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EPR Characterization of Organic Free Radicals in Marine Diesel

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Abstract. The intensive unresolved central line associated with organic free radicals in electron paramagnetic resonance (EPR) spectra of petroleum is interpreted as resulting from the superposition of signals from different radical species with very close g values. The mobility of a free radical in crude oil is relatively low due to the high oil viscosity. Aimed at characterizing free radicals in the oil byproduct, the present study is concerned with the investigation of marine diesel (bunker), a low-viscosity oil. Marine diesel was studied by EPR spectroscopy at X-band (9 GHz) in the temperature range from 170 to 400 K. Despite the viscosity at room temperature ($2.5 \cdot 10^{-3}$ kg/m \cdot s) and the tumbling correlation time for free radicals of about 10^{-7} s suggesting a high mobility of free radicals in marine diesel, the EPR spectra at room temperature did not exhibit resolved lines, but only an envelope with a poor signal-to-noise ratio. The same behavior was observed from 170 to 373 K. Above 373 K, the EPR spectrum exhibited resolved lines: a superposition of a septet-quartet, a sextet-quartet and a quintet-quartet group of lines was identified with the following parameters: $g = 2.003 \pm 0.001$, proton hyperfine couplings $A = 6.41 \pm 0.03$ G (septet) and $A' = 1.82 \pm 0.02$ G (quartet); $g = 2.003 \pm 0.001$, $A = 6.21 \pm 0.03$ G (sextet) and $A' = 1.64 \pm 0.02$ G (quartet); $g = 2.003 \pm 0.001$, $A = 6.16 \pm 0.03$ G (quintet) and $A' = 1.83 \pm 0.02$ G (quartet), which were attributed to phenalenyl radicals and their derivatives. Below 373 K, phenalenyl dimerization prevented its detection by EPR.

1 Introduction

The signal of free radicals in the electron paramagnetic resonance (EPR) spectra of petroleum consists of an unresolved line with a width of about 5 G [1–4]. This line results from the superposition of EPR spectra from different species of organic radicals in petroleum asphaltenes with very close g values [3]. Since petroleum is a high-viscosity liquid, the free radical mobility in crude oil at room temperature is relatively low; thus, the EPR lines of free radicals in this environment exhibit asymmetry due to the superposition of all possible orientations of the paramagnetic species in the system and contribution of different chemical species that interact with unpaired electrons [3]. The EPR signal due to free radi-

cals exhibited no resolution even at the W-band frequency at room temperature or 77 K [3].

Marine diesel (fluid catalytic cracking diesel, bunker, ship fuel) is produced in refineries and integrates mixtures with other products. This kind of diesel is formed through the mixture of several currents from several stages of crude oil processing, such as diesel, heavy naphtha, and light and heavy diesel. The interest in studying marine diesel is due to the fact that this low-viscosity oil byproduct ($2.5 \cdot 10^{-3} \text{ kg/m} \cdot \text{s}$ at room temperature) allows high mobility of a free radical in its environment. Dilute solutions of free radicals provide an abundant hyperfine structure (hfs) and the possibility of translating the structure into a map of unpaired electron density throughout the molecule [5]. Details are lost in high-viscosity liquids due to the line broadening resulting from the anisotropy of the g -factor and hfs coupling coefficients, plus the exchange and magnetic dipole–dipole interactions between the spins of neighboring radicals. Rapid molecular tumbling averages out these anisotropies and dilution minimizes the exchange and dipole–dipole effects. When stable radicals are dissolved in inert solvents, the spectra change from single broad lines for concentrated solutions to the hfs lines as dilution continues. The tumbling correlation time for free radicals in marine diesel at room temperature is about 10^{-7} s [6]. Although this value is larger than that obtained for nitroxyl radicals [7–9] and tempone [10] in solution with different viscosity, it is much lower than crude oil values (10^{-4} s) [3] and justifies the high mobility of free radicals in marine diesel.

Our group recently investigated marine diesel by EPR [6] and verified that the spectrum consisted of signals from free radicals with a typical hfs of protons, exhibiting a septet of lines with a ratio of intensities of 1:6:15:20:15:6:1. This ratio corresponds to different ways of forming spins $+3$, $+2$, $+1$, 0 , -1 , -2 , -3 caused by the interaction of six equivalent and strongly coupled protons [$A(^1\text{H})$]. Each of the seven hfs lines is split into four lines (quartet) caused by three weakly coupled protons [$A'(^1\text{H})$] with a ratio of intensities of 1:3:3:1 and corresponding to the different ways of forming spins $+3/2$, $+1/2$, $-1/2$, $-3/2$. The results obtained for the hfs interaction of free radicals in marine diesel and the discussion regarding the organic molecule models indicate that perinaphthenyl radicals are probably responsible for the septet-quartet EPR spectrum of this oil byproduct.

Our group subsequently verified that the signal attributed to the perinaphthenyl radical decreases in intensity and finally disappears with time of several minutes,

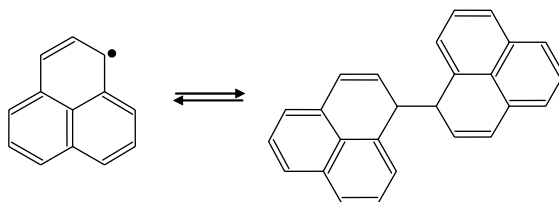


Fig. 1. Spontaneous self-associations of phenalenyl radicals forming the σ -dimer.

hours or days, depending on the time that the samples were exposed to air; this suggests that the radical undergoes a chemical reaction, probably with oxygen in air. Samples of marine diesel removed from containers which were opened sometimes exhibit no EPR lines or lines of very low intensity. Another possibility is that the perinaphthenyl radicals form a dimer (Fig. 1) becoming diamagnetic and, consequently, exhibiting no EPR signal. Concerning this possibility, marine diesel was investigated by EPR throughout the temperature range from 170 to 400 K. Investigations above room temperature are aimed at breaking the linkage between the perinaphthenyl radicals of the dimer. The reappearance of the perinaphthenyl signal above room temperature would characterize breaking of this linkage formed in the dimer.

2 Materials and Method

The oil used in this study was supplied by the Brazilian oil company Petrobras. The samples did not undergo modifications or dilutions and the experiments were repeated twice to guarantee the reliability of results. The specifications of marine diesel are outlined in ref. 6.

A variable-temperature EPR experiment was performed with the marine diesel samples at X-band (ca. 9 GHz) with a modulation amplitude of 1 G and a magnetic field modulation of 100 kHz on a JEOL (JES-PE-3X) spectrometer with a variable-temperature controller (JES-VT-3A) unit. The JES-VT-3A unit provides experiments in the temperature range from 100 to 570 K. $\text{Mn}^{2+}:\text{MgO}$ ($g = 1.981$) was used as a *g*-marker, its fourth spectrum line was used.

The experiment was performed in a sealed quartz tube in the temperature range from 170 to 400 K. Heating from 300 to 383 K was followed by cooling to 300 K and maintenance of this temperature for a few minutes, and then the same sample underwent further heating (from 300 to 403 K) and cooling.

3 Results and Discussion

Despite the viscosity of $2.5 \cdot 10^{-3} \text{ kg/m} \cdot \text{s}$ at room temperature and the tumbling correlation time for free radicals of about 10^{-7} s suggesting a high mobility of free radicals in marine diesel, the EPR spectra (X-band) at room temperature did not exhibit resolved lines, but only an envelope presenting a poor signal-to-noise ratio (Fig. 2a). Although the samples used were taken from the same container as in ref. 6, the spectra obtained in this paper under the same conditions differed a lot from those found for fresh samples of marine diesel (Fig. 2b). The exposure to air of the marine diesel stored in the container opened on several occasions for removing the samples may be responsible for this difference, since phenalenyl is sufficiently persistent in diluted deoxygenated solutions [11, 12]. The signal loss of radical spectra in fuel samples associated with the storage time was verified by Senglet et al. [13], who observed weak phenalenyl radical spectra after six months of storage.

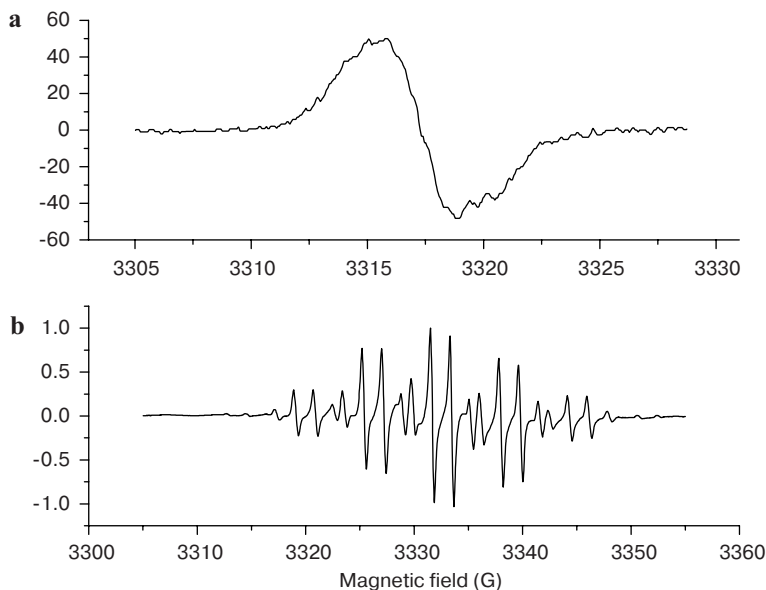


Fig. 2. **a** EPR spectrum of marine diesel (older sample) at 9.37 GHz at room temperature. Microwave power, 1 mW. **b** EPR spectrum of marine diesel (fresh sample) from ref. 6.

The free radical EPR spectrum in marine diesel revealed a progressive appearance of the typical hfs of protons with heating (Fig. 3a). The hfs lines were superposed over the single line with a peak-to-peak line width of about 9 G present in all spectra (Fig. 2a), whose intensity also increased with temperature. Up to 378 K, it was impossible to determine the interaction of a free electron with hydrogen atom protons. At 383 K, the EPR spectrum became very intensive (Fig. 3b) exhibiting resolved hfs lines. This spectrum was analyzed to determine the types of free radicals manifested in this experiment. In order to investigate only resolved hfs lines, the single unresolved line, such as observed in Fig. 2a and overlapping in all EPR spectra of marine diesel (Fig. 3b, dotted line), was subtracted from the spectrum (Fig. 3b, solid line). Since the radical rotates at a shorter correlation time than the reciprocal of the spectrum spread in frequency and considering the high mobility of free radicals in marine diesel [6], the spectrum resulting from the subtraction above can be interpreted in terms of the following isotropic spin Hamiltonian:

$$\mathcal{H} = g\beta BS + AIS + A'IS,$$

where $S = 1/2$ and $I = 1/2$.

The Bruker WINEPR SimFonia Version 1.25 software was used in the simulation to determine g , A , A' and ΔB (peak-to-peak line width) of the free radical species. Corrections were made for the second-order effects. The first attempt considered a septet-quartet EPR spectrum caused by the interaction of six equiva-

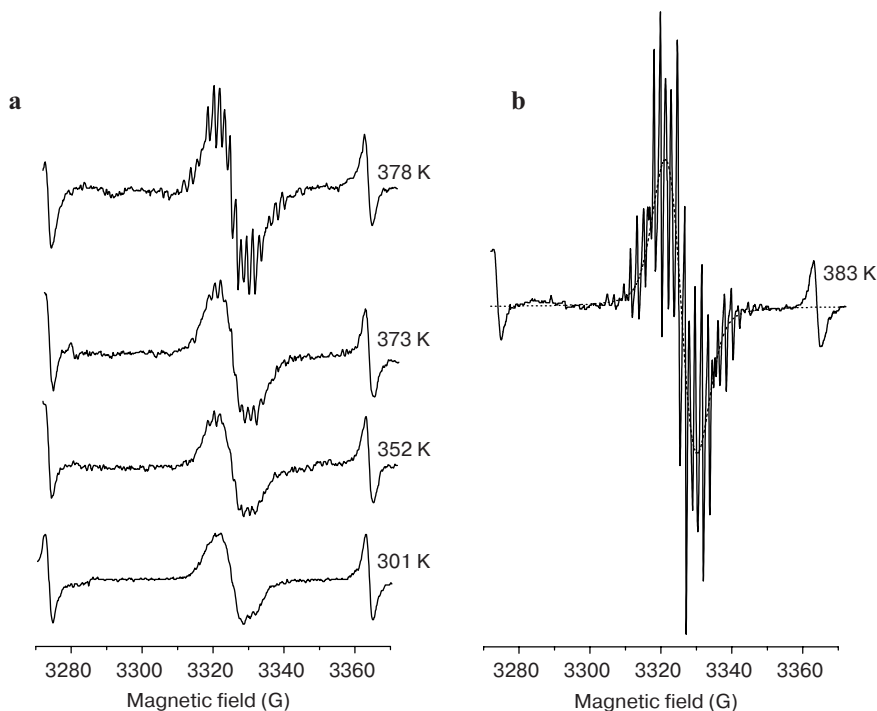


Fig. 3. **a** EPR spectra of marine diesel (older sample) at 9.37 GHz in the temperature range from 301 to 378 K. Microwave power, 1 mW. **b** Resolved hfs lines at 383 K.

lent and strongly coupled protons (septet) and the interaction of three weakly coupled protons (quartet) (Fig. 4a). The parameter values used were as follows: $g = 2.003 \pm 0.001$; $A = 6.41 \pm 0.03$ G for six equivalent protons; $A' = 1.82 \pm 0.02$ G for three equivalent protons, and $\Delta B = 0.50 \pm 0.02$ G. The uncertainty was estimated by matching the experimental spectrum to the simulated one. Therefore, with the parameters above and no superposition of the spectrum lines, 28 lines were expected with the following intensity ratio of 1:3:3:1:6:18:18:6:15:45:45:15:20:60:60:20:15:45:45:15:6:18:18:6:1:3:3:1. The simulation corresponded to the EPR spectrum of a fresh sample of marine diesel, as shown in Fig. 2b, which is attributed to the perinaphthenyl radical ($C_{13}H_9^{\cdot}$) (Fig. 5a). However, this interpretation was not sufficient to reproduce the spectrum resulting from the subtraction above (Fig. 3b), indicating the superposition with other groups of less intensive lines which could be due to phenalenyl radicals with a different number of splitting protons [14].

The investigation of the remaining lines in the EPR spectrum after subtraction of the first group of lines simulated in Fig. 4a revealed the need to add a second group of lines due to the interaction of five equivalent and strongly coupled protons (sextet) and the interaction of three weakly coupled protons (quartet) (Fig. 4b). The chemical structure corresponding to this interaction is presented in Fig. 5b. The parameter values used were as follows: $g = 2.003 \pm 0.001$; $A = 6.21 \pm 0.03$ G for

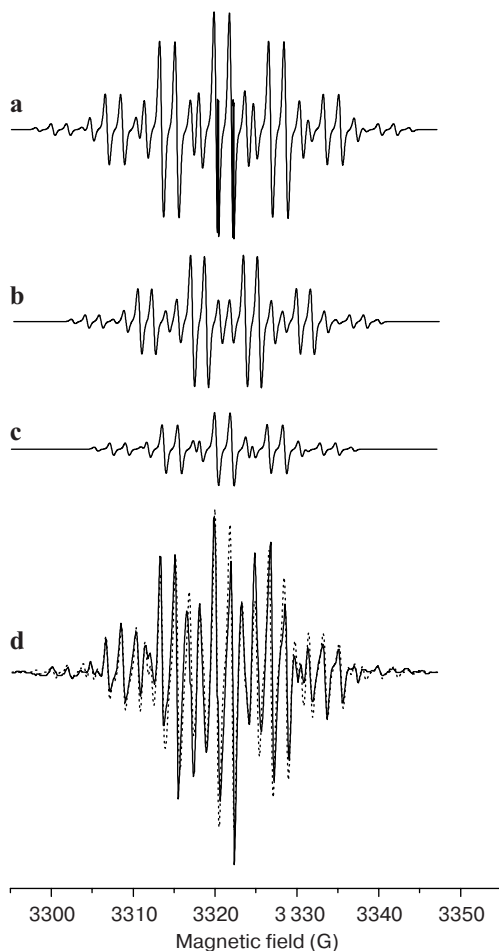


Fig. 4. **a** Simulation of the septet-quartet EPR spectrum with parameters $g = 2.003 \pm 0.001$, $A = 6.41 \pm 0.03$ G for six equivalent protons, $A' = 1.82 \pm 0.02$ G for three equivalent protons, and $\Delta B = 0.50 \pm 0.02$ G. **b** Simulation of the sextet-quartet EPR spectrum with parameters $g = 2.003 \pm 0.001$, $A = 6.21 \pm 0.03$ G for five equivalent protons, $A' = 1.64 \pm 0.02$ G for three equivalent protons, and $\Delta B = 0.50 \pm 0.02$ G. **c** Simulation of the quintet-quartet EPR spectrum with parameters $g = 2.003 \pm 0.001$, $A = 6.16 \pm 0.03$ G for four equivalent protons, $A' = 1.83 \pm 0.02$ G for three equivalent protons, and $\Delta B = 0.50 \pm 0.02$ G. **d** Superposition of the septet-quartet, sextet-quartet and quintet-quartet with weight percentages of 53.5, 30.0, and 16.5%, respectively (dotted line), and experimental spectrum (solid line) resulting from the subtraction in Fig. 3b.

five equivalent protons; $A' = 1.64 \pm 0.02$ G for three equivalent protons, and $\Delta B = 0.50 \pm 0.02$ G. The sum of these two simulated groups (Fig. 4a and b) reproduced all spectrum lines but not their intensities. The intensity problem was solved by the addition of a third group of lines due to the interaction of four equivalent and strongly coupled protons (quintet) and the interaction of three weakly coupled protons (quartet) (Fig. 4c) whose structure is presented in Fig. 5c. The parameter val-

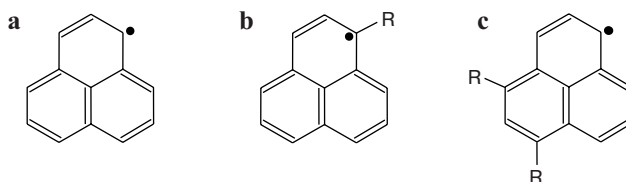


Fig. 5. Structures of the phenalenyl radical (a) and phenalenyl derivatives (b and c).

ues used were as follows: $g = 2.003 \pm 0.001$; $A = 6.16 \pm 0.03$ G for four equivalent protons; $A' = 1.83 \pm 0.02$ G for three equivalent protons, and $\Delta B = 0.50 \pm 0.02$ G. The superposition of three groups of lines generated a set of lines shown in Fig. 4d (dotted line). The theoretical model with the three groups of lines overlaps with the experimental spectrum (Fig. 4d, solid line) resulting from the subtraction represented in Fig. 3b. The weight percentages in the intensity of the lines was 53.5, 30.0, and 16.5% for the first, second and third groups, respectively.

The superposition of the first, second and third groups (Fig. 6, dotted line) with the simulation parameters $A = 6.30 \pm 0.03$ G (6H) and $A' = 1.75 \pm 0.02$ G (3H); $A = 6.12 \pm 0.03$ G (5H) and $A' = 1.66 \pm 0.02$ G (3H); $A = 6.03 \pm 0.03$ G (4H) and $A' = 1.74 \pm 0.02$ G (3H) resulted in the EPR spectrum (Fig. 6, solid line) obtained with a modulation amplitude of 0.5 G. The g -factor was 2.003 ± 0.001 and $\Delta B = 0.35 \pm 0.02$ G for all groups. The solid line in Fig. 6 is the result of a subtraction such as in Fig. 3b, where the unresolved line was excluded. This spectrum allowed a better observation of certain lines that the

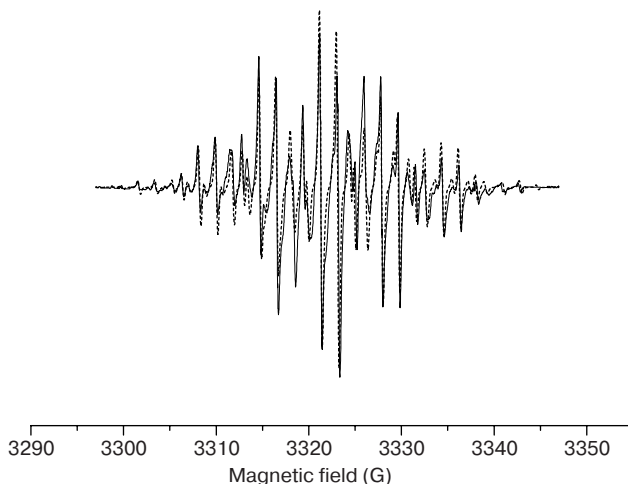


Fig. 6. EPR spectrum of marine diesel (younger sample) in X-band at room temperature (solid line) after heating. Modulation amplitude, 0.5 G; microwave power, 1 mW; microwave frequency, 9.34 GHz. Simulation of the EPR spectrum (dotted line) with parameters $A = 6.30 \pm 0.03$ G (6H) and $A' = 1.75 \pm 0.02$ G (3H); $A = 6.12 \pm 0.03$ G (5H) and $A' = 1.66 \pm 0.02$ G (3H); $A = 6.03 \pm 0.03$ G (4H) and $A' = 1.74 \pm 0.02$ G (3H) for the first, second and third groups, respectively.

EPR spectrum obtained with the modulation amplitude of 1 G (Fig. 4d, solid line) does not exhibit as resolved ones. The comparison shows that the proposed models (first, second and third groups) accurately reproduce the experimental lines (Fig. 6). The spectrum with the modulation amplitude of 0.5 G was obtained in the experiment with an intermediate sample (younger sample) that experienced a lower oxygen effect and consequently contained more paramagnetic species. This sample was submitted to the same temperature variation but in this case the spectrum (Fig. 6, solid line) was obtained at room temperature after heating. Despite the fact that this spectrum was not obtained in the same experiment described above, the spectrum with the modulation of 0.5 G served as a confirmation of the present model, since it concerned the same sample (marine diesel) under the variable-temperature experiment and provided a spectrum with resolved lines.

Three paramagnetic species, phenalenyl plus two of its derivatives, found after heating indicate that the system (older marine diesel) somehow preserved the phenalenyl structure. Let us consider these phenalenyl derivatives since this configuration was not observed in a fresh sample.

In the liquid state, usually all but the most stable free radicals rearrange or polymerize [15]. Studies [11, 16] indicate that the phenalenyl radical and its derivatives show self-association and the formation of a diamagnetic dimer (Fig. 1). More recently, quantitative EPR studies [14, 17] confirmed that the phenalenyl dimerization occurs reversibly in carbon tetrachloride, toluene and dichloromethane solutions, resulting in a complete signal loss at low temperatures due to the dimer formation. Given that the phenalenyl radical generally exists in equilibrium with its diamagnetic dimer [11] and taking into account the high mobility of this radical in marine diesel [6], dimerization even at room temperature should be considered. This mechanism could keep the phenalenyl radical in its diamagnetic dimer form. The thermal instability of the dimer form could be responsible for the appearance of a typical hfs of protons at heating.

Lewis and Singer [18] prepared the 1-methyl and 1-phenyl derivatives of phenalenyl by simple dissociation reactions and measured their EPR spectra in solution. Besides its interaction with phenalenyl protons, the substituent methyl caused splitting of 6.27 G with the three equivalent protons of the methyl group, exhibiting a spectrum containing 116 resolved lines. In contrast, for a solution of the 1-phenyl- d_5 -phenalenyl radical in benzene at 25 °C, the spectrum was simplified with the following coupling constant assignment: 5H, 6.12 ± 0.01 G; 3H, 1.781 ± 0.003 G. The spectra of the hydroxyperinaphthenyl radical described by Rabold et al. [19] presented a splitting due to a set of five equivalent protons (6.21 G) and another set of three equivalent protons (1.68 G). This configuration was reported by Wain et al. [20]. In the current simulation, this configuration is present: six main groups of lines (sextet), each group with four lines (quartet); however, because the paramagnetic species were overlapped by two other species, apart from the difficulty of obtaining a high-resolution spectrum that allowed the observation of the splitting due to the functional group protons, it is impossible to identify the functional group that substituted the hydrogen atom. The substituent radical caused a slight reduction in the magnitude of the hfs interaction at all phenalenyl ring positions, as observed by Lewis and Singer [18].

While preparing the phenalenyl radical [16], it was verified that the continued uptake of oxygen resulted in peroxide $C_{26}H_{18}O_2$ possessing no definitive melting point and breaking down into a mixture of peropyrene and perinaphthene upon heating in vacuum. Perinaphthene can be reduced to yield the neutral hydroxyperinaphthenyl radical [20]. The older marine diesel samples were exposed to oxygen and might have formed such a peroxide. The calculated hfs coupling constants for the second group reinforce this supposition which is in strong agreement with the values reported by Rabold et al. [19] for the hydroxyperinaphthenyl radical and the appearance of the second group of lines only after heating. Yamada and Toyoda [21] observed the formation of the 4,6-dimethylperinaphthenyl radical when acenaphthylene dissolved in an inert solvent was heated up to 440 °C, resulting in the EPR spectrum splitting due to the methyl protons. Singer and Lewis [22] suggested that the 4,6-dimethylperinaphthenyl radical also appears during the carbonization of acenaphthylene. The two methyl groups occupying two α -positions produce a spectrum similar to that of the third group (Fig. 4c). Despite the observation of this radical only at high temperatures, it appears upon heating and as an intermediate compound in the reaction. In the spectrum analyzed for marine diesel (older sample), the observation revealed that the weight percentage in intensity for the third group was the lowest (16.5%). The appearance of the third group of lines only after heating and the low weight percentage in intensity of this radical reinforce the idea of an intermediate substance.

When the system returned to room temperature, the intensity of the hfs splitting decreased with time. Upon further heating, it was impossible to reproduce the hfs splitting. This observation indicates the nonreversibility of the system. Upon cooling, the remaining hfs splitting disappeared at about 230 K, resulting in a single unresolved line. At progressive cooling to 170 K, the intensity of this line decreased but it did not collapse.

The proposed model of three overlapped paramagnetic species accurately reproduced the experimental lines. Despite the fact that it was impossible to describe the exact chemical transformations and the mechanisms involved in the appearance of paramagnetic species in marine diesel due to the complexity of this oil byproduct, the information provided by EPR spectroscopy, especially the hfs coupling, allowed us to monitor the modifications and to suggest the type of free radical species formed in this oil during heating. Thus, with organic molecule models, perinaphthenyl radicals are thermally recuperated by breaking the linkage formed in the dimer. According to the results obtained for hfs interaction and the discussion presented, hydroxyperinaphthenyl and 4,6-dimethylperinaphthenyl radicals are the most likely phenalenyl derivatives yielded upon heating the marine diesel.

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