Photoelectron Spectra and Electronic Structures of Substituted Pyrimidines

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The electronic structures of pyrimidine (**1**) and its substituted derivatives **2**–**15** have been investigated by ultraviolet photoelectron spectroscopy and quantum chemical methods. The ionisation potentials corresponding to the π MOs π_1-π_3 and the two n_N orbitals of the pyrimidine unit could be determined and assigned for **1**–**15**. Multiple linear regression analyses of the *IP*s related to these orbitals with different substituent constants indicated that Hammett σ_p values performed well for all these *IP*s, whereas the resonance parameters *R* and R^+ were satisfactory for π and poor for n_N ionisations.

Introduction

Substituents can modify the electronic structure of a parent molecule and knowledge of its electronic properties and the nature of its interactions with substituents could help in better understanding its chemical properties. Previously, we have investigated the ultraviolet photoelectron (PE) spectra and electronic structures of 1-substituted 1*H*-benzotriazoles.[1] With only a few exceptions, the ionisation potentials corresponding to all occupied π MOs (π_1-π_5) and the two n_N orbitals of the 1*H*-benzotriazole unit could be determined and assigned for the parent 1*H*-benzotriazole and 19 of its derivatives. Linear free energy (LFE) correlations of the ionisations related to these orbitals with inductive substituent parameters σ_I and *F* were reasonable except for *IP*(π_3). The energies of the π and n MOs, except for π_3, are thus affected primarily by the electronegativity of the substituents. The different behaviour of π_3 is caused by direct interactions with substituent orbitals. This work presents the results for substituted pyrimidines **1**−**15**. PE spectra of pyrimidine and some of its derivatives have been investigated previously[2−9] but no systematic research of substituent effects on the electronic structures has been performed until now.

Results and Discussion

PE Spectra and Electronic Structures of Pyrimidines 1−15

The molecular structure of pyrimidine (**1**) has been determined by X-ray structure analysis.[10] The molecule is planar and has C_{2v} symmetry. In **1** there are 15 occupied valence MOs, consisting of three π type MOs ($\pi_1-\pi_3$) belonging to the symmetry groups b_1 and a_2, and twelve σ type MOs which belong to the groups a_1 and b_2. The electron lone-pairs of the two N atoms occupy the n type orbitals n_N^- and n_N^+ of b_2 and a_1 symmetry, respectively. These two n type and the three π type MOs can be assumed to occur with more or less modified shapes and energies in all substituted pyrimidines and we call them the "characteristic pyrimidine MOs". These MOs, as calculated by the B3LYP method, are shown in Figure 1.

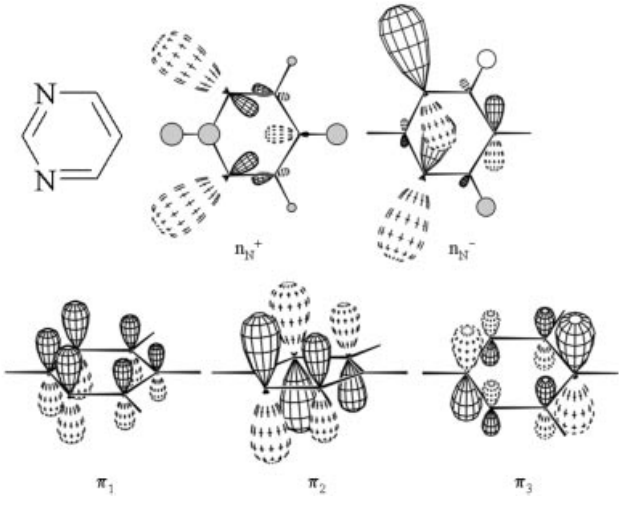

Figure 1. Characteristic MOs of pyrimidine (**1**) (B3LYP results)

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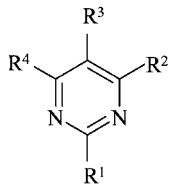

R^1	H	H	C≡CH	H	NH_2	NH_2	NH_2	NH_2	NH_2	NH_2	NH_2	NH_2	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$
R^2	H	CH_3	H	H	H	CH_3	Cl	OH	OCH_3	Cl	Cl	OCH_3	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$
R^3	H	H	H	C≡CH	H	H	H	H	H	H	H	H	H	CH_3	$CH(CH_3)_2$
R^4	H	H	H	H	H	CH_3	CH_3	CH_3	CH_3	Cl	OCH_3	OCH_3	CH_3	CH_3	CH_3
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**

Scheme 1

The PE spectra of compounds **1**−**15** (Scheme 1) are depicted in Figures 2 and 3. The measured ionisation potentials are summarised in Tables 1−15 together with the relevant results of quantum chemical calculations. In order to limit the amount of data, we have omitted some σ orbitals which are irrelevant for spectroscopic assignments.

We performed density functional theory (DFT) B3LYP[11,12] calculations with the basis set 6-31+G*. As-

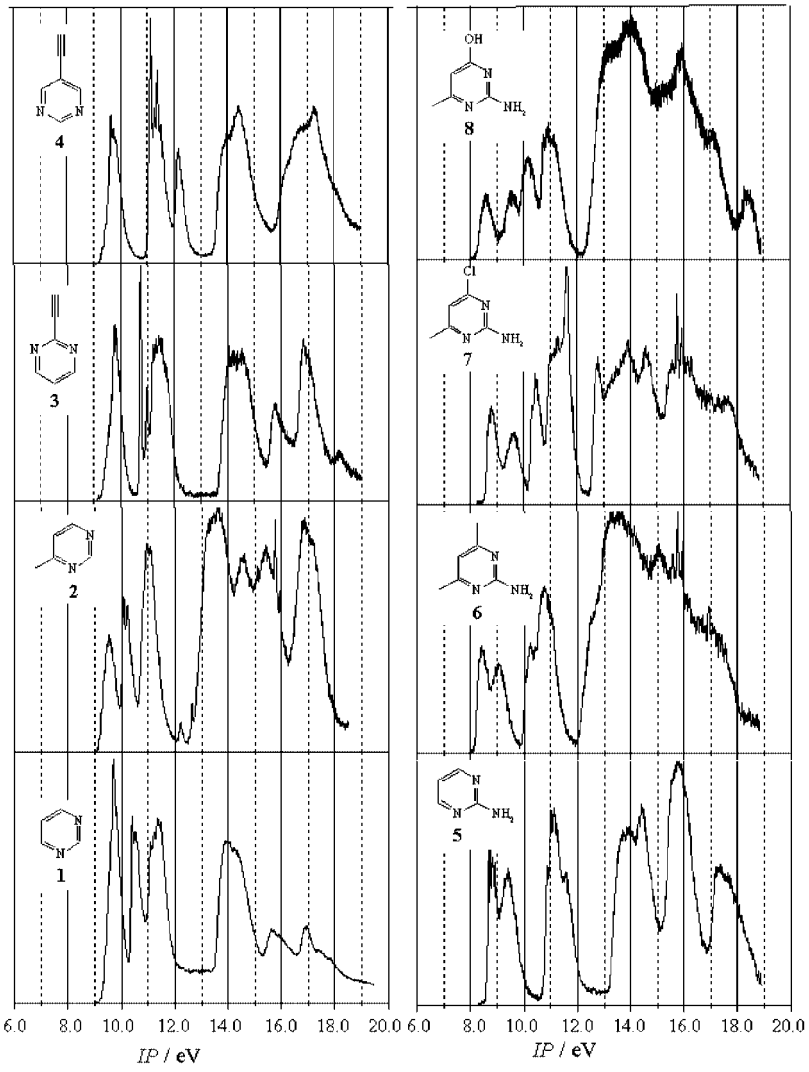

Figure 2. PE spectra of pyrimidines **1**−**8**

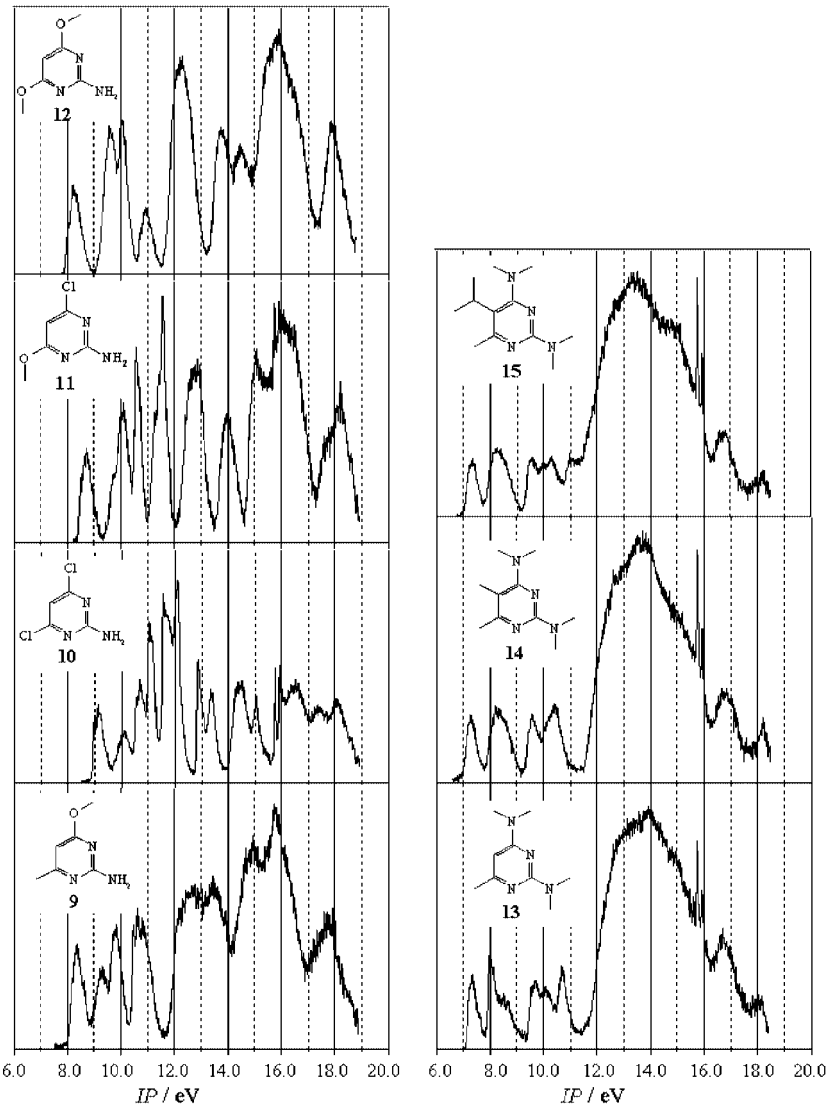

Figure 3. PE spectra of pyrimidines **9**−**15**

signments of the *IP*s can be achieved using Koopmans' theorem,[13] $IP_i = -\varepsilon_i$, by which vertical ionisation energies and SCF MO energies are related. Although Kohn−Sham (KS) orbitals obtained by DFT methods[14] are not SCF MOs and their physical meaning is still debated, it has been shown that they can be used with high confidence for the interpretation of PE spectra.[15,16] Much better agreement between experimental and theoretical values can be expected for the first vertical *IP* (IP_{1v}) when the energies of the molecule M and the radical cation $M^{\cdot+}$ are calculated by the B3LYP method. Since a vertical *IP* corresponds to the transition with the highest Franck−Condon factor without any structural change, a single point calculation can be performed for $M^{\cdot+}$ using the molecule's geometry in order to obtain IP_{1v}. The corresponding energy values, which do not include any zero-point corrections, are summarised in Table S1 (see Supporting Information). We can now correct the other ε^{B3LYP} values by the difference between $-\varepsilon$(HOMO) and the calculated IP_{1v} in order to obtain higher IP_v values.[16]

Whereas for the compounds studied here typical energy differences between IP_i and $-\varepsilon_i^{B3LYP}$ values are about 3 eV, experimental and calculated IP_i values differ only by 0.1−0.8 eV. Furthermore, both $-\varepsilon_i^{B3LYP}$ and calculated IP_i(calcd.) values are linearly correlated with the experimental IP_i(exp) values with correlation coefficients (both $r = 0.992$) close to 1.000.

In the following section, a brief interpretation and discussion of the PE spectra of compounds **1**−**15** are given. MOs are classified and labelled according to their symmetry properties. For the labelling, only valence MOs were taken into account. The core orbitals (i.e., 1s orbital except for hydrogen, 2s and 2p for third-row elements, etc.) were neglected. In certain cases (compounds **5**, **6** and **12**), the exact molecular symmetry may be lower than that used for the assignments but deviations are very small. Because of their

unsymmetrical substitution, compounds **7**−**9**, **11** and **13**−**15** have no molecular symmetry and accordingly their point group is C_1. Many of the observed ionisation bands, in particular those related to ionisations from π and n MOs, exhibit vibrational splitting. The corresponding frequencies are given in the respective tables. No attempt was made to assign the frequencies to certain vibrations of the respective radical cations but, generally, it can be stated that they belong to valence or deformation vibrations of the pyrimidine ring or a substituent. Sharp peaks at 15.76 and 15.94 eV, present in some spectra, originate from argon that was used as a calibration gas. *IP* values which could be determined only approximately from the spectra are given in parentheses.

The spectrum of pyrimidine (**1**) (Figure 2, Table 1) has been investigated previously by Gleiter and Heilbronner.[3] Most assignments given by these authors are confirmed by the present study. Our data and assignment (14.0 eV, σ, $6a_1$) deviate from those of the previous investigation (13.9 eV, π, $1b_1$) only for the fifth ionisation band. The spectrum of 4-methylpyrimidine (**2**) (Figure 2, Table 2) is rather similar to that of the parent compound **1**. The *IP*s related to the characteristic pyrimidine MOs (Figure 1) are lowered by the inductive effect of the methyl group by about 0.3 eV from those of **1**. C_s molecular symmetry can be assumed with a mirror plane lying in the molecular plane.

Table 1. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of pyrimidine (**1**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
9.70/1150	7.25	9.20	n_N^- ($5b_2$)
10.42/900	8.16	10.11	π_3 ($2b_1$)
11.22/950	8.58	10.53	n_N^+ ($7a_1$)
11.38/800	8.98	10.93	π_2 ($1a_2$)
14.0	11.54	13.49	σ ($6a_1$)
14.3	11.78	13.73	σ ($4b_2$)
	11.90	13.85	π_1 ($1b_1$)

Table 2. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 4-methylpyrimidine (**2**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
9.52/900	7.14	9.40	n_N^- (14a′)
10.08/1100	7.91	10.17	π_3 (4a′′)
10.95/900	8.41	10.67	n_N^+ (13a′)
11.09/1000	8.62	10.88	π_2 (3a′′)
13.36	10.89	13.15	σ (12a′)
13.66	11.16	13.42	π(CH_3) (2a′′)
14.54	12.32	14.58	π_1 (1a′′)

The molecular structure of 2-ethynylpyrimidine (**3**) has been determined by X-ray structure analysis[17] and the molecular symmetry is C_{2v}. In the spectrum of **3** (Figure 2, Table 3), the ionisation related to the orbital π′(C≡C) ($5b_2$) can be easily recognised by its distinct fine structure which is quite similar to that of the corresponding band in ethynylbenzene[18−20] which is isoelectronic with **3**. In contrast to the former compound, the second ionisation related to the triple bond, π(C≡C) ($2b_1$), is not characterised by a similar fine structure but is part of a composite band to which three ionisations contribute. The ionisations related to the two highest occupied MOs, n_N^- ($6b_2$) and π_3 ($3b_1$), are quite close in energy and form a common band. Interaction of the orbitals π_3 and π(C≡C), which are of the same symmetry, destabilises the former relative to its value in pyrimidine (**1**) by 0.66 eV. On the other hand, π_2 in **3** is stabilised relative to its value in **1** by about 0.3 eV. By the same value, n_N^+ of **3** is also shifted while n_N^- remains nearly unchanged. 5-Ethynylpyrimidine (**4**) has C_{2v} molecular symmetry and its structure has been determined by X-ray crystallography.[21] The spectrum of this compound (Figure 2, Table 4) is similar to that of its isomer **3** and that of ethynylbenzene[18−20] and the *IP* sequence is the same for **3** and **4** with only minor energy differences.

Table 3. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2-ethynylpyrimidine (**3**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
9.6 sh	7.31	9.04	n_N^- ($6b_2$)
9.76/700	7.41	9.14	π_3 ($3b_1$)
10.76/1950	8.04	9.77	π′(C=C) ($5b_2$)
11.50/1200	8.92	10.65	n_N^+ ($9a_1$)
11.7 sh	9.12	10.85	π_2 ($1a_2$)
11.8 sh	9.15	10.88	π(C=C) ($2b_1$)
14.2	11.92	13.65	σ ($4b_2$)
14.4	12.05	13.78	σ ($8a_1$)
14.55	12.24	13.97	π_1 ($1b_1$)
15.75	13.55	15.28	σ ($7a_1$)
16.81	14.53	16.26	σ ($6a_1$)

Table 4. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 5-ethynylpyrimidine (**4**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
9.65	7.34	9.27	n_N^- ($6b_2$)
9.75/800	7.40	9.33	π_3 ($3b_1$)
11.14/2000	8.53	10.46	π′(C=C) ($5b_2$)
11.27	8.88	10.81	n_N^+ ($9a_1$)
11.52/900	9.22	11.15	π_2 ($1a_2$)
12.19	9.68	11.61	π(C=C) ($2b_1$)
13.95	11.81	13.74	σ ($8a_1$)
14.08	12.01	13.94	σ ($4b_2$)
14.44	12.23	14.16	π_1 ($1b_1$)
16.25	14.04	15.97	σ ($7a_1$)
16.79	14.75	16.68	σ ($3b_2$)

In the spectrum of 2-aminopyrimidine (**5**) (Figure 2, Table 5) there are two groups of bands in the energy region below 12 eV which can be assigned to ionisations from the MOs π_3, π_2, n_N^-, n_N^+ and n(NH_2). The molecule has a pyramidal amino group and only one plane of symmetry.

Accordingly, the molecular symmetry is C_s. Again, most *IP*s related to the characteristic MOs of the pyrimidine system are lowered by about 0.3 eV relative to the values of **1**. A larger shift of 1.58 eV was found for $IP(\pi_3)$. This can be explained by the fact that π_3 has a rather large orbital coefficient on the C atom which carries the substituent and, because of this, substituents in this position will affect the MO energy to a greater extent than those on ring atoms with smaller coefficients. In the energy region below 12 eV there are three bands in the spectrum of 2-amino-4,6-dimethylpyrimidine (**6**) (Figure 2, Table 6). The band at about 10.8 eV is a superposition of two ionisations as indicated by its high intensity. The ionisations can be assigned to the orbitals π_3, n_N^-, π_2, n_N^+ and $n(NH_2)$. Again, C_s molecular symmetry is assumed. Compared with compound **5**, the additional two methyl groups induce a substantial destabilisation of π_2 by about 0.9 eV, while π_3 and the two n_N orbitals are shifted upwards by 0.2−0.4 eV.

Table 5. Vertical ionisation potentials *IP* [eV], fine structure *ν* [cm^{-1}] and orbital energies *ε* [eV] of 2-aminopyrimidine (**5**)

IP/ν	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.84/1000	6.50	8.99	π_3 (11a′)
9.44	6.98	9.47	n_N^- (7a′′)
11.01/1050	8.71	11.20	n_N^+ (6a′′)
11.14/950	8.71	11.20	π_2 (10a′)
11.6	9.17	11.66	$n(NH_2)$ (9a′)
14.0	11.33	13.82	σ (8a′)
14.43	11.69	14.18	σ (5a′′)
(15.0)	12.04	14.53	π_1 (7a′)

Table 6. Vertical ionisation potentials *IP* [eV], fine structure *ν* [cm^{-1}] and orbital energies *ε* [eV] of 2-amino-4,6-dimethylpyrimidine (**6**)

IP/ν	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.44	6.30	8.30	π_3 (14a′)
9.07	6.81	8.81	n_N^- (10a′′)
10.25/1200	8.05	10.05	π_2 (9a′′)
10.79	8.41	10.41	n_N^+ (13a′)
11.0	8.65	10.65	$n(NH_2)$ (12a′)
12.7	10.96	12.96	$\pi(CH_3)$ (11a′)
(13.6)	10.96	12.96	σ (7a")
(15.0)	12.30	14.30	π_1 (8a′)

Below 12 eV in the spectrum of 2-amino-4-chloro-6-methyl-pyrimidine (**7**) (Figure 2, Table 7), four bands occur again from the same orbitals as in **6** and an additional band from the orbital n_π'(Cl) of the chloro group. The latter orbital is localised in the molecular plane, in contrast to n_π(Cl) which is perpendicular to it. Three orbitals contribute to the fourth band ionisations, namely $n(NH_2)$, n_N^+ and n_π'(Cl). The ionisations of **7** differ by up to 0.7 eV from those of **2** and by around 1 eV from those of the parent compound **1**. In the latter case, an even greater deviation (1.64 eV) can be found only for π_3.

Table 7. Vertical ionisation potentials *IP* [eV], fine structure *ν* [cm^{-1}] and orbital energies *ε* [eV] of 2-amino-4-chloro-6-methyl-pyrimidine (**7**)

IP/ν	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.78/650	6.67	8.64	π_3 (24a)
9.63	7.37	9.34	n_N^- (23a)
10.46/550	8.16	10.13	π_2 (22a)
11.09	8.76	10.73	$n(NH_2)$ (21a)
11.28	9.04	11.01	n_N^+ (20a)
11.62	8.79	10.76	n_π'(Cl) (19a)
12.78	10.29	12.26	n_π(Cl) (18a)
13.3	10.96	12.93	σ (17a)
13.5	11.25	13.22	σ (16a)
13.93	11.61	13.58	$\pi(CH_3)$ (15a)
14.61	12.01	13.98	n_σ(Cl) (14a)
(14.9)	12.67	14.64	π_1 (13a)

In the spectrum of 2-amino-4-hydroxy-6-methylpyrimidine (**8**) (Figure 2, Table 8), there are four groups of bands in the energy region below 12 eV which can be assigned to ionisations from π_3, π_2, both n_N orbitals, $n(NH_2)$ and n_σ(O). The last mentioned orbital can be found above n_π(O) because the latter is stabilised considerably by its interaction with π_2. Compared with the unsubstituted parent compound **1**, all characteristic pyrimidine MOs are destabilised by between 0.15 eV (n_N^-) and 1.84 eV (π_3), whereas relative to 2-aminopyrimidine (**5**), destabilisation of these MOs amounts to between 0.11 eV (n_N^-) and 0.99 eV (π_2). In the spectrum of 2-amino-4-methoxy-6-methylpyrimidine (**9**) (Figure 3, Table 9), the same ionisation bands can be found as for compound **8**. However, all of them are shifted to lower values by 0.2−0.3 eV because of the replacement of the hydroxy by a methoxy group.

The spectrum of 2-amino-4,6-dichloropyrimidine (**10**) (Figure 3, Table 10) is dominated by three very strong and sharp ionisation bands between 11.0 and 12.5 eV which originate from the ejection of electrons from the chlorine atoms. For the assignment of these bands, a comparison with the spectrum of 1,3-dichlorobenzene[22,23] was helpful. Ionisations from the pyrimidine MOs π_3, n_N^- and π_2 can be found in the lower energy part of the spectrum while

Table 8. Vertical ionisation potentials *IP* [eV], fine structure *ν* [cm^{-1}] and orbital energies *ε* [eV] of 2-amino-4-hydroxy-6-methyl-pyrimidine (**8**)

IP/ν	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.58	6.38	8.40	π_3 (24a)
9.55	7.19	9.21	n_N^- (23a)
10.15/1200	7.79	9.81	π_2 (22a)
10.90/1350	8.53	10.55	$n(NH_2) + n_\pi$(O) (21a)
11.13	8.82	10.84	n_N^+ (20a)
12.8	10.57	12.59	n_σ(O) (19a)
13.1	10.74	12.76	$n(NH_2) - n_\pi$(O) (18a)
14.1	11.54	13.56	n_π(O) (16a)
(15.1)	12.56	14.58	π_1 (14a)

Table 9. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2-amino-4-methoxy-6-methylpyrimidine (**9**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.36	6.21	8.16	π_3 (27a)
9.33	7.04	8.99	n_N^- (26a)
9.82	7.57	9.52	π_2 (25a)
10.63/1350	8.34	10.29	$n(NH_2)$ (24a)
10.83	8.60	10.55	n_N^+ (23a)
11.1 sh	9.74	11.69	$n_\sigma(O)$ (22a)
12.3	9.92	11.87	$n_\pi(O)$ (21a)
12.8	10.53	12.48	σ (20a)
13.50	11.17	13.12	$\pi(CH_3)$ (19a)
(15.0)	13.08	15.03	π_1 (17a)

Table 10. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2-amino-4,6-dichloropyrimidine (**10**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
9.11/650	7.00	8.79	π_3 (14a′)
10.13	7.91	9.70	n_N^- (10a′′)
10.71/1100	8.41	10.20	π_2 (9a′′)
11.05/700	8.66	10.45	$n_\pi(Cl)^+$ (13a′)
11.56	8.99	10.78	$n_\pi'(Cl)^-$ (8a′′)
11.7	9.54	11.33	n_N^+ (12a′)
12.12/450	9.18	10.97	$n_\pi'(Cl)^+$ (11a′)
12.88	10.61	12.40	$n(NH_2)$ (10a′)
13.38	10.79	12.58	$n_\pi(Cl)^-$ (7a′′)
14.3	12.09	13.88	$n_\sigma(Cl)^-$ (6a′′)
14.47	12.48	14.27	$n_\sigma(Cl)^+$ (9a′)
15.02	13.04	14.83	π_1 (8a′)

that of n_N^+ occurs between the second and third n_{Cl} ionisations. The molecular point group is C_s.

The amino group of 2-amino-4-chloro-6-methoxypyrimidine (**11**) is pyramidal and there is only one mirror plane vertical to the molecular plane if the methoxy groups are arranged accordingly. We have assumed C_s symmetry for this molecule. As in the previous compound, the ionisation bands related to the chlorine atoms in the spectrum of **11** (Figure 3, Table 11) can be recognised by their high intensity and sharp appearance. The three pyrimidine bands at lower energies can be assigned as in compound **10**. The destabilising effect of the methoxy group, which has replaced a chlorine atom in the latter compound, is mainly manifested in the shift of $IP(\pi_2)$ by 0.61 eV. In the region below 13.0 eV, in the spectrum of 2-amino-4,6-dimethoxypyrimidine (**12**) (Figure 3, Table 12), four bands of different intensities may be found. Some of them are composite bands to which several ionisations contribute. In particular, this holds for the very strong and broad band between 10.8 and 13.0 eV to which four ionisations can be assigned. To the second band, which lies at about 9.6 eV, ionisations from n_N^- and π_2 contribute in such a way that individual *IP*s cannot be determined. C_s symmetry is assumed for the molecule, although this is probably a simplification since the methoxy groups may adopt different conformations.

Table 11. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2-amino-4-chloro-6-methoxypyrimidine (**11**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.71/1250	6.57	8.49	π_3 (27a)
9.78 sh	7.59	9.51	n_N^- (26a)
10.10	7.89	9.81	π_2 (25a)
10.58/750	8.22	10.14	$n_\pi(Cl)$ (24a)
11.31	9.10	11.02	n_N^+ (23a)
11.57/850	8.73	10.65	$n_\pi'(Cl)$ (22a)
12.80	10.05	11.97	$n_\sigma(O)$ (21a)
	10.25	12.17	$n(NH_2)$ (20a)
	10.33	12.25	$n_\pi(O)$ (19a)
14.00	11.51	13.43	$n_\sigma(Cl)$ (18a)
15.08	12.28	14.20	π_1 (17a)

Table 12. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2-amino-4,6-dimethoxypyrimidine (**12**)

IP/v	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
8.27/1700	6.32	8.27	π_3 (17a′)
9.62	7.13	9.08	n_N^- (13a′′)
	7.23	9.18	π_2 (12a′′)
10.05	7.80	9.75	$n_\pi(O)^+$ (16a′)
10.97	8.55	10.50	n_N^+ (15a′)
12.2	9.46	11.41	$n_\sigma(O)^-$ (11a′′)
12.29	9.87	11.82	$n(NH_2)$ (14a′)
12.5	10.08	12.03	$n_\sigma(O)^+$ (13a′)
12.7	10.21	12.16	$n_\pi(O)^-$ (10a′′)
13.84	11.84	13.79	$\pi(CH_3)$ (12a′)
14.60	12.06	14.01	σ (11a′)
(15.2)	13.40	15.35	π_1 (8a′)

In addition to the *IP*s related to the characteristic pyrimidine MOs, in the low-energy part of the spectrum of 2,4-bis(dimethylamino)-6-methylpyrimidine (**13**) (Figure 3, Table 13) two ionisations from orbitals that are mainly localised in the two dimethylamino groups can be expected. These are labelled as $n(NMe_2)^+$ and $n(NMe_2)^-$, although the molecule has no symmetry and linear combinations according to different symmetry properties can only refer to

Table 13. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2,4-bis(dimethylamino)-6-methylpyrimidine (**13**)

IP	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
7.33	5.45	7.12	π_3 (36a)
8.00	6.08	7.75	$n(NMe_2)^+$ (35a)
8.56	6.45	8.12	n_N^- (34a)
9.71	7.69	9.36	π_2 (33a)
10.08	8.01	9.68	n_N^+ (32a)
10.69	8.73	10.40	$n(NMe_2)^-$ (31a)
13.2	11.14	12.81	σ (23a)
13.9	11.71	13.38	σ (20a)
(15.0)	12.92	14.59	π_1 (16a)

the approximate local symmetry of the two groups in *meta* positions of the pyrimidine ring. Below 11.5 eV, there are six ionisation bands, the second and the sixth being assigned to the two n(NMe_2) ionisations and the remaining four can be related to the characteristic pyrimidine MOs. Because of the strong destabilising effect of the two NMe_2 groups, *IP*s related to the latter MOs are lowered by up to 3.09 eV relative to their positions in the parent compound (**1**). The appearance of the spectrum of 2,4-bis(dimethylamino)-5,6-dimethylpyrimidine (**14**) (Figure 3, Table 14) is similar to that of compound **13** although the bands are less well separated. The calculation shows no symmetry for the molecule (point group C_1) with relatively large deviations from C_s symmetry. The sequence of the *IP*s is the same as in **13**. The spectrum of 2,4-bis(dimethylamino)-5-isopropyl-6-methylpyrimidine (**15**) (Figure 3, Table 15) is little different from that of compound **14** but the assignments are the same for both compounds. As a new feature in the spectrum of **15**, a band at 11.1 eV appears which can be assigned to ionisation from a pseudo π type orbital mainly localised on the isopropyl group.

Table 14. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2,4-bis(dimethylamino)-5,6-dimethylpyrimidine (**14**)

IP	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
7.30	5.40	7.03	π_3 (39a)
8.30	6.19	7.82	$n(NMe_2)^+$ (38a)
8.6	6.47	8.10	n_N^- (37a)
9.58	7.66	9.29	π_2 (36a)
10.2 sh	8.16	9.79	n_N^+ (35a)
10.43	8.41	10.04	$n(NMe_2)^-$ (34a)
13.2	10.78	12.41	σ (26a)
13.9	10.99	12.62	σ (24a)
(15.0)	12.84	14.47	π_1 (17a)

Table 15. Vertical ionisation potentials *IP* [eV], fine structure *v* [cm^{-1}] and orbital energies ε [eV] of 2,4-bis(dimethylamino)-5-isopropyl-6-methylpyrimidine (**15**)

IP	$-\varepsilon^{B3LYP}$	IP^{B3LYP}	
7.32	5.44	7.01	π_3 (45a)
8.30	6.18	7.75	$n(NMe_2)^+$ (44a)
8.6 sh	6.47	8.04	n_N^- (43a)
9.59	7.63	9.20	π_2 (42a)
10.0	8.07	9.64	n_N^+ (41a)
10.30	8.31	9.88	$n(NMe_2)^-$ (40a)
11.1	9.39	10.96	π(iPr) (39a)
13.6	11.11	12.68	σ (28a)
14.8	11.66	13.23	σ (26a)
(15.1)	12.84	14.41	π_1 (19a)

Linear Free Energy Correlation Analysis of Ionisation Energies

In substituted compounds, the magnitude of substituent-induced shifts on an orbital is dependent upon the electronegativity of the substituent (through inductive effects) and on the ability of orbitals located on the substituent to interact with orbitals of the parent molecular core (resonance effect).[24] The orbitals of the parent moiety and those of the substituent generally become mixed in the composite system so that localisation on one subunit no longer exists. However, even though the orbitals of the substituted system are delocalised, it is helpful to refer to them in terms of their origin.

In Figure 4, a correlation diagram for the ionisation potentials *IP* associated with the characteristic pyrimidine MOs (Figure 1) is shown for compounds **1**−**15**. As is clear from Figure 4, for all pyrimidines studied here, there is a comparable influence of the substituents on the energies of these MOs. In particular, the MO sequence remains unchanged for compounds **6**−**12** and when the remaining compounds are included, only two MO crossings occur.

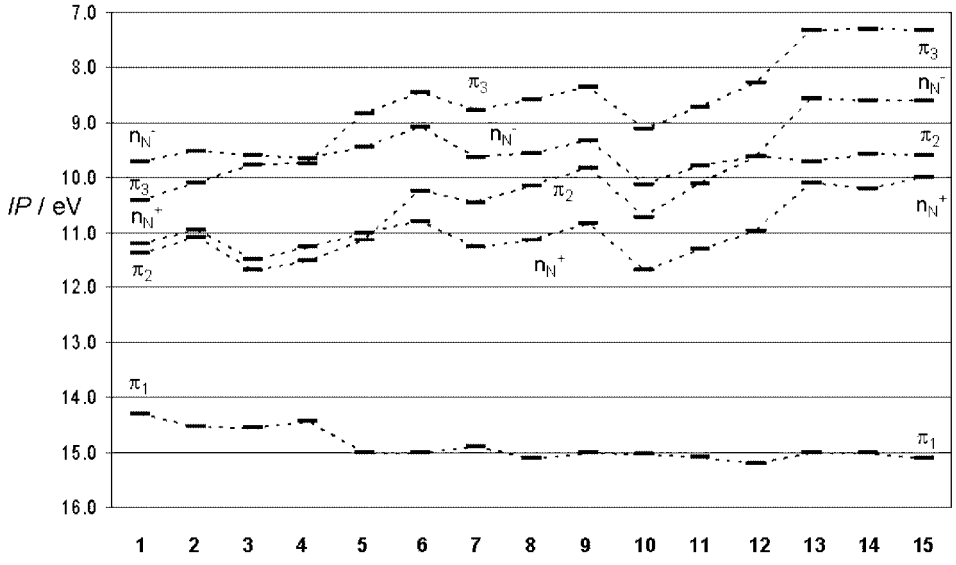

Figure 4. Correlation diagram of the ionisation potentials *IP* of pyrimidines **1**−**15**

Thus, π_3 is always the highest occupied MO (HOMO) except in compounds **1**−**4** in which it is replaced by n_N^- which is itself the second highest occupied MO (HOMO-1) in all other compounds. Furthermore, for most compounds, except for **1**−**5**, π_2 is found above n_N^+. However, a closer inspection of the data reveals that the spread of *IP* values differs for the individual MOs: π_3 (7.3−10.4 eV), π_2 (9.6−11.7 eV), π_1 (14.3−15.1 eV), n_N^- (8.6−10.1 eV) and n_N^+ (10.0−11.7 eV). From these observations it can be concluded that the substituents affect both types of MOs (n and π) in a comparable way but to different extents. The energy variation of $IP(\pi_3)$ is considerably larger then that of $IP(\pi_2)$ and nearly four times as large as that of $IP(\pi_1)$. On the other hand, the variations of $IP(n_N^-)$ and $IP(n_N^+)$ are quite similar. For a quantitative investigation of substituent effects, we have carried out linear free energy (LFE) correlation analyses of the *IP* values with the aid of substituent parameters in order to understand the nature of the electronic effects on the various energy levels.

Linear correlations of *IP* values with substituent parameters have been demonstrated repeatedly[25] and numerous benzene derivatives[9,26] have been investigated. Hammett σ values are usually used in such analyses for aromatic compounds. For other compounds, e.g., quinuclidines,[27] *IP*s were found to correlate well with Taft's σ values and, as we have recently shown for 1-substituted 1*H*-benzotriazoles,[1] *IP*s related to all occupied π MOs (π_1-π_5) and the two n_N orbitals of the parent 1*H*-benzotriazole unit correlate well with inductive substituent parameters σ_I and *F*. For some substituents, for which no σ_I or *F* parameters are known, these could be determined from their *IP*s by correlation analysis.

In the above-mentioned LFE analyses of *IP* data, series of compounds have been studied in which only one substituent was varied. Similar investigations could also be performed for subgroups of pyrimidines **1**−**15** which differ only in one of the four substituents R^1−R^4 (Scheme 1). Thus, compounds **6**−**9** differ only in R^2, compounds **1**, **3** and **5** in R^1, and compounds **7**, **10** and **11** in R^4, etc. Since none of these subgroups contains more than four members, single-parameter LFE analysis would only be of limited relevance. In order to analyse all relevant *IP*s of compounds **1**−**15**, we have performed multiple linear regression analyses[28] including all four substituents (R^1−R^4) simultaneously. The regression equation with substituent parameters $X(R^k)$ as independent variables has the form [Equation (1)]:

$$IP_i = a + c_1 X(R^1) + c_2 X(R^2) + c_3 X(R^3) + c_4 X(R^4) \quad (1)$$

Thus, regression coefficients c_k can be determined. The intercept term *a* should ideally be equal to the respective *IP* value of the parent compound (**1**) and c_1−c_4 indicate how important the substituent R^k is for *IP*s related to the respective MO. The statistical significance of the regression coefficients is given by their standard errors.

We have tested different substituent constants such as σ_I, σ_p, σ_m, σ_F, *R*, R^+, R^- and *F*[29] in LFE analyses according to Equation (1) using the *IP*s related to the pyrimidine MOs π_1−π_3, n_N^- and n_N^+ (Figure 1). Most of these substituent parameters performed rather poorly and only with Hammett σ_p and resonance constants *R* and R^+ were satisfactory to fair results obtained. As representative examples, the regression coefficients for the constants σ_p and *R* are summarised in Table 16. For σ_p, the multiple correlation coefficients *r* have values greater than 0.90 indicating quite satisfactory ($r > 0.95$) to fair ($r = 0.90$ to 0.95) correlations[28,30] for all *IP*s. For *R* (or R^+) the correlation is even a little better than for σ_p if only the π ionisations are considered. For the n_N *IP*s, the correlation is less satisfactory than with σ_p and *r* values of 0.81 and 0.83 can be considered as poor.[28,30] This may be taken as an indication that the two types of orbitals are affected in a somewhat different way by the substituents and the superior performance of σ_p can be explained by the fact that these constants represent the sum of electronic influences (inductive and mesomeric effects).

As is clear from the data in Table 16, the regression coefficients c_3 cannot be considered as significant since in most

Table 16. Regression parameters *a* and *c* and correlation coefficients *r* of multiple linear regression analyses of *IP*s related to the characteristic MOs of pyrimidines **1**−**15** with substituent parameters σ_p and *R*; values in parentheses are standard deviations

		π_3	π_2	π_1	n_N^-	n_N^+
σ_p	*r*	0.965	0.956	0.918	0.914	0.942
	a	9.92 (0.15)	11.34 (0.13)	14.53 (0.07)	9.65 (0.11)	11.29 (0.10)
	c_1	1.76 (0.29)	1.18 (0.25)	−0.68 (0.12)	0.04 (0.21)	0.15 (0.19)
	c_2	1.09 (0.27)	0.42 (0.23)	0.10 (0.12)	1.04 (0.20)	1.12 (0.18)
	c_3	−0.05 (1.21)	0.73 (1.05)	−0.18 (0.53)	0.27 (0.91)	0.13 (0.80)
	c_4	0.83 (0.67)	1.87 (0.58)	−0.24 (0.29)	0.36 (0.51)	0.43 (0.45)
R	*r*	0.965	0.975	0.947	0.810	0.832
	a	10.06 (0.15)	11.46 (0.10)	14.47 (0.05)	9.68 (0.16)	11.30 (0.16)
	c_1	1.54 (0.34)	0.61 (0.22)	−0.62 (0.12)	0.19 (0.36)	0.09 (0.37)
	c_2	0.90 (0.38)	1.00 (0.25)	−0.01 (0.12)	0.74 (0.41)	0.89 (0.42)
	c_3	1.85 (1.68)	0.01 (1.11)	0.43 (0.61)	1.99 (1.81)	2.01 (1.84)
	c_4	0.07 (0.75)	1.61 (0.49)	−0.29 (0.17)	−1.13 (0.81)	−0.77 (0.82)

cases the standard deviation is larger than its absolute value. This can be simply explained since there are only three compounds with a substituent $R^3 \neq H$, namely **4**, **14** and **15**.

If a multiple correlation analysis is performed simultaneously with two constants for each substituent such as *F* and *R* (or R^+), which represent only the inductive and the mesomeric electronic influences, respectively, a considerable improvement is obtained. The correlation coefficients for all *IP*s become excellent ($r > 0.99$) to satisfactory ($r > 0.95$). However, since eight regression coefficients instead of four have now been determined, the significance level is reduced accordingly.

If the characteristic pyrimidine MOs of the investigated compounds are only slightly perturbed by substituents, the effects of substituents may be expected to be more or less additive in polysubstituted pyrimidine derivatives. In order to test this assumption, we performed a final linear regression of the *IP*s with the sum of the σ_p constants for each compound. Only for π_3 ($r = 0.951$) and π_2 ($r = 0.917$) were fair correlations found, while for π_1 ($r = 0.669$), n_N^- ($r = 0.809$) and n_N^+ ($r = 0.860$) only poor relations were obtained.

Conclusion

In this study, a relatively large number of compounds has been investigated. The PE spectra were analysed according to standard procedures including quantum chemical computations. The set of *IP*s for ionisations related to all characteristic pyrimidine MOs presented a good basis for investigating the relationship between the electronic structure of the parent molecule and the substituents. This was achieved by multiple regression analysis using different substituent constants. To the best of our knowledge, this is the first analysis of this type for ionisation potentials obtained by PE spectroscopy.

It was found that all *IP*s of compounds **1**−**15** related to the characteristic pyrimidine MOs can be correlated with substituent constants such as σ_p indicating that these parameters can be used as "explanatory variables"[28] or "descriptors" for the MO energies and thus the electronic structures of pyrimidines. It is essential to include both inductive and mesomeric effects in correlation analyses of the *IP*s with substituent constants, in order to obtain satisfactory results for π and n levels. A model that systematically describes the nature and extent of substituent effects on π and n_N ionisations of pyrimidines is certainly of high interest. Additivity of substituent effects in polysubstituted pyrimidines could only be proved for Hammett σ_p constants to a satisfactory degree of approximation for the two highest occupied π MOs.

Experimental Section

General: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500 and 125.8 MHz, respectively. NMR signals were referenced to TMS ($\delta = 0$ ppm) or solvent signals recalculated relative to TMS. IR spectra were measured on a Bio-Rad FTS 135 instrument. For mass spectra, a VG Prospec 3000 instrument from Fisons was used. PE spectra were recorded on a Leybold-Heraeus UPG200 spectrometer equipped with a He(I) radiation source (21.21 eV). The temperature of the inlet system was varied between 25 and 225 °C according to the different volatilities of the compounds in order to reach sufficient vapour pressure. Compound **9** was measured at 450 °C. The energy scale was calibrated with an argon/xenon mixture. The accuracy of the ionisation potentials is ±0.03 eV for sharp peaks but only ±0.1 eV for broad and overlapping signals.
Becke3LYP[11,12] calculations were performed with the program GAUSSIAN 98.[31] The latter DFT method was employed with the basis set 6-31+G*. All calculations were carried out with full geometry optimisation. MOs were plotted by using the program PERVAL.[32]

Materials: Compounds **1**, **2** and **5**−**12** were purchased from Sigma−Aldrich Chemie GmbH, Steinheim, Germany. Syntheses of compounds **4**[33] and **13**−**15**[34] have been described previously.

2-Ethynylpyrimidine (3): To a mixture of 2-bromopyrimidine (2.8 g, 17.6 mmol) and 2-methyl-3-butyne-2-ol (1.8 g, 21.5 mmol) in diethylamine (25 mL) were added bis(triphenylphosphane)palladium dichloride (126 mg, 0.2 mmol) and copper(I) iodide (19.8 mg, 0.1 mmol). The reaction mixture was stirred under argon at room temperature for 15 h and the solvent was then removed under reduced pressure. Water (3 mL) was added and the mixture extracted with diethyl ether (2 × 40 mL). Toluene (67 mL) and sodium hydroxide (560 mg, 140 mmol) were added and the mixture heated to reflux for 1 h. After removal of the solvent in vacuo, the product was recrystallised from chloroform. Yield 66 mg (4%), m.p. 95−96 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.12$ [s, 1 H, C(8)−H], 7.27 [t, $J = 4.9$ Hz, 1 H, C(5)−H], 8.71 [d, $J = 4.9$ Hz, 2 H, C(4)−H] ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 75.9$ [C(8)], 81.8 [C(7)], 120.5 [C(5)], 152.2 [C(2)], 157.3 [C(4)] ppm. IR: $\tilde{\nu} = 3257$ cm^{-1} [s, C≡C−H], 3077 [s, Aryl-H], 2122 [s, C≡C], 1632, 1567, 1504 [s, C=C, C=N], 803 [s]. MS (70 eV, EI): *m*/*z* (%) = 104 (100) [M^+], 105 (7) [M^+ + H], 77 (11) [M^+ − HCN], 52 (11) [$C_3H_2N^+$], 26 (7) [$C_2H_2^+$]. MS (high-resolution): *m*/*z* = 104.0359 [calcd. for $C_6H_4N_2$: 104.0374].

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