

The investigation of different properties of Sarin: A theoretical study

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ABSTRACT

At the present study, different properties of Sarin with the formula $[(\text{CH}_3)_2\text{CHO}]\text{CH}_3\text{POF}$ was studied in gas phase. Geometrical optimizations of Sarin, single point calculation, NMR and Electrical parameters were carried out in gas phase with the Hartree-Fock method coupled to 6-31g* basis sets for all atoms. The results obtained from a comparison between tables and charts came up for discussion and analysis.

Keywords: Sarin; Quantum Mechanic; Chemical warfare

INTRODUCTION

Sarin is an organo phosphorus compound with the formula $[(\text{CH}_3)_2\text{CHO}]\text{CH}_3\text{POF}$. It is a colorless, odorless liquid. So, it is a chiral molecule because it has four chemically different substituent attached to the tetrahedral phosphorus center [1]. The P-F bond is easily broken by nucleophilic agents, such as water and hydroxide. At high pH, sarin decomposes rapidly to nontoxic phosphonic acid derivatives [2-4].

Sarin originally was developed in 1938 in Germany as a pesticide; until in mid 1939 German army to the chemical warfare section ordered that it be brought

into mass production for wartime use because [5] it has been classified as a weapon of mass destruction in UN Resolution 687. Production and stockpiling of sarin was outlawed by the Chemical Weapons Convention of 1993 and it is classified as a Schedule 1 substance. Also, Sarin was used in the deadly attacks of the Iran-Iraq war [6].

Sarin is 26 times more deadly than cyanide. When pure is, can be readily absorbed into the body by breathing, eating or drinking and skin or eye contact. Short-term health effects seen from sarin include runny nose, tightness in the chest,

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shortness of breath, excessive drooling and sweating, increased urination, abnormal heart rate and blood pressure, nausea, vomiting, abdominal cramps, muscle twitching, confusion, seizures, paralysis, coma, respiratory paralysis, and death. These incapacitating and/or lethal effects can be seen as early as 1 to 10 minutes after exposure. Sarin is a agent classified as a nerve agent. Nerve agents are the most toxic and rapidly acting of the known chemical warfare agents. Animal studies have shown that exposure to low levels of sarin can lead to adverse effects such as suppression of immune system response, subtle changes in brain activity, and learning and memory impairments [7,8].

METHODOLOGY

In our model, all calculations were performed using Gaussian 09 software package. Geometrical optimizations of sarin, single point calculation, NMR and Electrical properties [9] parameters were carried out in gas phase with the Hartree - Fock method coupled to 6-31g* basis sets for all atoms.

The most common type of ab initio calculation is called a Hartree- Fock calculation (abbreviated HF), in which the primary approximation is called the central field approximation. A method, which avoids making the HF mistakes in the first place, is called Quantum Monte Carlo (QMC). There are several flavors of QMC variational, diffusion and Green's functions. These methods work with an explicitly correlated wave function and evaluate integrals numerically using a Monte Carlo integration [10, 11]. In general, ab initio calculations give very good qualitative results and can give increasingly accurate quantitative results as the molecules in question become smaller [12]. There are three steps in carrying out any quantum mechanical calculation. First,

prepare a molecule with an appropriate starting geometry. Second, choose a calculation method and its associated options. Third, choose the type of calculation with the relevant options.

RESULTS AND DISCUSSION

Molecular Geometry

Fig. 1, Shows the graphical representations of the optimized geometry of Sarin. In the figure, the F atom are shown by blue color, white spheres are H atoms, yellow sphere is P, red sphere is O and gray sphere is C.

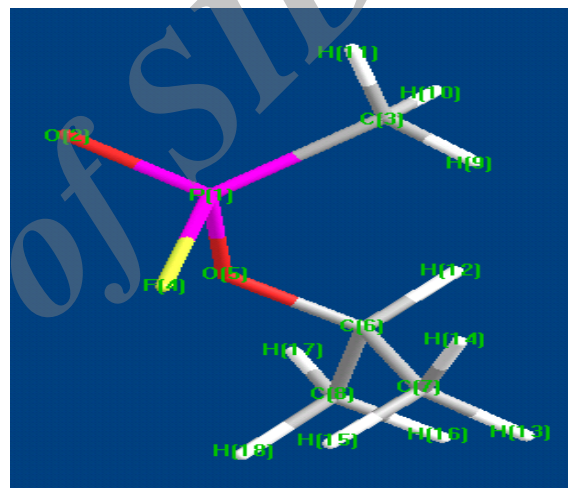


Fig. 1. Optimized geometry of Sarin obtained at HF/6-31G* level.

Nuclear Magnetic Resonance Parameters

In general, the electron distribution around a nucleus in a molecule is more spherically symmetric. Therefore, the size of the electron current around the field, and hence the size of the shielding, will depend on the orientation of the molecule within the applied field. NMR spectroscopy is a research technique that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of nuclear magnetic resonance and can provide detailed

information about the structure, dynamics, reaction state, and chemical environment of molecules. Ab initio calculation of nuclear magnetic shielding has become an aid in the analysis of molecular structure and accurate assignment of NMR spectra of compounds. So, NMR is based on the quantum mechanical property of nuclei. The chemical shielding refers to the phenomenon, which is associated with the secondary magnetic field created by the induced motions of the electrons that surrounding the nuclei when in the presence of an applied magnetic field [13].

In the present paper, total dipole moments of Sarin in gas phase have been

explored and NMR computations were done by Gaussian 09 suite of programs. The calculated magnetic shielding tensor (σ , ppm), shielding asymmetry (η) and the chemical shift tensor (δ) calculated for C, H, P, O and F nuclei in the active site of Sarin in gas phase are presented in Table 1. Also, the graphs of calculated isotropic magnetic shielding constants σ_{iso} (ppm), anisotropic magnetic shielding tensors σ_{aniso} (ppm), chemical shifts δ (ppm) and shielding asymmetry (η) versus the number of atomic centers for selected atoms of Sarin are displayed in Figs. 2a-d respectively.

Table1. Components of the magnetic shielding tensor (σ , ppm), magnetic shielding anisotropy ($\Delta\sigma$, ppm), shielding asymmetry (η) and the chemical shift tensor (δ) calculated for C, H, P, O and F nuclei in the active site of Sarin in gas phases at HF level with the 6-31G* basis set

Atoms	σ_{iso}	σ_{11}	η	Atoms	σ_{iso}	σ_{11}	η
	σ_{aniso}	σ_{22}	δ		σ_{aniso}	σ_{22}	δ
		σ_{33}				σ_{33}	
1P	215.8256	-103.7315	0.28	10H	32.6527	28.6811	0.45
	524.6979	330.2418	319.5571		9.4126	31.1834	5.441
		420.9664				38.0937	
2O	-0.3998	-333.6428	0.98	11H	31.4879	27.0417	0.56
	668.3793	-2.2931	335.1363		10.8404	29.5400	4.4462
		334.7365				37.8821	
3C	175.7315	143.5473	0.89	12H	32.0012	28.7391	0.31
	66.1823	173.9175	33.9981		8.2346	30.2908	4.9725
		209.7296				36.9737	
4F	389.2421	305.5423	0.90	13H	29.5303	26.7728	0.45
	163.5954	393.0463	-83.6998		6.5628	28.4825	3.8053
		469.1377				33.3356	
5O	219.9356	75.5891	0.16	14H	32.7356	27.9366	0.41
	228.7613	279.8671	-144.3465		11.6124	30.7211	6.8134
		304.3504				39.5490	
6C	140.8474	114.6185	0.18	15H	31.8451	25.8315	0.80
	44.3766	122.6997	44.3766		11.4541	32.4181	-6.0136
		185.2240				37.2856	
7C	184.0629	166.2094	0.61	16H	32.1171	29.4074	0.10
	40.0033	179.7668	22.1498		7.6213	29.9152	4.9116
		206.2127				37.0287	
8C	181.8303	161.8672	0.65	17H	32.5862	28.0570	0.34
	44.1465	177.6100	24.1834		11.286	30.3586	6.7568
		206.0137				39.3430	
9H	31.6700	28.0472	0.24	18H	31.6288	26.9467	0.39
	8.8294	30.0861	28.0472		11.3936	29.5995	6.7115
		36.8766				38.3403	

According to Figure 2a, it is obvious that one atom in Sarin has maximum σ_{iso} value in compare to the other atoms of this structure and this value belongs to 4F. Anisotropic chemical shielding is one of the other parameters that were checked in this work. From Figure 2b it has been found that the maximum value of σ_{aniso} in

sarin is related to 2O.

The results of investigating chemical shift tensor indicate that 2O have been shown to be the largest value of (δ) in Sarin and our knowledge about sarin has been specified that O number 2 show the largest intermolecular effects in (η) component (Fig. 2d).

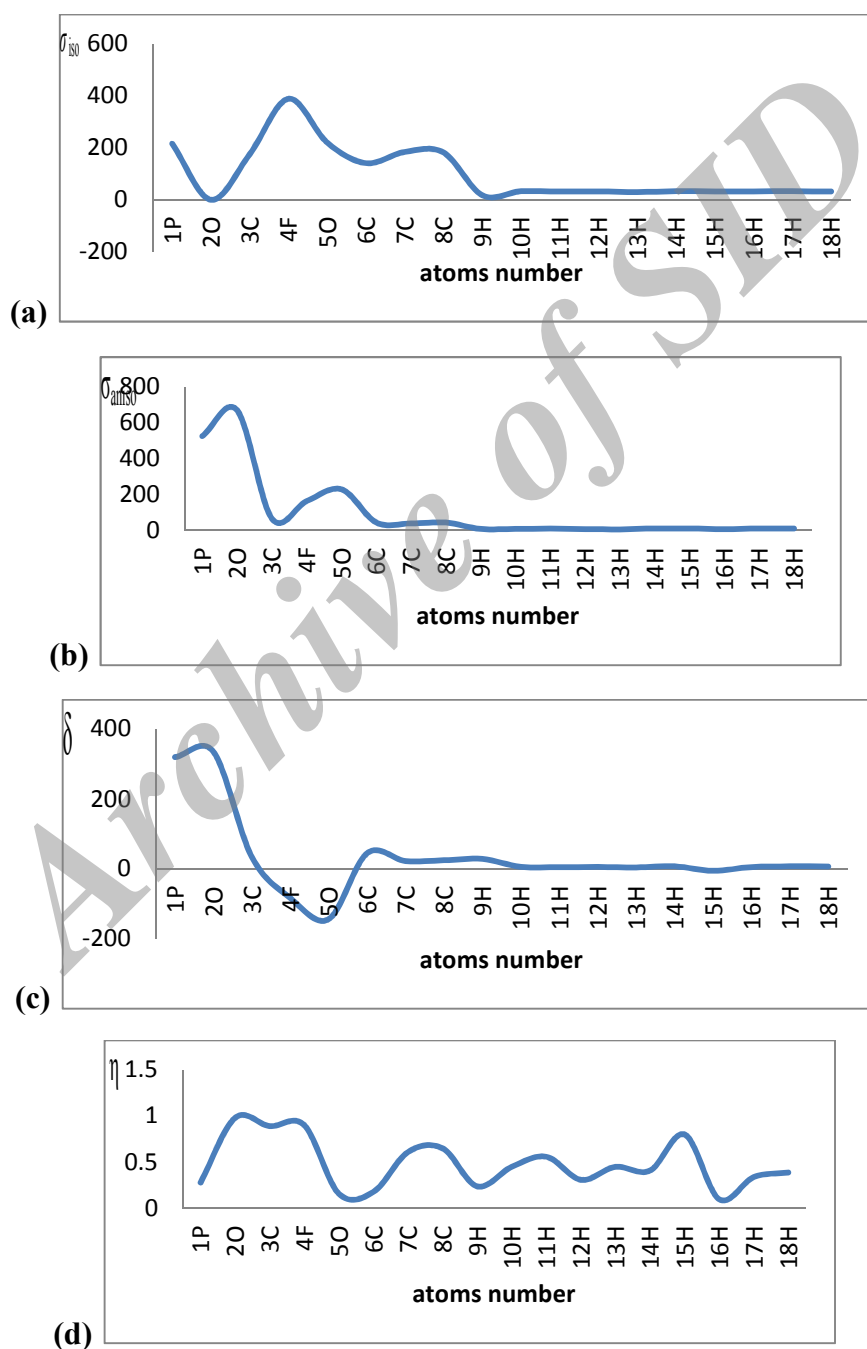


Fig. 2. The graphs of a) σ_{iso} , b) σ_{aniso} , c) δ , d) η of sarin in gas phases at the HF/6-31G* basis sets.

Electromagnetic Hyperfine Parameters

In this section, the major point is embedded in the investigation of the electrostatic interaction of sarin in gas phase by the HF/6-31g*method. Length bonds, total atomic charges, electric potential in different bonds of Sarin are reported in table 2. Also, graphs of calculated electric potential in different bonds of Sarin are shown in Figs. 3.

The calculations were performed in two methods, $\Delta V^* = (Q_2 - Q_1)/4\pi\epsilon r$ and different electrostatic properties.

CONCLUSION

NMR chemical shielding tensors in the methods framework makes it possible to

study the chemical shift of sarin. The calculated parameters reveal that 2O and 13H atoms have the largest and smallest anisotropic magnetic shielding (σ_{aniso}) constants among the other nuclei, respectively.

The 2O has the largest but 5O has the smallest chemical shift (δ) constants among and other atoms, respectively. The diagram consist of η show all shielding values η are between 0 to 1.

Also, Length bonds, total atomic charges and electric potential were calculated in different bonds of Sarin that can be compared with each other. Also, graph of calculated electric potential in different bonds of Sarin are shown.

Table 2. Length bond, total atomic charges, electric potential in different bonds of Sarin at HF level With the 6-31G* basis set

Bond	(r) Length bond	($Q_2 - Q_1$) Total atomic charges	(ΔV^*) electric potential	($\Delta V = V_2 - V_1$) electric potential
B1(1P-2O)	1.68748	-2.07154	-17.6601	31.69629
B2(1P-3C)	1.83757	-2.18755	-17.1259	39.25695
B3(1P-4F)	1.39101	0.290872	3.008226	-42.166
B4(1P-5O)	1.69845	-2.217	-18.7781	31.71411
B5(5O-6C)	1.43452	1.000827	10.03671	7.654283
B6(6C-7C)	1.55365	-0.63305	-5.86168	-0.08315
B7(6C-8C)	1.54843	-0.56591	-5.2577	-0.0876
B8(3C-9H)	0.9861	1.262017	18.41124	21.60484
B9(3C-10H)	1.08303	1.012007	13.44256	13.66527
B10(3C-11H)	1.0834	1.026902	13.63575	13.6528
B11(6C-12H)	1.08312	0.998217	13.25828	13.66316
B12(7C-13H)	1.09949	0.02418	0.316376	13.55127
B13(7C-14H)	1.08517	0.651802	8.640856	13.63975
B14(7C-15H)	1.08601	0.671168	8.890706	13.6365
B15(8C-16H)	1.08556	0.663159	8.788256	13.63431
B16(8C-17H)	1.08572	0.568977	7.539034	13.6363
B17(8C-18H)	1.08555	0.595458	7.891147	13.62867

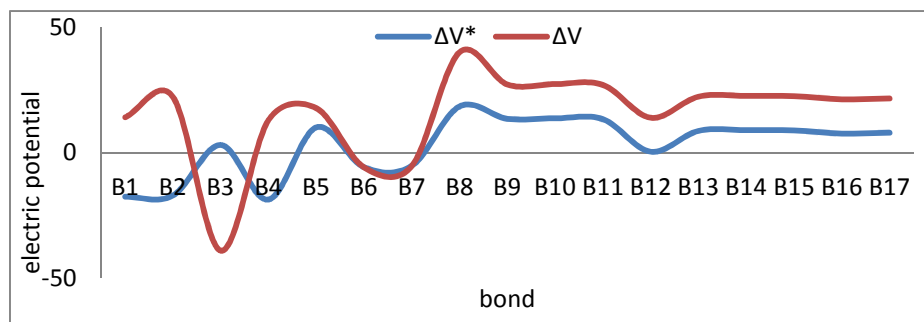


Fig 3. The graph of calculated electric potential in different bonds of Sarin at the HF/6-31G* basis sets.

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