.54 (0.87)	15.52	15.52	14.64
$7a_1$	σ		16.28	15.30 (0.87)	14.78	14.79	14.70
$1b_1$	π_1	15.25	17.12	15.50 (0.80)	15.49	15.49	15.09
$6a_1$	σ	17.28	20.01	18.14 (0.84)	18.11	18.11	17.13
$3b_2$	σ		20.43	18.44 (0.84)	18.42	18.42	17.55

Table 6. Experimental band energies derived from the He I PES of 5-bromo-2-chloropyrimidine together with the assignments of each band. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

Supporting Information for

“An Experimental and Computational Study of the Valence Photoelectron Spectra of Halogenated Pyrimidines”

Patrick O'Keeffe, Paola Bolognesi, Anna Rita Casavola, Daniele Catone, Nicola Zema, Stefano Turchini and Lorenzo Avaldi.

1. Pyrimidine:

1.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C,1,B1
C,2,B2,1,A1
C,3,B3,2,A2,1,D1,0
N,1,B4,4,A3,3,D2,0
N,1,B5,5,A4,4,D3,0
H,1,B6,4,A5,3,D4,0
H,2,B7,1,A6,4,D5,0
H,3,B8,2,A7,1,D6,0
H,4,B9,3,A8,2,D7,0
```

Variables:

```
B1=2.26549454
B2=1.39104925
B3=1.39104925
B4=1.33514491
B5=1.33514491
B6=1.08595857
B7=1.08648567
B8=1.0829271
B9=1.08648567
A1=90.23498617
A2=116.5577385
A3=32.0180741
A4=127.00843738
A5=148.51385542
A6=148.51866006
A7=121.72113075
A8=121.24635377
D1=0.
D2=180.
D3=0.
D4=180.
D5=180.
D6=180.
D7=180.
```

1.2 Total Energy

1
2
3
4
5
6
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11
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18
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44
45
46
47
48
49
50
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52
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56
57
58
59
60

E(RB+HF-LYP) = -264.393935420 Hartrees

1.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

			1				2			3
			B1				A2			B2
Frequencies	--		346.9748				406.8478			636.1803
Red. masses	--		2.6629				4.1300			7.9786
Frc consts	--		0.1889				0.4028			1.9025
IR Inten	--		3.4903				0.0000			9.9897
Atom	AN		X	Y	Z		X	Y	Z	
1	6		0.20	0.00	0.00		0.00	0.00	0.00	-0.14
2	6		-0.12	0.00	0.00		0.23	0.00	0.00	0.26
3	6		0.24	0.00	0.00		0.00	0.00	0.00	0.21
4	6		-0.12	0.00	0.00		-0.23	0.00	0.00	0.26
5	7		-0.10	0.00	0.00		0.27	0.00	0.00	-0.28
6	7		-0.10	0.00	0.00		-0.27	0.00	0.00	-0.28
7	1		0.59	0.00	0.00		0.00	0.00	0.00	0.20
8	1		-0.38	0.00	0.00		0.61	0.00	0.00	0.40
9	1		0.47	0.00	0.00		0.00	0.00	0.00	-0.25
10	1		-0.38	0.00	0.00		-0.61	0.00	0.00	0.40
			4				5			6
			A1				B1			B1
Frequencies	--		696.0192				732.9806			820.9289
Red. masses	--		7.3288				1.7381			1.7356
Frc consts	--		2.0918				0.5502			0.6891
IR Inten	--		3.0989				43.7288			6.8741
Atom	AN		X	Y	Z		X	Y	Z	
1	6		0.00	0.00	-0.34		-0.10	0.00	0.00	0.09
2	6		0.00	-0.26	0.02		-0.07	0.00	0.00	0.13
3	6		0.00	0.00	0.40		0.14	0.00	0.00	0.01
4	6		0.00	0.26	0.02		-0.07	0.00	0.00	0.13
5	7		0.00	0.26	-0.02		0.11	0.00	0.00	-0.10
6	7		0.00	-0.26	-0.02		0.11	0.00	0.00	-0.10
7	1		0.00	0.00	-0.35		-0.55	0.00	0.00	-0.02
8	1		0.00	-0.12	-0.26		-0.52	0.00	0.00	-0.31
9	1		0.00	0.00	0.40		-0.31	0.00	0.00	-0.87
10	1		0.00	0.12	-0.26		-0.52	0.00	0.00	-0.31
			7				8			9
			B1				A2			B1
Frequencies	--		975.9093				993.2509			1010.7519
Red. masses	--		1.3674				1.3792			1.4915
Frc consts	--		0.7673				0.8017			0.8978
IR Inten	--		0.0274				0.0000			0.0024
Atom	AN		X	Y	Z		X	Y	Z	
1	6		-0.12	0.00	0.00		0.00	0.00	0.00	-0.15
2	6		-0.05	0.00	0.00		-0.13	0.00	0.00	0.08
3	6		0.11	0.00	0.00		0.00	0.00	0.00	-0.08
4	6		-0.05	0.00	0.00		0.13	0.00	0.00	0.08
5	7		0.02	0.00	0.00		-0.02	0.00	0.00	0.02
6	7		0.02	0.00	0.00		0.02	0.00	0.00	0.02
7	1		0.67	0.00	0.00		0.00	0.00	0.00	0.64
8	1		0.28	0.00	0.00		0.70	0.00	0.00	-0.47
9	1		-0.60	0.00	0.00		0.00	0.00	0.00	0.33
10	1		0.28	0.00	0.00		-0.70	0.00	0.00	-0.47
			10				11			12
			A1				A1			B2
Frequencies	--		1011.1710				1079.5348			1093.8032
Red. masses	--		9.8208				3.5422			1.5209
Frc consts	--		5.9163				2.4322			1.0721

URL: <http://mc.manuscriptcentral.com/tandf/tmph>

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			22			23			24		
			B2			A1			A1		
Frequencies	--		3154.7726			3167.4200			3197.5350		
Red. masses	--		1.0918			1.0917			1.0964		
Frc consts	--		6.4024			6.4533			6.6045		
IR Inten	--		18.1584			13.7417			9.0240		
Atom	AN		X	Y	Z	X	Y	Z	X	Y	Z
1	6		0.00	0.00	0.00	0.00	0.00	-0.09	0.00	0.00	0.00
2	6		0.00	0.06	0.03	0.00	0.01	0.00	0.00	0.02	0.00
3	6		0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.09
4	6		0.00	0.06	-0.03	0.00	-0.01	0.00	0.00	-0.02	0.00
5	7		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	7		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	1		0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.04
8	1		0.00	-0.63	-0.32	0.00	-0.07	-0.04	0.00	-0.16	-0.08
9	1		0.00	0.01	0.00	0.00	0.00	0.08	0.00	0.00	-0.96
10	1		0.00	-0.63	0.32	0.00	0.07	-0.04	0.00	0.16	-0.08

2. 2-bromopyrimidine:

2.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C,1,B1
C,2,B2,1,A1
C,3,B3,2,A2,1,D1,0
N,1,B4,2,A3,3,D2,0
N,2,B5,1,A4,5,D3,0
H,3,B6,2,A5,1,D4,0
H,4,B7,3,A6,2,D5,0
H,2,B8,1,A7,5,D6,0
Br,1,B9,5,A8,4,D7,0
```

Variables:

```
B1=2.25061328
B2=1.39063884
B3=1.39063884
B4=1.32426991
B5=1.33722206
B6=1.08214206
B7=1.08585572
B8=1.08585572
B9=1.91679851
A1=90.1662816
A2=116.33613981
A3=95.76921093
A4=32.085896
A5=121.83193009
A6=121.60067615
A7=148.23304224
A8=115.89643756
D1=0.
D2=0.
D3=180.
D4=180.
D5=180.
D6=180.
D7=180.
```

2.2 Total Energy

E(RB+HF-LYP) = -2837.93615700 Hartrees

2.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

		1		2		3				
		B1		B2		A1				
Frequencies	--	141.9332		270.5296		322.6271				
Red. masses	--	6.3832		7.7210		15.1030				
Frc consts	--	0.0758		0.3329		0.9262				
IR Inten	--	5.1145		5.0751		5.9056				
Atom	AN	X	Y	Z	X	Y	Z			
1	6	-0.29	0.00	0.00	0.00	0.36	0.00	0.00	0.18	
2	6	0.03	0.00	0.00	0.00	-0.02	-0.22	0.00	0.04	0.33
3	6	0.37	0.00	0.00	0.00	-0.15	0.00	0.00	0.00	0.39

1												
2												
3	4	6	0.03	0.00	0.00	0.00	-0.02	0.22	0.00	-0.04	0.33	
4	5	7	-0.31	0.00	0.00	0.00	0.27	0.19	0.00	-0.06	0.30	
5	6	7	-0.31	0.00	0.00	0.00	0.27	-0.19	0.00	0.06	0.30	
6	7	1	0.76	0.00	0.00	0.00	-0.35	0.00	0.00	0.00	0.39	
7	8	1	0.05	0.00	0.00	0.00	-0.12	0.42	0.00	-0.01	0.28	
8	9	1	0.05	0.00	0.00	0.00	-0.12	-0.42	0.00	0.01	0.28	
9	10	35	0.08	0.00	0.00	0.00	-0.12	0.00	0.00	0.00	-0.30	
10				4			5			6		
11				A2			B1			B2		
12	Frequencies	--	409.6389				472.2586			633.7788		
13	Red. masses	--	4.2212				3.0790			8.2498		
14	Frc consts	--	0.4173				0.4046			1.9524		
15	IR Inten	--	0.0000				1.8957			9.8586		
16	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
17	1	6	0.00	0.00	0.00		0.30	0.00	0.00	0.00	-0.10	0.00
18	2	6	-0.23	0.00	0.00		-0.15	0.00	0.00	0.00	0.26	-0.26
19	3	6	0.00	0.00	0.00		0.22	0.00	0.00	0.00	0.20	0.00
20	4	6	0.23	0.00	0.00		-0.15	0.00	0.00	0.00	0.26	0.26
21	5	7	-0.28	0.00	0.00		-0.01	0.00	0.00	0.00	-0.26	0.27
22	6	7	0.28	0.00	0.00		-0.01	0.00	0.00	0.00	-0.26	-0.27
23	7	1	0.00	0.00	0.00		0.25	0.00	0.00	0.00	-0.30	0.00
24	8	1	0.61	0.00	0.00		-0.61	0.00	0.00	0.00	0.39	0.02
25	9	1	-0.61	0.00	0.00		-0.61	0.00	0.00	0.00	0.39	-0.02
26	10	35	0.00	0.00	0.00		-0.01	0.00	0.00	0.00	-0.01	0.00
27				7			8			9		
28				A1			B1			B1		
29	Frequencies	--	749.3143				784.0197			818.4156		
30	Red. masses	--	7.8907				7.6713			1.2156		
31	Frc consts	--	2.6103				2.7783			0.4797		
32	IR Inten	--	37.9108				11.1410			27.2525		
33	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
34	1	6	0.00	0.00	0.36		0.51	0.00	0.00	-0.03	0.00	0.00
35	2	6	0.00	-0.29	0.04		0.20	0.00	0.00	0.08	0.00	0.00
36	3	6	0.00	0.00	-0.38		-0.23	0.00	0.00	0.06	0.00	0.00
37	4	6	0.00	0.29	0.04		0.20	0.00	0.00	0.08	0.00	0.00
38	5	7	0.00	0.27	0.06		-0.30	0.00	0.00	-0.03	0.00	0.00
39	6	7	0.00	-0.27	0.06		-0.30	0.00	0.00	-0.03	0.00	0.00
40	7	1	0.00	0.00	-0.38		-0.08	0.00	0.00	-0.85	0.00	0.00
41	8	1	0.00	0.15	0.33		0.46	0.00	0.00	-0.36	0.00	0.00
42	9	1	0.00	-0.15	0.33		0.46	0.00	0.00	-0.36	0.00	0.00
43	10	35	0.00	0.00	-0.03		-0.01	0.00	0.00	0.00	0.00	0.00
44				10			11			12		
45				A2			B1			A1		
46	Frequencies	--	997.4480				998.1127			1002.1739		
47	Red. masses	--	1.3704				1.4104			9.9849		
48	Frc consts	--	0.8033				0.8278			5.9085		
49	IR Inten	--	0.0000				0.1154			0.3353		
50	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
51	1	6	0.00	0.00	0.00		-0.04	0.00	0.00	0.00	0.00	-0.08
52	2	6	0.13	0.00	0.00		0.10	0.00	0.00	0.00	0.05	0.04
53	3	6	0.00	0.00	0.00		-0.13	0.00	0.00	0.00	0.00	0.47
54	4	6	-0.13	0.00	0.00		0.10	0.00	0.00	0.00	-0.05	0.04
55	5	7	0.02	0.00	0.00		0.00	0.00	0.00	0.00	0.44	-0.23
56	6	7	-0.02	0.00	0.00		0.00	0.00	0.00	0.00	-0.44	-0.23
57	7	1	0.00	0.00	0.00		0.59	0.00	0.00	0.00	0.00	0.50
58	8	1	0.70	0.00	0.00		-0.56	0.00	0.00	0.00	-0.07	0.09
59	9	1	-0.70	0.00	0.00		-0.56	0.00	0.00	0.00	0.07	0.09
60	10	35	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
				13			14			15		
				A1			B2			A1		
	Frequencies	--	1087.0553				1109.2006			1169.1629		
	Red. masses	--	2.9448				1.4452			3.8904		
	Frc consts	--	2.0503				1.0476			3.1333		

IR Inten	--	7.0117			0.6871			194.5912		
Atom AN		X	Y	Z	X	Y	Z	X	Y	Z
1 6		0.00	0.00	0.10	0.00	0.08	0.00	0.00	0.00	0.43
2 6		0.00	0.26	-0.03	0.00	-0.07	0.01	0.00	0.05	-0.14
3 6		0.00	0.00	-0.14	0.00	0.10	0.00	0.00	0.00	0.13
4 6		0.00	-0.26	-0.03	0.00	-0.07	-0.01	0.00	-0.05	-0.14
5 7		0.00	0.06	0.03	0.00	-0.04	0.07	0.00	-0.04	-0.05
6 7		0.00	-0.06	0.03	0.00	-0.04	-0.07	0.00	0.04	-0.05
7 1		0.00	0.00	-0.16	0.00	0.96	0.00	0.00	0.00	0.13
8 1		0.00	-0.49	0.40	0.00	-0.12	0.08	0.00	0.16	-0.58
9 1		0.00	0.49	0.40	0.00	-0.12	-0.08	0.00	-0.16	-0.58
10 35		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01
		16			17			18		
		B2			B2			A1		
Frequencies	--	1226.3659			1289.5484			1417.8813		
Red. masses	--	9.5816			1.5900			2.1216		
Frc consts	--	8.4904			1.5579			2.5130		
IR Inten	--	0.2547			8.2626			242.4240		
Atom AN		X	Y	Z	X	Y	Z	X	Y	Z
1 6		0.00	-0.30	0.00	0.00	0.19	0.00	0.00	0.00	0.11
2 6		0.00	0.10	0.34	0.00	-0.05	0.04	0.00	-0.07	0.03
3 6		0.00	-0.24	0.00	0.00	0.01	0.00	0.00	0.00	0.06
4 6		0.00	0.10	-0.34	0.00	-0.05	-0.04	0.00	0.07	0.03
5 7		0.00	0.14	0.37	0.00	-0.04	0.03	0.00	-0.10	-0.15
6 7		0.00	0.14	-0.37	0.00	-0.04	-0.03	0.00	0.10	-0.15
7 1		0.00	0.22	0.00	0.00	-0.26	0.00	0.00	0.00	0.07
8 1		0.00	0.11	-0.32	0.00	0.23	-0.62	0.00	-0.23	0.63
9 1		0.00	0.11	0.32	0.00	0.23	0.62	0.00	0.23	0.63
10 35		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		19			20			21		
		B2			B2			A1		
Frequencies	--	1452.1664			1587.6783			1596.9566		
Red. masses	--	1.8935			6.2180			4.7210		
Frc consts	--	2.3526			9.2347			7.0937		
IR Inten	--	0.4779			107.8272			141.3138		
Atom AN		X	Y	Z	X	Y	Z	X	Y	Z
1 6		0.00	0.12	0.00	0.00	-0.29	0.00	0.00	0.00	0.05
2 6		0.00	-0.01	0.13	0.00	-0.23	-0.09	0.00	0.11	0.32
3 6		0.00	0.14	0.00	0.00	0.44	0.00	0.00	0.00	-0.18
4 6		0.00	-0.01	-0.13	0.00	-0.23	0.09	0.00	-0.11	0.32
5 7		0.00	-0.06	0.04	0.00	0.16	0.07	0.00	-0.02	-0.18
6 7		0.00	-0.06	-0.04	0.00	0.16	-0.07	0.00	0.02	-0.18
7 1		0.00	-0.61	0.00	0.00	-0.56	0.00	0.00	0.00	-0.22
8 1		0.00	-0.30	0.43	0.00	-0.05	-0.33	0.00	0.26	-0.49
9 1		0.00	-0.30	-0.43	0.00	-0.05	0.33	0.00	-0.26	-0.49
10 35		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		22			23			24		
		A1			B2			A1		
Frequencies	--	3162.1133			3165.0691			3207.8318		
Red. masses	--	1.0901			1.0922			1.0965		
Frc consts	--	6.4220			6.4467			6.6477		
IR Inten	--	11.8041			12.4157			5.1310		
Atom AN		X	Y	Z	X	Y	Z	X	Y	Z
1 6		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2 6		0.00	0.05	-0.02	0.00	-0.06	0.03	0.00	0.02	0.00
3 6		0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	-0.09
4 6		0.00	-0.05	-0.02	0.00	-0.06	-0.03	0.00	-0.02	0.00
5 7		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6 7		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7 1		0.00	0.00	-0.24	0.00	-0.01	0.00	0.00	0.00	0.97
8 1		0.00	0.61	0.30	0.00	0.63	0.31	0.00	0.15	0.07
9 1		0.00	-0.61	0.30	0.00	0.63	-0.31	0.00	-0.15	0.07
10 35		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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3 **3. 5-bromopyrimidine:**
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5
6 **3.1 Geometry**
7

8 optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory
9

10 C
11 C,1,B1
12 C,2,B2,1,A1
13 C,3,B3,2,A2,1,D1,0
14 N,1,B4,2,A3,3,D2,0
15 N,2,B5,1,A4,5,D3,0
16 H,4,B6,3,A5,2,D4,0
17 H,2,B7,1,A6,5,D5,0
18 Br,3,B8,2,A7,1,D6,0
19 H,1,B9,5,A8,4,D7,0
20 Variables:
21 B1=2.2703905
22 B2=1.39179689
23 B3=1.39179689
24 B4=1.33437731
25 B5=1.33403597
26 B6=1.08527625
27 B7=1.08527625
28 B8=1.90578858
29 B9=1.0851449
30 A1=89.49191149
31 A2=117.72118914
32 A3=94.98740399
33 A4=31.70146814
34 A5=121.31626098
35 A6=149.19182753
36 A7=121.13940543
37 A8=116.66008996
38 D1=0.
39 D2=0.
40 D3=180.
41 D4=180.
42 D5=180.
43 D6=180.
44 D7=180.

45 **3.2 Total Energy**
46

47 E(RB+HF-LYP) = -2837.93398026 Hartrees
48
49

50 **3.3 Frequencies**
51

52 Output from the "b3lyp/6-311++g(d,p) freq" calculation
53

		1			2			3		
		B1			B2			A1		
Frequencies	--	163.3838			241.8699			321.2182		
Red. masses	--	4.1375			6.2541			13.3842		
Frc consts	--	0.0651			0.2156			0.8137		
IR Inten	--	0.2971			1.1221			2.6204		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.27	0.00	0.00	0.00	-0.12	0.00	0.00	0.00	0.37
2	6	-0.24	0.00	0.00	0.00	0.24	-0.18	0.00	0.04	0.28
3	6	-0.25	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.12

4	6	-0.24	0.00	0.00	0.00	0.24	0.18	0.00	-0.04	0.28
5	7	0.04	0.00	0.00	0.00	-0.02	0.20	0.00	-0.04	0.32
6	7	0.04	0.00	0.00	0.00	-0.02	-0.20	0.00	0.04	0.32
7	1	-0.40	0.00	0.00	0.00	0.34	0.37	0.00	0.00	0.37
8	1	-0.40	0.00	0.00	0.00	0.34	-0.37	0.00	0.00	0.37
9	35	0.06	0.00	0.00	0.00	-0.10	0.00	0.00	0.00	-0.29
10	1	0.64	0.00	0.00	0.00	-0.30	0.00	0.00	0.00	0.37
		4			5			6		
		A2			B1			B2		
Frequencies	--	412.6071			420.6792			629.1750		
Red. masses	--	4.2054			4.3323			8.9424		
Frc consts	--	0.4218			0.4517			2.0857		
IR Inten	--	0.0000			0.4197			13.8198		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.13	0.00
2	6	0.23	0.00	0.00	-0.07	0.00	0.00	0.00	-0.24	-0.25
3	6	0.00	0.00	0.00	0.46	0.00	0.00	0.00	-0.21	0.00
4	6	-0.23	0.00	0.00	-0.07	0.00	0.00	0.00	-0.24	0.25
5	7	0.28	0.00	0.00	-0.15	0.00	0.00	0.00	0.30	0.30
6	7	-0.28	0.00	0.00	-0.15	0.00	0.00	0.00	0.30	-0.30
7	1	-0.61	0.00	0.00	-0.49	0.00	0.00	0.00	-0.37	0.02
8	1	0.61	0.00	0.00	-0.49	0.00	0.00	0.00	-0.37	-0.02
9	35	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	-0.01	0.00
10	1	0.00	0.00	0.00	0.47	0.00	0.00	0.00	-0.26	0.00
		7			8			9		
		B1			A1			B1		
Frequencies	--	729.9382			744.8655			907.7513		
Red. masses	--	2.4451			9.5447			1.6123		
Frc consts	--	0.7676			3.1201			0.7828		
IR Inten	--	29.5164			6.2089			6.6819		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.15	0.00	0.00	0.00	0.00	-0.33	0.09	0.00	0.00
2	6	-0.12	0.00	0.00	0.00	-0.32	0.05	0.13	0.00	0.00
3	6	0.12	0.00	0.00	0.00	0.00	0.42	-0.10	0.00	0.00
4	6	-0.12	0.00	0.00	0.00	0.32	0.05	0.13	0.00	0.00
5	7	0.17	0.00	0.00	0.00	0.33	0.06	-0.05	0.00	0.00
6	7	0.17	0.00	0.00	0.00	-0.33	0.06	-0.05	0.00	0.00
7	1	-0.47	0.00	0.00	0.00	0.19	-0.21	-0.60	0.00	0.00
8	1	-0.47	0.00	0.00	0.00	-0.19	-0.21	-0.60	0.00	0.00
9	35	0.00	0.00	0.00	0.00	0.00	-0.04	0.00	0.00	0.00
10	1	-0.66	0.00	0.00	0.00	0.00	-0.34	-0.47	0.00	0.00
		10			11			12		
		A2			B1			A1		
Frequencies	--	975.1222			992.7439			1028.7472		
Red. masses	--	1.3708			1.4830			8.2121		
Frc consts	--	0.7680			0.8611			5.1206		
IR Inten	--	0.0000			0.0048			61.2852		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	-0.03
2	6	-0.13	0.00	0.00	-0.06	0.00	0.00	0.00	0.24	-0.01
3	6	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	-0.38
4	6	0.13	0.00	0.00	-0.06	0.00	0.00	0.00	-0.24	-0.01
5	7	-0.02	0.00	0.00	-0.03	0.00	0.00	0.00	0.37	0.17
6	7	0.02	0.00	0.00	-0.03	0.00	0.00	0.00	-0.37	0.17
7	1	-0.70	0.00	0.00	0.34	0.00	0.00	0.00	-0.37	-0.26
8	1	0.70	0.00	0.00	0.34	0.00	0.00	0.00	0.37	-0.26
9	35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
10	1	0.00	0.00	0.00	-0.85	0.00	0.00	0.00	0.00	-0.03
		13			14			15		
		A1			A1			B2		
Frequencies	--	1099.9895			1161.1637			1205.9251		
Red. masses	--	5.2004			2.2578			2.3954		
Frc consts	--	3.7074			1.7936			2.0524		

1											
2											
3	IR Inten	--	8.1337			30.2899			13.6869		
4	Atom AN	X	Y	Z	X	Y	Z	X	Y	Z	
5	1 6	0.00	0.00	-0.29	0.00	0.00	0.23	0.00	-0.04	0.00	
6	2 6	0.00	0.29	0.13	0.00	0.02	-0.10	0.00	0.02	0.20	
7	3 6	0.00	0.00	0.29	0.00	0.00	0.17	0.00	0.04	0.00	
8	4 6	0.00	-0.29	0.13	0.00	-0.02	-0.10	0.00	0.02	-0.20	
9	5 7	0.00	-0.06	-0.05	0.00	0.04	-0.04	0.00	0.01	0.14	
10	6 7	0.00	0.06	-0.05	0.00	-0.04	-0.04	0.00	0.01	-0.14	
11	7 1	0.00	-0.48	-0.18	0.00	-0.27	-0.58	0.00	-0.11	-0.46	
12	8 1	0.00	0.48	-0.18	0.00	0.27	-0.58	0.00	-0.11	0.46	
13	9 35	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	
14	10 1	0.00	0.00	-0.31	0.00	0.00	0.25	0.00	-0.66	0.00	
15			16			17			18		
16			B2			B2			A1		
17	Frequencies	--	1217.6389			1360.9646			1436.3278		
18	Red. masses	--	5.3970			1.2322			2.1819		
19	Frc consts	--	4.7145			1.3447			2.6521		
20	IR Inten	--	2.3611			3.1059			78.7633		
21	Atom AN	X	Y	Z	X	Y	Z	X	Y	Z	
22	1 6	0.00	0.40	0.00	0.00	0.03	0.00	0.00	0.00	0.12	
23	2 6	0.00	-0.17	0.09	0.00	0.00	0.07	0.00	0.08	0.00	
24	3 6	0.00	0.25	0.00	0.00	-0.10	0.00	0.00	0.00	0.10	
25	4 6	0.00	-0.17	-0.09	0.00	0.00	-0.07	0.00	-0.08	0.00	
26	5 7	0.00	-0.16	0.13	0.00	0.02	0.00	0.00	0.11	-0.13	
27	6 7	0.00	-0.16	-0.13	0.00	0.02	0.00	0.00	-0.11	-0.13	
28	7 1	0.00	0.04	0.36	0.00	0.31	0.54	0.00	0.23	0.63	
29	8 1	0.00	0.04	-0.36	0.00	0.31	-0.54	0.00	-0.23	0.63	
30	9 35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
31	10 1	0.00	0.59	0.00	0.00	-0.46	0.00	0.00	0.00	0.12	
32			19			20			21		
33			B2			A1			B2		
34	Frequencies	--	1450.7022			1581.4764			1583.1277		
35	Red. masses	--	1.8683			5.6690			5.8096		
36	Frc consts	--	2.3166			8.3538			8.5788		
37	IR Inten	--	13.8141			1.9578			57.7146		
38	Atom AN	X	Y	Z	X	Y	Z	X	Y	Z	
39	1 6	0.00	0.08	0.00	0.00	0.00	0.10	0.00	0.37	0.00	
40	2 6	0.00	-0.07	-0.07	0.00	-0.11	0.34	0.00	0.20	-0.12	
41	3 6	0.00	0.16	0.00	0.00	0.00	-0.19	0.00	-0.33	0.00	
42	4 6	0.00	-0.07	0.07	0.00	0.11	0.34	0.00	0.20	0.12	
43	5 7	0.00	0.00	-0.11	0.00	0.05	-0.22	0.00	-0.17	0.04	
44	6 7	0.00	0.00	0.11	0.00	-0.05	-0.22	0.00	-0.17	-0.04	
45	7 1	0.00	-0.15	-0.07	0.00	-0.28	-0.46	0.00	-0.03	-0.38	
46	8 1	0.00	-0.15	0.07	0.00	0.28	-0.46	0.00	-0.03	0.38	
47	9 35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
48	10 1	0.00	-0.93	0.00	0.00	0.00	0.10	0.00	-0.53	0.00	
49			22			23			24		
50			B2			A1			A1		
51	Frequencies	--	3171.2125			3171.2227			3178.9094		
52	Red. masses	--	1.0924			1.0910			1.0935		
53	Frc consts	--	6.4729			6.4647			6.5106		
54	IR Inten	--	2.6874			10.4263			5.7922		
55	Atom AN	X	Y	Z	X	Y	Z	X	Y	Z	
56	1 6	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.08	
57	2 6	0.00	-0.06	-0.03	0.00	0.05	0.02	0.00	-0.02	-0.01	
58	3 6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
59	4 6	0.00	-0.06	0.03	0.00	-0.05	0.02	0.00	0.02	-0.01	
60	5 7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	6 7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	7 1	0.00	0.63	-0.32	0.00	0.59	-0.30	0.00	-0.21	0.11	
	8 1	0.00	0.63	0.32	0.00	-0.59	-0.30	0.00	0.21	0.11	
	9 35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	10 1	0.00	0.00	0.00	0.00	0.00	-0.34	0.00	0.00	-0.94	

4. 2-chloropyrimidine:

4.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

C

```
C,1,B1
C,2,B2,1,A1
C,3,B3,2,A2,1,D1,0
N,1,B4,4,A3,3,D2,0
N,1,B5,5,A4,4,D3,0
H,2,B6,1,A5,6,D4,0
H,3,B7,2,A6,1,D5,0
H,4,B8,3,A7,2,D6,0
Cl,1,B9,6,A8,2,D7,0
```

Variables:

```
B1=2.25087191
B2=1.39055831
B3=1.39055831
B4=1.32504869
B5=1.32504869
B6=1.08579192
B7=1.08201766
B8=1.08579192
B9=1.75082293
A1=90.19963159
A2=116.29673926
A3=32.41441955
A4=128.13283666
A5=148.21565593
A6=121.85163037
A7=121.58471247
A8=115.93358167
D1=0.
D2=180.
D3=0.
D4=0.
D5=180.
D6=180.
D7=180.
```

4.2 Total Energy

b3lyp/6-311++g(d,p) level of theory

E(RB+HF-LYP) = -724.017721191 Hartrees

3.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

		1			2			3		
		B1			B2			A2		
Frequencies	--	156.9259			329.3429			412.6434		
Red. masses	--	6.6929			8.6759			4.2137		
Frc consts	--	0.0971			0.5545			0.4227		
IR Inten	--	4.0106			3.7167			0.0000		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.25	0.00	0.00	0.00	0.35	0.00	0.00	0.00	0.00
2	6	0.02	0.00	0.00	0.00	-0.02	-0.21	-0.23	0.00	0.00
3	6	0.37	0.00	0.00	0.00	-0.15	0.00	0.00	0.00	0.00
4	6	0.02	0.00	0.00	0.00	-0.02	0.21	0.23	0.00	0.00
5	7	-0.31	0.00	0.00	0.00	0.28	0.17	-0.28	0.00	0.00
6	7	-0.31	0.00	0.00	0.00	0.28	-0.17	0.28	0.00	0.00

1												
2												
3	7	1	0.01	0.00	0.00	0.00	-0.12	-0.41	-0.61	0.00	0.00	
4	8	1	0.76	0.00	0.00	0.00	-0.34	0.00	0.00	0.00	0.00	
5	9	1	0.01	0.00	0.00	0.00	-0.12	0.41	0.61	0.00	0.00	
6	10	17	0.17	0.00	0.00	0.00	-0.26	0.00	0.00	0.00	0.00	
7				4			5			6		
8				A1			B1			B2		
9	Frequencies	--	440.1012				490.9697			638.0703		
10	Red. masses	--	16.3001				2.9718			8.1824		
11	Frc consts	--	1.8601				0.4221			1.9628		
12	IR Inten	--	9.8159				1.7882			8.8438		
13	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
14	1	6	0.00	0.00	0.01		0.28	0.00	0.00	0.00	-0.09	0.00
15	2	6	0.00	0.08	0.28		-0.15	0.00	0.00	0.00	0.26	-0.27
16	3	6	0.00	0.00	0.41		0.22	0.00	0.00	0.00	0.20	0.00
17	4	6	0.00	-0.08	0.28		-0.15	0.00	0.00	0.00	0.26	0.27
18	5	7	0.00	-0.11	0.23		0.00	0.00	0.00	0.00	-0.25	0.27
19	6	7	0.00	0.11	0.23		0.00	0.00	0.00	0.00	-0.25	-0.27
20	7	1	0.00	0.03	0.19		-0.62	0.00	0.00	0.00	0.39	-0.03
21	8	1	0.00	0.00	0.41		0.22	0.00	0.00	0.00	-0.31	0.00
22	9	1	0.00	-0.03	0.19		-0.62	0.00	0.00	0.00	0.39	0.03
23	10	17	0.00	0.00	-0.54		-0.04	0.00	0.00	0.00	-0.03	0.00
24				7			8			9		
25				A1			B1			B1		
26	Frequencies	--	771.0900				794.6226			818.9335		
27	Red. masses	--	7.8502				8.8428			1.2088		
28	Frc consts	--	2.7501				3.2897			0.4777		
29	IR Inten	--	41.8704				9.7078			30.1620		
30	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
31	1	6	0.00	0.00	0.32		0.56	0.00	0.00	-0.05	0.00	0.00
32	2	6	0.00	-0.29	0.07		0.22	0.00	0.00	0.07	0.00	0.00
33	3	6	0.00	0.00	-0.35		-0.22	0.00	0.00	0.07	0.00	0.00
34	4	6	0.00	0.29	0.07		0.22	0.00	0.00	0.07	0.00	0.00
35	5	7	0.00	0.27	0.07		-0.33	0.00	0.00	-0.02	0.00	0.00
36	6	7	0.00	-0.27	0.07		-0.33	0.00	0.00	-0.02	0.00	0.00
37	7	1	0.00	-0.15	0.36		0.37	0.00	0.00	-0.36	0.00	0.00
38	8	1	0.00	0.00	-0.35		-0.22	0.00	0.00	-0.85	0.00	0.00
39	9	1	0.00	0.15	0.36		0.37	0.00	0.00	-0.36	0.00	0.00
40	10	17	0.00	0.00	-0.11		-0.02	0.00	0.00	0.00	0.00	0.00
41				10			11			12		
42				A2			B1			A1		
43	Frequencies	--	998.8553				1000.7750			1004.2248		
44	Red. masses	--	1.3712				1.4171			9.9668		
45	Frc consts	--	0.8060				0.8362			5.9220		
46	IR Inten	--	0.0000				0.1791			0.1534		
47	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
48	1	6	0.00	0.00	0.00		0.04	0.00	0.00	0.00	0.00	-0.08
49	2	6	0.13	0.00	0.00		-0.10	0.00	0.00	0.00	0.06	0.03
50	3	6	0.00	0.00	0.00		0.13	0.00	0.00	0.00	0.00	0.48
51	4	6	-0.13	0.00	0.00		-0.10	0.00	0.00	0.00	-0.06	0.03
52	5	7	0.02	0.00	0.00		0.00	0.00	0.00	0.00	0.43	-0.23
53	6	7	-0.02	0.00	0.00		0.00	0.00	0.00	0.00	-0.43	-0.23
54	7	1	-0.70	0.00	0.00		0.56	0.00	0.00	0.00	0.07	0.08
55	8	1	0.00	0.00	0.00		-0.58	0.00	0.00	0.00	0.00	0.50
56	9	1	0.70	0.00	0.00		0.56	0.00	0.00	0.00	-0.07	0.08
57	10	17	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.01
58				13			14			15		
59				A1			B2			A1		
60	Frequencies	--	1089.8833				1111.3335			1190.3909		
	Red. masses	--	2.7526				1.4327			4.2108		
	Frc consts	--	1.9264				1.0425			3.5156		
	IR Inten	--	5.1067				0.5982			186.4327		
	Atom AN		X	Y	Z		X	Y	Z	X	Y	Z
	1	6	0.00	0.00	0.08		0.00	0.08	0.00	0.00	0.00	0.47

2	6	0.00	0.24	-0.02	0.00	-0.07	0.00	0.00	0.07	-0.15
3	6	0.00	0.00	-0.14	0.00	0.10	0.00	0.00	0.00	0.11
4	6	0.00	-0.24	-0.02	0.00	-0.07	0.00	0.00	-0.07	-0.15
5	7	0.00	0.06	0.04	0.00	-0.04	0.06	0.00	-0.03	-0.04
6	7	0.00	-0.06	0.04	0.00	-0.04	-0.06	0.00	0.03	-0.04
7	1	0.00	0.48	0.42	0.00	-0.12	-0.09	0.00	-0.13	-0.58
8	1	0.00	0.00	-0.17	0.00	0.96	0.00	0.00	0.00	0.11
9	1	0.00	-0.48	0.42	0.00	-0.12	0.09	0.00	0.13	-0.58
10	17	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00	-0.03
		16			17			18		
		B2			B2			A1		
Frequencies	--	1233.1390			1293.3151			1423.2475		
Red. masses	--	9.6511			1.5742			2.1258		
Frc consts	--	8.6467			1.5514			2.5370		
IR Inten	--	0.7996			8.7442			219.3075		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	-0.31	0.00	0.00	0.19	0.00	0.00	0.00	0.11
2	6	0.00	0.10	0.34	0.00	-0.06	0.04	0.00	-0.07	0.02
3	6	0.00	-0.24	0.00	0.00	0.01	0.00	0.00	0.00	0.06
4	6	0.00	0.10	-0.34	0.00	-0.06	-0.04	0.00	0.07	0.02
5	7	0.00	0.15	0.37	0.00	-0.04	0.04	0.00	-0.10	-0.14
6	7	0.00	0.15	-0.37	0.00	-0.04	-0.04	0.00	0.10	-0.14
7	1	0.00	0.10	0.30	0.00	0.23	0.63	0.00	0.23	0.63
8	1	0.00	0.27	0.00	0.00	-0.23	0.00	0.00	0.00	0.08
9	1	0.00	0.10	-0.30	0.00	0.23	-0.63	0.00	-0.23	0.63
10	17	0.00	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		19			20			21		
		B2			B2			A1		
Frequencies	--	1455.2160			1592.1744			1602.2692		
Red. masses	--	1.9360			6.3151			4.8984		
Frc consts	--	2.4155			9.4321			7.4093		
IR Inten	--	0.4549			109.4327			128.9889		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.12	0.00	0.00	-0.31	0.00	0.00	0.00	0.06
2	6	0.00	-0.01	0.14	0.00	-0.23	-0.09	0.00	0.11	0.32
3	6	0.00	0.14	0.00	0.00	0.44	0.00	0.00	0.00	-0.18
4	6	0.00	-0.01	-0.14	0.00	-0.23	0.09	0.00	-0.11	0.32
5	7	0.00	-0.06	0.05	0.00	0.16	0.07	0.00	-0.02	-0.19
6	7	0.00	-0.06	-0.05	0.00	0.16	-0.07	0.00	0.02	-0.19
7	1	0.00	-0.30	-0.42	0.00	-0.05	0.34	0.00	-0.26	-0.49
8	1	0.00	-0.62	0.00	0.00	-0.54	0.00	0.00	0.00	-0.22
9	1	0.00	-0.30	0.42	0.00	-0.05	-0.34	0.00	0.26	-0.49
10	17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
		22			23			24		
		A1			B2			A1		
Frequencies	--	3162.7949			3165.6497			3209.1206		
Red. masses	--	1.0901			1.0923			1.0965		
Frc consts	--	6.4251			6.4492			6.6529		
IR Inten	--	10.9331			12.2231			4.7280		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6	0.00	-0.05	0.02	0.00	-0.06	0.03	0.00	0.02	0.00
3	6	0.00	0.00	-0.02	0.00	0.00	0.00	0.00	0.00	-0.09
4	6	0.00	0.05	0.02	0.00	-0.06	-0.03	0.00	-0.02	0.00
5	7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	1	0.00	0.61	-0.30	0.00	0.63	-0.31	0.00	-0.15	0.07
8	1	0.00	0.00	0.24	0.00	-0.01	0.00	0.00	0.00	0.97
9	1	0.00	-0.61	-0.30	0.00	0.63	0.31	0.00	0.15	0.07
10	17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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5. 5-bromo-2-chloropyrimidine

5.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C,1,B1
C,2,B2,1,A1
C,3,B3,2,A2,1,D1,0
N,1,B4,2,A3,3,D2,0
N,2,B5,1,A4,5,D3,0
H,4,B6,3,A5,2,D4,0
H,2,B7,1,A6,5,D5,0
Br,3,B8,2,A7,1,D6,0
Cl,1,B9,5,A8,4,D7,0
Variables:
B1=2.25652417
B2=1.39139133
B3=1.39139133
B4=1.32538811
B5=1.33418218
B6=1.08535985
B7=1.08535985
B8=1.90159178
B9=1.74627798
A1=89.55344634
A2=117.33113531
A3=95.63639006
A4=31.83805397
A5=121.61662495
A6=148.82992871
A7=121.33443234
A8=116.14459594
D1=0.
D2=0.
D3=180.
D4=180.
D5=180.
D6=180.
D7=180.
```

5.2 Total Energy

b3lyp/6-311++g(d,p) level of theory
E(RB+HF-LYP) = -3297.55621429

5.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

		1			2			3		
		B1			B2			A1		
Frequencies	--	76.3961			186.4347			271.2891		
Red. masses	--	12.2663			11.4942			30.5523		
Frc consts	--	0.0422			0.2354			1.3248		
IR Inten	--	0.1853			0.3974			0.0335		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.17	0.00	0.00	0.00	0.17	0.00	0.00	0.00	-0.36
2	6	0.34	0.00	0.00	0.00	0.34	0.08	0.00	0.06	-0.18
3	6	0.24	0.00	0.00	0.00	0.38	0.00	0.00	0.00	0.01
4	6	0.34	0.00	0.00	0.00	0.34	-0.08	0.00	-0.06	-0.18
5	7	0.31	0.00	0.00	0.00	0.22	-0.11	0.00	-0.06	-0.24

6	7	0.31	0.00	0.00	0.00	0.22	0.11	0.00	0.06	-0.24
7	1	0.42	0.00	0.00	0.00	0.39	-0.17	0.00	0.00	-0.29
8	1	0.42	0.00	0.00	0.00	0.39	0.17	0.00	0.00	-0.29
9	35	-0.14	0.00	0.00	0.00	-0.16	0.00	0.00	0.00	0.44
10	17	-0.33	0.00	0.00	0.00	-0.27	0.00	0.00	0.00	-0.55
			4				5			
			B1				B2			
Frequencies	--		287.7225				362.9228			
Red. masses	--		11.2682				7.4664			
Frc consts	--		0.5496				0.5794			
IR Inten	--		1.9768				4.6253			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.36	0.00	0.00	0.00	0.31	0.00	0.00	0.00	0.00
2	6	0.25	0.00	0.00	0.00	-0.13	-0.20	-0.24	0.00	0.00
3	6	0.62	0.00	0.00	0.00	-0.24	0.00	0.00	0.00	0.00
4	6	0.25	0.00	0.00	0.00	-0.13	0.20	0.24	0.00	0.00
5	7	-0.32	0.00	0.00	0.00	0.23	0.18	-0.28	0.00	0.00
6	7	-0.32	0.00	0.00	0.00	0.23	-0.18	0.28	0.00	0.00
7	1	0.27	0.00	0.00	0.00	-0.25	0.45	0.60	0.00	0.00
8	1	0.27	0.00	0.00	0.00	-0.25	-0.45	-0.60	0.00	0.00
9	35	-0.06	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00
10	17	0.11	0.00	0.00	0.00	-0.19	0.00	0.00	0.00	0.00
			7				8			
			B1				A1			
Frequencies	--		485.8950				505.6901			
Red. masses	--		3.1004				14.7294			
Frc consts	--		0.4313				2.2192			
IR Inten	--		2.6247				32.6460			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.26	0.00	0.00	0.00	0.00	0.15	0.00	-0.07	0.00
2	6	-0.13	0.00	0.00	0.00	0.03	0.34	0.00	0.25	-0.31
3	6	0.29	0.00	0.00	0.00	0.00	0.30	0.00	0.19	0.00
4	6	-0.13	0.00	0.00	0.00	-0.03	0.34	0.00	0.25	0.31
5	7	-0.02	0.00	0.00	0.00	-0.08	0.33	0.00	-0.27	0.33
6	7	-0.02	0.00	0.00	0.00	0.08	0.33	0.00	-0.27	-0.33
7	1	-0.64	0.00	0.00	0.00	-0.03	0.34	0.00	0.36	0.11
8	1	-0.64	0.00	0.00	0.00	0.03	0.34	0.00	0.36	-0.11
9	35	0.00	0.00	0.00	0.00	0.00	-0.11	0.00	0.01	0.00
10	17	-0.03	0.00	0.00	0.00	0.00	-0.42	0.00	-0.04	0.00
			10				11			
			B1				A1			
Frequencies	--		783.5255				797.5251			
Red. masses	--		9.1074				9.3889			
Frc consts	--		3.2942				3.5185			
IR Inten	--		10.9571				3.0298			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.58	0.00	0.00	0.00	0.00	0.30	0.06	0.00	0.00
2	6	0.21	0.00	0.00	0.00	-0.35	0.04	-0.13	0.00	0.00
3	6	-0.24	0.00	0.00	0.00	0.00	-0.35	0.09	0.00	0.00
4	6	0.21	0.00	0.00	0.00	0.35	0.04	-0.13	0.00	0.00
5	7	-0.33	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00
6	7	-0.33	0.00	0.00	0.00	-0.33	0.00	0.00	0.00	0.00
7	1	0.39	0.00	0.00	0.00	0.22	0.32	0.69	0.00	0.00
8	1	0.39	0.00	0.00	0.00	-0.22	0.32	0.69	0.00	0.00
9	35	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00
10	17	-0.02	0.00	0.00	0.00	0.00	-0.10	0.00	0.00	0.00
			13				14			
			A2				A1			
Frequencies	--		983.0345				1023.6157			
Red. masses	--		1.3628				7.8833			
Frc consts	--		0.7759				4.8667			
IR Inten	--		0.0000				35.0351			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z

1											
2											
3	1	6	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	-0.13
4	2	6	0.13	0.00	0.00	0.00	0.24	0.03	0.00	-0.21	0.04
5	3	6	0.00	0.00	0.00	0.00	0.00	0.36	0.00	0.00	0.30
6	4	6	-0.13	0.00	0.00	0.00	-0.24	0.03	0.00	0.21	0.04
7	5	7	0.02	0.00	0.00	0.00	0.38	-0.15	0.00	0.01	-0.06
8	6	7	-0.02	0.00	0.00	0.00	-0.38	-0.15	0.00	-0.01	-0.06
9	7	1	0.70	0.00	0.00	0.00	-0.37	0.29	0.00	0.47	-0.42
10	8	1	-0.70	0.00	0.00	0.00	0.37	0.29	0.00	-0.47	-0.42
11	9	35	0.00	0.00	0.00	0.00	0.00	-0.02	0.00	0.00	-0.01
12	10	17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
13				16			17			18	
14				A1			B2			B2	
15	Frequencies	--	1189.5070				1220.4837			1278.6112	
16	Red. masses	--	3.9208				11.9234			2.0429	
17	Frc consts	--	3.2686				10.4644			1.9678	
18	IR Inten	--	301.5755				0.6996			9.7829	
19	Atom AN		X	Y	Z		X	Y	Z		
20	1	6	0.00	0.00	0.44	0.00	0.47	0.00	0.00	0.20	0.00
21	2	6	0.00	0.05	-0.14	0.00	-0.20	-0.32	0.00	-0.07	0.09
22	3	6	0.00	0.00	0.12	0.00	0.38	0.00	0.00	0.03	0.00
23	4	6	0.00	-0.05	-0.14	0.00	-0.20	0.32	0.00	-0.07	-0.09
24	5	7	0.00	-0.03	-0.03	0.00	-0.19	-0.33	0.00	-0.04	0.10
25	6	7	0.00	0.03	-0.03	0.00	-0.19	0.33	0.00	-0.04	-0.10
26	7	1	0.00	0.17	-0.58	0.00	-0.13	0.11	0.00	0.19	-0.65
27	8	1	0.00	-0.17	-0.58	0.00	-0.13	-0.11	0.00	0.19	0.65
28	9	35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	10	17	0.00	0.00	-0.03	0.00	0.01	0.00	0.00	-0.01	0.00
30				19			20			21	
31				B2			A1			B2	
32	Frequencies	--	1386.9337				1425.7893			1564.8893	
33	Red. masses	--	2.1207				2.1546			7.7993	
34	Frc consts	--	2.4035				2.5807			11.2531	
35	IR Inten	--	6.5546				263.8659			80.5431	
36	Atom AN		X	Y	Z		X	Y	Z		
37	1	6	0.00	0.06	0.00	0.00	0.00	0.11	0.00	0.40	0.00
38	2	6	0.00	-0.04	0.14	0.00	-0.07	0.01	0.00	0.25	0.13
39	3	6	0.00	0.19	0.00	0.00	0.00	0.09	0.00	-0.43	0.00
40	4	6	0.00	-0.04	-0.14	0.00	0.07	0.01	0.00	0.25	-0.13
41	5	7	0.00	-0.04	0.08	0.00	-0.10	-0.14	0.00	-0.20	-0.09
42	6	7	0.00	-0.04	-0.08	0.00	0.10	-0.14	0.00	-0.20	0.09
43	7	1	0.00	-0.39	0.55	0.00	-0.23	0.63	0.00	-0.01	0.45
44	8	1	0.00	-0.39	-0.55	0.00	0.23	0.63	0.00	-0.01	-0.45
45	9	35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	10	17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47				22			23			24	
48				A1			B2			A1	
49	Frequencies	--	1582.7715				3173.8549			3174.4721	
50	Red. masses	--	5.4647				1.0928			1.0935	
51	Frc consts	--	8.0659				6.4857			6.4925	
52	IR Inten	--	43.5463				1.2304			4.9072	
53	Atom AN		X	Y	Z		X	Y	Z		
54	1	6	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00
55	2	6	0.00	0.11	0.34	0.00	-0.06	0.03	0.00	0.06	-0.03
56	3	6	0.00	0.00	-0.20	0.00	0.00	0.00	0.00	0.00	0.00
57	4	6	0.00	-0.11	0.34	0.00	-0.06	-0.03	0.00	-0.06	-0.03
58	5	7	0.00	-0.04	-0.21	0.00	0.00	0.00	0.00	0.00	0.00
59	6	7	0.00	0.04	-0.21	0.00	0.00	0.00	0.00	0.00	0.00
60	7	1	0.00	0.28	-0.48	0.00	0.63	0.31	0.00	0.63	0.31
	8	1	0.00	-0.28	-0.48	0.00	0.63	-0.31	0.00	-0.63	0.31
	9	35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10	17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00