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A DFT study of the chemical reactivity of thiobencarb and its oxidized derivatives in the aqueous phase

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Abstract: In the present work, the global and local reactivity of *S*-(4-chlorobenzyl)-*N*,*N*-diethylthiocarbamate (TB) and its oxidized derivatives (sulfone (TBSu) and sulfoxide (TBS) were analyzed. In addition, the chemical reactivities of the dechlorinated forms of TB (DTB), TBSu (DTBSu) and TBS (DTBS) were studied. The calculations were performed at the wB97XD/6-311++G(2d,2p) level of theory in the aqueous phase. The condensed Fukui functions indicated that for TB and DTB, the most preferred sites for donating electron in a reaction are located on the S and N atoms, while the most reactive sites for accepting electrons are associated with the aromatic ring (AR). For TBS and DTBS, the more reactive sites are located on AR, S and AR for nucleophilic, electrophilic and free radical attacks, respectively. In the case of TBSu and DTBSu, the results showed AR to be the more reactive zone for the three kinds of attacks. These last results suggest that cleavage of the C–S bond in TB, TBS and their dechlorinated forms is favored by electrophilic attacks. Additionally, the obtained results suggest that in TB, it is plausible that the cleavage of the C–N is favored on attack of this molecule by electrophiles.

Keywords: thiobencarb; Fukui function; dual descriptor; DFT.

INTRODUCTION

Rice is one of the most important crops in the world,[1] and one of the staple foods for more than half of the world's population.[2] Therefore, different methods have been developed to increase its production. In this sense, rice crop production is higher when herbicide treatments are used in comparison with non-treated crops.[2] The herbicide thiobencarb (*S*-(4-chlorobenzyl)-*N*,*N*-diethylthiocarbamate), also called benthiocarb, see Fig. 1a, has been widely applied in rice paddy fields in Japan and other Asian countries to control various weeds, especially barnyard grass.[3] Thiobencarb (TB) is considered safe for rice plants when used at the recommended rates. TB does not inhibit the germination of seeds, but potently inhi-

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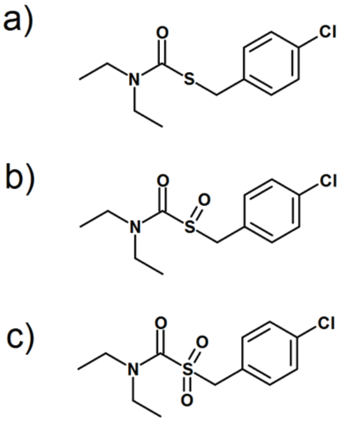


Fig. 1. Chemical structures of thiobencarb derivatives a) thiobencarb, b) thiobencarb sulfoxide and c) thiobencarb sulfone.

bits shoot elongation of germinated seeds.[4] The resultant syndrome is called delayed phytotoxicity syndrome.[3,5] Additionally, when TB is used on paddy fields, its residues in standing water may harm beneficial flora and fauna.[6,7] Moreover, TB is toxic for tadpoles at concentrations found in waters where rice is cultivated.[8] Here, it is interesting to mention that TB is naturally transformed to dechlorinated thiobencarb (DTB) in certain field soils in Japan and the USA, but DTB is highly toxic to rice crops.[8] Additionally, in aqueous phase, TB can easily be oxidized to thiobencarb sulfoxide (TBS) and thiobencarb sulfone (TBSu) under environmental and biological conditions,[9–11] since these oxidized forms are the active forms of TB.[4] Although, thiobencarb is considered as photostable,[12] TB degradation in natural water may occur abiotically through photooxidation,[13] and indirect photolysis *via* hydroxyl radicals.[12,13] If laser flash photolysis is employed, TB degradation involves the photocleavage of the C–S bond.[11] Furthermore, it has been reported that during chlorination of drinking water, thiobencarb is rapidly degraded, producing chlorobenzyl alcohol, chlorotoluene, chlorobenzyl chloride, chlorobenzoic acid and chlorobenzaldehyde as chlorination by-products.[14] Nevertheless, it has recently been reported that the pollution levels of thiobencarb are increasing in drainage canals close to the irrigation systems of rice fields.[15] Moreover, TB was shown to be persistent in water,[16] resulting in an accelerated increase in the concentration of TB and its oxidized metabolites in surface-water,[16] which would constitute a potential risk for drinking water contamination.[17] Moreover, this pollution is a great risk to animals inhabiting freshwater bodies near fields of application.[18] Despite its potential risk as an emerging water contaminant, literature data concerning the chemical behavior of TB and their oxidized derivatives in aqueous phase are very scarce. Thus, a detailed study of the chemical reactivity exhibited by TB, TBS and TBSu and their dechlorinated forms at the molecular level may be fundamental for understanding its degradation mechanism in aqueous phase. In this sense, the values of the frontier orbitals (HOMO and LUMO) of thiobencarb were determined and employed to predict its genotoxicity by artificial neural network simulation.[19] In addition, a quantitative structure–activity relationship study was performed to evaluate the toxicity of TB employing its molecular structure.[20] However, to the best of our knowledge, there is no report in the literature in which the chemical reactivities of TB and its oxidized derivatives are analyzed employing the global and local reactivity descriptors derived from the density functional theory (DFT). Here, it is important to mention that this kind of study may become useful to propose new alternative degradation mechanisms of this herbicide. Therefore, it was considered that this kind of study could contribute to a better understanding of the chemical behavior of this herbicide and its derivatives in the aqueous phase.

Theory

Within the framework of the DFT, it is possible to define global reactivity parameters that yield information about the general chemical behavior of a molecule. These parameters are the electronic chemical potential (μ), the electronegativity (χ) and hardness (η), which are defined as:[21–27]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\frac{1}{2}(I + A) \quad (1)$$

$$\chi = -\mu \quad (2)$$

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = (I - A) \quad (3)$$

In Eqs. (1)–(3), E, N and $v(r)$ are the energy, number of electrons and the external potential of the system, respectively. The chemical potential measures the escaping tendency of an electron and is the negative of the Mulliken electronegativity of molecules,[28] while η is related to the polarizability.[29,30] In addition to μ, χ and η, the global electrophilicity index ω was defined by Parr and can be calculated using μ and η, Eq. (4):[31]

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

According to this definition, ω measures the susceptibility of chemical species to accept electrons. Thus, low values of ω suggest a good nucleophile while higher values indicate the presence of a good electrophile. From this reactivity index, it is possible to define the electrodonating (ω^-) and electroaccepting (ω^+) powers as:[32]

$$\omega^- = \frac{\left(\mu^-\right)^2}{2\eta} \tag{5}$$

$$\omega^+ = \frac{\left(\mu^+\right)^2}{2\eta} \tag{6}$$

where

$$\mu^- = -\frac{1}{4}(3I + A) \tag{7}$$

and

$$\mu^+ = -\frac{1}{4}(I + 3A) \tag{8}$$

In addition to the global reactivity parameters, it is possible to define local reactivity parameters that enable the reactivity on different sites within a molecule to be analyzed. In this sense, the Hard and Soft Acids and Bases principle (HSAB) is useful to predict the reactivity of chemical systems.[33–35] Thus, from the HSAB principle in combination with the DFT, it was possible to identify many useful and important reactivity concepts, such as the Fukui Function $\left(f(\vec{r})\right)$.[33,34] The Fukui function (FF) is defined as:[33,34]

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(r)} = \left(\frac{\partial \mu(\vec{r})}{\partial v(r)}\right) \tag{9}$$

where $\rho(\vec{r})$ is the electronic density. The FF can be evaluated using a finite difference approximation. However, due to the discontinuity of the electron density with respect to the number of electrons (N), this approximation leads to three types of FF for a molecular system, namely, $f^-(\vec{r})$, $f^+(\vec{r})$ and $f^0(\vec{r})$ for electrophilic, nucleophilic, and free radical attacks, respectively, which can be evaluated as:[29]

$$f^-(\vec{r}) = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}) \tag{10}$$

$$f^+(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}) \tag{11}$$

$$f^0(\vec{r}) = \frac{1}{2}\left[\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})\right] \tag{12}$$

On the other hand, it was reported that the dual descriptor is a more accurate tool than nucleophilic and electrophilic Fukui functions.[36] This dual descriptor is able to expose unambiguously truly nucleophilic and electrophilic regions, and can be written as:

$$f^2(\bar{r}) \approx f^+(\bar{r}) - f^-(\bar{r}) = \rho_{N+1}(\bar{r}) - 2\rho_N(\bar{r}) + \rho_{N-1}(\bar{r}) \qquad (13)$$

The dual descriptor allows the preferable sites for nucleophilic attacks ($f^2(\bar{r}) > 0$) and the preferable sites for electrophilic attacks ($f^2(\bar{r}) < 0$) to be obtained simultaneously over the system at point **r**.

COMPUTATIONAL

The optimal conformations of TB, TBS and TBSu were subjected to full geometry optimization in the gas phase employing the hybrid functional wB97XD and the basis set 6-311++G(2d,2p).[37,38] The optimized molecules in the gas phase were further re-optimized in an aqueous solvent employing the wB97XD/6-311++G(2d,2p) level. Solvent phase optimization was performed using the polarizable continuum model (PCM) developed by Tomasi and coworkers.[39,40] The vibrational frequencies were computed to ensure that the stationary points were minima in the potential energy surface (not shown). All the calculations reported herein were performed with the Gaussian 09 package,[41] and visualized with GaussView V. 2.08.[42]

RESULTS AND DISCUSSION

The structures of TB, TBS and TBSu, and their dechlorinated forms DTB, DTBS and DTBSu, respectively, optimized at the wB97XD/6-311++G(2d,2p) level of theory and in the aqueous phase are depicted in Fig. 2; the *xyz* coordinates of these molecules are reported in Tables S-I–S-VI in the Supplementary material to this paper. The total electronic energy calculated for TB, TBS and TBSu are −1455.319899, −1530.503507, and −1605.726321 Ha, while the electronic energies of DTB, DTBS and DTBSu are –995.7099588, –1070.893676 and –1146.116732 Ha, respectively. Note that the bond lengths and angle values are similar in the chlorinated and dechlorinated forms, see Fig. 2–4, suggesting similar molecular structures.

The global chemical reactivity descriptors (η, μ and ω) for TB and its derivatives were evaluated employing Eqs. (1), (3) and (4). In these equations, the value of the vertical affinity energy was calculated as $A=E(\mathrm{N})–E(\mathrm{N}+1)$, where $E(\mathrm{N})$ and $E(\mathrm{N}+1)$ are the total ground-state energies in the neutral (N) and singly charged (N+1) configurations, while the ionization potential was calculated as $I=E(\mathrm{N}–1)–E(\mathrm{N})$, where $E(\mathrm{N}–1)$ corresponds to the energy of the cationic configuration. The values of η, μ and ω for the chlorinated and dechlorinated forms are reported in Table I. Observe that in all cases the hardness values are similar for the chlorinated and dechlorinated forms, which suggests similar chemical stability of TB and its derivatives. If the values of μ and ω of the six molecules studied in the present work are compared, similar results are observed, suggesting equivalent global chemical behavior of the chlorinated and dechlorinated forms of TB.

Here, it is interesting to mention that the origin of toxicity is supposed to be governed by possible charge transfer between a toxin and a biosystem,[43] for example electrophilic substances could form covalent bonds to proteins and DNA,

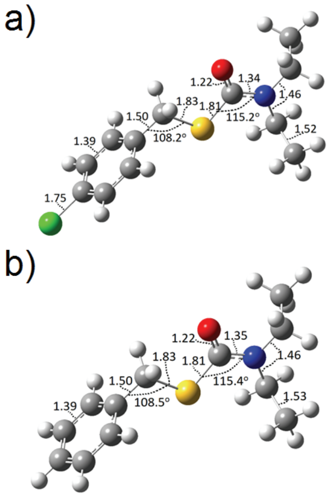


Fig. 2. Chemical structures of a) thiobencarb and b) dechlorinated thiobencarb, optimized at the wB97XD/6-311++G(2d,2p) level of theory in the aqueous phase employing the PCM solvation model.

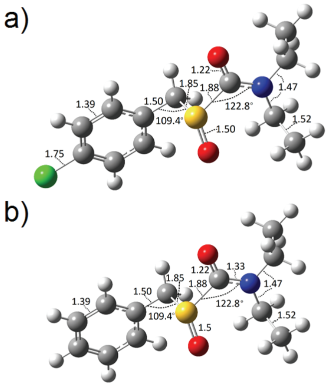


Fig. 3. Chemical structures of a) thiobencarb sulfoxide and b) dechlorinated thiobencarb sulfoxide, optimized at the wB97XD/6-311++G(2d,2p) level of theory in the aqueous phase employing the PCM solvation model.

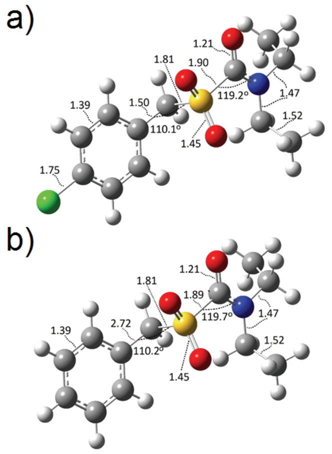


Fig. 4. Chemical structures of a) thiobencarb sulfone and b) dechlorinated thiobencarb sulfone, optimized at the wB97XD/6-311++G(2d,2p) level of theory in the aqueous phase employing the PCM solvation model.

resulting in reactive toxicity and according diseases such as dermal or respiratory sensitization and mutagenicity.[44] In this sense, the origin of the toxicity may be attributed to the electron-accepting nature of a compound,[43] which may be evaluated through Eq. (6).[45] The values of ω^+ for the compounds analyzed in the present work are reported in Table II. Observe that DTB exhibits a lower value of ω^+ in comparison to TB, suggesting major toxicity of DTB. Indeed, this result is coincident with reported experiments in which DTB was found to be more toxic than TB.[8] Moreover, note that the ω^+ value of DTBSu is lower than that obtained for TBSu, suggesting that the former is more toxic than the latter. In the case of DTBS and TBS, these compounds show similar ω^+ values, indicating similar toxicity. According to these results, the more toxic thiobencarb derivatives are DTB and DTBSu.

TABLE I. Global reactivity descriptors evaluated for TB and its dechlorinated forms at the wB97XD/6-311++G(2d,2p) level of theory in the aqueous phase, employing the PCM solvation model, according to the Eqs. (1), (3) and (4)

Species	η / eV	μ / eV	ω / eV	Species	η / eV	μ / eV	ω / eV
TB	0.22	–0.15	0.05	DTB	0.22	–0.14	0.04
TBS	0.22	–0.15	0.05	DTBS	0.22	–0.15	0.05
TBSu	0.22	–0.15	0.05	DTBSu	0.24	–0.15	0.05

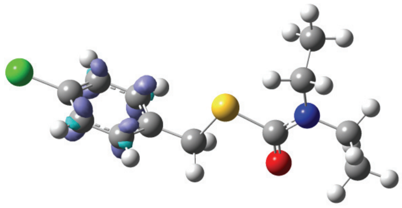
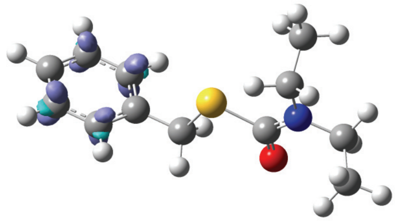
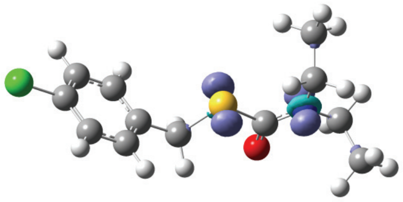
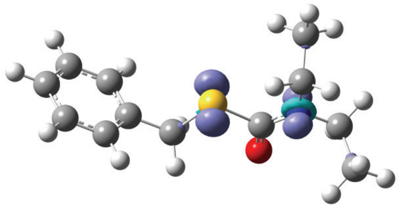
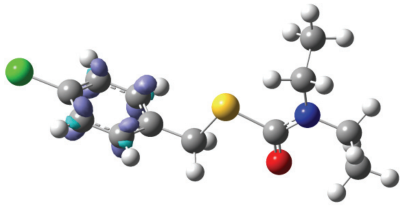
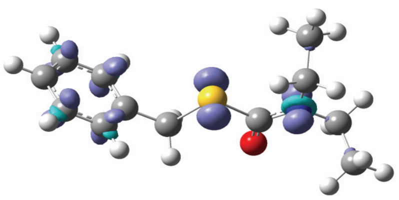
TABLE II. Electron-accepting (ω^+) powers evaluated at the wB97XD/6-311++G(2d,2p) level of theory in the aqueous phase, employing the PCM solvation model, according to Eq. (6)

Species	ω^+ / eV	Species	ω^+ / eV
TB	0.0195	DTB	0.0158
TBS	0.0201	DTBS	0.0202
TBSu	0.0204	DTBSu	0.0167

Local reactivity descriptors

In order to pinpoint the distribution of the active sites of TB and its derivatives, Eqs. (10)–(12) were employed to calculate the distribution of FF on the respective molecule. The obtained FF isosurfaces for TB and DTB obtained are depicted in Table III. In the case of TB the more susceptible sites to nucleophilic and free radical attack are located in the aromatic ring (AR), while for electrophilic attack, the more reactive sites are on the S and N atoms, see Fig. 2. For the case of DTB, the sites more reactive to electrophilic and free radical attack are on the N and S atoms, while the more nucleophilic active sites are on AR. Thus, the dechlorination process does not modify the positions of the sites more reactive to nucleophilic and electrophilic attacks observed on TB, TBS and TBSu. Free radical attacks on DTB are expected on the AR and S atom. Furthermore, electrophilic and free radical attacks on S may start the DTB degradation process by cleavage of the C–S bond.

TABLE III. Isosurfaces of the Fukui Functions for nucleophilic ($f^{+}(\vec{r})$), electrophilic ($f^{-}(\vec{r})$) and free radical attacks ($f^{0}(\vec{r})$) on TB and DTB according to Eqs. (10), (11) and (12) at the wB97XD/6-311++G(2d,2p) level of theory, employing the PCM solvation model. In all cases the isosurfaces were obtained at 0.01 e/a.u.^{3}

FF	TB	DTB
$f^{+}(\vec{r})$		
$f^{-}(\vec{r})$		
$f^{0}(\vec{r})$		

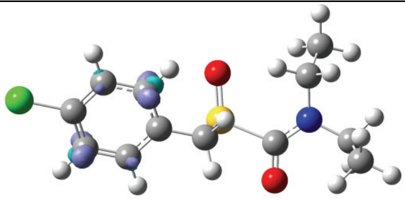
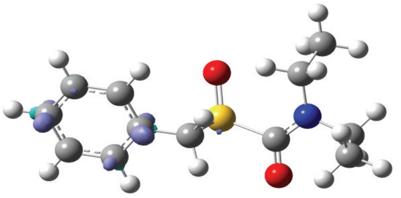
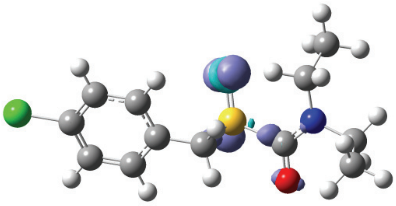
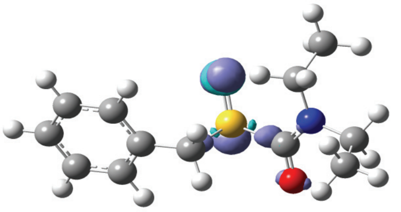
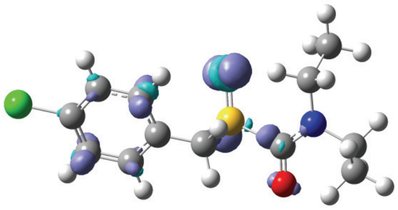
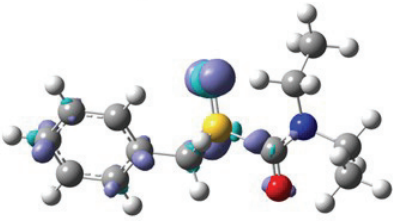
The FF isosurfaces for TBS and its dechlorinated form are shown in Table IV. For this molecule, the more nucleophilic reactive sites are located in the AR, for electrophilic attack, the more reactive sites are on the N and S atoms, while those for free radical attacks are in the AR and on the N and S atoms. Interestingly, the dechlorination process does not modify the reactivity distribution because DTBS exhibited the same chemical behavior as TBS. From these results, it is possible to suggest that the fragmentation of both molecules is possible if the S atom is attacked by either electrophiles or free radicals, favoring the cleavage of the C–S bond, as was experimentally observed for TB.[11]

The FF isosurfaces for TBSu and DTBSu are shown in Table V, note that in all cases the AR is the most susceptible site to the three kinds of attack, which suggests aromatic substitutions instead of direct degradation of these molecules.

The most reactive sites for each molecule are summarized in Table VI, note that in all cases, nucleophilic attacks favor aromatic substitutions on the AR.

In addition, the local chemical reactivity of TB and its derivatives were analyzed by means of the dual descriptor, Eq. (13). This descriptor allows the preferred sites for nucleophilic and electrophilic attacks on a system at point **r** to be simultaneously

TABLE IV. Isosurfaces of the Fukui Functions for nucleophilic ($f^{+}(\vec{r})$), electrophilic ($f^{-}(\vec{r})$) and free radical attacks ($f^{0}(\vec{r})$) on TBS and DTBS according to Eqs. (10), (11) and (12) at the wB97XD/6-311++G(2d,2p) level of theory employing the PCM solvation model. In all cases, the isosurfaces were obtained at 0.01 e/a.u.^{3}

FF	TBS	DTBS
$f^{+}(\vec{r})$		
$f^{-}(\vec{r})$		
$f^{0}(\vec{r})$		

obtained. The distribution of the dual descriptor for the thiobencarb derivatives is reported in Table VII. The more reactive sites for TB and TBS were found in the AR, and on the S atom for nucleophilic and electrophilic attacks, respectively. For TBSu, the more reactive sites are in the AR. In the case of the dechlorinated molecules, the nucleophilic attacks are in the AR for DTB, DTBS and DTBSu, while the electrophilic attacks are located on the AR, S and AR for DTB, DTBS and DTBSu, respectively. A summary of the more reactive sites is reported in Table VIII. These results are coincident with those obtained from Eqs. (10), (11) and (12). The last results suggest that cleavage of the C–S bond, experimentally observed during TB degradation,[11,46] may be obtained by electrophiles attacking TB, TBS and their dechlorinated forms. Moreover, the presented results indicate that this electrophilic attack might cause cleavage of the C–N bond in TB and DTB.

In addition to the global and local reactivity descriptors, the reactivity of TB, TBS, and TBSu and their dechlorinated forms through maps of the electrostatic potential was also analyzed. This kind of maps may provide insight into reactivity.[47] In these maps, a reactive site is a particularly charged region of a molecule

TABLE V. Isosurfaces of the Fukui Functions for nucleophilic ($f^{+}(\vec{r})$), electrophilic ($f^{-}(\vec{r})$) and free radical attacks ($f^{0}(\vec{r})$) on TBSu and DTBSu according to Eqs. (10), (11) and (12) at the wB97XD/6-311++G(2d,2p) level of theory employing the PCM solvation model. In all cases the isosurfaces were obtained at 0.01 e/a.u.^{3}

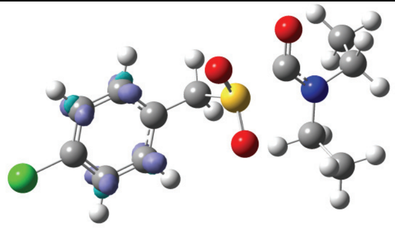
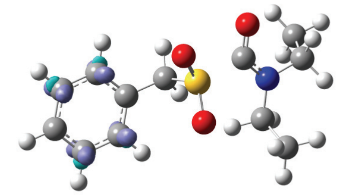
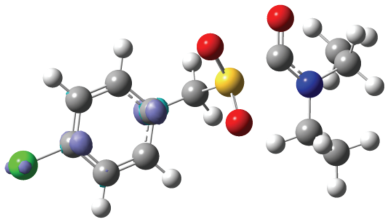
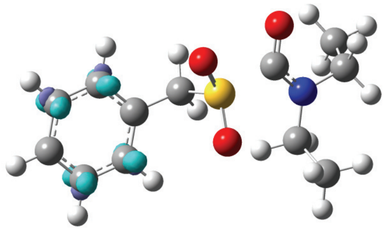
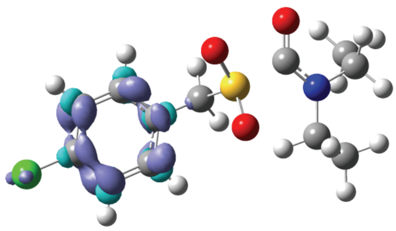
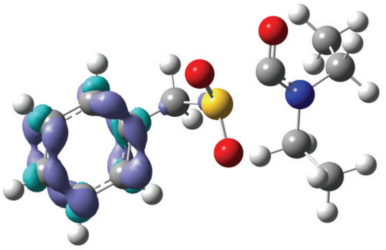
FF	TBSu	DTBSu
$f^{+}(\vec{r})$		
$f^{-}(\vec{r})$		
$f^{0}(\vec{r})$		

TABLE VI. More reactive sites according to the condensed Fukui functions determined at the wB97XD/6-311++G(2d,2p) level of theory employing the PCM solvation model

Species	$f^{+}(\vec{r})$	$f^{-}(\vec{r})$	$f^{0}(\vec{r})$	Species	$f^{+}(\vec{r})$	$f^{-}(\vec{r})$	$f^{0}(\vec{r})$
TB	AR	S,N	AR	DTB	AR	S,N	S,N
TBS	AR	S	AR,S	DTBS	AR	S	AR,S
TBSu	AR	AR	AR	DTBSu	AR	AR	AR

that has an affinity for interacting with charged particles. Thus, a region of very low potential energy would have a very strong influence on positively charged particles or regions of particles nearby. In Fig. S-1 (see Supplementary material), areas of low potential (red color) are characterized by an abundance of electrons, while areas of high potential (blue color) are characterized by a relative lack of electrons. Note that the oxygen atoms have the lowest potential values in comparison to the other atoms and consequently have a higher electron density around them.

TABLE VII. Dual descriptors evaluated at the wB97XD/6-311++G(2d,2p) level of theory employing the PCM solvation model according to equation (13). In all cases the isosurfaces were obtained at 0.01 e/a.u.^{3}

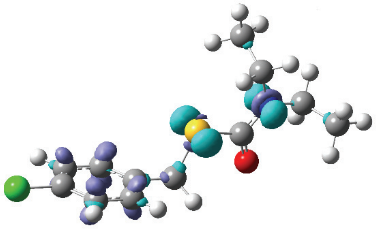
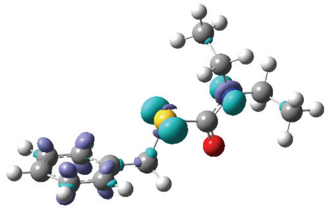
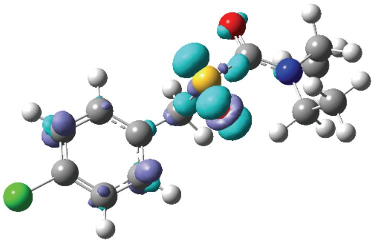
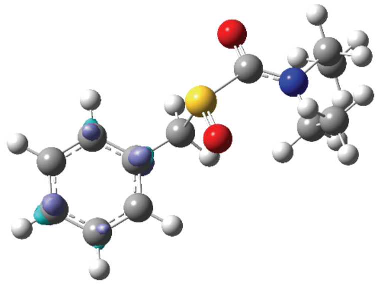
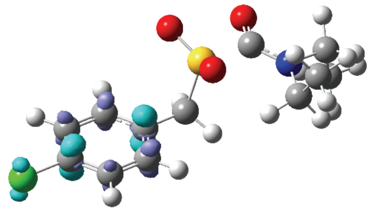
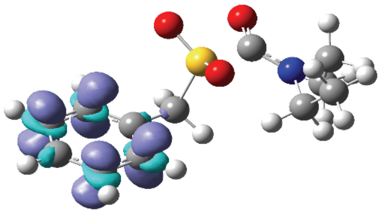
Species	$f^2(\bar{r})$ -chloro	$f^2(\bar{r})$ -without chloro
TB		
TBS		
TBSu		

TABLE VIII. Summary of the more reactive sites according to the dual descriptor at the wB97XD/6-311++G(2d,2p) level of theory employing the PCM solvation model according to Eq. (13)

Species	Nucleophilic	Electrophilic	Species	Nucleophilic	Electrophilic
TB	AR	S,N	DTB	AR	S,N
TBS	AR	S	DTBS	AR	AR
TBSu	AR	AR	DTBSu	AR	AR

CONCLUSIONS

In the present work, the chemical reactivity of chlorinated and dechlorinated *S*-(4-chlorobenzyl)-*N*,*N*-diethylthiocarbamate and its oxidized derivatives were analyzed in the aqueous phase. The results suggest that the six molecules studied have a similar global chemical behavior. However, Fukui functions isosurfaces revealed that the AR is the most susceptible zone to nucleophilic attacks in all cases. Only TB and TBS, and their dechlorinated forms show a main susceptibility to electrophilic attacks on the N and S atoms. These results suggest that the photocleavage of the C–S bond is favored in aqueous media by electrophiles. In addition, except for DTB, free radical attacks are favored in the aromatic ring for the other chemical species analyzed.

SUPPLEMENTARY MATERIAL

Additional computational data are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

DFT ПРОУЧАВАЊЕ ХЕМИЈСКЕ РЕАКТИВНОСТИ У ВОДЕНОЈ ФАЗИ ТИОБЕНКАРБА И ЊЕГОВИХ ОКСИДОВАНИХ ДЕРИВАТА

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У овом раду, анализиране су глобална и локална реактивност *S*-(4-хлоробензил)-*N*,*N*-диетилтиокарбамата (TB) и њихових оксидованих деривата (сулфона (TBSu) и сулфоксида (TBS). Проучавана је и хемијска реактивност дехлорованих облика TB (DTB), TBSu (DTBSu) и TBS (DTBS). Израчунавања су изведена на wB97XD/6-311++G(2d,2p) нивоу теорије у воденој фази. Кондензоване функције Fukui указују да су у TB и DTB најповољнија места за давање електрона лоцирана на S и N атомима, док су најреактивнија места за прихватање електрона придружена ароматичном прстену (AR). За TBS и DTBS, најреактивнија места су лоцирана на AR, S и AR за нуклеофилне, електрофилне односно слободнорадикалске нападе. У случају TBSu и DTBSu, AR је најреактивнија зона за све три врсте напада. Последњи резултати сугеришу да је раскидање C–S везе у TB, TBS и њиховим дехлорованим облицима фаворизовано електрофилним нападима. Поред тога, резултати сугеришу да је у TB вероватно раскидање C–N фаворизовано нападањем електрофилима на овај молекул.

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