Semiempirical Studies of Core Electron Binding Energies
Part 10. The SCC-MO Calculations on some Purines

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Z. Naturforsch. **38 a,** 866 – 873 (1983); received February 2, 1983

The solid state binding energies of 8-azaguanine, 8-azaxanthine, hypoxanthine and xanthine were calculated by using semiempirical self-consistent charge intramolecular electrostatic potentials expressed in the point-charge approximation. The results are essentially in good agreement with the experimental data giving in the same time a very simple and transparent interpretation of ESCA spectra which is close to the chemical intuition. Splitting of some unresolved N(1s) peaks is proposed and separate binding energies are attributed to particular nitrogen atoms. Since the point-charge model describes a number of molecular properties, it is concluded that formal atomic charges are meaningful within the adopted theoretical framework despite the fact that they can not be defined in a unique fashion. The relaxation energy and work functions of the studied molecular crystals are briefly discussed.

1. Introduction

Electron spectroscopy for chemical analysis (ESCA) is a useful vehicle for exploring gross molecular properties in gaseous [1], liquid [2] and solid [3] samples. It is also a convenient method for discussing electronic features in polymers [4], chemisorption and physisorption phenomena [5], homogeneous catalysis [6] etc. The measured ESCA chemical shifts give probably the best insight into the charge distribution in molecular systems. The relation between inner-core energy shifts and formal atomic charges was first suggested by Siegbahn *et al.* [1]. It was subsequently used in a number of semiempirical calculations. However, by far the best results are obtained with the self consistent charge method (SCC-MO) as we have conclusively shown in a series of papers [7 – 9]. The backbone of this approach is the calculation of the potential at the nucleus in the point-charge approximation. The relaxation of the electron density upon ionization is taken explicitly into account employing the equivalent core concept [10] or the transition potential formalism [11]. The results for a large number of atoms in a wide variety of different chemical environments were in good agreement with the experimental data. Since the quality of the results is much higher than that obtained by e.g. the CNDO/2 method, it is desirable to apply our simple and efficient procedure to large compounds of chemical interest. Here we consider inner-shell binding energies in some biologically important purines. Their charge distributions and ESCA base lines will be examined. The relaxation energies and solid state work functions are also briefly discussed.

2. Outline of the Method

Basch [12] and Schwartz [13] have shown that the ESCA chemical shifts of 1s levels are mostly affected by the changes in electrostatic potential exerted on the host nucleus

$$\Delta BE_A = k_A \Delta V_A + l_A , \qquad (1)$$

where

$$V_A = \sum_{B}{}' [(Z_B - 2)/R_{AB}] - \langle 0 | (1/r_A) | 0 \rangle \qquad (2)$$

and k_A, l_A are adjustable parameters. Calculating the one-center $1/r$ integrals and approximating the polycenter ones by point-charges, one obtaines the

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simple formula [7]

$$\Delta BE_{\mathrm{A}} = k_1 Q^{\mathrm{A}}_{2\mathrm{s}} + k_2 Q^{\mathrm{A}}_{2\mathrm{p}} + k_3 \sum_{\mathrm{B}}{}' (Z_{\mathrm{B}} - 2 - Q_{\mathrm{B}})/R_{\mathrm{AB}} + k_4, \quad (3)$$

where $Q^{\mathrm{A}}_{2\mathrm{p}} = \sum_{\alpha} Q^{\mathrm{A}}_{2\mathrm{p}\alpha} (\alpha = x, y, z)$ $\underset{\mathrm{B}}{\text{and}}$ Q_μ is the orbital population $Q_\mu = P_{\mu\mu} + \sum_{\mathrm{B}} \sum_{\nu}{}' P_{\mu\nu} S_{\mu\nu}$. The valence shell electron density on atom B is denoted by Q_{B}. The weighting factors $k_i (i = 1, 2, 3, 4)$ put the potentials in line with the energy shifts. The k_4 parameter is related to the reference level. The remaining factors absorb a large portion of the relaxation energy [7]. The factor k_3 multiplying the Madelung term deserves some more comments. Careful analysis of the ab initio DZ results reveals that the electrostatic potential at the nucleus can be accurately calculated in the point-charge approximation where the constant k_3 is unity [14]. The fact that k_3 is generally different from unity ($k_3 \neq 1$) in the formula (3) reveals the influence of the intramolecular charge transfer reorganization on the binding energy shifts (vide infra).

Thus the use of $k_3 = 1$ in the ground state potential (GPM) formulas of the type (3) by other workers is not quite justified. The one-center relaxation due to the contraction of atomic orbitals is included in the weighting factors k_1 and k_2 as discussed by Snyder [15]. Hence, a great deal of the relaxation energy is taken into account even in the approach involving only ground state charge distribution. The parameters k_1 and k_2 could be contracted to a single constant $k_1 = k_2$. Then the ΔBE_{A} shifts depend explicitly on the ground state charge of the ionized atom A denoted by q_{A}. Depending on the number of the weighting factors and their interrelations one can distinguish several models. They are signified as q ($k_1 = k_2$, $k_3 = 0$) if the Madelung term is neglected. Inclusion of the Madelung contribution ($k_1 = k_2$, $k_3 \neq 0$), abbreviated by M, is denoted by $q + M$ etc. If molecules with special structural characteristics regarding shape and size are considered, then the relaxation energy can play a significant role. It can be conveniently treated by invoking the equivalent core approximation [10] which simulates the ΔSCF procedure yielding the extended formula

$$\Delta BE_{\mathrm{A}} = k_1 (Q_{\mathrm{A}} + Q_{\tilde{\mathrm{A}}}) + k_3 (M_{\mathrm{A}} + M_{\tilde{\mathrm{A}}}) + k_4, \quad (4)$$

where Ã stands for the $Z_{\mathrm{A}} + 1$ atom ionized in the valence shell. An analogous formula obtained by the transition potential operator reads

$$\Delta BE_{\mathrm{A}} = k_1 Q^{\mathrm{TP}}_{\mathrm{A}} + k_3 M^{\mathrm{TP}}_{\mathrm{A}} + k_4, \quad (5)$$

where the transition potential is simulated by the pseudoatom possessing $Z_{\mathrm{A}} + 1/2$ nuclear charge. Somewhat more elaborate formulas for the equivalent core approach distinguishing 2s and 2p orbitals placed on the host atom take the forms

$$\Delta BE_{\mathrm{A}} = k_1 [(\xi_{2\mathrm{s}} Q_{2\mathrm{s}} + \xi_{2\mathrm{p}} Q_{2\mathrm{p}}) + (\tilde{\xi}_{2\mathrm{s}} \tilde{Q}_{2\mathrm{s}} + \tilde{\xi}_{2\mathrm{p}} \tilde{Q}_{2\mathrm{p}})] + k_3 (M_{\mathrm{A}} + M_{\tilde{\mathrm{A}}}) + k_4 \quad (6)$$

and

$$\Delta BE_{\mathrm{A}} = k_1 (\xi_{2\mathrm{s}} Q_{2\mathrm{s}} + \xi_{2\mathrm{p}} Q_{2\mathrm{p}}) + k_2 (\tilde{\xi}_{2\mathrm{s}} \tilde{Q}_{2\mathrm{s}} + \tilde{\xi}_{2\mathrm{p}} \tilde{Q}_{2\mathrm{p}}) + k_3 (M_{\mathrm{A}} + M_{\tilde{\mathrm{A}}}) + k_4, \quad (7)$$

which have three and four-parameters, respectively. The atomic charges and orbital populations were computed by the SCC-MO method, which in turn is described elsewhere [7]. The experimental X-ray geometries were used for 8-azaguanine [16a] and 8-azaxanthine [16b]. Since experimental data were not available for xanthine and hypoxanthine, here MINDO/3 [16c] optimized structural parameters were employed. Although MINDO/3 geometries leave much to be desired exhibiting appreciable errors, several test cases showed that ESCA shifts are not very sensitive on the relatively small deviations of the structural parameters from the precise values. This is to be expected because interatomic distances enter the denominator of the $1/r$ operator and the first order correction is given by $\Delta r/r^2$. This is also one of the reasons why the calculations on molecules involving pseudoatoms or equivalent cores were executed for ground state geometries. The other reason is that heavy nuclei can not follow completely the fast photoionisation process due to their inertness. Finally, Clementi-Raimondi AOs were employed in computations since they have different screening constants for s and p-type orbitals [16d].

3. Results and Discussion

ESCA shifts

The estimated solid state ESCA shifts for 8-azaguanine, 8-azaxanthine, hypoxanthine and xanthine are compared with the corresponding experimental data [17] in Table 1. The C(1s) and N(1s) shifts were determined relative to the gas phase reference levels of CH_4 and N_2, which take values of 290.7 and 409.9 (in eV), respectively. The empirical weighting factors were taken from the earlier work [8]. Survey of the results shows that the overall agreement with measured values is quite good for all five formulas. Their performance is best illustrated by the average absolute errors which are 0.4, 0.3, 0.2, 0.2 and 0.2 (in eV) starting from the q model and ending up with the results obtained by the (7), respectively. The simple two parameter q model works well particularly if one takes into account the fact that other semiempirical methods face serious troubles in treating nitrogen shifts [7]. Slight improvement is observed with the q^{TP} model since the charge on the host atom calculated by the transition potential method reflects better the effect of the electronic reorganisation. Additional gain in accuracy is obtained by the inclusion of the transition potential Madelung term M_A^{TP}. It yields results with the average absolute error of 0.2 eV which is ac-

Table 1. Comparison between SCC-MO inner-shell binding energy shifts in some purines as calculated by several electrostatic potential models and the available experimental data (in eV).

Compound	Atom	Eq. (3) ($k_1 = k_2, k_3 = 0$)	Eq. (5) ($k_3 = 0$)	Eq. (5)	Eq. (6)	Eq. (7)	ΔBE(exp.)
8-azaguanine							
	C_6	− 2.1	− 2.0	− 1.9	− 1.8	− 1.8	− 1.8
	C_5	− 3.7	− 4.2	− 4.3	− 4.3	− 4.3	− 4.9
	C_4	− 2.7	− 3.1	− 3.3	− 3.4	− 3.4	− 3.3
	C_2	− 2.1	− 2.3	− 2.5	− 2.6	− 2.6	− 2.0
	N_3	−10.0	−10.1	−10.6	−10.6	−10.4	−10.3
	N_1	− 8.8	− 9.1	− 9.2	− 9.2	− 8.9	− 8.9
	N_7	− 9.9	− 9.9	− 9.3	− 9.3	− 9.4	− 9.7
	N_9	− 8.6	− 8.9	− 8.4	− 8.4	− 8.2	− 8.9
	N_8	− 9.5	− 9.7	− 8.9	− 8.9	− 8.9	− 8.9
	N_{10}	− 9.8	− 9.4	−10.0	−10.0	−10.3	−10.3
8-azaxanthine							
	C_6	− 1.8	− 1.6	− 1.6	− 1.6	− 1.6	− 1.9
	C_2	− 1.2	− 0.8	− 0.9	− 0.9	− 0.9	− 1.0
	C_4	− 2.7	− 3.0	− 3.4	− 3.4	− 3.4	− 3.4
	C_5	− 3.5	− 3.9	− 4.2	− 4.3	− 4.3	− 4.7
	N_3	− 8.8	− 9.1	− 9.2	− 9.2	− 8.9	− 9.0
	N_1	− 8.8	− 9.1	− 9.4	− 9.4	− 9.1	− 9.0
	N_7	− 9.6	− 9.8	− 9.9	− 9.7	− 9.7	− 9.6
	N_8	− 8.3	− 8.6	− 7.9	− 7.9	− 7.7	− 8.1
	N_9	− 9.7	− 9.9	−10.2	−10.2	−10.0	−10.6
Hypoxanthine							
	C_6	− 2.4	− 2.3	− 2.0	− 2.0	− 2.0	− 1.9
	C_5	− 4.0	− 4.6	− 4.9	− 4.5	− 4.6	− 5.0
	C_4	− 3.1	− 3.6	− 3.7	− 3.8	− 3.8	− 3.6
	C_2	− 3.1	− 3.1	− 3.3	− 3.3	− 3.3	− 3.2
	C_8	− 3.7	− 3.8	− 3.8	− 3.8	− 3.8	− 4.7
	N_3	−10.1	−10.1	−10.5	−10.5	−10.3	−10.1
	N_1	− 8.9	− 9.2	− 9.1	− 9.1	− 8.8	− 8.9
	N_7	−10.3	−10.3	−10.3	−10.3	−10.3	−10.1
	N_9	− 8.9	− 9.2	− 9.3	− 9.3	− 9.0	− 8.9
Xanthine							
	C_8	− 3.7	− 3.9	− 4.0	− 4.0	− 4.0	− 4.0
	C_6	− 2.2	− 2.0	− 1.9	− 1.9	− 1.9	− 1.9
	C_5	− 4.1	− 4.7	− 4.8	− 4.8	− 4.8	− 4.9
	C_4	− 2.5	− 2.9	− 3.5	− 3.5	− 3.5	− 3.5
	C_2	− 1.2	− 0.9	− 1.0	− 1.0	− 1.0	− 1.0
	N_3	− 8.8	− 9.1	− 9.1	− 9.1	− 8.9	− 9.1
	N_1	− 8.8	− 9.1	− 9.5	− 9.5	− 9.2	− 9.1
	N_7	−10.3	−10.3	−10.5	−10.5	−10.5	−10.4
	N_9	− 8.9	− 9.1	− 9.6	− 9.6	− 9.3	− 9.1

ceptable. One should mention in this respect that the experimental standard deviation for C(1s) levels is about 0.2 eV while the N(1s) experimental data have even larger uncertainty due to the poor resolution of the spectra. Hence the N(1s) errors are sometimes as high as ±0.4 eV [17] leading to some unresolved peaks like N_8 and N_9 lines in **1,** N_1 and N_9 in **3,** and finally N_1, N_3 and N_9 in **4**. The equivalent core formulas (6) and (7) exhibit errors of 0.3 and 0.2 eV, respectively, giving thus a good overall picture of the ESCA shifts.

Let us focus our attention on the C(1s) levels first. It is interesting to observe variations in bonding energy with changes in chemical environment of the considered atoms. According to the simple rule of thumb the atoms with lower electron density have higher inner-core binding energies. Hence the smallest absolute values of the shifts from the reference level are expected for carbons surrounded by three highly electronegative heteroatoms. Indeed, the most stable C(1s) level is found at C_2 positions in 8-azaxanthine and xanthine where the carbons are linked to the two nitrogens and one oxygen atom. Concomitantly the valence shell electron density at C_2 is low being 3.75 e. The C_2(1s) binding energies in 8-azaguanine and hypoxanthine are according to the formula (7) 288.1 and 287.4 eV, respectively, compatible with number of neighbouring (three and two) nitrogen atoms. The corresponding gross atomic populations 3.81 and 3.87 e are consistent with the aforementioned simple picture. A comparison between C_2(1s) and C_6(1s) levels is instructive. These atoms have the same effective charges in 8-azaguanine and the same shifts within the *q* model. However, the relaxation energies are different indicating that the C_6(1s) level is more stable by ~ 0.8 eV (Table 1) according to calculations. Experiment predicts a difference of only ~ 0.2 eV. In any case, this example shows limits of the simple ground state effective charge of the host atom model and underlines the importance of the reorganisation energy in some particular situations. Interestingly, the C_6(1s) binding energy is higher although there are only two heteroatoms in the neighbourhood. This is a consequence of the high electronegative power of the keto-oxygen which is comparable to the joint action of N(sp^3) and N(sp^2) nitrogens. The C_6 carbon in 8-azaxanthine has higher electron density (3.79 e) then the C_2 carbon (3.75 e) as expected. Therefore, the binding energy of the former atom is lower by ~ 0.7 eV. Here the criterion of the charge of the ionized atom works well again. One can say that it is generally quite good providing a useful tool for the tentative assignment of the experimental spectra. Finally, the C_4(1s) binding energies are always higher than the C_5(1s) values. This is not surprising because the C_4(1s) positions are bound to two nitrogens while C_5 carbons have only one neighbour of this kind. It is noteworthy that carbon atoms with similar immediate environment have very close binding energies. For example, the C_6(1s) energies variations are all within the ±0.2 eV range measuring from the C_6 value in 8-azaguanine. Slightly larger deviations exhibit positions C_4 and C_5.

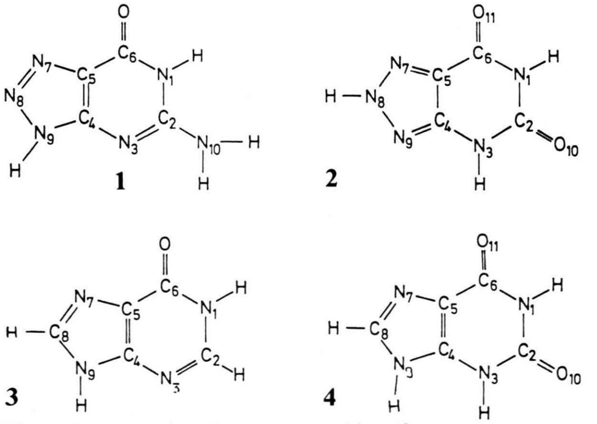

Fig. 1. 8-azaguanine (**1**) : 8-azaxanthine (**2**) : hypoxanthine (**3**) : xanthine (**4**).

The changes of N(1s) levels follow a similar pattern. One can distinguish basically three types of nitrogens in a series of studied molecules: amino group (NH_2), pyrimidine-like (−N=) and pyrrole-like (−NH−) atoms. The gross atomic populations of the atoms N_{10} and N_3 in **1** are very close, 5.15 and 5.17 (in e), respectively, and their binding energies are practically the same being ~ 399.5 eV. The reasons for the relatively high concentration of the electronic charge on these atoms are different. The sp^3 nitrogen of the amino-group has three channels leading to the pool of electrons provided by the electropositive carbon and two hydrogen atoms. The pyridine-like nitrogens have two channels but they are rather effective because the localized sp^2 σ-lone pairs are energetically very convenient to accomodate electrons. Different situation is found at the pyrrole-like nitrogens N_1. Here, the lone pair is placed in the π-orbital and consequently it is substantially delocalized over the ring. This is evidenced by the $2p^{\pi}(N_1)$ populations. Let us consider numerical values found in 8-azaguanine in more detail. The corresponding entities in other compounds are very similar if not identical. The population of the $2p^{\pi}(N_1)$ orbital is as low as ~ 1.55 e. Hence, the charge density on N_1 is significantly lower than that of N_3 which is reflected in higher N(1s) binding energy of the former atom the difference being 1.5 eV. The N_7 and N_8 atoms have also a localised σ-lone pair each in the plane of the five membered ring but their BEs are higher than that of N_3 by 1.0 and 1.5 eV, respectively. The reason is again found in their immediate neighbourhood, because they are linked to one or two nitrogens. Their shifts relative to the $N_3(1s)$ level are further enhanced by the differences in the relaxation energy (vide infra, Table 2). The unresolved peaks will be of our concern next. According to the results of the Eq. (7), the $N_9(1s)$ level should be higher by 0.7 eV than that of $N_8(1s)$ in **1** while $N_8(1s)$ and $N_1(1s)$ seem to be virtually the same. The binding energies $N_1(1s)$ and $N_9(1s)$ in **3** are very close the difference being only 0.2 eV (Table 1). The spectrum of xanthine has three unresolved levels of atoms N_1, N_3 and N_9. The $N_3(1s)$ level appears to be more stable by 0.3 and 0.4 eV than $N_1(1s)$ and $N_9(1s)$ levels, respectively.

The similarities between the binding energies of nitrogens in similar bonding situations is remarkable. For example, the $N_3(1s)$ level in 8-azaxanthine is virtually the same as $N_1(1s)$ in 8-azaguanine. Further, $N_1(1s)$ BEs in **2** and **4** are practically the same. The shifts of N_7 and N_9 1s electrons in **3** are close to the corresponding values in **4** etc. It is gratifying that the point-charge model corrected when necessary with explicit treatment of relaxation effect yields results which are so close to the chemical intuition and so useful for the interpretation of ESCA spectra.

Relaxation energies

As Hedin and Johansson have shown [18], the relaxation energy is given by

$$E_A^r = \tfrac{1}{2}\,[V_{\tilde{A}}(Z_A + 1) - V_A(Z_A)]\,, \qquad (8)$$

where $V_A(Z_A)$ and $V_{\tilde{A}}(Z_A + 1)$ are potentials exerted on the sites of the atom A undergoing ionization and its equivalent core counterpart $\tilde{A}$, respectively. In the point-charge approximation, the relaxation energy E_A^r can be partitioned into three terms

$$E_A^r = E_A^r\,(\text{contr.}) + E_A^r\,(\text{flow}) + E_A^r\,(\text{mix})\,. \qquad (9)$$

Here

$$E_A^r\,(\text{contr.}) = 13.6\, Q_A(\xi_A - \xi_{\tilde{A}})/n \text{ eV}\,, \qquad (10\,\text{a})$$

$$E_A^r\,(\text{flow}) \;=\; 7.2\,(M_{\tilde{A}} - M_A) \text{ eV}\,, \qquad (10\,\text{b})$$

$$E_A^r\,(\text{mix.}) \;=\; 13.6\, \xi_{\tilde{A}}(Q_{\tilde{A}} - Q_A)/n \text{ eV}\,. \qquad (10\,\text{c})$$

Similar expressions hold for the TP model. It is only necessary to substitute $\xi_{\tilde{A}}$, $Q_{\tilde{A}}$ and $M_{\tilde{A}}$ by the corresponding pseudoatom entities and divide each term by 2. The three contributions (10a–c) have simple physical interpretation. The first term (10a) arises from the contraction of the valence orbitals in the field of the host atom due to the increase in effective positive charge of the nucleus. The second term (10b) is polycentric in nature and appears because of the electron density migration toward the positive hole which leads to the difference in Madelung potentials. It is called charge flow contribution. The last term (10c) is again monocentric but includes both the charge flow and contraction of atomic orbitals. It reflects the fact that the transferred charge feels the field of the nucleus with the charge $n\,\xi_{\tilde{A}}$. Thus it is called a mixed term.

The estimated relaxation energies are given in Table 2. Their extent is large. However, the variations of E_A^r are at least an order of magnitude smaller. It is interesting to notice that the dominating term is E_R(mix) and that the charge flow contribution is relatively small and of the opposite sign. The corresponding values of E_A^r(contr.) and E_A^r(flow) are virtually the same in the equivalent core and transition potential approaches. They are also fairly constant in a series of studied compounds. The E_A^r(contr.) term is proportional to the valence charge population of the host term A in the ground state, as observed first by Snyder [15]. The largest variations exhibits the E_A^r(mix.) term which also differs in the EC and TP methods by ~ 1 eV. The equality of E_A^r (contr.) and E_A^r(flow) as well as discrepancies for E_A^r(mix.) term are easily understood if the following approximate relation between the corresponding EC and TP entities are taken into account [9]:

$$\zeta_A^{TP} \cong (\zeta_{\tilde{A}} + \zeta_A)/2 \quad \text{and} \quad M_A^{TP} \cong (M_{\tilde{A}} + M_A)/2\,.$$

Table 2. Reorganization energies upon inner-shell ionization in some purines as estimated by equivalent core (EC) and transition potential (TP) methods (in eV).

Compound	Carbon atoms						
	Atom	E_R (contr.)	E_R (flow)	E_R (mix.)		E_R (tot.)	
				EC	TP	EC	TP
8-azaguanine							
	C_6	−8.4	3.7	−12.5	−11.5	−17.3	−16.2
	C_5	−8.6	3.8	−13.2	−12.1	−18.1	−17.0
	C_4	−8.5	3.8	−13.2	−12.1	−17.9	−16.8
	C_2	−8.4	3.8	−13.1	−12.0	−17.7	−16.6
8-azaxanthine							
	C_6	−8.5	3.8	−13.0	−12.0	−17.7	−16.6
	C_2	−8.3	3.8	−12.3	−11.3	−16.8	−15.7
	C_4	−8.4	3.7	−12.4	−11.4	−17.1	−16.1
	C_5	−8.6	3.8	−13.1	−12.0	−17.9	−16.9
Hypoxanthine							
	C_6	−8.6	3.8	−13.3	−12.2	−18.0	−16.9
	C_5	−8.7	3.8	−13.3	−12.2	−18.2	−17.2
	C_4	−8.5	3.7	−12.5	−11.5	−17.3	−16.3
	C_2	−8.6	3.7	−12.6	−11.6	−17.5	−16.4
	C_8	−8.6	3.8	−12.7	−11.6	−17.5	−16.5
Xanthine							
	C_6	−8.5	3.8	−13.3	−12.2	−18.0	−16.9
	C_5	−8.7	3.7	−13.3	−12.2	−18.2	−17.1
	C_4	−8.4	3.6	−12.5	−11.5	−17.3	−16.3
	C_2	−8.3	3.8	−12.4	−11.8	−16.9	−16.3
	C_8	−8.6	3.7	−12.7	−11.6	−17.6	−16.5
	Nitrogen atoms						
8-azaguanine							
	N_3	−11.4	3.4	−15.2	−14.2	−23.3	−22.2
	N_1	−11.1	3.8	−15.1	−14.0	−22.3	−21.2
	N_7	−11.4	3.6	−14.7	−13.6	−22.5	−21.4
	N_9	−11.0	3.9	−14.8	−13.8	−22.0	−20.9
	N_8	−11.3	3.5	−14.9	−13.8	−22.7	−21.6
	N_{10}	−11.4	3.9	−12.2	−11.4	−19.7	−18.9
8-azaxanthine							
	N_3	−11.1	3.9	−14.9	−13.8	−22.0	−21.0
	N_1	−11.1	3.8	−14.9	−13.8	−22.1	−21.1
	N_7	−11.3	3.6	−15.2	−14.1	−22.9	−21.8
	N_8	−10.9	3.9	−14.8	−13.8	−21.8	−20.8
	N_9	−11.4	3.5	−15.3	−14.2	−23.1	−22.0
Hypoxanthine							
	N_3	−11.5	3.5	−15.1	−14.1	−23.1	−22.1
	N_1	−11.1	3.9	−15.1	−14.0	−22.3	−21.2
	N_7	−11.5	3.5	−14.9	−13.9	−22.9	−21.3
	N_9	−11.1	3.9	−14.9	−13.9	−22.2	−21.1
Xanthine							
	N_3	−11.1	3.9	−14.8	−13.8	−22.0	−21.0
	N_1	−11.1	3.8	−14.9	−13.9	−22.2	−21.2
	N_7	−11.5	3.5	−14.8	−13.8	−22.8	−21.8
	N_9	−11.1	3.9	−14.9	−13.8	−22.1	−21.1

The difference in $E_{\mathrm{A}}^{\mathrm{r}}$(mix.) contribution is then proportional to $\zeta_{\bar{\mathrm{A}}} - \zeta_{\mathrm{A}}^{\mathrm{TP}} = (\zeta_{\bar{\mathrm{A}}} - \zeta_{\mathrm{A}})/2$. It should be pointed out that nonequivalence of the ΔSCF and transition operator methods in some 3d inorganic complexes was discussed at length by Böhm [19]. Although the relaxation energies estimated by the EC and TP methods differ in absolute values, their changes relative to the given reference $E_{\mathrm{A}}^{\mathrm{r}}$ energy are practically the same. Hence EC and TP models have the same performance when ESCA shifts are considered. The amount of the charge flow toward the ionized atom possessing a positive hole is noteworthy. It neutralizes almost completely the created positive charge in most cases. We shall illustrate this statement with data for hypoxanthine giving the valence populations for the atom in question and its equivalent core counterpart $\mathrm{A}(Q_{\mathrm{A}}, Q_{\bar{\mathrm{A}}})$. They read: C_2(3.87, 4.82), C_4(3.83, 4.87), C_5(3.39, 4.93), C_6(3.87, 4.77), N_1(5.02, 6.00), N_3(5.18, 6.16), N_7(5.22, 6.18) and N_9(5.03, 5.99). One observes that the carbon C_4 is overcompensated by the charge flow since it gets slightly more than one electron. Apart its influence on the ESCA chemical shifts, the relaxation energy is related to the proton affinity [20, 21].

Comparison of the gas and solid state binding energies gives an estimate of the sum of the work function φ and the extramolecular reorganization energy according to the equation

$$BE_{\mathrm{A}}(\mathrm{gas}) - BE_{\mathrm{A}}(\mathrm{solid}) = \varphi + E_{\mathrm{A}}^{\mathrm{r}}(\mathrm{extra})\,. \quad (11)$$

It is difficult, unfortunately, to delineate the last two entities. Furthermore, they are obtained as a difference of the two big number so that one gets a rough idea about $\varphi + E_{\mathrm{A}}^{\mathrm{r}}$(extra). They are given in the last column of the Table 3. The average values for carbon and nitrogen atom in the studied purines are 4.9 and 5.6 eV, respectively. Thus $E_{\mathrm{N}}^{\mathrm{r}}$(extra) is on average by 0.7 eV higher than the $E_{\mathrm{C}}^{\mathrm{r}}$(extra) which is exactly the result obtained earlier on nucleic acids and related heterocyclic compounds [8]. This finding is compatible with greater electronegativity of the nitrogen. The work function of the molecular solids is surprisingly constant and one can take ~ 4.0 eV as a rough estimate. Then the average $\bar{E}_{\mathrm{C}}^{\mathrm{r}}$(extra) and $\bar{E}_{\mathrm{N}}^{\mathrm{r}}$(extra) values are ~ 0.9 and ~ 1.6 eV, respectively. Hence the extramolecular relaxation energies are very small and their variations on different molecular sites should be an order of magnitude smaller. It should be mentioned that variation of $E_{\mathrm{A}}^{\mathrm{r}}$(extra) in studied purines (Table 3) is too exaggerated. This is a consequence of the inaccuracy inherent in (11) and possibly due to the presence of hydrogen bonds in solids which are not treated in this work.

4. Conclusion

The solid state ESCA chemical shifts of the studied purines are well described by the semiempirical SCC-MO ground state potentials calcu-

Table 3. Estimated gas phase energy levels as calculated by the SCC-MO method and $\varphi + E_{\mathrm{A}}^{\mathrm{r}}$ (extra) values.

Compound	Atom	Gas phase BE	
		calcd.	$\varphi + E_{\mathrm{A}}^{\mathrm{r}}$ (extra)
8-azaguanine			
	C_6	293.9	5.0
	C_5	291.3	5.5
	C_4	292.0	4.6
	C_2	292.8	4.1
	N_3	404.5	4.9
	N_1	406.5	5.5
	N_7	406.3	6.1
	N_9	407.6	6.6
	N_8	407.0	6.0
	N_{10}	405.3	5.7
8-azaxanthine			
	C_6	294.0	5.2
	C_2	294.5	4.8
	C_4	291.8	4.5
	C_5	291.1	5.1
	N_3	406.6	5.7
	N_1	406.2	5.3
	N_7	405.5	5.2
	N_8	408.5	6.7
	N_9	405.0	5.7
Hypoxanthine			
	C_6	291.8	5.1
	C_5	290.8	5.4
	C_4	293.9	4.7
	C_2	292.1	4.6
	C_8	291.8	5.8
	N_3	404.6	4.8
	N_1	406.7	5.7
	N_7	404.0	4.2
	N_9	406.4	5.4
Xanthine			
	C_6	293.9	5.1
	C_5	290.7	4.9
	C_4	291.5	4.3
	C_2	294.5	4.8
	C_8	291.5	4.8
	N_3	406.7	5.9
	N_1	406.1	5.3
	N_7	404.6	5.1
	N_9	405.9	5.1

lated in the point-charge approximation. Explicit consideration of the relaxation effect by invoking the EC or TP formalism offers sometimes a more reliable account of the inner-shell photoionization phenomenon, but generally speaking the GPM approach is satisfactory. The results are in good agreement with the experimental data and support the partial assignment of the measured spectra [17]. Splittings of some unresolved N(1s) peaks are proposed illustrating the usefullness of the simple point-charge model. Although the calculated binding energies and charge distributions are interesting per se due to the biochemical importance of the examined compounds, they have much broader impact yielding an additional piece of evidence that atomic point charges are a useful tool for studying molecular behaviour. Indeed, earlier work [7−9] and present results conclusively show that the point-charge model interprets ESCA chemical shifts in a simple and transparent way which is close to chemical intuition. It should be mentioned in this connection that the point-charge model gives a rationale for a number of other molecular properties like diamagnetic shielding [22] and the diamagnetic part of the magnetic susceptibility [23−25], and that they are closely related to the total molecular SCF energies [26]. Thus we can draw the important conclusion that atomic charges do have a certain meaning within the adopted theoretical framework inspite of the fact that they can not be defined in a unique way. By using the effective charges of atoms one can express a number of molecular properties as a sum of atom-like entities.

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