



Investigation molecular and radical structures of three-carboxyfurans by DFT and EPR on gas-phase

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Abstract: Three-carboxyfurans ($C_5H_4O_3$) is a member of organic compounds. The structure, radical properties, and Electron paramagnetic resonance (EPR) parameters of this organic compound were studied using computational methods. Conformational analysis, which examines the potential energy surface of the molecule in order to determine the stable structure of the molecule, was performed with the Spartan program. Then the conformations obtained as a result of this calculation were optimized by using B3LYP functional of DFT with using 6-311++G(d,p) basis sets. Thanks to geometry optimization calculations, conformations energies were obtained. And stable conformer was detected. And then radicals were modeled by using the conformer that has the lowest energy. Finally, calculated values are compared with experimental data.

Keywords: Three-carboxyfurans; Molecular Modelling; DFT; Conformational Analysis; Radical models.

1. Introduction

Three-carboxyfurans (3-FCA), also known as 3-furancarboxylic acid or 3-furoate, belongs to the class of organic compounds known as furoic acids. These are organic compounds containing a furoic acid moiety, with a structure characterized by a furan ring bearing a carboxylic acid group at the C_2 or C_3 carbon atom. 3-FCA is neutral compound and partly weak basic. 3-FCA has been detected asparagus. This could make 3-FCA a potential biomarker for the consumption of these foods (Liebich & Först, 1990; Nozal et al., 2001; Tunaru et al., 2003). Furans are five-membered aromatic heterocyclic rings formed by one oxygen and four carbon atoms. These organic compounds play important roles in the pharmaceutical and chemical industries. Also, a wide range of furan derivatives has been found to be hazardous to both animals and human beings (Kus et al., 2010). 3-FCA is a furan and therefore, its structure and radical properties are important. This study is a purely theoretical study where the structure of 3-FCA is revealed and experimental data are taken from references to compare the data in the study. Because the most of physical and chemical properties of a molecule depend on the molecular structure, information about molecular structure and conformational behaviour of a compound are very important. Density-functional theory (DFT) is a successful theory to calculate the electronic structure of atoms, molecules, and solids. Its goal is the quantitative understanding of material properties from the fundamental laws of quantum mechanics. While traditional construction methods try to solve the Schrödinger equation of N

electrons, DFT solves it using some approximations. DFT has two advantages over traditional construction methods. First, because it uses approximate methods, the complexity of the calculations is reduced. The second is to decrease the time which is required for calculations and to reduce the need for a powerful computer. (Kurth et al., 2005). For this reason, I preferred the DFT method. The aim of this study is to determine the stable structure of 3-FCA and to determine the radicals that may form by determining this structure by DFT.

2. Materials and methods

EPR is a magnetic resonance technique and is one of a method for studying materials with unpaired electrons. EPR has been widely used in the identification of irradiation damage centers in many substances. Experimental EPR study of 3-FCA was reported by Aras et al. (Aras et al., 2006). The experimental data used in this study are entirely taken from their work. The aim of the theoretical study is comparing modelled radicals with the one that proposed by experimental one to validate which radical corresponds to the experimental EPR spectra (Aras et al., 2006). As a result, calculated EPR parameters were compared with the experimental values. Thus, the accuracy of the theoretically obtained stable structure will also be tested.

In this study, to reveal the molecular structure, the conformational space of 3-FCA was scanned with molecular mechanic calculations. In order to establish the stable possible conformations, the same methodology with our previous similar study (Dereli et al., 2017; Dereli et al., 2018; Sarıkaya et al., 2017; Sarıkaya & Dereli, 2014; Sarıkaya et al., 2013; E. K. Sarıkaya & Ö. Dereli, 2017; Sarıkaya & Dereli, 2013; Sarıkaya et al., 2013; Sarıkaya et al., 2018) was applied in this study. Conformational analysis of 3-FCA was performed by Spartan 08 program (Irvine, 2008). After the conformers determined, using Gaussian 03W program package (Frisch & al., 2003), geometry optimizations and the other calculations of these conformers were performed by Becke's three-parameter hybrid-exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) method and with 6-311++G(d, p) level of DFT. Thus, the most stable conformer was detected. With respect to the radical structure calculations, I employed optimized structural parameters of this conformer upon obtaining the most stable conformer of 3-FCA determined. And then, twenty-three different radicals were chosen to be a model for DFT calculations. Initially, geometry optimisations of the molecule and model radicals were performed by using B3LYP functional of DFT with using 6-311++G(d,p) basis sets. Afterwards, calculations of EPR parameters were performed by using GIAO method with B3LYP functional of DFT and generic TZVP basis set obtained from Basis Set Exchange (BSE) software and the EMSL Basis Set (Schuchardt et al., 2007) Library.

3. Results and discussion

In the experimental study, the crystal structure of the 3-FCA was examined by irradiation with EPR. The low and high temperature measurements were carried out between 120 and 350 K. Aras et al. suggested that the EPR spectra of 3-FCA were exhibited a sextet with an intensity distribution 1:1:2:2:1:1 and other hyperfine splittings which they could not identify. And also they propose that caused by H1 and H2 protons, triplet intensity ratios (1:2:1) have occurred in spectra and that each of the lines (1:2:1) divided into doublets because of the H3 proton (Aras et al., 2006). The experimental spectrum was taken from as shown in Figure 1.

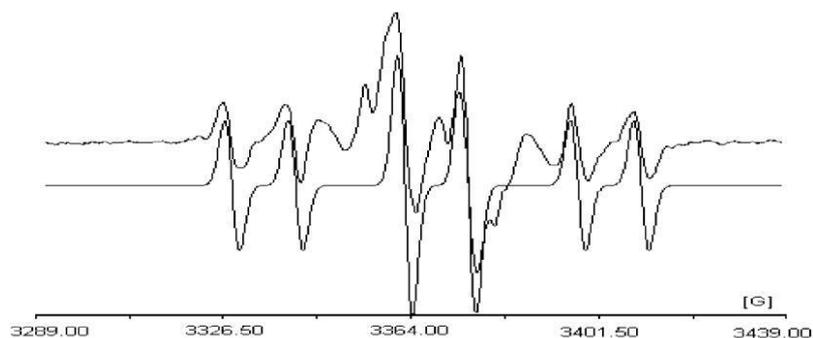


Figure 1. The experimental spectrum was taken from (Aras et al., 2006).

Spartan 08 program was used for conformational analysis and the conformational space of 3-FCA was scanned with Merck Molecular Force Field (MMFF) method. Hence, four conformers have been obtained. Geometry optimizations were performed with B3LYP method and the standard 6-311++G(d,p) basis set. The optimizations were performed without any constraints (full optimization). Then geometry optimizations calculations were performed. Thanks to geometry optimizations calculations, conformations energies were obtained. Energies and dipole moments of all calculated structures are given in Table 1. Molecular structures of the calculated conformers of 3-FCA molecule are shown in Figure 2.

Table 1. Conformational energies and dipole moment of 3-FCA molecule.

Conformations	Energies (Hartree)	Dipole Moment (D)
Conformer 1	-418.725673	1.469
Conformer 2	-418.725299	2.026
Conformer 3	-418.714574	4.823
Conformer 4	-418.714081	4.229

And stable conformer was detected. Dipole moment and energy of the lowest energy conformer calculated as 1.469 Debye and -418.725673 Hartree, respectively. Conformer 1 is the most stable conformer, seen in Figure 2.

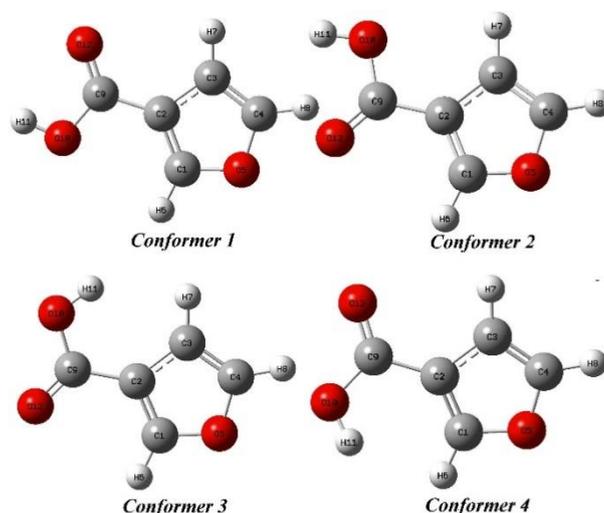


Figure 2. Molecular structure of the calculated conformers of 3-FCA molecule.

Subsequently, using the most stable structure twenty-three possible radicals were modeled, and EPR parameters were calculated by theoretical calculations for all modeled radicals after geometry optimizations of model radicals were performed. Hyperfine coupling constants (hfccs) and g-factors of model radicals were performed with NMR/GIAO method. Table 2 shows how the model radicals are modeled and model radicals were shown in Figure 3.

Measuring g values more accurately than by $\sim 10^{-3}$ is difficult. Thus, a deviation of 500 ppm between theory and experiment usually falls within the experimental error, and even an agreement with theory with in 1000ppm (1ppt) is considered satisfactory” (Neese, 2001). They said that they found the g value as 2.00310 experimentally. It is seen from Table 3, calculated g factor of the Rad2, Rad15, Rad18 and Rad21 are closer to the experimental g factor than that of other model radicals.

Table 2. Modelled radicals of the 3-FCA molecule.

Modelled Radical 1	Positive Molecular Ion	Modelled Radical 13	H7 Removed (+)
Modelled Radical 2	Negative Molecular Ion	Modelled Radical 14	H7 Removed (-)
Modelled Radical 3	H11 Removed	Modelled Radical 15	Adding H13 to C4
Modelled Radical 4	H11 Removed (+)	Modelled Radical 16	Adding H13 to C4 (+)
Modelled Radical 5	H11 Removed (-)	Modelled Radical 17	Adding H13 to C4 (-)
Modelled Radical 6	H6 Removed	Modelled Radical 18	Adding H13 to C3
Modelled Radical 7	H6 Removed (+)	Modelled Radical 19	Adding H13 to C3 (+)
Modelled Radical 8	H6 Removed (-)	Modelled Radical 20	Adding H13 to C3(-)
Modelled Radical 9	H8 Removed	Modelled Radical 21	Adding H13 to C1
Modelled Radical 10	H8 Removed (+)	Modelled Radical 22	Adding H13 to C1 (+)
Modelled Radical 11	H8 Removed (-)	Modelled Radical 23	Adding H13 to C1 (-)
Modelled Radical 12	H7 Removed		

In this case, the radical can be determined by looking at the hfccs values. “Similarly, a criterion is used when comparing experimental and theoretical hfccs values. For most purposes of interpretation and assignment, 20% deviations would be quite acceptable for calculated isotropic hyperfine splitting values of experimentally isolated radicals” (Chipman, 1994). The calculated hfccs of Rad 21 are A_{H7} : 1.25, A_{H8} : 9.82, A_{H11} :0.78 and identical two $A_{H6}=A_{H13}$: 33.28 as seen as Table 3. The experimental counterparts are A_{H7} : 1.71, A_{H8} : 11.31, and identical two $A_{H6}=A_{H13}$: 34.91 (Aras et al., 2006). When the results are examined, the experimentally observed radical is the theoretically calculated Rad21.

As in many studies we have done before (Dereli et al., 2017; Dereli et al., 2018; Ebru Karakaş Sarıkaya & Ömer Dereli, 2017; E. K. Sarıkaya & Ö. Dereli, 2017; Sarıkaya et al., 2018), these results have shown us how successful theoretical calculations are in determining the structure and creating the radical structure. In addition, after the structure has been determined and radical structures are modeled, using the calculated EPR parameters, even highly complex spectra can be reliably resolved.

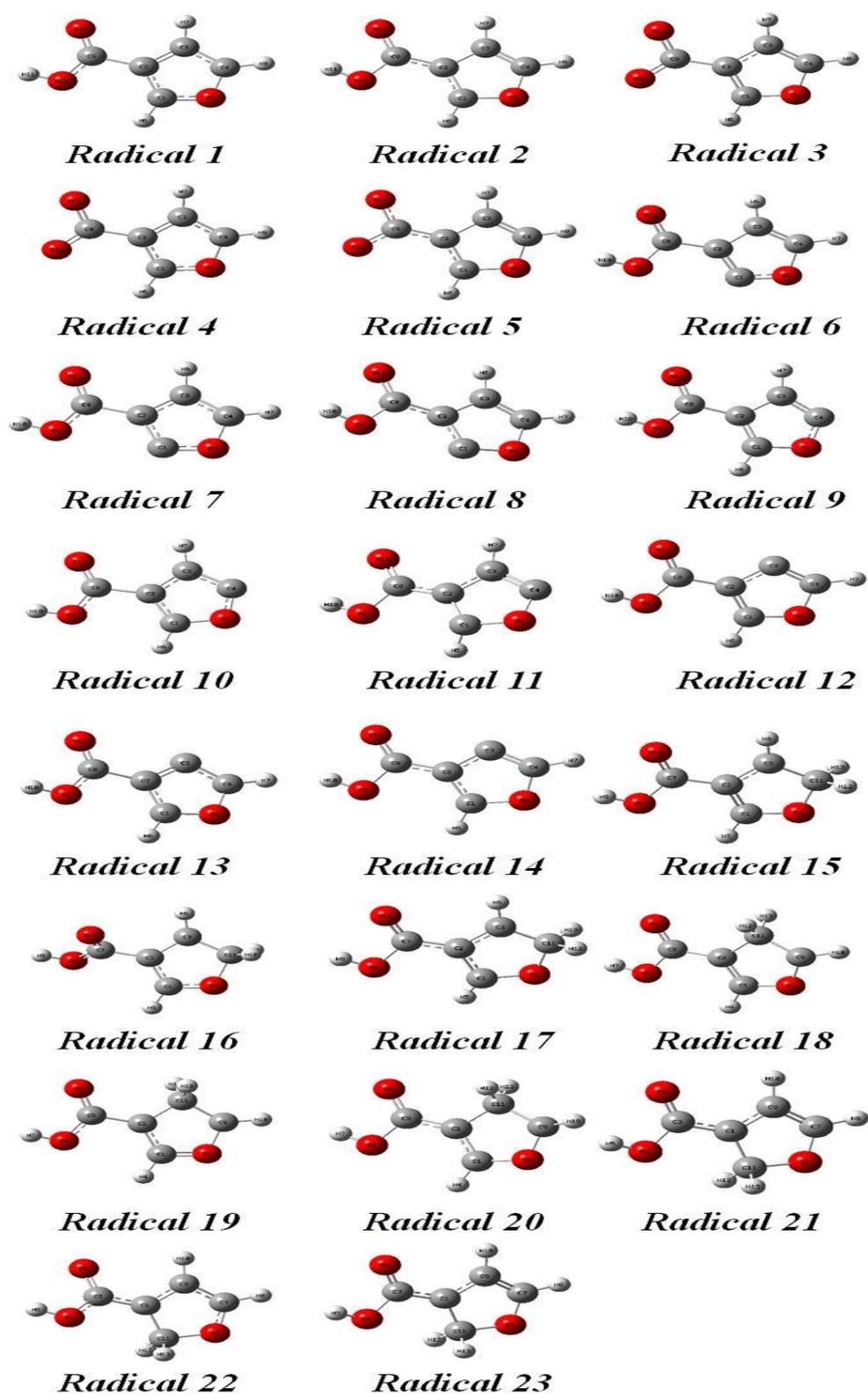


Figure 3. Modelled radicals of the 3-FCA molecule.

Table 3. Calculated (B3LYP/TZVP) values of a_{iso} (Gauss) and g_{iso} values of the 3-FCA radicals (radicals obtained by removing hydrogen).

Atom	Rad1	Rad2	Rad3	Rad4	Rad5	Rad6	Rad7	Rad8	Rad9
H(6)	11.86	13.82	0.15	6.45	7.12	-	-	-	2.98
H(7)	1.10	0.46	0.06	1.32	0.23	2.46	1.32	1.29	2.73
H(8)	12.15	0.33	0.31	6.64	0.32	2.88	5.22	1.62	-
H(11)	0.12	0.71	-	-	-	0.01	0.19	0.38	1.06
g	2.00572	2.00370	2.01030	2.02525	2.02047	2.00188	2.00181	2.00434	2.00196
	Rad10	Rad11	Rad12	Rad13	Rad14				
H(6)	5.16	2.82	2.69	4.20	5.19				
H(7)	2.14	1.18	-	-	-				
H(8)	-	-	3.11	6.79	1.75				
H(11)	0.49	0.12	0.18	0.15	0.41				
g	2.00124	2.00534	2.00204	2.00165	2.00445				

Calculated (B3LYP/TZVP) values of A (Gauss) and g values of the 3-FCA radicals (radicals obtained by adding hydrogen).

Atom	Rad15	Rad16	Rad17	Rad18	Rad19	Rad20	Rad21	Rad22	Rad23
H(6)	11.52	4.76	4.05	0.31	4.55	1.52	33.28	15.14	12.63
H(7)	15.28	10.16	7.87	47.18	36.90	20.83	1.25	3.27	5.24
H(8)	40.64	21.63	18.45	15.45	12.58	2.16	9.82	3.32	10.00
H(11)	0.08	0.17	0.59	0.14	0.55	0.31	0.78	1.18	0.89
H(13)	40.54	21.97	17.82	51.94	36.90	18.89	33.28	13.74	12.64
g	2.00319	2.00938	2.00644	2.00304	2.00596	2.00690	2.00393	2.02011	2.00630

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