Ionization Energies of Triazines and Tetrazines. Application of Green's Function Method Coupled with Semiempirical Molecular Orbital Calculations†

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The ionization energies of the valence electrons of eighteen 1,2,4,5-tetrazines, six 1,2,3-triazines and seven 1,2,4-triazines derivatives have been calculated with the Outer Valence Green Function (OVGF) technique, using as the zeroth order approximation the wavefunctions obtained with semiempirical AM1 and PM3 approximations. In many cases the SCF(AM1), SCF(PM3), HAM/3 and OVGF(AM1) methods fail to reproduce correctly the ordering of the ionization energies for the azines under consideration. On the other hand, the OVGF(PM3) method gives quite satisfactory quantitative agreement with the experimental ionization potentials and for dimethoxy-*s*-tetrazine, it is of comparable accuracy to ADC(3) *ab initio* calculations with a polarized basis set. OVGF(PM3) calculations predict reliably the effect of substituents on the ionization potentials of azines, confirming previous suggestions that strong electron-donating groups lead to inversion of the ordering of the two highest orbitals, relative to their ordering in the parent *s*-tetrazine. In 1,2,3-triazine and 1,2,4-triazine methyl substitution does not change the ordering of the ionization energies relative to the corresponding parent molecules.

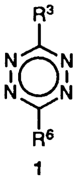
Photoelectron spectroscopy (PES) has developed during the last decades into an extremely useful experimental technique for the study of the electronic structure of atoms and molecules, and in particular the bonding characteristics of orbitals and their mutual interactions.[1] In order to interpret a PE spectrum and to exploit the information contained in it, a theoretical determination of the ionization potentials (E_i) is required. Usually Koopman's theory,[2] equating E_i with the negative value of the energy of the molecular orbital from which the electron is removed, is used in the interpretation.

A large number of theoretical methods and techniques, semiempirical as well as *ab initio*, is now available for calculating the energies of molecular orbitals. However, in some cases these theoretical methods fail to give the correct quantitative E_i or even to reproduce the correct orbital ordering. Cederbaum and co-workers have shown recently that in a variety of systems the combination of *ab initio* techniques with Green's function methods can improve significantly the ability of theoretical calculations accurately to predict E_i.[3] In this method the many-body perturbation theory is used to obtain equations that calculate ionization potentials which include corrections for electron correlation and for relaxation effects.[3] Hartree–Fock solutions obtained from *ab initio* calculations serve as the zeroth approximation in the perturbation series. In particular, the Algebraic Diagramic Construction [ADC(3)] method, which gives an exact summation of the perturbation series for the self-energy part in terms of a simple algebraic form introducing effective higher-order quantities, has been shown to be an appropriate theoretical framework for the investigation of ionic states even when the one-particle model of ionization does not apply and when ionic satellite states acquire substantial spectral intensity.[3b]

Unfortunately, at present the application of *ab initio*-Green function methods is practical only for relatively small molecules,[3] *i.e.* containing up to 6–7 non-hydrogen atoms. To overcome this difficulty, one of us has described recently[4,5] the coupling of the Outer-Valence Green Function (OVGF) approach with semiempirical methods such as AM1[6] [denoted in this paper as OVGF(AM1)]. The OVGF(AM1) method was used successfully to calculate the ionization potentials of the valence electrons of a variety of nitrogen-heterocycles, such as substituted pyridines (30 compounds), pyrimidines, pyridazines and azoles.[4,5] In general it was found that inclusion of Green's function method in the calculations improved substantially the quantitative theoretical–experimental agreement, and that this agreement was better than that obtained with the HAM/3 method[7] which was designed specifically for calculating ionization potentials.[4,5] In cases where comparisons were available the OVGF(AM1) and the OVGF (*ab initio* with polarized basis sets) calculations gave results of comparable quality.[4,5] A computer program combining the outer-valence Green's function formalism with the AM1 method or with the recently introduced PM3[8] semiempirical method is now available from *QCPE*.[9]

Azines, *i.e.* a benzene ring where at least one carbon atom is replaced by nitrogen, have attracted considerable interest from a variety of aspects.[10] The PES of azines is of particular interest, owing to the fact that the highest lone-pair orbitals on nitrogen and the highest π-orbitals are close in energy, and it has therefore been studied quite extensively.[11–16] We have studied previously, using the combination of OVGF and semiempirical methods, azines with one nitrogen (*i.e.* substituted pyridines)[5a] and with two nitrogens (*i.e.* pyrimidines, imidazoles and pyrazoles).[4,5b]

In this paper we extend our previous studies[4,5] to azines with 3 or 4 nitrogens and report OVGF calculations coupled with the semiempirical AM1 and PM3 methods for a number of substituted *s*-tetrazines (**1**), 1,2,3-triazines (**2**) and 1,2,4-triazines (**3**) and compare our ionization potentials (of the valence electrons) with experimental values as well as with the results of



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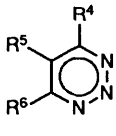

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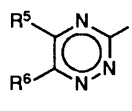

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† This paper was submitted to mark the 150th anniversary of the Chemical Society/Royal Society of Chemistry.

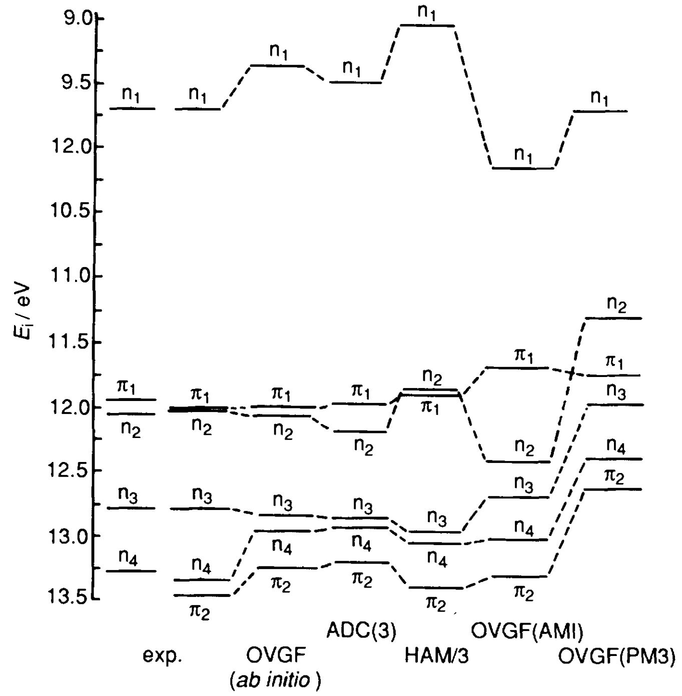


Fig. 1 Comparison of the experimental ionization energies of 1,2,4,5-tetrazine (**1a**) with those obtained by several theoretical methods (data from Table 1)

previous semiempirical and *ab initio* calculations. In general, our discussion of the PE spectra will be short, as for most of the compounds studied here the PES were already analysed in detail in previous studies. We will concentrate on cases in which our calculations lead to interpretations of the experimental spectra which are different from those in the literature, and on comparisons of the reliability of the different theoretical methods.

Computational Method

The OVGF method is described in detail in ref. 3. The application of this method for the case of semiempirical wavefunctions has been discussed in refs. 4 and 5 and a computer program implementing the method is available from *QCPE*.[9] Here we outline briefly some of the main points and the interested reader is referred to refs. 3–5 for more details.

The OVGF technique was used with the self-energy part extended to include third-order perturbation corrections.[3] The higher-order contributions were estimated by the renormalization procedure. The actual expression used to calculate the self-energy part, $\Sigma_{pp}(w)$, chosen in the diagonal form, is given in eqn. (1), where $\Sigma^{(2)}_{pp}$ and $\Sigma^{(3)}_{pp}$ are the second- and third-order corrections, and A is the screening factor accounting for all the contributions of higher orders.

$$\Sigma_{pp}(w) = \Sigma^{(2)}_{pp}(w) + (1 + A)^{-1}\Sigma^{(3)}_{pp}(w). \qquad (1)$$

The particular expression which was used for the second-order corrections is given in eqn. (2).

$$\Sigma^{(2)}_{pp}(w) = \sum_{a}\sum_{i,j}\frac{(2V_{paij} - V_{paji})V_{paij}}{w + \varepsilon_a - \varepsilon_i - \varepsilon_j} + \sum_{a,b}\sum_{i}\frac{(2V_{piab} - V_{piba})V_{piab}}{w + \varepsilon_i - \varepsilon_a - \varepsilon_b}. \qquad (2)$$

where

$$V_{pqrs} = \iint \varphi^*_p(1)\varphi^*_q(2)(1/r_{12})\varphi_r(1)\varphi_s(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

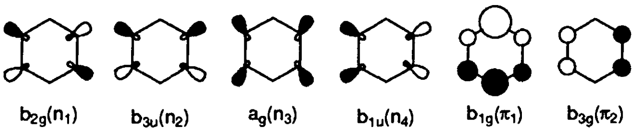


Fig. 2 Schematic drawing of the six highest MOs of 1,2,4,5-tetrazine (**1a**)

In eqn. (2), i and j denote occupied orbitals, a and b denote virtual orbitals, p denotes orbitals of unspecified occupancy and ε denotes the orbital energy. The equations were solved by means of an iterative procedure which is given in eqn. (3).

$$w_p^{i+1} = \varepsilon_p + \Sigma_{pp}(w^i) \qquad (3)$$

The SCF energies and the corresponding integrals calculated by a semiempircal method (AM1 or PM3) were taken as the zeroth approximation and all MOs were included in the active space for the OVGF calculations. The expressions used for $\Sigma^{(3)}_{pp}$ and A are give in ref. 3(*b*).

The geometries of all compounds under consideration were fully optimized with the AM1 and PM3 semiempirical molecular orbital methods.

Results and Discussion

The Parent 1,2,4,5-Tetrazine (s-*Tetrazine*), **1a**.—The PE spectrum of the parent 1,2,4,5-tetrazine (**1a**) was first determined by Heilbroner *et al.*[11] and by Fridh *et al.*[12] who both concluded that the lowest E_i (at 9.72 eV) corresponds to ionization of a 'lone-pair' electron on nitrogen.[11,12] This band is well separated from a group of five very close-lying bands between 12 and 14 eV (Fig. 1).

The results of our calculations for the six highest ionization potentials of the parent *s*-tetrazine **1a** are presented in Table 1 together with the experimental data,[12,13] as well as previous computational data.[13,14] For convenience the results are also displayed graphically in Fig. 1, together with the experimental data. A schematic drawing of these molecular orbitals is given in Fig. 2.

The first point to note in Table 1 is the very good general agreement between the experimental ionization potentials and the OVGF(PM3) and OVGF(AM1) calculations. The OVGF(AM1) calculations with an average deviation of 0.3 eV from the experimental E_i values are somewhat superior to the OVGF(PM3) calculations, except for the first E_i which is better reproduced by OVGF(PM3). The major failure of the OVGF(AM1) calculations is in predicting the b_{1g}–b_{3u} splitting which is 0.0–0.2 eV experimentally, but 0.8 eV computationally. The experimental–theoretical agreement with the OVGF(AM1) method is only slightly inferior to that obtained by the much more elaborate and costly OVGF (*ab initio*) and ADC(3) calculations.[14] The HAM/3 method also gives quite satisfactory results for **1a** (Table 1). It is noteworthy that the first ionization potential of **1a**, which at the *ab initio* SCF level is 1.65 eV too high (1.3 eV by AM1), is by PM3 only 0.6 eV higher than the experimental value.

The OVGF (semiempirical) results for **1a** converge very fast (Table 2), so that in general it is sufficient to expand the perturbation corrections to the self-energy part only up to second-order. Further expansion to third-order and to the complete expression for $\Sigma_{pp}(w)$ has only a small effect on the calculated ionization energies (Table 2). This observation is important for larger molecules, *i.e.* for the disubstituted derivatives of **1**, where full OVGF calculations are not always feasible. Similarly, it was found that the inclusion of perturbation corrections higher than second-order did not improve the OVGF(AM1) calculated ionization energies of pyridines and

Table 1 Experimental and calculated ionization energies (eV) of *s*-tetrazine (**1a**)

MO[a]	Expt.		SCF (*ab initio*)[b]	OVGF (*ab initio*)[b]	ADC(3)[b]	HAM/3[c]	AM1	OVGF-(AM1)	PM3	OVGF(PM3)
n_1 (b_{2g})	9.7[d]	9.7[c]	11.36	9.42	9.54	9.08	11.03	10.18	10.30	9.73
π_1 (b_{1g})	11.9	12.05	11.98	12.05	12.01	11.89[f]	11.76	11.68	11.82	11.74[f]
n_2 (b_{3u})	12.1	12.05	14.47	12.11	12.20	11.85[f]	13.40	12.47	12.06	11.36[f]
n_3 (a_g)	12.8	12.8	14.52	12.82	12.86	12.96	13.86[f]	12.72	12.62	11.98
n_4 (b_{1u})	13.3	13.4	15.36	12.97	12.95	13.10	14.14[f]	13.05	13.20[f]	12.41
π_2 (b_{3g})		13.5	13.50	13.23	13.19	13.42	13.78[f]	13.34	12.93[f]	12.69
$\bar{\Delta}$[e]			1.32	0.18	0.19	0.25	0.84	0.30	0.28	0.59

[a] Symmetries in D_{2h} point group are given in parentheses. [b] From ref. 14. [c] From ref. 13. [d] From ref. 12. [e] The mean deviation for all orbitals of the calculated ionization energies from the experimental values (eV). [f] The relative ordering of this orbital is different from the ordering according to the experimental and the ADC(3) interpretations.

Table 2 Dependence of the ionization energies of *s*-tetrazine (**1a**) on the expansion order of the self-energy part of the OVGF method[a]

MO	PM3	OVGF(PM3)		
		2nd[b]	3rd[c]	Full[c]
n_1	10.3	9.73	9.78	9.76
π_1	11.82	11.74	11.74	11.74
n_2	12.06	11.36	11.37	11.37
n_3	12.62	11.98	12.07	12.00
n_4	13.20	12.41	12.44	12.44
π_2	12.93	12.69	12.69	12.69

[a] See eqn. (1). [b] See eqn. (2). [c] For the expression used, see ref. 3(*b*).

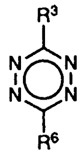
azoles.[4] On the other hand, when SCF *ab initio* calculations were used as the zeroth approximation it was found that a good quantitative agreement with experiment is achieved only if the complete expansion of the self-energy part is included in the calculations.[14]

3,6-*Disubstituted* 1,2,4,5-*Tetrazines* (s-*Tetrazines*, **1**).—The PE spectra of 3,6-disubstituted *s*-tetrazines have recently attracted considerable interest.[11-16]

Gleiter *et al.* have recently undertaken a PE(HeI) study of an extensive series of disubstituted *s*-tetrazines (including **1a**–**r**). In particular, they were interested in the possibility of influencing the ionization energies of *s*-tetrazines by attaching, at the 3- and 6-positions, π-electron-donating or π-electron-accepting substituents and, more specifically, in reversing the level ordering exhibited by the parent molecule (Table 1).[13] The interpretation of the PES was based on the comparison of the experimental spectra with the results of HAM/3 calculations.[13] According to Gleiter's study the HOMO of disubstituted *s*-tetrazines has π-character with strong electron-donating substituents whereas with alkyl or electron-accepting groups it is n-type (see Fig. 2).[13] This change in the symmetry of the HOMO is interesting because it may have consequences for the reactivity of tetrazines towards electrophiles, such as metal fragments.[13] Fisher *et al.* studied a similar group of disubstituted *s*-tetrazines using electron spin resonance and cyclic voltammetry in order to try to detect this crossover in the HOMO wavefunction from σ- to π-character.[16] These authors have reached conclusions similar to those of Gleiter and co-workers[13] and have detected the switch in the HOMO symmetry in compounds substituted with two strong π-donors, such as mercapto (**1d**), aziridine (**1g**) and combinations of amino and thio groups (**1p**).[16]

More recently Cederbaum *et al.* studied computationally the PES in the low-energy valence region of several of these compounds (*i.e.* **1a**; **1**, $R^3 = R^6 = OH$; **1c**; **1**, $R^3 = R^6 = SH$ and **1**, $R^3 = R^6 = NH_2$). These authors used the ADC(3)[3b] approximation coupled with *ab initio* SCF calculations (using a relatively large polarized basis set) and the OVGF methods.[14] This study confirmed that in *s*-tetrazines substituted with two strong electron-donating groups the first line of the PES is of π-symmetry, and the general agreement with experiment was good to excellent.[14] However, Cederbaum's study also demonstrated that within the SCF approximation the one-particle model of ionization is, to a large extent, inadequate and that many-body effects must be included in the calculations in order to interpret correctly the PE spectra (in particular the n_2 ionization) of these compounds.

We now discuss in detail the results of our calculations for the eighteen 3,6-disubstituted *s*-tetrazines **1a**–**r** and compare our results [AM1, PM3, OVGF(AM1), OVGF(PM3)] with previous theoretical studies[11-16] and with experiment.[13]



	$R^3 = R^6$				R^3	R^6
1a	H	**1g**	aziridin-1-yl	**1m**	$NHCH_3$	OCH_3
1b	CH_3	**1h**	azetan-1-yl	**1n**	$N(CH_3)_2$	OCH_3
1c	OCH_3	**1i**	Cl	**1o**	pyrrolidin-1-yl	OCH_3
1d	SCH_3	**1j**	F	**1p**	$NHCH_3$	SCH_3
1e	$NHCH_3$	**1k**	CN	**1q**	$N(CH_3)_2$	SCH_3
1f	$N(CH_3)_2$	**1l**	CF_3	**1r**	pyrrolidin-1-yl	SCH_3

(*a*) 3,6-*Dimethoxy*-s-*tetrazine* (**1c**). The 3,6-dimethoxy-*s*-tetrazine **1c** is discussed separately from the other disubstituted *s*-tetrazines because it is the only compound for which both experimental data and OVGF (*ab initio*) calculations are available. The results of the OVGF(PM3) and the OVGF-(AM1) calculations for 3,6-dimethoxy-*s*-tetrazine (**1c**) are presented in Table 3 together with the experimental ionization energies and other available calculated data.[13,14]

As mentioned above, Cederbaum *et al.* have studied in detail the PES of **1c** using both the OVGF (*ab initio*) and the ADC(3) methods.[14] They found that the *ab initio* SCF approximation is, to a large extent, inadequate for the interpretation of the PES of **1c**. The OVGF model is much more successful. The ionization energies are shifted on average by about 1–3 eV in the OVGF results owing to the inclusion of correlation and relaxation effects and for the four first ionizations the average deviation between the experimental ionization potentials and the ADC(3) calculations is only 0.27 eV, but for the π_2-level it is as high as 0.6 eV.[14]

The HAM/3 method reproduces correctly the ordering of the energy levels of **1c**; however the quantitative theoretical–experimental agreement is rather poor. The average deviation

Table 3 Experimental and calculated ionization energies (eV) of dimethoxy-*s*-tetrazine (**1c**)

MO	Expt.[a]	OVGF (*ab initio*)[b]	ADC(3)[b]	HAM/3[a]	AM1	OVGF(AM1)	PM3	OVGF(PM3)
n_1	9.05	8.76	9.09	8.09	10.64[d]	9.68[d]	10.15[d]	9.46
π_1	9.6	9.44	9.56	9.23	9.92[d]	9.48[d]	10.01[d]	9.65
n_2	11.2	—	11.63	10.77	13.24[d]	12.39[d]	11.96	11.13
π_2	11.8	12.25	12.37	11.45	12.39[d]	11.39[d]	12.27	11.43
$\bar{\Delta}$[c]		—	0.27	0.53	1.14	0.59	0.69	0.22

[a] From ref. 13. [b] From ref. 14. [c] The mean deviation for all orbitals of the calculated ionization energies from the experimental values (eV). [d] The relative ordering of this orbital is different from the ordering according to the experimental and the ADC(3) interpretations.

from the experimental E_i values is 0.53 eV and for the first ionization potential it is 1.0 eV.[13]

As with the SCF (*ab initio*) calculations,[14] SCF(AM1) and SCF(PM3) calculations also show large deviations from the experimental values, in particular for the n-type MOs. The deviations from experiment are somewhat smaller with PM3 than with AM1. Furthermore, with both methods the ordering of the n- and π-type levels is inverted (Table 3). The AM1 method overestimates so strongly the ionization potentials from the n-levels that the corrections introduced by the OVGF method are too small to compensate this inherent deficiency and the OVGF(AM1) method also fails to reproduce even qualitatively the correct ordering of the orbital energy levels of **1c** (Table 3).

On the other hand, as the errors of the SCF(PM3) calculations are smaller than those of the SCF(AM1) method, the corrections introduced by the OVGF method in this case are sufficient, and the OVGF(PM3) calculations do predict correctly the ordering of the orbital levels in **1c** [*i.e.* the same as in the ADC(3) and HAM/3 calculations]. The average deviation of the OVGF(PM3) calculated ionization energies of **1c** from experiment is only 0.22 eV; comparable (even slightly lower) to that achieved by the OVGF (*ab initio*) calculations.

We now discuss the PE spectra of the other sixteen 3,6-disubstituted *s*-tetrazines **1b** and **1d–r**.

(*b*) *Other* 3,6-*disubstituted* s-*tetrazines* (**1**). 3,6-Disubstituted *s*-tetrazines (**1**), especially those with strong π-conjugating substituents, present, as described above, a special theoretical challenge owing to the breakdown of the one-particle molecular orbital model.[14] The calculated [PM3, AM1, HAM/3, OVGF(AM1) and OVGF(PM3)] and the experimental ionization energies (usually the first four) of 3,6-disubstituted *s*-tetrazines with first-row substituents are presented in Table 4 and those with second-row substituents are listed in Table 5. HAM/3 results are reported only for first-row substituents, as this method is not parametrized for second-row elements.

The HAM/3 method predicts that the first ionization of the first-row substituted *s*-tetrazines occurs from an n-type orbital (Table 4). In contrast, experimental studies show that for most derivatives the first ionization occurs from π-type orbital (Table 4). The reason for this failure is that the ionization potentials from n_1 (Fig. 2) calculated with HAM/3 are generally lower by *ca.* 1.0 eV than the experimental values, while the deviations for the π_1-orbital (Fig. 2) are considerably smaller. Consequently HAM/3 predicts incorrectly that n_1 lies above π_1 in **1g**, **1m**, **1n** and **1o** and that in **1e**, **1f** and **1h** the π_1 and n_1 levels are nearly degenerate. For the 13 *s*-tetrazines studied by HAM/3, the average deviation from experiment is 0.4 eV, and for six of these molecules the predicted ordering of the energy levels is wrong. We conclude that HAM/3 calculations are entirely unsatisfactory for the prediction of the ionization potentials of substituted *s*-tetrazines.

The conclusions drawn above for 3,6-dimethoxy-*s*-tetrazine (**1c**), namely that both the SCF(AM1) and the OVGF(AM1) methods do not properly describe, either qualitatively or quantitatively, the ionization energies are also valid for other 3,6-disubstituted *s*-tetrazines. For the 18 *s*-tetrazines **1a–r** the average experimental–theoretical deviation for the OVGF-(AM1) calculations is 0.44 eV, and for ten of these compounds the predicted ordering of the energy levels is wrong. The OVGF(AM1) method gives satisfactory results only for **1i** and **1k**, but this is probably coincidence.

As with the AM1 method, SCF(PM3) calculations also give poor results; the mean deviation from the experimental data is 0.76 eV (18 compounds) and in four of these compounds (**1b**, **1c**, **1d**, **1i**) the calculated level ordering is the reverse of the experimentally determined one.

In contrast with these failures very satisfactory results are obtained with the OVGF(PM3) calculations. For 17 out of the 18 *s*-tetrazines studied (excluding **1a**) the experimental orbital ordering is correctly reproduced. Furthermore, the average experimental–calculated difference is only 0.39 eV (18 compounds). The assignments predicted by OVGF(PM3) for **1d**, **1i** and **1p–1r** correspond to the empirical assignments made in ref. 13. For **1a–c** and **1i–l** the OVFG(PM3) calculations find that the HOMO is an n-type MO. This is in agreement with EPR studies of the radical cations of these molecules which also concluded that the SOMO is σ-type, confined to the four nitrogens of the heterocycle.[16] In the amino-substituted *s*-tetrazines **1f** and **1h** the EPR study revealed a π-radical with the unpaired electron mainly localized at the amine nitrogens, again in agreement with the OVGF(PM3) calculations (Table 4). According to the OVGF(PM3) calculations the diamino derivatives **1e–h** and the amino, methoxy derivatives **1m–o** have a π-type HOMO, with the highest orbital coefficient localized on the amino nitrogen atoms. The amino, thio derivatives **1p–r** also possess a π-type HOMO which is delocalized over the sulfur (orbital coefficient 0.65) and the amino nitrogen (orbital coefficient 0.45). In only three cases, the parent molecule **1a** (see the discussion above), the dicyano derivative **1k** and the dichloro derivative **1i** is the agreement between the calculations and the experiment worse at the OVGF(PM3) level than at the SCF level. For the dichloro *s*-tetrazine **1i** unsatisfactory results were obtained with the SCF(PM3) and the OVGF(PM3) methods, the mean deviation of the calculated three highest ionization potentials from the experimental data being 0.6 eV for SCF(PM3) and 0.96 eV for OVGF(PM3). Similarly, for the dicyano *s*-tetrazine **1k** this value is 0.62 eV for OVGF(PM3) and 0.74 eV for the HAM/3 calculations. For both **1i** and **1k** the mean deviation is smaller with OVGF(AM1) than with OVGF(PM3), but this is probably coincidence.

In summary OVGF(PM3) calculations fully support the conclusions of previous studies that strong electron-donating groups lead to inversion of the ordering of the highest two orbitals (*i.e.* π_1 above n_1), relative to their ordering in the parent *s*-tetrazine and in *s*-tetrazines substituted with alkyl groups or electron-accepting substituents (where π_1 is below n_1).[13,14] According to our calculations this interesting reversal in orbital

Table 4 Experimental and calculated energies (eV) of 3,6-disubstituted *s*-tetrazines (**1**)

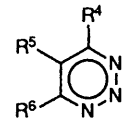
Molecule	MO	Expt.[a]	PM3	OVGF-(PM3)	Δ[b]	AM1	OVGF-(AM1)	Δ[b]	HAM/3[a]	Δ[b]
1b	n_1	9.08	10.02	9.40	0.32	10.52	9.63	0.55	8.28	0.80
$R^3 = R^6 = CH_3$	π_1	10.72	10.84	10.68	0.04	10.69	10.46	0.26	10.55	0.17
	n_2	11.15	11.82	11.07	0.08	13.21	12.21	1.06	11.08	0.07
	n_3	11.98	12.67	11.93	0.05	13.41	12.40	0.42	12.10	0.12
	n_4	12.0	12.91[d]	12.09	0.09	13.65[d]	12.53	0.53	12.16	0.16
	π_2	12.66	12.76[d]	12.41	0.25	13.59[d]	13.03		12.56	0.12
	n_5					13.91[d]	13.03	0.37		
	π_3	13.50	13.78	13.22	0.28	13.80	13.13	0.37	13.41	0.09
	$\bar{\Delta}^c$		0.53	0.16		1.14	0.43		0.22	
1e	π_1	8.00	8.68	8.24	0.24	8.49	8.0	0.0	7.62[d]	0.38
$R^3 = R^6 = NHCH_3$	n_1	8.50	9.77	9.06	0.56	10.12	9.14	0.64	7.57[d]	0.93
	π_2	9.9	10.37	9.55	0.35	10.73	9.67	0.23	9.57	0.33
	n_2	10.5	11.56	10.71	0.21	12.24[e]	11.44[e]	0.96	10.63	0.27
	$\bar{\Delta}^c$		0.87	0.34		1.17	0.46		0.48	
1f	π_1	7.5	8.51	7.99	0.49	8.03	7.45	0.05	7.40[d]	0.1
$R^3 = R^6 = N(CH_3)_2$	n_1	8.2	9.64	8.99	0.69	9.89	8.85	0.65	7.37[d]	0.83
	π_2	9.2	10.03	9.17	0.03	10.16	9.05	0.15	9.24	0.04
	n_2	9.5	11.47	10.56	1.06	12.56[d]	11.62[d]	2.12	10.03	0.53
	π_3	11.05	11.88	11.22	0.17	11.93[d]	11.08[d]	0.03	11.04[f]	0.01
	$\bar{\Delta}^c$		1.22	0.51		1.42	0.6		0.31	
1g	π_1	8.8	9.39	8.93	0.13	9.50	8.94	0.16	8.87[d]	0.07
$R^3 = R^6$ = aziridin-1-yl	n_1	8.8	9.96	9.21	0.41	10.34	9.33	0.53	7.82[d]	0.98
	π_2	10.2	10.72	9.94	0.26	11.22	10.17	0.03	10.15	0.05
	n_2	10.6	11.79	10.90	0.30	12.53[e]	11.62[e]	1.02	10.67	0.07
	$\bar{\Delta}^c$		0.87	0.27		1.30	0.44		0.29	
1h	π_1	7.7	8.67	8.15	0.45	7.85	7.28	0.42	7.27[d]	0.43
$R^3 = R^6$ = azetan-1-yl	n_1	8.2	9.70	8.94	0.74	9.74	8.68	0.48	7.10[d]	1.1
	π_2	9.3	10.16	9.32	0.02	10.12	9.00	0.3	8.96	0.34
	n_2	9.4	11.53	10.61	1.21	11.56	10.82	1.42	9.87	0.47
	$\bar{\Delta}^c$		1.35	0.60		1.17	0.65		0.59	
1j	n_1	10.6	10.95	10.36	0.24	11.32	10.45	0.15	9.89	0.71
$R^3 = R^6 = F$	π_1	12.0	11.79	11.61	0.39	11.31	11.06	0.94	12.07	0.07
	n_2	12.5	12.78	12.05	0.45	14.62	13.38	0.88	12.77	0.27
	n_3	13.5	13.91[d]	13.08	0.42	15.18[d]	13.94	0.44		
	π_2		13.76[d]	13.40	0.10	14.69[d]	14.08	0.58	14.19	0.69
	$\bar{\Delta}^c$		0.27	0.37		1.28	0.62		0.43	
1k	n_1	10.8	11.07	10.34	0.46	11.74	10.75	0.05	9.55	1.25
$R^3 = R^6 = CN$	π_1	12.08	11.88	11.64	0.44	11.96	11.64	0.44	11.66	0.42
	n_2	12.85	12.87	12.01	0.84	14.46	13.24	0.39	12.37	0.48
	n_{CN}	13.4	13.15	12.63	0.77	14.75[f]	13.51[f]	0.11	12.61[g]	0.79
	$\bar{\Delta}^c$		0.19	0.62		1.01	0.25		0.74	
1l	n_1	10.6	11.38	10.78	0.18	12.13	11.19	0.59	9.75	0.85
$R^3=R^6=CF_3$	n_2	12.9	13.09	12.36	0.54	13.83[d]	12.84[d]	0.06	12.57	0.33
	π_1	12.9	13.13	12.93	0.03	12.93[d]	12.61[d]	0.29	12.69	0.21
	n_3	13.6	13.78	13.05	0.55	14.31	13.26	0.34	13.52	0.08
	$\bar{\Delta}^c$		0.34	0.32		0.8	0.32		0.37	
1m	π_1	8.55	9.17	8.74	0.19	9.12	8.64	0.09	8.30[d]	0.25
$R^3 = NHCH_3$	n_1	8.55	9.94	9.23	0.68	10.35	9.38	0.83	7.80[d]	0.75
$R^6 = OCH_3$	π_2	10.85	11.32	10.56	0.29	11.57	10.57	0.28	10.59	0.26
	n_2	10.85	11.75	10.89	0.04	12.77[e]	11.98[e]	1.13	10.67	0.18
	$\bar{\Delta}^c$		0.96	0.30		1.25	0.58		0.36	
1n	π_1	8.25	9.02	8.52	0.27	8.81	8.26	0.01	8.13[d]	0.12
$R^3 = N(CH_3)_2$	n_1	8.5	9.87	9.14	0.64	10.22	9.22	0.72	7.66[d]	0.84
$R^6 = OCH_3$	π_2	10.5	11.13	10.38	0.12	11.28	10.29	0.21	10.34	0.16
	n_2	10.6	11.67	10.81	0.21	12.66[e]	11.84[e]	1.25	10.44	0.16
	$\bar{\Delta}^c$		0.96	0.31		1.29	0.55		0.32	
1o	π_1	8.1	8.90	8.35	0.25	8.89	8.27	0.17	7.96[d]	0.14
R^3 = pyrrolidin-1-yl	n_1	8.5	9.82	9.07	0.57	10.23	9.21	0.71	7.47[d]	1.03
$R^6 = OCH_3$	π_2	10.4	11.01	10.25	0.15	11.09	10.13	0.27	10.12	0.28
	n_2	10.6	11.64	10.81	0.21	11.66[e]	11.11[e]	0.51	10.25	0.35
	$\bar{\Delta}^c$		0.94	0.29		1.07	0.41		0.45	

[a] From ref. 13. [b] The difference, for a particular orbital, between the experimental and the calculated data (eV). [c] The mean deviation for all orbitals of the calculated ionization energies from the experimental values (eV). [d] The relative ordering of this orbital is different from the order based on the experimental interpretation[13] and on the OVGF(PM3) calculations. [e] π_3-type MO. [f] n_3-type MO. [g] π_{CN}-type MO.

Table 5 Experimental and calculated ionization energies (eV) of S- and Cl-containing 3,6-disubstituted *s*-tetrazines

Molecule	MO	Expt.[a]	PM3	OVGF-(PM3)	Δ^b	AM1	OVGF-(AM1)	Δ^b
1d	π_1	8.63	8.99	8.54	0.09	8.34	7.88	0.75
$R^3 = R^6 = SCH_3$	n_1	9.0	10.12[d]	9.30	0.30	10.54[d]	9.48[d]	0.48
	π_2	9.79	10.10[d]	9.51	0.28	9.85[d]	9.13[d]	0.66
	n_2	10.4	11.88	11.03	0.63	11.95	11.22	0.82
	$\bar{\Delta}^c$		0.82	0.32		0.86	0.68	
1i	n_1	10.1	10.35[d]	9.68	0.42	11.06[d]	10.15	0.05
$R^3 = R^6 = Cl$	π	11.0	10.29[d]	9.96	1.04	10.96[d]	10.64	0.36
	n_{Cl}	12.16	11.33	10.74	1.42	13.12	12.36	0.20
	$\bar{\Delta}^c$		0.60	0.96		0.65	0.20	
1p	π_1	8.3	8.75	8.31	0.01	8.27	7.80	0.5
$R^3 = NHCH_3, R^6 = SCH_3$	n_1	8.6	9.90	9.14	0.54	10.31	9.31	0.71
	π_2	9.8	10.22	9.54	0.26	10.33	9.49	0.31
	n_2	9.9	11.67	10.78	0.88	11.68	11.06	1.16
	$\bar{\Delta}^c$		0.99	0.42		1.01	0.67	
1q	π_1	8.0	8.47	8.0	0.0	8.13	7.65	0.35
$R^3 = N(CH_3)_2, R^6 = SCH_3$	n_1	8.5	9.74	8.95	0.45	10.20[d]	9.17[d]	0.67
	π_2	9.4	9.94	9.24	0.16	10.04[d]	9.16[d]	0.24
	n_2		11.51	10.59		11.60	10.97	
	$\bar{\Delta}^c$		0.75	0.20		0.82	0.42	
1r	π_1	7.9	8.56	8.06	0.16	8.13	7.63	0.27
R^3 = pyrrolidin-1-yl	n_1	8.4	9.77	8.96	0.56	10.17[d]	9.13[d]	0.73
$R^6 = SCH_3$	π_2	9.3	9.94	9.19	0.11	9.99[d]	9.05[d]	0.25
	n_2		11.55	10.61		11.58	10.95	
	$\bar{\Delta}^c$		0.89	0.28		0.90	0.42	

[a] From ref. 13. [b] The difference, for a particular orbital, between the experimental and the calculated data (eV). [c] The mean deviation for all orbitals of the calculated ionization energies from the experimental values. [d] The relative ordering of this orbital is different from the order based on the experimental data[13] and on the OVGF(PM3) calculations.



	R^4	R^5	R^6
2a	H	H	H
2b	CH_3	H	H
2c	H	CH_3	H
2d	CH_3	CH_3	H
2e	CH_3	H	CH_3
2f	CH_3	CH_3	CH_3

ordering occurs for bis-dialkylamino substitution (*i.e.* **1e–h**), for combinations of methoxy and alkylamino groups (**1m–o**), for bis-methylthio substitution (**1d**) and for combinations of mercapto and alkylamino groups (**1p–r**).

(*c*) *Calculated geometries.* Although the major issue of this paper is the PES of substituted triazines and tetrazines it is probably appropriate also to comment on the performance of the AM1 and PM3 methods for calculating the equilibrium geometries of these molecules. Unfortunately, the comparison is relatively limited as experimental geometries are available only for four *s*-tetrazines, **1a–c** and **1g**,[17] and to the best of our knowledge such data is not available for triazines. Both AM1 and PM3 calculate C–N bonds which are too long by *ca.* 0.025 Å and N–N bonds which are too short by *ca.* 0.03 Å in comparison with the X-ray data of **1a–c** and **1g**.[17] This deficiency of the AM1 and PM3 methods was noted previously in other molecules with C–N or N–N bonds.[8] The calculated C–O bond length in **1c** is longer by 0.026 Å (PM3) and 0.044 Å (AM1) than the experimental value, again a deficiency of these methods noted previously for other C–O bonds.[8]

According to the calculations the effect of substituents on the C–N and N–N bond lengths is relatively small, in agreement with the available X-ray structures. Thus, the range of the C–N bond lengths in the 18 *s*-tetrazines **1a–r** is 1.372–1.384 Å by PM3 and 1.396–1.416 Å by AM1, and the range of the N–N bond distances is 1.272–1.286 Å by PM3 and 1.257–1.270 Å by AM1. Only in two molecules are the calculated bond distances slightly out of this range. In the parent *s*-tetrazine (**1a**) the calculated C–N distance is 1.364 Å by PM3 and 1.384 Å by AM1, and the calculated N–N bond length is 1.290 Å by PM3 and 1.279 Å by AM1. Similarly, in the CF_3-disubstituted *s*-tetrazine **1l**, the calculated C–N bond length is 1.364 Å (PM3) and 1.384 Å (AM1), and the calculated N–N bond length is 1.290 Å (PM3) and 1.276 Å (AM1).

The CNN and NCN bond angles are calculated by both methods to be in the range 117.7–121.2° and 118.2–123.9°, respectively.

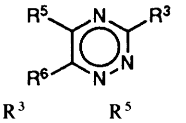
1,2,3-*Triazines* (**2**).—The OVGF(AM1) and OVGF(PM3) methods were applied to the parent 1,2,3-triazine **2a** and to several methyl-substituted derivatives **2b–f**. Our calculated data and the available experimental E_i values[18] are collected in Table 6.

All the theoretical methods including the two OVGF methods predict the same orbital ordering for the parent 1,2,3-triazine, *i.e.* n_1 (lowest E_i), n_2, π_1, π_2 and n_3 (highest E_i). However, the various theoretical methods have different predictions regarding the effect of methyl substitution on this orbital ordering. The energy difference between the n_2 and the

Table 6 Experimental and calculated ionization energies (eV) of 1,2,3-triazine (**2a**) and its mono-, di- and tri-methyl derivatives

Molecule	MO	Expt.[a]	PM3	OVGF(PM3)	Δ^c	AM1	OVGF-(AM1)	Δ^c
2a	n_1	10.0	10.48	9.87 (9.60)[b]	0.13 (0.4)[b]	11.30	10.35	0.35
$R^4 = R^5 = R^6 = H$	n_2	10.4	10.85	10.21 (10.3)[b]	0.19 (0.1)[b]	11.76[e]	10.87	0.47
	π_1	11.6	11.65	11.51 (11.6)[b]	0.09 (0.0)[b]	11.66[e]	11.44	0.16
	π_2	12.0	11.69	11.53 (11.7)[b]	0.47 (0.3)[b]	11.98	11.67	0.33
	n_3	13.1	13.31	12.46 (13.3)[b]	0.64 (0.2)[b]	14.02	12.87	0.23
	$\bar{\Delta}^d$		0.30	0.30 0.20[b]		0.74	0.31	
2b	n_1	9.7	10.37	9.72	0.02	11.17	10.19	0.49
$R^4 = CH_3$	n_2	10.1	10.81	10.11	0.01	11.61[e]	10.68	0.58
$R^5 = R^6 = H$	π_1	11.1	11.15	10.95	0.15	11.18[e]	10.89	0.21
	π_2	11.6	11.60	11.40	0.20	11.75	11.42	0.18
	n_3	12.7	13.22	12.36	0.34	13.90	12.72	0.02
	$\bar{\Delta}^d$		0.39	0.14		0.88	0.30	
2c	n_1	9.8	10.43	9.78	0.02	11.14[e]	10.18	0.38
$R^5 = CH_3$	n_2	10.3	10.75	10.08	0.22	11.73[e]	10.78	0.48
$R^4 = R^6 = H$	π_1	11.0	11.12	10.94	0.06	11.05[e]	10.79	0.21
	π_2	11.8	11.63	11.42	0.38	11.91	11.56	0.24
	n_3	12.8	13.21	12.33	0.47	13.86	12.72	0.08
	$\bar{\Delta}^d$		0.36	0.23		0.80	0.28	
2d	n_1	9.5	10.32	9.64	0.14	11.03[e]	10.03	0.53
$R^4 = R^5 = CH_3$	n_2	9.9	10.71	9.99	0.09	11.54[e]	10.59[e]	0.69
$R^6 = H$	π_1	10.6	10.83	10.60	0.0	10.74[e]	10.43[e]	0.17
	π_2	11.3	11.38	11.12	0.18	11.59	11.19	0.11
	n_3	12.6	13.13	12.26	0.34	13.76	12.67	0.07
	$\bar{\Delta}^d$		0.49	0.15		0.95	0.31	
2e	n_1	9.5	10.26	9.59	0.09	11.08[e]	10.04	0.54
$R^4 = R^6 = CH_3$	n_2	9.9	10.75	10.01	0.11	11.45[e]	10.51	0.61
$R^5 = H$	π_1	10.8	11.0	10.75	0.05	11.05[e]	10.73	0.07
	π_2	11.0	11.15	10.92	0.08	11.20	10.80	0.20
	n_3	12.5	13.17	12.27	0.23	13.78	12.59	0.09
	$\bar{\Delta}^d$		0.53	0.11		0.97	0.30	
2f	n_1	9.4	10.21	9.51	0.11	10.93[e]	9.88	0.48
$R^4 = R^5 = R^6 = CH_3$	n_2	9.7	10.65	9.89	0.19	11.36[e]	10.40[e]	0.7
	π_1	10.3	10.71	10.45	0.15	10.57[e]	10.22[e]	0.08
	π_2	10.9	10.94	10.65	0.25	11.14	10.70	0.20
	n_3	12.4	13.11	12.18	0.22	13.21	12.61	0.21
	$\bar{\Delta}^d$		0.58	0.18		0.90	0.33	

[a] From ref. 18. [b] HAM/3 results from ref. 18. [c] The difference, for a particular orbital, between the experimental and the calculated data (eV). [d] The mean deviation for all orbitals of the calculated ionization energies from the experimental values (eV). [e] The relative ordering of this orbital is different from the order based on experimental data [18] and on the OVGF(PM3) calculations.



	R^3	R^5	R^6
3a	H	H	H
3b	CH_3	H	H
3c	H	CH_3	H
3d	H	H	CH_3
3e	CH_3	CH_3	H
3f	H	CH_3	CH_3
3g	CH_3	CH_3	CH_3

π_1 levels in the parent 1,2,3-triazine (**2a**) is *ca.* 1.0 eV according to experiment and according to PM3, HAM/3 and OVGF-(PM3) calculations. Methyl substitution lowers the E_i of both n_2 and π_1 MOs (by *ca.* 0.3–0.6 eV per methyl, see Table 6 and ref. 18) and the orbital order in the methyl-substituted 1,2,3-triazines remains therefore the same as in **2a** (see the experimental results in Table 6). AM1 calculations fail to predict even the correct ordering of the energy levels in methyl-substituted 1,2,3-triazines, *i.e.* it predicts that π_1 is higher in energy than n_2 (see for example **2b**, Table 6). PM3 calculations give the correct qualitative ordering of the orbital energies, but the average deviation from the experimental results is considerable (0.44 eV for six compounds). OVGF(AM1) calculations give better results than the SCF(AM1) calculations (the average deviation from experiment is 0.29 eV), but this method fails to reproduce the correct ordering of the orbital energy levels in the dimethyl and trimethyl derivatives **2d** and **2f**, respectively.

As with the *s*-tetrazines, OVGF(PM3) is also the most reliable method for predicting the E_i values for 1,2,3-triazines. The average deviation between the calculated and the experimental ionization potentials is only 0.18 eV (for six compounds). OVGF(PM3) calculations agree with the experimental conclusions of Glieter *et al.* that methyl, dimethyl and trimethyl substitution of 1,2,3-triazines does not change the ordering of the molecular orbitals, which remain the same as in the parent 1,2,3-triazine, **2a**.

1,2,4-*Triazines* (**3**).—The results of the calculations for 1,2,4-triazine (**3a**) and its various methyl-substituted derivatives **3b**–**g**

Table 7 Experimental and calculated ionization energies (eV) of 1,2,4-triazine (**3a**) and its mono-, di- and tri-methyl derivatives

Molecule	MO	Expt.[a]	PM3	OVGF-(PM3)	Δ[b]	AM1	OVGF-(AM1)	Δ[b]
3a	n_1	9.61	10.14	9.54	0.07	10.70	9.84	0.23
$R^3 = R^5 = R^6 = H$	π_1	11.30	11.19	11.08[d]	0.22	11.08	10.92	0.38
	n_2	11.82	11.74	11.05[d]	0.77	12.77[d]	11.81	0.01
	n_3	12.14	12.30[a]	11.58	0.56	13.42[d]	12.28	0.14
	π_2	12.43	12.08[d]	11.85	0.58	12.70[d]	12.31	0.12
	$\bar{\Delta}$[c]		0.18	0.44		0.92	0.18	
3b	n_1	9.26	10.02	9.39	0.13	10.50	9.61	0.35
$R^3 = CH_3$	π_1	10.60	10.76	10.60	0.0	10.63	10.41	0.29
$R^5 = R^6 = H$	n_2	11.46	11.70	10.94	0.52	12.68[d]	11.67	0.23
	n_3	11.7	12.25[d]	11.49	0.21	13.19[d]	12.08[d]	0.35
	π_2	12.1	11.96[d]	11.68	0.42	12.50[d]	12.05[d]	0.02
	$\bar{\Delta}$[c]		0.37	0.26		0.88	0.25	
3c	n_1	9.31	10.07	9.43	0.12	10.59	9.68	0.37
$R^5 = CH_3$	π_1	10.73	10.87	10.71	0.02	10.76	10.54	0.19
$R^3 = R^6 = H$	n_2	11.48	11.65	10.92	0.56	12.56[d]	11.59	0.11
	n_3	12.0	12.20[d]	11.44	0.56	13.29[d]	12.10[d]	0.10
	π_2	12.0	11.81[d]	11.55	0.45	12.29[d]	11.85[d]	0.15
	$\bar{\Delta}$[c]		0.29	0.34		0.79	0.18	
3d	n_1	9.35	10.03	9.40	0.05	10.52	9.64	0.29
$R^6 = CH_3$	π_1	10.65	10.71	10.57	0.08	10.57	10.36	0.29
$R^3 = R^5 = H$	n_2	11.53	11.66	10.93	0.60	12.74[d]	11.74	0.21
	n_3	11.82	12.33[d]	11.56	0.26	13.29[d]	12.12	0.30
	π_2	12.17	12.02[d]	11.74	0.43	12.61[d]	12.16	0.01
	$\bar{\Delta}$[c]		0.30	0.28		0.87	0.22	
3e	n_1	9.02	9.96	9.30	0.18	10.40	9.45	0.43
$R^3 = R^5 = CH_3$	π_1	10.27	10.55	10.36	0.09	10.41	10.15	0.12
$R^6 = H$	n_2	11.2	11.63[d]	10.83	0.37	12.49[d]	11.47	0.27
	n_3	11.7	12.15[d]	11.36	0.34	13.07[d]	11.99	0.29
	π_2	11.7	11.59[d]	11.26	0.44	11.99[d]	11.49	0.21
	$\bar{\Delta}$[c]		0.44	0.28		0.89	0.26	
3f	n_1	9.15	9.97	9.31	0.16	10.41	9.48	0.33
$R^5 = R^6 = CH_3$	π_1	10.33	10.47	10.28	0.05	10.30	10.05	0.28
$R^3 = H$	n_2	11.27	11.59	10.82	0.45	12.46[d]	11.52	0.25
	n_3	11.7	12.20[d]	11.42	0.32	13.14[d]	11.92	0.22
	π_2	11.7	11.70[d]	11.38	0.28	12.17[d]	11.68	0.02
	$\bar{\Delta}$[c]		0.36	0.25		0.88	0.22	
3g	n_1	8.84	9.88	9.18	0.34	10.24	9.27	0.43
$R^3 = R^5 = R^6 = CH_3$	π_1	9.86	10.19	9.97	0.11	10.05	9.27	0.14
	n_2	11.0	11.55	10.73	0.27	12.40[d]	11.42	0.02
	π_2	11.4	11.52	11.16	0.24	11.93[d]	11.38	0.38
	n_3	11.4	12.17	11.35	0.05	12.94	11.74	0.34
	$\bar{\Delta}$[c]		0.56	0.20		1.01	0.26	

[a] From ref. 19. [b] The difference, for a particular orbital, between the experimental and the calculated data (eV). [c] The mean deviation for all orbitals of the calculated ionization energies from the experimental values (eV). [d] The relative ordering of this orbital is different from the order predicted by the OVGF(PM3) calculations and the experimental conclusions.[19]

are presented in Table 7 together with the relevant experimental data.[19]

The assignments of the ionization potentials for the parent 1,2,4-triazine (**3a**) given in Table 7 are based on the results of the OVGF(PM3) and the OVGF(AM1) calculations and also on the calculated orbital energies by the ZDO procedure[11,19] and the Energy Weighted Maximum Overlap (EWMO) approximation.[20] SCF procedures with either AM1 or PM3 do not reproduce correctly the ordering of the n_3 and π_2-orbitals (*i.e.* n_3 above π_2). However, the general quantitative agreement between the PM3 calculations and the experimental PE spectra of **3a** is good (average deviation of 0.18 eV), except for the HOMO (n_1) where the deviation is 0.5 eV. For **3a**, the inclusion of correlation and relaxation effects by means of the OVGF-(PM3) method produces ionization energies which are too low and the experimental–theoretical agreement is actually poorer (the average deviation is 0.44 eV) than with the SCF(PM3) method. For **3a** the OVGF(AM1) method gives much better results with $\bar{\Delta}$ being only 0.18 eV.

In contrast with the poor performance of the OVGF(PM3) calculations for **3a**, for methyl-substituted 1,2,4-triazines, the average deviation from the experimental results of the OVGF-(PM3) calculations is smaller than that of SCF(PM3) calculations. The average deviation for the seven 1,2,4-triazines studied is 0.89, 0.36, 0.29 and 0.24 eV for SCF(AM1), SCF-(PM3), OVGF(PM3) and OVGF(AM1) calculations, respectively. The average deviation is slightly smaller for the OVGF(AM1) calculations than for the OVGF(PM3) calculations, but only the OVGF(PM3) method reproduces correctly the observed degeneracy of the n_3- and π_2-levels of 5-methyl-1,2,4-triazine (**3c**) and of the dimethyl-(**3e** and **3f**) and the trimethyl-(**3g**) substituted derivatives.

Conclusions

In this work we have studied the ability of the OVGF technique coupled with semiempirical methods correctly to predict the PE spectra of the valence electrons of substituted triazines and tetrazines. Significant improvement of the agreement between experiment and theory is achieved for both AM1 and PM3 SCF calculations when OVGF techniques are used. Thus, calculations using OVGF methods give consistently lower quantitative deviations from experiment in comparison with the SCF methods. Furthermore while the SCF procedures fail in many cases to predict correctly even the correct ordering of the orbitals this failure is much less frequent with the OVGF methods. Between the two semiempirical methods, the OVGF(PM3) method gives significantly more satisfactory results.* In particular the OVGF(PM3) calculations predict more reliably the effect of substituents on the ionization potentials of triazines and tetrazines. In cases where comparisons are available the OVGF(PM3) and the OVGF (*ab initio*) methods give similar mean deviations from the experimental E_i values. The OVGF(AM1) method, which gave good results for azoles and pyridines[4,5] is less satisfactory for the triazines and tetrazines. In many cases the OVGF(AM1) method fails to reproduce even qualitatively the correct orbital ordering; yet it presents considerable improvement over the SCF(AM1) results.*

In conclusion, we have demonstrated that the inclusion of electron correlation and relaxation effects by using the outer-valence Green function formalism coupled with PM3 or AM1 methods as the zeroth approximation, is a very reliable computational method for the prediction of the ionization potentials of heterocyclic molecules with two,[4,5] three and four nitrogen atoms, and that these methods can serve as a reliable and useful tool to assist the interpretation of the PES of these molecules. These methods present a significant improvement over the corresponding SCF methods, with only a modest increase in the computer resources required to perform the calculations and they can be therefore used for relatively large molecules, where the corresponding *ab initio* procedures are prohibitively expensive and outside the computer capabilities of most laboratories.

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* The mean deviation of the calculated ionization energies from the experimental values for the 31 molecules studied in this paper are as follows: 0.95, 0.60, 0.39 and 0.33 eV for the SCF(AM1), SCF(PM3), OVGF(AM1) and OVGF(PM3) methods, respectively. For the 14 molecules for which HAM/3 calculations are available (see the text) the mean deviation is 0.40 eV. Note however, that in addition to the mean deviations it is important also to examine the ability of a particular method to reproduce correctly the ordering of the molecular orbitals.