Theoretical study of the molecular properties of dimethylanthracenes as properties for the prediction of their biodegradation and mutagenicity

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HIGHLIGHTS

- Electronic properties of dimethylanthracenes (DMAs) and biodegradation by bacteria.
- DFT methods are employed.
- Ionization potentials and electron affinities of DMAs are almost constant.
- Obtained polarizabilities can be used as predictors of biodegradation rates of DMAs.
- Vibrational property/observed mutagenic activity relationship is determined.

GRAPHICAL ABSTRACT
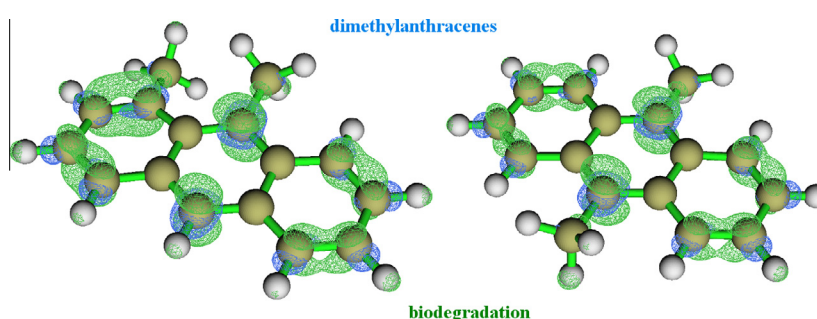
ABSTRACT

There is little information available on methyl derivatives of anthracene and their interaction with the enzymes of bacterial consortia that could be found in petroleum sludge. In this study a theoretical investigation of all dimethylanthracenes (DMA) isomers and their relation to biodegradation are presented. Equilibrium geometries, ionization potentials (*IP*), electronic affinities (*EA*), dipole moments and electronic dipole polarizabilities of DMA isomers calculated by Density Functional Theory (DFT) methods are reported. The calculated *IP* and *EA* values vary little along the series of isomers. The polarizability values ($\langle\alpha\rangle$, $\Delta\alpha$, and α_{yy}) increase on passing from meso,meso- and α,meso- to β,β-DMA isomers. The computed polarizability values of DMAs can be used as predictors in determining differences in biodegradation rates of DMAs. The summation over Raman activity $\sum A_{Raman}$ over 3N-6 vibrational modes is sensitive to the position of the methyl substituent. The $\sum A_{Raman}$ values of 1-methylanthracene (MA), 2-MA, 2,9-DMA and 9,10-DMA are consistent with observed mutagenic activities in *Salmonella Typhimurium* strains TA98 and TA100.

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1. Introduction

Alkylaromatic molecules are structural features of coals, heavy oils and residua. The methylated forms of PAHs are shown to be more carcinogenic than their parent counterparts (Slaga et al., 1974; Hecht et al., 1977; La Voie et al., 1981; Hoffman et al., 1982; Myers et al., 1988; Kurihara et al., 1996; Flesher et al., 2010). The bioalkylation of non-methylated PAHs occurs *in vivo* and non-carcinogenic PAHs may be converted to carcinogenic (Flesher et al., 2010, Flesher and Myers, 1991a,b; Myers et al., 1988). Anthracene can be found in coal tar pitch and certain

petroleum distillate fractions. The levels of anthracene and other PAHs in gasoline and diesel lubricating oils increase with mileage of use. Methylanthracenes have also been identified in diesel exhaust. Sjögren et al. (1996) observed a significant correlation of mutagenic effects with the content of polycyclic aromatic compounds of the diesel fuels, particularly of picene, phenanthrene, 2-methylanthracene, 3-methylphenanthrene and fluoranthene. A cigarette smoke is a rich source of PAHs. It contains methylated anthracenes and phenanthrenes as the predominant PAHs. The previous results on mutagenic activities of methylated derivatives of anthracene in *Salmonella Typhimurium* TA98 and TA100 showed that methylanthracenes are mutagenic and have tumor-initiating activity on mouse skin (La Voie et al., 1985). The bioassays indicate that increased mutagenic potency and tumor-initiating activity are associated with the presence of a methyl substituent at both the 9- and 10- position of anthracene. Anthracene and 2-methylanthracene do not inhibit significantly gap junction intercellular communication (GJIC) in rat liver epithelial cells, whereas anthracene methylated in the 1 or 9 position reversibly inhibited GJIC (Upham et al., 1996).

The microbial degradation is believed to be one of the major processes for cleaning up PAH-contaminated sediments. However, it is also important to keep in mind that although it is a cheap method, it sometimes leads to metabolites that are more or less carcinogenic than the parent compound. The interaction of alkyl derivatives of PAHs with the enzymes of bacterial consortia has gained increasing interest during recent years. The biodegradation of DMAs is of environmental interest and it is particularly important to have the prediction of the biodegradation rates of these molecules. Wammer and Peters (2005) performed a structure-based study of the biodegradation rates of 22 PAHs in aqueous systems. The consortium of aerobic PAH-degraders enriched on a broad range of PAHs was used in their study. The number of rings of PAHs studied varied from two to four and the PAHs with different alkyl substituents and different positions of substituent were examined. Wammer and Peters concluded that the presence of the alkyl substituents in the α position significantly decrease the rate of biodegradation. Librando and Alparone investigated theoretically the dipole polarizabilities and vibrational properties of dimethylnaphthalene (DMN) isomers (Librando and Alparone, 2007a; Alparone and Librando, 2012c). They revealed that the computed averaged dipole polarizabilities and the summation of the Raman activities over vibrational degrees of freedom of DMNs are in excellent linear correlation with the observed first-order bio-mass-normalized rate coefficient of DMNs, a parameter related to the rate of biodegradation of DMNs investigated experimentally by Wammer and Peters (2005).

The present work on methylanthracenes is part of our continuing study of molecules found in complex fossil fuels (Ostojić and Đorđević, 2012a,b; Ostojić et al., 2013a; Ostojić and Đorđević, 2013a,b). In our previous study on trimethylnaphthalenes (TMNs) (Ostojić and Đorđević, 2012b) the presented results on the theoretical prediction of biodegradation rates of 2,3,6-TMN, 1,3,6-TMN and 1,3,7-TMN follow exactly the experimental order of susceptibility of these isomers to biodegradation, 2,3,6-TMN > 1,3,6-TMN > 1,3,7-TMN (Huang et al., 2004). We know of neither experimental nor theoretical study on the biodegradation of dimethylanthracenes. To the best of our knowledge electronic and spectroscopic properties of most of dimethylanthracenes are reported here for the first time. The main aim of this study is to investigate the effects of methyl substituents on the selected physico-chemical properties of methylated anthracenes such as relative energies, ionization potential (*IP*), electron affinity (*EA*), dipole moment (μ), electronic polarizability (α) and vibrational properties through computational methods and to explore possible relation-

ships with the observed mutagenic activities and to predict the biodegradation rates.

2. Computational details

The equilibrium geometries of all dimethylanthracene isomers were fully optimized using the B3LYP (Becke3-Lee–Yang–Parr) DFT method (Lee et al., 1988; Becke, 1993) with the 6-311+G(2df,p) basis set which consists of 628 contracted basis functions on the carbon and hydrogen atoms. We performed the optimizations in the framework of the C_1 point group. The frequency B3LYP/6-311+G(2df,p) calculations showed no imaginary values, implying that all the structures are minima on the potential energy surface of the ground electronic state. The vertical first ionization potentials and vertical electron affinities were calculated according to the formulas:

$$IP = E_{cation} - E_{neutral}$$
$$EA = E_{neutral} - E_{anion}$$

where E_{cation}, E_{anion}, and $E_{neutral}$ are the energy of the cation, anion, and neutral, respectively, calculated using the optimized geometry of the neutral ground state at the B3LYP/6-311+G(2df,p) level of theory. The energies of the ground electronic states of the cation and anion were calculated using the unrestricted B3LYP method (UB3LYP) while neutral ground state energies were calculated employing the B3LYP level of theory. In the calculations the spin contamination in the UB3LYP procedure was acceptably low – the calculated $\langle S^2 \rangle$ value differs from the exact $S(S + 1)$ value by about 0.01%. We employed the 6-311++G(2d,2p) basis set for calculation of the *IP* and *EA* values of the dimethylanthracene isomers. For the determination of the relative energies of the isomers the B3LYP/6-311+G(2df,p) level of theory was employed too. The zero-point vibrational energies (*ZPVE*) were scaled using the scaling factor of 0.9889 determined for the B3LYP method and the 6-311+G(2df,p) basis set (Merrick et al., 2007). From the calculated components of the zero-frequency (static) dipole polarizability tensor along the principal axes, α_{xx}, α_{yy}, α_{zz}, at the B3LYP/6-311+G(2df,p) level, the following quantities (Long, 1982) are obtained:

the electronic contribution to the average polarizability, $\langle\alpha\rangle$:

$$\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

and the electronic contribution to the polarizability anisotropy, $\Delta\alpha$:

$$\Delta\alpha = \left\{ \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6\left(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2\right)^2 \right]/2 \right\}^{1/2}$$

The dipole moment values were calculated at the B3LYP/cc-pVTZ level of theory.

The Fukui function (Parr and Yang, 1984) for 1,9-DMA, 2,7-DMA, 2,9-DMA, 9,10-DMA, 1,3-DMA, and 1,8-DMA was calculated employing the natural population analysis (NPA) (Reed et al., 1988) and Bader's topological population analysis scheme (Bader, 1990) at the B3LYP/cc-pVTZ level of theory as implemented in the Gaussian 09 package (Frisch et al., 2010). A good performance of the B3LYP functional and the cc-pVTZ basis set for the calculation of the Fukui function $f^-(r)$ has been reported by De Proft et al. (1996). The Fukui function $f^-(r)$ was obtained as a finite difference approximation from the population in an *N*-electron and $(N - 1)$-electron system using the equilibrium geometry of the *N*-electron system. The figures showing the Fukui function were obtained with the help of the program Multiwfn (Lu and Chen, 2012). All calculations have been performed with the Gaussian 09 (Frisch et al., 2010) and Gaussian 03 (Frisch et al., 2004) program packages.