

Proton affinity of S-containing aromatic compounds: Implications for crude oil hydrodesulfurization

Isidoro García-Cruz^{a,*}, Diego Valencia^b, Tatiana Klimova^b, Raúl Oviedo-Roa^a,
José Manuel Martínez-Magadán^{a,c}, Rodolfo Gómez-Balderas^c, Francesc Illas^d

^a Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte,
152 Colonia San Bartolo Atepehuacán, México, 07730, D.F., Mexico

^b Facultad de Química, Universidad Nacional Autónoma de México, México, D.F., México

^c Depto de Química, FES-Cuautitlán, UNAM, Av. 1 de Mayo s/n, C. Izcalli, Edo. México, 54700, México

^d Departament de Química Física i Centre especial de Recerca en Química Teòrica, Universitat
de Barcelona i Parc Científic de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

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Abstract

The electronic structure and proton affinities of a series of organosulfur compounds such as thiophene, dibenzothiophene and a series of their derivatives have been studied by means density functional theory. The molecular structure of these compounds and their protonated species has been obtained by means of geometry optimization and characterized as potential energy surface minima by harmonic frequency analysis. The analysis of frontier orbitals, aromaticity and proton affinity permits one to make quantitative predictions about the difficulty to remove sulfur from these molecules. In particular, it is suggested that the proton affinities provide a descriptor of the activity of these molecules towards hydrodesulfurization. © 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrodesulfurization; Proton affinity; NICS; HOMO; LUMO

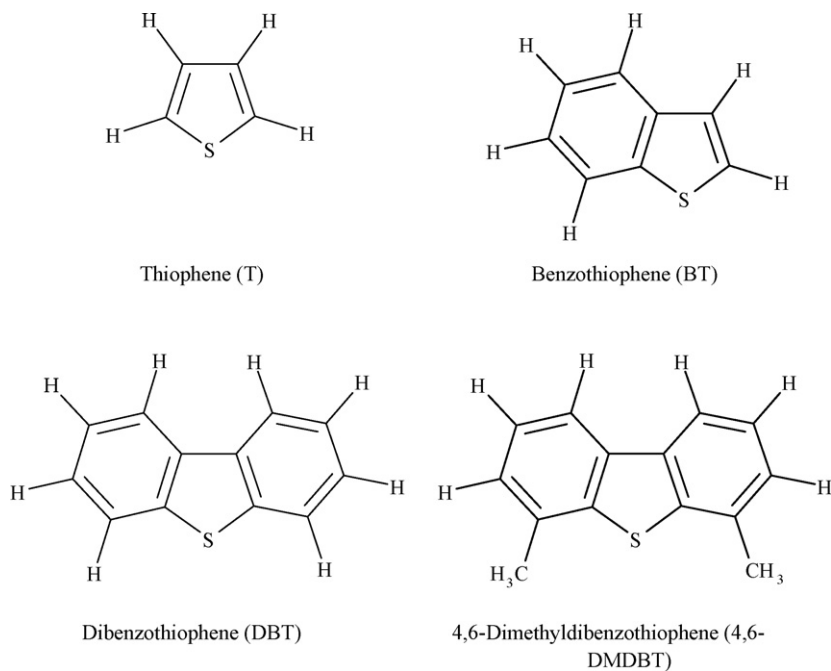
1. Introduction

Crude oil contain organosulfur compounds such as thioles, thioethers, thiophene, benzothiophenes, dibenzothiophene and other derivatives which need to be treated before using petroleum derivatives as fuels. Hydrodesulfurization (HDS) is the usual process used in industry to eliminate sulfur from these potential pollutants. In the HDS process, sulfur containing molecules react with hydrogen on Co(Ni)MoS₂/Al₂O₃ catalysts [1,2] to yield hydrocarbons and H₂S [3–6]. This is indeed one of the most important steps in oil refining. Thus, HDS aims at reducing the sulfur content in the petroleum feedstock to a sufficient low level so as to accomplish the set of severe conditions recently introduced in the environmental legislation of many developed countries. New environmental regulations will impose a further reduction of the sulfur emissions (SO_x) produced upon fuel combustion. This implies the production of cleaner fuels and thereby

the need to improve the efficiency of the hydrodesulfurization of the petroleum feedstock. Currently, sulfur concentrations of the middle-distillate fraction can range widely from 500 to 5000 ppm or even higher in the case of distillate from heavy or extra heavy crude oils. Future specifications for ultra-low sulfur diesel fuel (ULSD) of 10–15 ppm will require significant hydrotreating catalysts improvement [7,8].

Sulfur removal by HDS of components of feedstock such as thioles and thioethers is rather easy but this becomes difficult for sulfide aromatic and even harder for alkyl-substituted sulfide aromatic compounds which resist HDS treatment under classical conditions. Recent progress in catalyst design have yielded catalytic mixtures capable of succeeding in S removal in thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), and di-alkyl-dibenzothiophenes, such as 4,6-di-methyl-dibenzothiophene (4,6-DMDBT). The position of alkyl groups in these substituted dibenzothiophenes (Scheme 1) is believed to play an important role in controlling their reactivity with respect to HDS. For instance, desulfuration activity over a CoMoS₂/Al₂O₃ catalysts goes in the order 2,8-DMDBT > 3,7-DMDBT > 4,6-DMDBT, the last compound exhibiting the

* Corresponding author. Tel.: +52 55 9175 6903; fax: +52 55 9175 6380.
E-mail address: igarcia@imp.mx (I. García-Cruz).



Scheme 1.

lowest conversion rate. The electronic effects of the alkyl groups are recognized to be responsible for the relatively higher activity of 2,8-DMDBT towards HDS whereas the poor reactivity of the 4,6-DMDBT has been attributed to the steric hindrance provoked by the methyl groups, which render the sulfur atom inaccessible to the active sites of the catalysts.

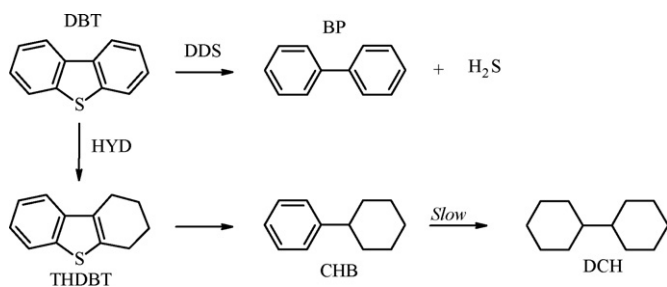
Two major pathways to desulfurized products have been proposed, the first one is called direct desulfurization (DDS) and the second one is usually referred to as the hydrogenation route (HYD). In the DDS pathway, the sulfur atom is removed from the structure and replaced by hydrogen, without hydrogenation of any of the other carbon–carbon double bonds (Scheme 2). On the other hand, in the HYD route, also shown in Scheme 2, it is assumed that at least one aromatic ring is hydrogenated before the sulfur atom is removed.

A few attempts exist aiming at understanding the activity of these compounds towards HDS through the analysis of kinetic data, mainly apparent reaction rate constants [9–12,13]. This is because it is customary to treat these chemical processes as pseudo-first order reactions although these hydrogenation and hydrogenolysis reactions are better treated as complex mechanisms [14–16]. It is also important to point out that there are

few studies aiming at correlating molecular properties with the HDS activity of these compounds [17–19]. In this respect, a more systematic analysis of the electronic effects caused by the presence of alkyl-groups in the different positions of di-alkyl-dibenzothiophenic compounds seems to be needed since these effects are likely to have an influence in their activity towards HDS. To this end, a systematic study of the electronic structure and various reactivity indexes is carried out for a series of sulfur containing molecules using a computational electronic structure approach with the goal of obtaining molecular descriptors which allow one to derive a quantitative relationship between activity towards HDS and molecular properties. Thiophene, benzothiophene, dibenzothiophene and several alkyl-derivatives, have been chosen on the basis of their different activity towards HDS. The present work also explores whether these molecular descriptors can be used to provide information about the preferred desulfurization route followed by a given species.

2. Computational strategy and details

A detailed structural study of thiophene, benzothiophene, dibenzothiophene and some alkyl derivatives, protonated and unprotonated, has been carried using *ab initio* quantum chemical methods. The list of compounds studied includes thiophene (T), α methyl thiophene (α -MT), β -methyl thiophene (β -MT), benzo thiophene (BT), 4 methyl benzo thiophene (4MBT), di benzo thiophene (DBT), 1 methyl di benzo thiophene (1MDBT), 2 methyl di benzo thiophene (2MDBT), 3 methyl di benzo thiophene (3MDBT), 4 methyl di benzo thiophene (4MDBT), 1,9 di methyl di benzo thiophene (19DMDBT), 2, 8 di methyl di benzo thiophene (28DMDBT), 3,7 di methyl di benzo thiophene (37DMDBT), 4,6 di methyl di benzo thiophene (46DMDBT), 4 methyl 8 ethyl di benzo thiophene (4M8EDBT),



Scheme 2.

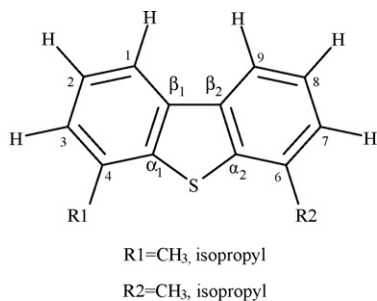


Fig. 1. Schematic representation of the dibenzothiophene and the different substituted compounds.

3,4,6 tri methyl 8 ethyl di benzo thiophene (346TM8EDBT), and 4,6 di isopropyl di benzo thiophene (46DIISOPRDBT). The electronic structure of these compounds (see Fig. 1) has been studied within of frame of the hybrid density functional theory (DFT). The well-known B3LYP hybrid exchange-correlation [20,21] functional, in combination with a 6-311++G** basis sets [22] have been used. All the geometries were fully optimized from starting geometries obtained through the semiempirical PM3 method [23]. Next, the first principles B3LYP optimized geometries were characterized as true minima by harmonic frequency analysis. All the calculations were performed with the Gaussian 98 package [24].

The electronic structure and several properties have been obtained and analyzed. These are the widely used HOMO–LUMO energy gap (Δ_{H-L}); the nucleus independent chemical shifts (NICS) [25], and the proton affinities. The NICS are defined as the absolute magnetic shielding computed at the ring center; which in turn is defined as the unweighted average of the heavy atom coordinates. To have a correspondence with the familiar nuclear magnetic resonance (NMR) chemical shift convention, negative NICS indicate aromaticity. The NICS have been calculated at the same level of theory used for the geometry

optimization using the continuous set of the gauge transformation method [26,27]. NICS values have been computed at the center of the thiophenic and benzenic rings of the unprotonated and protonated species. This methodology has been applied of successfully in our research group in different studies on neutral and free radical species [28–31]. The proton affinity (PA) is defined as the negative of the enthalpy change at 298.15 K for the $A + H^+ \rightarrow AH^+$, therefore

$$PA = -\Delta H_{298} = -\{\Delta E_0 + \Delta E_{\text{therm}} + \Delta(PV)\} \quad (1)$$

where ΔE_0 is the difference in the total electronic energies of the species at 0 K, ΔE_{therm} includes contributions from zero-point vibrational energy differences, thermal vibrational energy differences, rotational energy differences, and thermal translational energy differences. $\Delta(PV)$ is the standard conversion from internal energy to enthalpy and for all proton affinity reactions equals $-RT$ ($=-2.48$ kJ/mol). [32] The thermal corrections for the rotational and translational contributions account $3/2RT$ and the vibrational one is negligible with respect to the zero point vibrational energy. Therefore proton affinities are finally computed as in the following equation:

$$PA = -\Delta H_{298} = -\left\{ \Delta E_0 + \Delta E_{\text{ZPE}} - \frac{5}{2}RT \right\} \quad (2)$$

3. Results and discussion

3.1. Geometries

The optimized geometrical parameters for the thiophene, benzothiophene, dibenzothiophene and their alkyl-derivatives (Fig. 1) calculated at B3LYP/6-311++G** levels are displayed in Table 1. X-ray diffraction values for thiophene are also given for comparison. From Table 1 it is clear that differences between the structural parameters of these molecules are very small. The

Table 1
Bond lengths in various sulfur containing as predicted at the B3LYP/6-311++G** level of theory

Parameters	T	BT	4MBT	DBT	4MDBT	19DMDBT	28DMDBT	37DMDBT	46DMDBT	Exp. (Ref. [32])
Bond length (Å)										
C ₁ –C ₂		1.385	1.384	1.388	1.387	1.397	1.391	1.383	1.387	
C ₂ –C ₃		1.405	1.405	1.401	1.401	1.395	1.409	1.409	1.401	
C ₃ –C ₄		1.388	1.392	1.389	1.394	1.386	1.388	1.393	1.394	
C ₁ –C β_1		1.406	1.406	1.401	1.401	1.420	1.402	1.402	1.401	
C ₄ –C α_1		1.397	1.404	1.394	1.402	1.392	1.395	1.396	1.402	
C α_1 –S	1.733	1.756	1.758	1.766	1.769	1.757	1.766	1.767	1.768	1.71
C α_2 –S	1.733	1.749	1.749	1.766	1.765	1.757	1.766	1.767	1.768	1.71
C α_1 –C β_1	1.366	1.416	1.414	1.411	1.410	1.420	1.409	1.409	1.409	1.37
C α_2 –C β_2	1.366	1.356	1.355	1.411	1.410	1.420	1.409	1.409	1.409	1.37
C β_1 –C β_2	1.427	1.439	1.439	1.453	1.454	1.476	1.454	1.452	1.454	1.40
Bond angle (°)										
C ₁ C ₂ C ₃		120.7	120.9	120.5	120.7	122.7	118.7	121.6	120.7	
C ₂ C ₃ C ₄		120.8	121.9	120.7	121.8	119.6	121.7	118.8	121.8	
C ₃ C ₄ C α_1		118.4	116.5	118.5	116.7	118.1	118.7	119.6	116.7	
C ₄ C α_1 C β_1		121.6	122.6	121.6	122.6	123.4	121.1	121.8	122.6	
C ₁ C β_1 C α_1		118.7	118.9	118.7	118.9	116.8	118.9	118.2	118.9	
C α_1 S C α_2	91.4	90.9	90.9	90.9	91.0	90.9	90.8	90.9	91.0	92.2
C β_1 C α_1 S	111.5	111.1	110.9	112.4	112.2	113.1	112.5	112.2	112.2	

Table 2
HOMO energy, LUMO energy, HOMO-LUMO gap (Δ_{H-L}), proton affinity (PA) and net charge of S (Q_S) in thiophene and its derivatives at B3LYP/6-31++G** level

Compound	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	(Δ_{H-L}) (eV)	PA (J/mol)	Q_S
Thiophene	-0.24344	-0.02438	5.961	730.2	0.023
α -MT	-0.23119	-0.02110	5.717	754.2	-0.024
β -MT	-0.23628	-0.01852	5.926	746.7	0.004
BT	-0.22579	-0.03774	5.117	776.7	-0.140
4MBT	-0.22204	-0.03544	5.078		-0.133
DBT	-0.22311	-0.04925	4.731	806.4	0.013
1MDBT	-0.21914	-0.04543	4.727		-0.07
2MDBT	-0.21859	-0.04750	4.656		-0.053
3MDBT	-0.22087	-0.04499	4.786		-0.04
4MDBT	-0.22055	-0.04630	4.742	813.2	-0.082
19DMDBT	-0.21410	-0.04606	4.573	820.6	-0.035
28DMDBT	-0.21473	-0.04590	4.594	825.2	-0.039
37DMDBT	-0.21877	-0.04090	4.840	821.5	-0.028
46DMDBT	-0.21830	-0.04355	4.755	818.3	-0.200
4M8EDBT	-0.21573	-0.04359	4.684		-0.079
346TM8EDBT	-0.21018	-0.03845	4.673	844.4	-0.251
46DIISOPRDBT	-0.21543	-0.04406	4.663		-0.416

average variation in the distances C_1-C_2 is 0.002 Å, C_2-C_3 and C_3-C_4 is 0.001 Å, $C_1-C\beta_1$ is 0.001 Å, $C_1-C\alpha_1$ is 0.0003 Å, whereas the changes in the bond angles are negligible, $C_1C_2C_3$ is 0.8 (°), $C_3C_4C\alpha_1$ is 0.2 (°) and $C\alpha_1SC\alpha_2$ is 0.1 (°). The last angle is only 1 (°) smaller than the experimental value for thiophene [33].

Notice that all the studied molecules present a nearly planar structure, the exception being the 1,9-DMDBT that displays a distorted geometry due to the methyl groups hindrance. As it is well-known planar geometries favor aromaticity.

3.2. Electronic properties

The relevant electronic structure features of thiophene, benzothiophene, dibenzothiophene and its alkyl-derivatives, the HOMO-LUMO gap, proton affinity, S charges as obtained at the B3LYP/6-311++G** level of theory, are summarized in Table 2.

For all these organosulfur compounds, the HOMO energies display a variation going from -0.243 a.u. for the thiophene to -0.210 a.u. for the 3,4,6-trimethyl-8-ethylidibenzothiophene, whereas those of the LUMO energies present a smaller variation going from -0.049 a.u. for the DBT to -0.019 a.u. for the β -methyl-thiophene. An interesting electronic parameter is the energy difference between the HOMO and LUMO orbitals (Δ_{H-L}). Results show a small gap variation of 1.4 eV, but interestingly enough, the molecules displaying a (Δ_{H-L}) between 4.73 and 4.57 eV are those presenting two aromatic rings with and without alkyl-substituents. The Mulliken population analysis indicates that those compounds with charges more concentrated in the sulfur atom are more refractory to the hydrodesulfurization process (Table 2 and Fig. 2). The methyl groups have the effect of providing hydrogen bridges to sulfur atom by means of the HOMO electrons. This could give an electronic explanation to the experimentally observed

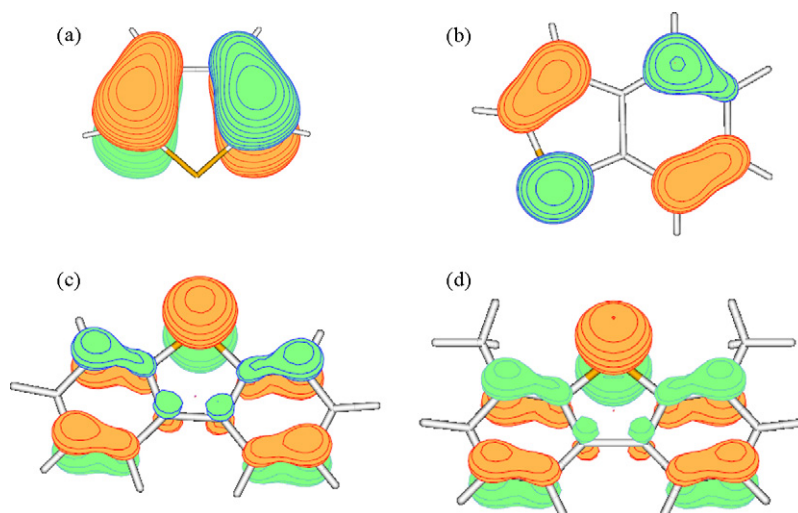


Fig. 2. Highest occupied molecular orbital (HOMO), (a) thiophene, (b) benzothiophene, (c) dibenzothiophene and (d) 4,6-dimethyldibenzothiophene at B3LYP/6-311++G** level of theory.

Table 3

Nucleus independent chemical shifts (NICS) in ppm on thiophenic and benzenic rings for thiophene, benzothiophene dibenzothiophene and its derivatives at B3LYP/6-311++G** level

Species	Thiophenic ring		Unprotonated benzenic ring		Protonated benzenic ring	
	Unprotonated	Protonated				
Thiophene	-12.90	-5.30				
α -MT	-11.54	-4.32				
β -MT	-12.05	-5.01				
BT	-9.02	-2.70	-10.36		-8.60	
DBT	-7.42	-1.01	-9.05	-9.05	-7.70	-7.70
4-MDBT	-7.12	-1.25	-8.69	-8.42	-7.68	-7.58
1,9-DMDBT	-6.60	-0.55	-8.60	-8.60	-7.70	-7.70
2,8-DMDBT	-7.31	-0.99	-8.02	-8.02	-7.30	-7.30
3,7-DMDBT	-7.19	-1.09	-8.70	-8.70	-7.50	-7.50
4,6-DMDBT	-7.08	-1.86	-8.60	-8.60	-7.70	-7.70
3,4,6-TM-8-EDBT	-7.01	-1.51	-8.00	-8.60	-7.70	-6.90

refractory properties of the alkyl-substituted organosulfur compounds.

The study of the aromaticity of thiophene, benzothiophene, dibenzothiophene and its alkyl-derivatives has been carried out in two steps. First, we focus on the aromaticity index in the thiophenic ring for protonated and unprotonated molecules. Next, we consider the aromaticity index for the benzenic rings for both, protonated and unprotonated molecules. All NICS values are reported in Table 3. It is very important to keep in mind that, at the B3LYP/6-31+G* level of theory, the NICS at the center of the benzene ring for benzene is -9.7 ppm, and the NICS for thiophene, also at the center of the ring, is -13.6 ppm [25]. In all the studied cases values show a clear and interesting trend. Unprotonated molecules display a planar structure with the exception of 1,9-DMDBT that present a distorted structure. This planar structure allows them a better electronic density delocalization with a concomitant stabilization. In these molecules, the five-member ring presents a NICS value of -12.90 ppm, that is to say a very aromatic ring, but alkyl and/or benzenic substituents decreases its aromaticity, from -12.90 for pyrrol to -7.01 ppm for 3,4,6-TM-8-EDBT (Table 3). The aromaticity is severely reduced upon protonation because this also involves a loss of planarity. In these cases the aromaticity goes from -5.30 ppm for thiophene to -0.55 ppm for 1,9-DMDBT. This aromaticity reduced for 1,9-DMDBT is due to its distorted structure.

The aromaticity for the benzenic rings of the unprotonated molecules also changes upon substitution. Thus, only the benzene ring of benzothiophene displays an aromaticity of -10.36 ppm, slightly larger than the value for benzene. All the other molecules display slightly lower aromaticity NICS measure than benzene, from -9.05 ppm for the DBT to -8.0 ppm for 3,4,6-TM-8-EDBT. This shows a clear tendency on the stability of these molecules. For the protonated molecules, the aromaticity only shows small variations because of the non-planar structure of these species.

3.3. Proton affinity

Previously we mentioned that a few studies attempt to correlate the molecular properties with the reactivity of these compounds towards HDS [17–19]. Here, we analyze the relationship between the proton affinity and the pseudo-first order reaction rate constants available in literature [13]. These rate constants for hydrodesulfurization catalyzed were obtained using a Co-MoS₂/ γ -Al₂O₃ catalyst at 300 °C and 102 atm. In spite of a slight dispersion for those compounds with lowest rate constants, Fig. 3a shows a clear linear behavior between proton affinity and these experimental rate constants; the correlation factor being 0.96 suggests that this correlation is even semiquantitative. Therefore, one can conclude that the compounds with larger proton affinity are also those exhibiting a

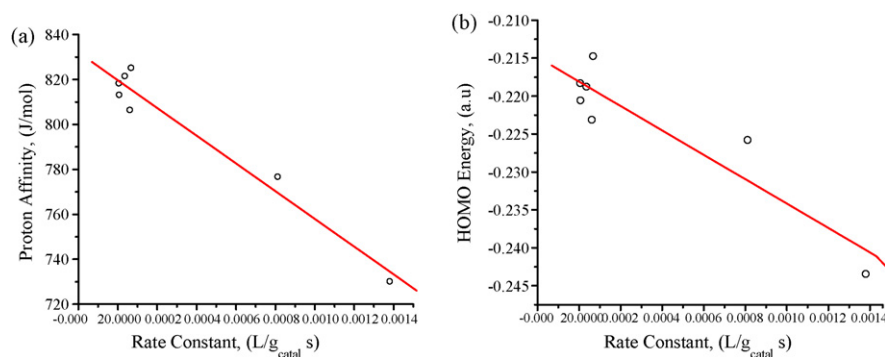


Fig. 3. Linear relationship: (a) rate constant vs. proton affinity; (b) rate constant vs. HOMO energy.

more refractory character towards HDS. A similar relationship ($r=0.95$), is observed when correlating the rate constants and highest occupied molecular orbital (HOMO) energy (Fig. 3b). However, we must warn the number of experimental points used in Fig. 3 is not large enough and they are surely affected by a given error bar. This is especially the case for the compounds where hydrodesulfuration is most difficult which also exhibit the largest dispersion. Likewise, one needs to realize that the pseudo order rate constants represent an average for the overall HDS process and that operation conditions such as temperature, pressure, catalyst preparation, concentration of reactant molecule will influence these apparent rate constants.

On the basis of our studies of proton affinity, the activity of dibenzothiophene and their derivatives are towards HDS can be ordered as 3,4,6-TM-8-E-DBT < 2,8-DMDBT < 3,7-DMDBT < 1,9-DMDBT < 4,6-DMDBT < 4MDBT < DBT, which agrees with the established by Bej et al. [2]. This ordering could be probably attributed to a combination of inductive and hyperconjugative effects of the methyl groups *para* to the two alpha carbons which could enrich the electronic density and increase the HDS activity. For thiophene and its derivatives, α - and β -methylthiophenes, the reactivity order is: α -methylthiophene > β -methylthiophene > thiophene. On the basis of this scale of reactivity, it is easier to hydrodesulfurized DBT than the di-alkyl and tri-alkyl derivatives, thiophene being the easiest hydrodesulfurizable compound.

4. Conclusions

The results obtained in the present work, allow us to establish a possible explanation on the relative difficulty to remove S from a series organosulfur compounds. From the aromaticity index one cannot really extract conclusions since for unprotonated molecules the almost planar molecular structure reveals only little changes in the aromaticity as measured from the NICS index while for the protonated species the similar loss of planarity results also in similar losses of aromaticity. From the analysis of proton affinities a clearer trend emerges. In fact, this descriptor allows one to order the activity of thiophenes and their derivatives towards HDS as T > BT > DBT > 4,6-DMDBT, whereas for thiophene and its derivatives (α - and β -methylthiophenes) the HDS activity of these compounds is predicted to follow the α -methylthiophene < β -methylthiophene < thiophene trend. On the basis of this scale of activity towards HDS, it is predicted that DBT is easier to desulfurize than its di-alkyl and tri-alkyl derivatives, whereas the easiest HDS occurs for thiophene. While some of these trends are well-known from experiment, the present results permit one to use proton affinity as a suitable predictor of a given S-containing molecule towards desulfurization through the HDS process, for molecules without steric hindrance.

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