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Research Article

EPR Analysis of Dinitrobenzoic Acid Anion Radicals

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Abstract:

EPR hyperfine coupling constants of dinitrobenzoic acid anion radicals were calculated by using (DFT) with the use of B3LYP functional at LanL2DZ, LanL2MB, EPR-II, EPR-III, 6-31+G(d) and 6-31++ G(d,p) basis sets. It was found that LanL2DZ is the best basis set from the correlation graphs between the theoretical and experimental results. Thus, in this set, the hyperfine structures formed EPR spectra and the distributions of the spin density of all the anion radicals were determined. From the optimized structures of all the radicals it was decided whether the nitro groups are out of plane or not. The reason of the different distributions of the spin density on the nitro groups were also investigated by Natural Bond Orbital (NBO) and Mulliken charge analyses. In these analyses, the interactions of the nitro groups with the ring were examined. The NBO analysis the anion radical of 2,4-dinitrobenzoic acid showed that there is a strong O-H…O hydrogen bond interaction (182.8 kcal/mol) between the carboxyl and nitro groups. The simulated EPR spectra of some radicals obtained by EPR Simulator software program were harmoniously given with together their experimental spectra.

1. Introduction

Dinitrobenzoic acid is one of the most important organic synthesis intermediates and, is widely used in the preservative and chemical industry. Dinitrobenzoic acid has four different isomers according to the different placement of the carboxyl and nitro groups in the benzene ring. These are 2,4-, 2,5-, 3,4- and 3,5-dinitrobenzoic acid. All of them are used in different fields. For example, 2,4-dinitrobenzoic acid is an important pharmaceutical intermediate, often used in the synthesis of antibacterial. It is also used in clinical and medical research. Similarly, 3,5-dinitrobenzoic acid is used to synthesize intermediates for dyes and liquid crystals. The optical properties of dinitrobenzoic acid isomers, both experimentally and theoretically, have been studied by Zhang and et al. [1]. The investigation of the electronic structures of the radical anions of aromatic nitro derivatives has attracted attention [2, 3]. EPR spectra of dinitro-derivatives of benzoic acid reduced by electrolysis in dimethyl formamide solution were obtained [4]. They suggested that one of the two nitro groups in some dinitro-derivatives must be out of plane. They have attributed the out-of-plane nature of one of the nitro groups to the bigger coupling constant belonging to the nitrogen in that nitro group. In addition, the hyperfine splitting belonging to the proton in the carboxyl group attached to the benzene ring was not observed in the studies [5, 6]. In this study, Electron Paramagnetic Resonance (EPR) hyperfine coupling constants and spin density distributions of dinitrobenzoic acid anion radicals were theoretically calculated in different sets by Density Functional Theory (DFT) with the use of B3LYP functional. Since the optimized structures of the radicals were determined by this study, it was easily decided, theoretically, whether the nitro groups in the radicals are out of plane or not. Consistent with the literature, it was observed that the hyperfine coupling constant belonging to the nitrogen in the out-of-plane nitro group is also bigger than the other nitro group. In addition, the hyperfine coupling constant belonging to the hydrogen in the carboxyl group of all the radicals, which could not

be determined in the literature, is determined theoretically by this study, even though it is small.

2. Computational Methods

The calculations of the optimized structures and hyperfine coupling constants of the radicals were done by the Gaussian 09 software package [7], and the results were displayed with the GaussView 5.0 program [8]. Density Functional Theory (DFT) has been widely used both in the gas phase [9] and on catalytic surfaces [10] in modeling the chemical interactions of atoms and molecules by considering their internal structures. Therefore, in our calculations, we have also used DFT [11, 12] with the use of Becke hybrid three-parameter variable functionality [13], and electronic correlation of Lee, Yang, and Par (B3LYP) [14]. Our previous studies have showed that DFT(B3LYP)/ LanL2DZ basis set gives very good values in hyperfine coupling constant calculations in terms of agreement with experimental results [15, 16]. Therefore, we have used LanL2DZ as well as LanL2MB, EPR-II, EPR-III, 6-31+G(d) and 6-31++ G(d,p) basis sets to determine the reality of this. Simulated EPR spectra were obtained using the EPR Simulator software program [17].

3. Results and Discussion

The hyperfine coupling constants (hfccs) calculated at different basis sets by DFT(B3LYP) for all the radicals are given in Table 1. The table also includes experimental values for comparison [4]. Considering that the calculated values are obtained for a single gas molecule, a full agreement cannot be expected with the experimental results having multiple interactions, we can say that the experimental and theoretical values are in good agreement. For all the anion radicals the correlation values between the theoretical and experimental hffcs are given in the bottom line of the table. From these correlation values, we can say that the best basis set is LanL2DZ, which is in agreement with our previous studies [15, 16]. Figure 1 shows its correlation graph as an example. The optimized structures and unpaired electron spin density distributions of all the anion radicals calculated at DFT(B3LYP)/LanL2DZ basis set are given in Fig.2. As can be seen, the spin density distributions of 2,4- and 2,5-dinitrobenzoic acid anion radicals are concentrated on only one nitro group. It can be seen from table 1that the nitrogen hfcc value of this nitro group is bigger than that of the other nitro group. For an example, from Table 1, for 2,4-dinitrobenzoic acid, the nitrogen hfcc value of one nitro group is calculated as

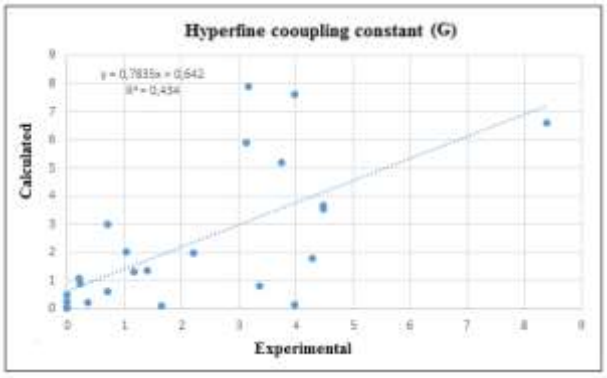


Figure 1. *Correlation graph between the calculated and experimental nitrogen hffcs of all the anion radicals.*

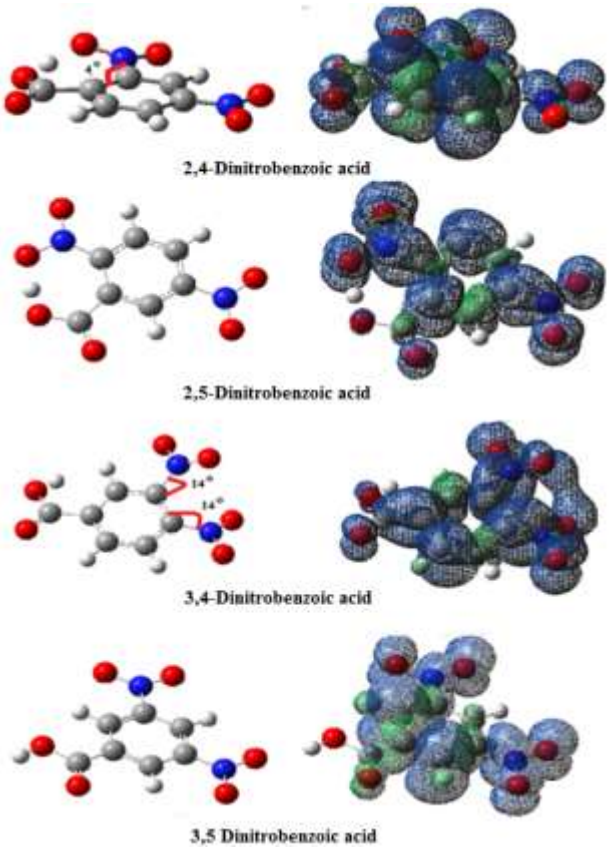
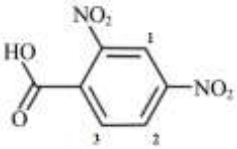
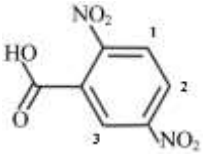
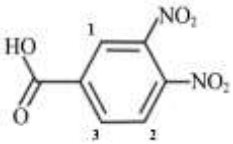
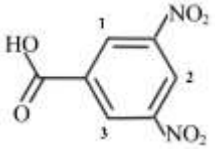


Figure 2. *The optimized structures and spin densities of all the anion radicals.*

6.68 G, while the other is calculated as 1.07 G. These values are experimentally found to be 8.38 and 0.20 G, respectively. However, the spin densities for 3,4- and 3,5-dinitrobenzoic acid anion radicals are almost equally distributed in the both nitro groups. Thus, the nitrogen hfcc values of the nitro groups of these radicals should be quite close to each other. For an example, for 3,5-dinitrobenzoic acid, these values are calculated as 3.66 and 3.54 G, respectively, and they are experimentally found to be equal and 4.47 G (see Table 1). As seen from the optimized structures of the anion radicals in Fig.2, one nitro group of 2,4-dinitrobenzoic acid is out of the ring plane with a dihedral angle of 4°.

Table 1. *Experimental [4] and calculated hyperfine coupling constants for all the anion radicals.*

			DFT(B3LYP)					
Anion Radical	**Hfcc (G)**	**Exp.**	**LanL2DZ**	**LanL2MB**	**EPR-II**	**EPR-III**	**6-31+G(d)**	**6-31 ++G(d,p)**
 2,4-Dinitrobenzoic acid	a_{N1}	8.38	6.62	1.73	2.95	3.17	3.83	4.12
	a_{N2}	0.20	1.07	0.22	0.48	0.51	0.78	0.71
	a_{H1}	3.36	-0.79	-2.03	-0.44	-0.41	-0.23	-0.45
	a_{H2}	3.13	-5.92	-5.31	-0.86	-5.72	-5.99	-5.96
	a_{H3}	1.04	2.04	1.75	1.86	1.81	1.88	1.88
	a_{H4}	0.00	-0.06	-0.68	0.23	0.07	0.15	0.05
 2,5- Dinitrobenzoic acid	a_{N1}	3.74	5.21	2.09	2.17	2.42	3.20	3.36
	a_{N2}	0.36	0.22	1.65	-0.40	-0.25	0.15	0.11
	a_{H1}	2.20	-1.97	-0.95	-1.75	-1.74	-1.82	-1.88
	a_{H2}	1.65	-0.11	-1.31	-0.37	-0.38	-0.51	-0.39
	a_{H3}	0.22	0.88	0.30	0.82	0.74	0.78	0.77
	a_{H4}	0.00	-0.51	0.26	-0.02	-0.30	-0.30	-0.33
 3,4-Dinitrobezoic acid	a_{N1}	4.28	1.78	0.06	0.52	0.59	1.04	1.04
	a_{N2}	1.40	1.37	-0.41	0.09	0.35	0.93	0.92
	a_{H1}	1.16	1.30	1.20	1.45	1.58	1.54	1.53
	a_{H2}	0.70	0.60	0.84	0.63	0.63	0.54	0.56
	a_{H3}	0.70	-3.00	-3.60	-2.61	-2.77	-2.97	-2.93
	a_{H4}	0.00	-0.27	-0.16	-0.30	-0.31	-0.30	-2.29
 3,5- Dinitrobenzoic acid	a_{N1}	4.47	3.66	0.70	1.55	1.81	2.44	2.42
	a_{N2}	4.47	3.54	0.68	1.45	1.66	2.25	2.24
	a_{H1}	3.98	-7.63	-2.18	-7.60	-7.25	-7.76	-7.65
	a_{H2}	3.98	- 0.13	-11.95	0.00	-0.03	-0.02	-0.01
	a_{H3}	3.17	-7.89	-2.04	-7.94	-7.72	-8.04	-7.95
	a_{H4}	0.00	0.04	-0.30	0.03	0.01	0.03	0.02
R^2(all)			0.43	0.08	0.14	0.18	0.23	0.22
R^2(for only a_N's)			0.77	0.08	0.71	0.73	0.73	0.74

This result is also consistent with the literature [4]. Thus, since this nitro group will interact more effectively with the π system of the ring, it is expected that the hfcc value of its nitrogen will be bigger. Again from the optimized structures in Fig. 2, it can be seen that the nitro groups in 3,4-dinitrobenzoic acid anion radical are out of the ring plane with a dihedral angle of about 14° up and down, respectively. This is suitable for their nitrogen hfcc values o be quite close to each other. These values are calculated as 1.78 and 1.37 G, respectively (see Table 1). In Table 1, the hfcc value of the proton in the carboxyl group of all the anion radicals, which cannot be observed according to the literature, is calculated and given, albeit small. In Figs. 3 and 4, the experimental and simulation EPR spectra of 2,4- and 3,5-dinitrobenzoic acid anion radicals of which the experimental spectra were obtained from the literature [4], are given. The simulation spectra were found by using the theoretical hfcc values of the radicals in the EPR Simulator program [17]. The optimal linewidth values are given in the figures. As can be seen, the simulation spectra are compatible with the experimental spectra. The highest occupied molecular orbital HOMO (or SOMO for half-filled molecular orbitals, i.e. radicals) energy indicates electron donating ability, while the lowest unoccupied molecular orbital LUMO energy indicates electron accepting ability. The LUMO-HOMO energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$)

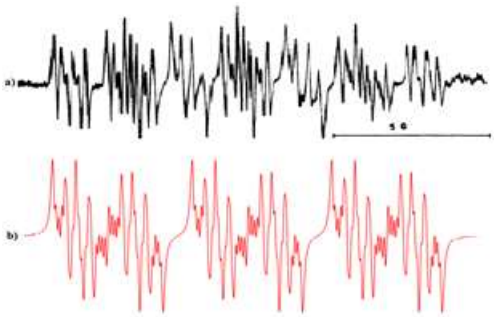


Figure 3. *a) Experimental [4] and b) simulation spectra of 2,5-dinitrobenzoic acid anion radical. The linewidth for the simulation spectrum is 0.11 G.*

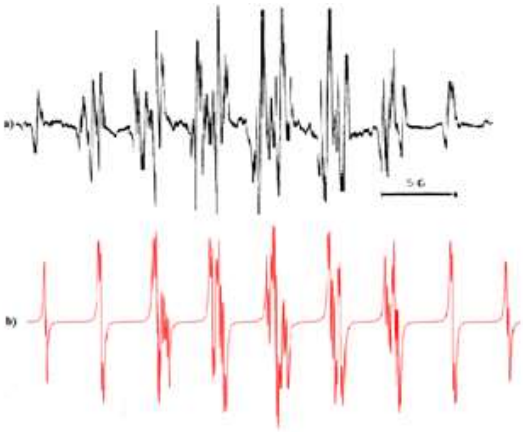


Figure 4. *a) Experimental [4] and b) simulation spectra of 3,5-dinitrobenzoic acid anion radical. The linewidth for the simulation spectrum is 0.10 G.*

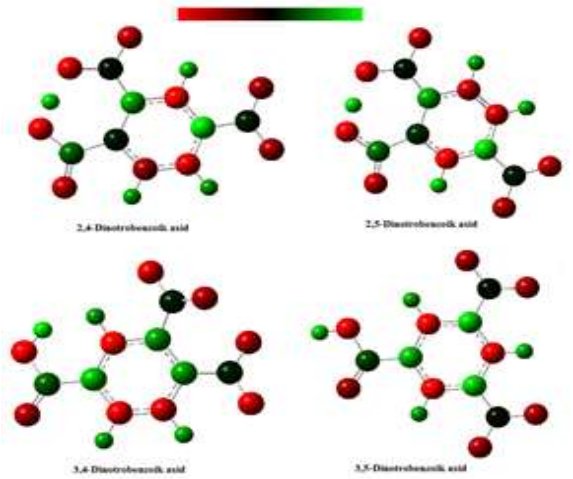


Figure 5. *The Mulliken atomic charges for all the anion radicals.*

Table 2. *Electronic, relative and LUMO-HOMO energy difference values of all the radicals calculated at the B3LYP/LanL2DZ basis set.*

Anion Radical	Electronic (Hartree/par.)	Relative (kkal/mol)	$\Delta E = E_{LUMO} - E_{HOMO}$ (Hartree/par.)
2,4- Dinitrobenzoic acid	-829.793137	5.17	0.04268
2,5- Dinitrobenzoic acid	-829.801385	0.0	0.07477
3,4- Dinitrobenzoic acid	-829.768096	20.89	0.07006
3,5- Dinitrobenzoic acid	-829.786248	9.50	0.03672

value is an important parameter as a function of a molecule's reactivity. A molecule with the low energy gap (also called soft molecule) has high chemical reactivity, while the one with the high energy gap (also called hard molecule) has low chemical reactivity [18]. The electronic, relative and E_{LUMO}-E_{HOMO} energy gap values calculated at the DFT(B3LYP)/ LanL2DZ basis set for all the anion radicals are given in Table 2. From the table, we can say that 2,5-dinitrobenzoic acid anion radical has the most stable structure while 3,5-dinitrobenzoic acid anion radical has the highest chemical reactivity. The stabilization energy values E(2) between the atom and bond orbitals at DFT(B3LYP)/ LanL2DZ basis set were calculated using the second order perturbation theory of Fock Matrix on the basis of natural bond orbital (NBO) of all the anion radicals. A large E(2) value means that the interactions between electron donors and electron acceptors are stronger. NBO analysis of 2,4-dinitrobenzoic acid shows that there is a strong hydrogen bonding interaction between the carboxyl and the near-nitro group, namely the O-H…O interaction, between the LP(O) (donor) atom orbital and the O…H (acceptor) unbounded orbital. This interaction energy is found to be 182.8 kcal/mol. The optimized structure was also checked for an imaginary frequency on suspicion of a trans structure. The O···H distance is 1.40 A^o, and the hydrogen atom is very close to the nitro group oxygen. It is also seen from the optimized structure in Fig. 2 that this nitro group is out of plane as we said before. Thus, it can be understood that the nitrogen of this nitro group will have a bigger hfcc value since it can interact more easily with the π system of the ring. In NBO analysis of 2,5-dinitrobenzoic acid, the charge transfer occurs (133.2 kcal/mol) from the ring carbon atom to which the first nitro group is attached, to the N-O bonds while the charge transfer (319.6 kcal/mol) to the ring carbon atom to which the second nitro group is attached, from the N-O bonds, on the contrary. This is resulted in a bigger nitrogen hfcc value of the former group and the smaller one of the latter group. From Table 1 these values are calculated as 5.22 G versus 0.21 G for this radical. We can say that in 3,4-dinitrobenzoic acid anion radical, the repulsion between the oxygens in the closely related carboxyl and nitro groups causes the nitro groups to be out of the ring plane with an almost equal dihedral angle in opposite directions in the optimized structure (see Figure 2). Its NBO analysis shows that there is a very high interaction (798.01 kcal/mol) between the ring carbon atoms to which the nitroxy groups are attached, and the high charge transfer (330.0 kcal/mol) from the ring carbon atom to which the second nitro group is attached, to the N-O bonds of the same group. This explains the close nitrogen hfcc values for the both groups (see Table 1). Finally, the optimized structure of 3,5 dinitrobenzoic acid anion radical is planar as seen in Fig. 2, and its NBO analysis is based on the LP(N) (donor) atom orbital in the both nitro groups and the BD(O…O) (acceptor) orbitals in the same groups. It shows that there is a high and almost equal energy interaction of E(2)= 320.0 kcal/mol between those orbitals. This result explains their close nitrogen hfcc values in

Table 1. The above comments can also be supported by the Mulliken charges given in Fig. 5. As can be seen in the figure, for 2,4- and 2,5-dinitrobenzoic acid anion radicals the charges on the ring carbon atoms which enable the interaction of the nitro groups with the ring are different (different colors) and so, their nitrogen hfcc values are far from each other. But for 3,4- and 3,5- dinitrobenzoic acid anion radicals these charges are approximately same (similar colors) and so their nitrogen hfcc values are close to each other (see Table 1).

4. Conclusions

In this study, EPR hyperfine coupling constants and spin density distributions of dinitrobenzoic acid anion radicals were calculated at different basis sets with DFT(B3LYP). The LanL2DZ basis set was found to be the best basis set in hfcc calculations in terms of agreement with experimental results. For 2,4- and 2,5-dinitrobenzoic acid anion radicals, the spin density distribution is concentrated on a single nitro group, while for 3,4- and 3,5-dinitrobenzoic acid, it is observed that it concentrates almost equally on the both nitro groups. In 2,4-dinitrobenzoic acid anion radical, the nitro group with high spin density is observed to be out of plane in accordance with the literature. The distribution differences of the spin density on the nitro groups were investigated by NBO and Mulliken charge analyzes of the anion radicals. NBO analyzes showed that there is a strong hydrogen bonding interaction between the carboxyl and nitro groups in 2,4-dinitrobenzoic acid, and in 2,5-dinitrobenzoic acid the charge is transferred from the ring carbon atom to the first nitro group while the opposite is calculated for the second nitro group. Again, the NBO analysis of 3,4-dinitrobenzoic acid showed that there is a high charge transfer from the ring carbon atom to the N-O bonds of the second nitro group. Finally, in 3,5 dinitrobenzoic acid it showed a high and almost equal charge transfer from the nitrogen atom in the both nitro groups to the BD(O…O) orbitals in the same groups. In summary, NBO analyzes explain the nitrogen hfcc values of the nitro groups which are far or close to each other for all the anion radicals. In addition, the EPR simulation spectra obtained by using the theoretical hfcc values in the EPR Simulator software program for some radicals were harmonically given with their experimental spectra.

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper
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- **Author contributions:** The authors declare that they have equal right on this paper.
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- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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