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Accurate computational prediction of the structural and vibrational properties of s-triazine derivatives *in vacuo*. A DFT approach

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ABSTRACT

The well-known class of herbicides, s-triazine derivatives, are commonly used as reagents in the manufacture of resins and pharmaceuticals, and also of solvent-refined coals. Recently, triazine derivatives have been observed to form self-assembling nanostructures on metallic surfaces. In this paper, we present a study using a DFT approach for the computational prediction of the structural and vibrational properties *in vacuo* of three s-triazine derivatives, *viz*., atrazine (*N,N′*-ethyl-isopropyl-6-chloro-1,3,5-triazine,2,4-diamine), prometryn (*N,N′*-diisopropyl-6-methyl-thio-1,3,5-triazine,2,4-diamine) and simetryn (*N,N′*-diethyl-6-methyl-thio-1,3,5-triazine,2,4-diamine). In particular we show that the employment of the Becke three-parameter Lee–Yang–Parr (B3-LYP) exchange-correlation functional using the aug-cc-pVQZ basis set provides an accurate prediction of the structural and vibrational properties of atrazine, prometryn, and simetryn.

1. Introduction

Triazine is a heterocyclic six-membered ring. It is formally analogous to the benzene ring but with three carbon atoms replaced by nitrogen atoms. By changing the relative position of the nitrogen atoms, three isomers of triazine can be distinguished, *viz*., 1,2,3-triazine, 1,2,4-triazine, and 1,3,5-triazine. The 1,3,5 isomer, also called s-triazine, is the best known and most used. It is a common reagent, and readily forms derivatives, which are used in the manufacture of resins [1,2], pharmaceuticals and herbicides [3]. Moreover, recent investigations have underlined the use of triazine derivatives as self-assembling nanostructures [4,5]. Triazines were originally developed by J. R. Geigy to be used as selective herbicides for cereals [6]. These compounds inhibit photosynthesis in plants by blocking the electron transfer from the quinone and cytochrome *b*-559 at the reducing site of chloroplast photosystem II [7,8]. They were first introduced into the environment about 50 years ago, and more than 2 billion pounds have been applied globally. Among s-triazines, particularly *atrazine* (*N,N′*-ethyl-isopropyl-6-chloro-1,3,5-triazine,2,4-diamine) and *prometryn* (*N,N′*-diisopropyl-6-methyl-thio-1,3,5-triazine,2,4-diamine) [9,10] and *simetryn* (*N,N′*-diethyl-6-methyl-thio-1,3,5-triazine,2,4-diamine) which were both synthesised later [11] are the most used triazine herbicides. These three were initially found to biodegrade poorly and to be surprisingly soluble in water (70 mg/L for atrazine and 450 mg/L for simetryn [12]) and with high mobility in soil; but today a more rapid biodegradation [13] and a lower water solubility [14] can be observed. In fact, it was recently shown [15–19] that s-triazine herbicides are readily metabolised by dedicated enzymes [20,21], encoded by bacteria genes. From a chemical point of view (Scheme 1), all of them have two secondary amino-groups bonded to the central ring. The two alkyl chains are identical in the cases of prometryn and simetryn, whereas atrazine presents different groups. Atrazine differs with respect to the other two species also for one chlorine atom instead of the thio-methyl group.

In spite of the applicative interest of these chemicals, there is no theoretical or computational prediction of the vibrational properties of s-triazines at Density Functional Theory (DFT) level in Literature. The formation of complexes by triazines and their derivatives with metal ions [22,23] or water [24] has been computationally investigated. Oliva et al. [25] have recently carried out a thorough study of the low-lying excited states of atrazine (1,3,5-triazine, and ametryn) from both a computational and an experimental point of view. In that work, the Authors determine the ground state geometry of atrazine at DFT level, by employing the B3-LYP functional and the 6-31G(d) basis set, and then other basis sets (cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ) are also used for the calibration of results. Nevertheless, the structural and vibrational properties are not treated in detail.

The main goal of this paper is to provide a valid description of the three triazines under study at DFT level with reasonable computational cost, with particular emphasis on the structural and vibrational properties. This description is of interest, especially if

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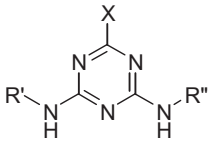


atrazine	X = Cl	R' = CH_2CH_3 ; R" = $CH(CH_3)_2$
prometryn	X = SCH_3	R' = R" = $CH(CH_3)_2$
simetryn	X = SCH_3	R' = R" = CH_2CH_3

Scheme 1.

the interaction with biomolecules (e.g. enzymes and biomembranes [8]) or the environment (clays and humic acids [26–31]) is investigated.

2. Computational details

A full geometry optimisation of the electronic ground state of atrazine, prometryn and simetryn was obtained *in vacuo* phase at DFT level using the Becke three-parameter Lee–Yang–Parr (B3-LYP) exchange-correlation functional with the 6-311G(d, p), 6-311+G(d, p), and aug-cc-pVQZ basis sets. This is the first time that such a high level of theory is applied to predict the properties of these three molecules. Subsequently, the optimised geometries were submitted to vibration calculation, in order to predict the vibrational properties and to determine whether the convergence points are "genuine" energy minima.

Lastly, starting from the optimised structures, the potential energy hypersurface was explored at the DFT B3-LYP/aug-cc-pVQZ level of theory along rotations around the most significant dihedral angles (*vide infra*), with and without relaxation, in order to evaluate the torsional freedom. The scans were obtained with 48 + 1 steps of 7.5 degrees.

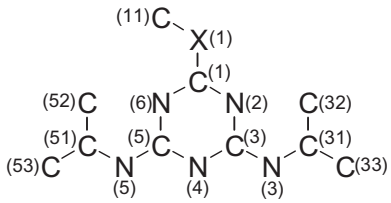
Gaussian 09 computational package [32] was used for all these calculations.

3. Results and discussion

During the presentation and the discussion of the results, we shall refer to the numbering of the atoms as reported in Scheme 2, where X(1) = Cl for atrazine, S for prometryn and simetryn. (C(11) and C(33) do not exist for atrazine; C(33) and C(53) do not exist for simetryn.)

3.1. Optimised geometries

Table 1 shows the main geometrical parameters for atrazine, prometryn and simetryn (see Fig. 1). Some mean values are also shown. In general, if we compare the experimental X-ray data, when available, with those computed using the three different basis sets, we reach a more accurate level of description if the aug-cc-pVQZ basis set is employed with respect to the 6-311G(d, p) or 6-311+G(d, p) basis sets. So we shall principally refer to the geometries relaxed by using the aug-cc-pVQZ basis set. (In Table S1, we provide the results obtained with the other two basis sets.)



Scheme 2.

In the case of prometryn, the presence of two independent but similar molecules (labelled as A and B) was shown [33] in the unit cell. Weak interactions were observed between these two molecules: weak hydrogen bonding, between A and B in the asymmetric unit, and intra-unit associations, involving only nitrogen atoms. Regrettably, the differences between A and B species are not presented nor discussed: they can be evinced by comparison with the geometrical parameters. In general, the comparison between computed and experimental geometries gives a good match for the B structure, whereas there exists a greater deviation from the A structure. Concerning the C—N—C and N—C—N bond angles, we find that 6-311G(d, p) or 6-311+G(d, p) basis sets provide values close to those obtained for A structure, whereas the aug-cc-pVQZ basis set gives a description closer to B structure.

Regarding the C—N bond lengths inside the ring, they are similar for the three molecules. For prometryn, the mean value is close to that found experimentally for the B molecule. Also for simetryn, the mean value is in agreement with the experimental geometry. For atrazine, no experimental structure was found. In Ref. [25], where the geometry was optimised at the DFT B3-LYP/6-31G(d) basis set, only few bonds look similar to those obtained at the B3-LYP/6-311+G(d, p) and aug-cc-pVQZ levels in the present study. In particular, those data seem to demonstrate that the technique employed is not sensitive to the two different substituents in R′ and R″, since their ring geometry shows a perfect C_{2v} symmetry, whereas our calculations using all the three basis sets provide non-symmetric geometries.

If we consider the mean value for C—N distances outside the ring, where C=C(3), C(5), and N=N(3), N(5), the description obtained for both prometryn and simetryn is satisfactory. For atrazine, the mean value is similar to that for prometryn. The differences between C(3)—N(3) and C(5)—N(5) are less than 0.005 Å; in particular, for symetrin and atrazine, the two bonds have almost the same length. (The difference is 0.003 Å in the X-ray structure, and <0.002 Å in the optimised geometries.)

The external amino-bond lengths are significantly longer than those discussed above. This may be put in correlation with the different bond order, which is higher for those directly linked to the ring. For prometryn, the mean value for N(*i*)—C(*i*1) (*i* = 3, 5) matches well with that for B structure. In the case of simetryn, the computed value coincides with the experimental one. In atrazine, this mean bond length is longer than in prometryn and simetryn. Also in the case of this geometrical parameter, the difference between the two bonds N(3)—C(31) and N(5)—C(51) is particularly remarkable, both computationally and experimentally, especially for prometryn; for symetrin and atrazine, it is more significant than the difference between C(3)—N(3) and C(5)—N(5).

If we calculate the mean squared deviations σ^2 for the bond lengths of the optimised geometries compared to the experimental ones, we note that the aug-cc-pVQZ basis always provides the closest values to the experimental ones ($\sigma^2 < 5 \times 10^{-5}$). In any case, the ring is well-described by employing all the three basis sets.

Concerning the bond angles inside the ring, C—N—C and N—C—N angles are remarkably different each other. In the experimental geometries of prometryn (simetryn), C(3)—N(4)—C(5) is smaller (larger) than the other two C—N—C angles. For both simetryn and prometryn A, N(2)—C(1)—N(6) is larger than the other two N—C—N angles; for prometryn B, the largest angle is the N(3)—C(4)—N(5) one. This confirms that the substituents influence the global geometry and especially the ring. Also in the case of the bond angles formed by the ring and the two terminals, C—N—C and N—C—N angles are different from each other, and in particular those of C—N—C are larger than those of N—C—N. In the amino chains, the angles involving the nitrogen atoms are moderately distorted. Moreover, the two lateral chains do not have the same tilt values. Considering C—N—C angles, C(3)—N(3)—C(31) is smaller than C(5)—N(5)—C(51),