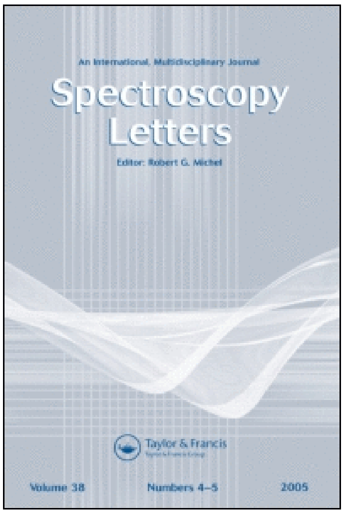

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GIAO Calculations of Chemical Shifts in Ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate

Y. Atalay[a]; D. Avcı[a]
[a] Sakarya niversitesi Fen Edebiyat, Fakültesi Fizik, Bölümü, Sakarya, Turkey

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GIAO Calculations of Chemical Shifts in Ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate

Y. Atalay and D. Avcı
Sakarya Üniversitesi Fen
Edebiyat, Fakültesi Fizik,
Bölümü, Sakarya, Turkey

ABSTRACT Geometric optimization and gauge including atomic orbital (GIAO). ^1H and ^{13}C NMR chemical shift calculations with Hartree–Fock (HF) method and density functional method (B3LYP), using the 6-31G(d) and 6-31 + G(d) basis sets, are proposed as a tool to be applied in the structural characterization of ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate, thus providing useful support in the interpretation of experimental NMR data. Parameters related to linear correlation plot of computed versus experimental ^{13}C NMR chemical shifts in DMSO-d_6 are provided.

KEYWORDS calculation, DFT, GIAO, ^1H and ^{13}C NMR, HF

INTRODUCTION

Many aromatic or aliphatic nitriles are close relatives of iminoesters, thioamides, carboxamidines, and hydrazones. These compounds have been used as starting materials for triazole, thiazole, thiadiazole, and imidazole compounds, which are important components of antimicrobial, antiviral, anticancer, and antifungal agents.[1–4] Some thiadiazole compounds with unsaturated double bonds that were synthesized from nitriles have been shown to have high anticancer activity.[5] Nibentan, a member of a new class of antiarrhythmic drug, was obtained from phenyl acetonitrile derivatives.[6] Moreover, phthalonitriles have been used as key reagents in the syntheses of phthalocyanines,[7] which are useful in the production of dyes, optical limiters, and liquid crystals.

NMR spectroscopy has been proved to be an exceptional tool to elucidate structure and molecular conformation. Ab initio and DFT calculation of NMR shielding at very accurate levels of approximation are available in the literature.[8–12] The most common methods to calculate chemical shifts are IGLO (individual gauge for localized orbitals), LORG (localized or loacaorbital origin), and GIAO (gauge-invariant orbital). The GIAO/DFT approach[13] is known to give satisfactory chemical shifts for different nuclei[13–15] with larger molecules. These quantum chemical calculations, however, often have to be limited to isolated (gas-phase) molecules and to some preferred (optimized) structures

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Address correspondence to
Y. Atalay, Sakarya Üniversitesi Fen
Edebiyat, Fakültesi Fizik, Bölümü,
Sakarya 54100, Turkey. Tel.: +90
264 2956083; Fax: +90 264 2955950;
E-mail: yatalay@sakarya.edu.tr

while experimental NMR spectra are commonly static averages affected by dynamic processes such as conformational equilibria as well as intramolecular and/or intermolecular interactions.

The current paper applies the Hartree–Fock (HF) and DFT methods to analyze the experimental ^{1}H and ^{13}C data of ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate published by Ustabaş et al.[16] The aim of this work is to calculate the theoretical chemical shifts of the title compound molecular structure based on proper assignment of observed ^{1}H and ^{13}C resonances by using proper computational method and basis set. The calculated chemical shifts are then compared with the experimental values.

CALCULATIONS

The molecular structure of ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate in the ground state (*in vacuo*) is optimized Becke–3 Lee–Yang–Parr (B3LYP) with 6-31G(d) basis set. The geometry of the title compounds, together with that of tetramethylsilane (TMS), is fully optimized. ^{1}H and ^{13}C NMR chemical shifts are calculated with GIAO approach[17,18] applying B3LYP and HF method[19] with 6-31G(d)[20] and 6-31 + G(d)[21] basis sets. The theoretical ^{1}H and ^{13}C NMR chemical shift values were obtained by subtracting the GIAO calculated.[15,22] ^{13}C isotropic magnetic shielding (IMS) of any X carbon atom, to the average ^{13}C IMS of TMS is calculated using the following equation: $CS_x = IMS_{TMS}\text{-}IMS_x$. Molecular geometry is restricted, and all the calculations were performed by using Gauss-View molecular visualization program[23] and the Gaussian 98 program package on a personal computer.[24]

RESULTS AND DISCUSSION

Ustabaş et al.[16] determined the crystal structure of the title compound ($C_{10}H_8N_4S_4$). The title compound is monoclinic, the space group $P2_1/c$, with cell dimensions $a = 11.514$ Å, $b = 8.682$ Å, $c = 14.155$ Å, and $V = 1344.3$ Å^3. The theoretical and experimental crystal structures of the title compound are shown in Fig. 1. In previous work,[25] we selected the optimized geometric parameters (bond lengths and angles) by HF and B3LYP methods with 6-31G(d) basis set. In the current work, we selected the optimized geometric parameters (bond lengths and angles) by HF and B3LYP methods with 6-31 + G(d) basis set, and these parameters are shown in Table 1. The molecule has an approximate center of symmetry at the middle of the C5–C6 bond and also approximates the other symmetry elements (a twofold axis perpendicular to a mirror plane) that constitute the C_{2h} point group. However, because it crystallizes in a general position, the packing environment did not fit this point group, and there are some significant deviations. For example, the four torsion angles C11–S1–C1–C5, C21–S2–C2–C6, C31–S3–C3–C5, and C41–S4–C4–C6 would all be equal in magnitude if C_{2h} were the symmetry group, but instead they have the values 72.5 (2), −58.9 (2), −39.4 (2) and 48.6 (2)°, respectively.[16]

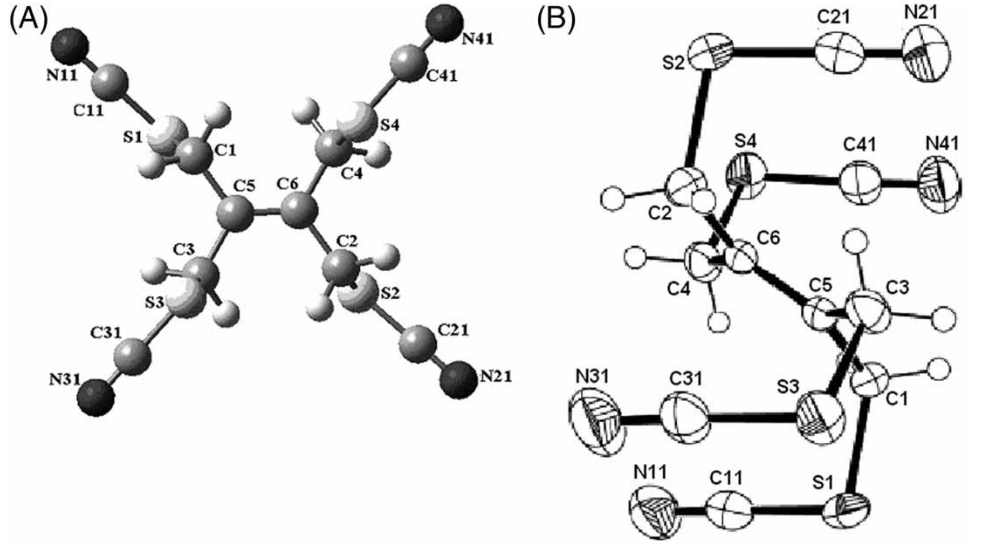

FIGURE 1 **(A) The Theoretical Geometric Structure of the Title Compound ($C_{10}H_8N_4S_4$). (B) The Experimental Geometric Structure of the Title Compound ($C_{10}H_8N_4S_4$) (the Displacement Ellipsoids are Drawn at 50% Probability level) Taken from Ref. [16].**

TABLE 1 **Optimized and Experimental Geometries of the Title Compound ($C_{10}H_8N_4S_4$) in the Ground State**

		Calculated			
		HF		B3LYP	
Parameters	Experimental[a]	6-31G(d)[b]	6-31 + G(d)	6-31G(d)[b]	6-31 + G(d)
Bond lengths (Å)					
C11≡N11	1.39(3)	1.137	1.138	1.166	1.167
C41≡N41	1.142(3)	1.137	1.138	1.166	1.167
S1–C11	1.684(3)	1.706	1.843	1.701	1.877
Bond angles (°)					
S2–C21–N21	179.7(3)	179.9	178.6	179.9	178.6
Torsion angles (°)					
C11–S1–C1–C5	75.2(2)	169.3	169.2	167.0	167.3
C21–S2–C2–C6	−58.9(2)	169.3	169.1	167.0	167.2
C31–S3–C3–C5	−39.4(2)	169.3	169.2	167.0	167.3
C41–S4–C4–C6	48.6(2)	169.3	169.1	167.0	167.2

[a,b] Taken from Refs. [16] and [25]. Bond lengths in angstroms, bond angles and torsion angles in degrees.

However, we have calculated the four torsion angles of the title compound (C11–S1–C1–C5, C21–S2–C2–C6, C31–S3–C3–C5, and C41–S4–C4–C6) at same values 169.3° for HF and 167.0° for B3LYP with 6-31G(d) basis set, respectively. Therefore, we can say that theoretically the title compound seems to show C_{2h} symmetry, as can be seen from Table 1 and Fig. 1.

GIAO calculations with X-ray geometry lead to more accurate chemical shifts compared with B3LYP optimized geometry. The theoretical chemical shift values of the title compound have been calculated by using B3LYP and HF methods with 6-31G(d) and 6-31 + G(d) basis sets. The ^1H and ^{13}C chemical shift values (with respect to TMS) calculated for the

TABLE 2 **Theoretical and Experimental ^1H and ^{13}C Isotropic Chemical Shifts (with Respect to TMS) of the Title Compound ($C_{10}H_8N_4S_4$)**

		Calculated chemical shift, δ (ppm)[a]			
		HF		B3LYP	
Atom	Experimental[b] NMR (ppm) (DMSO-d_6)	6-31G(d)	6-31G + (d)	6-31G(d)	6-31G + (d)
C5	126.02	134.90	135.85	133.44	135.96
C6	126.02	134.90	136.01	133.44	135.98
C31	113.08	111.89	103.33	99.45	112.91
C11	113.08	111.89	103.33	99.45	112.87
C21	113.08	111.88	103.33	99.45	112.91
C41	113.08	111.88	103.33	99.45	112.87
C1	20.18	24.30	23.88	24.06	22.83
C2	20.18	24.30	23.96	24.06	22.88
C3	20.18	24.30	23.96	24.06	22.88
C4	20.18	24.30	23.88	24.06	22.83
H1(C1)	3.44	3.86	3.99	3.99	3.86
H3(C2)	3.44	3.86	3.99	3.99	3.86
H5(C3)	3.44	3.86	3.99	3.99	3.86
H8(C4)	3.44	3.86	3.99	3.99	3.86
H2(C1)	3.44	3.43	3.63	3.61	3.43
H4(C2)	3.44	3.43	3.67	3.61	3.43
H6(C3)	3.44	3.43	3.64	3.61	3.43
H7(C4)	3.44	3.43	3.63	3.61	3.43

[a] All calculations performed with the 6-31G(d) and 6-31G + (d) basis sets.
[b] Taken from Refs. [16].

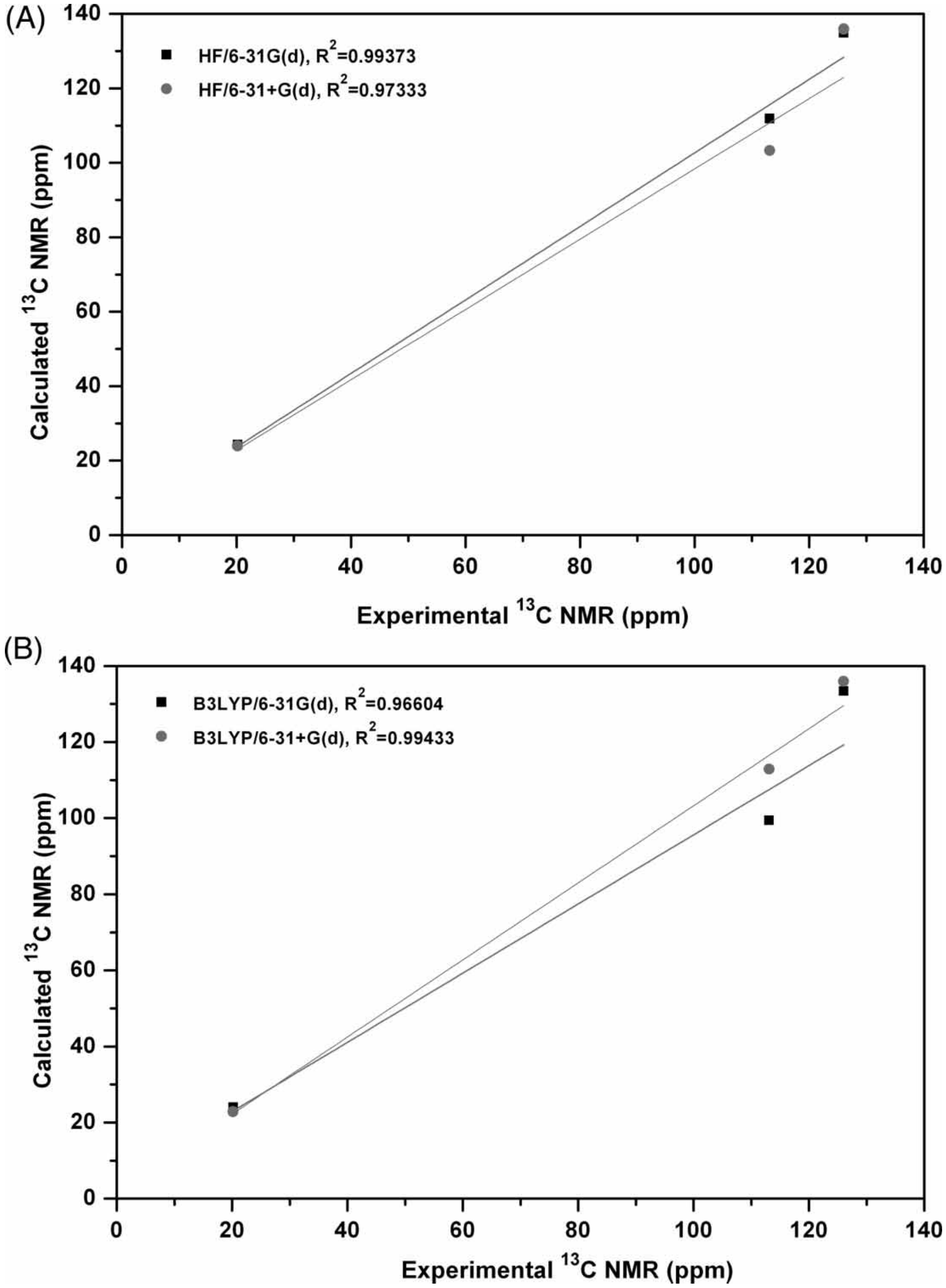

FIGURE 2 Correlation Plot of Calculated Versus Experimental ^{13}C NMR Chemical Shift, at the (A) HF and (B) B3LYP Level with 6-31G(d), 6-31 + G(d) Basis Sets for Ethene-1,1,2,2-Tetrayltetramethylene Tetrathiocyanate.

optimized structures of the title compound and experimental ^{1}H and ^{13}C chemical shift values[16] are shown in Table 2. As can also be seen in Fig. 1A, the title compound has C_{2h} symmetry. If one looks at the theoretical and experimental ^{1}H and ^{13}C spectra of the title compound, the spectra will imply the symmetry explicitly, as can be seen in Table 2. We can see in Table 2 that experimental ^{1}H and ^{13}C chemical shift values are in better agreement with the theoretical ^{1}H and ^{13}C chemical shift values and are found to have better agreement with the B3LYP than the HF method.

Figure 2 shows the correlation plot of the ^{13}C chemical shift values (with respect to TMS), calculated at HF and B3LYP level with 6-31G(d) and 6-31 + G(d) basis sets versus the corresponding experimental data shown in Table 2. As we can see from the correlation graphic in Fig. 2, experimental ^{13}C chemical shift values are in better agreement with the theoretical ^{13}C chemical shift values.

CONCLUSIONS

In this work, we have calculated the geometric parameters and ^{1}H and ^{13}C chemical shift values of ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate by using B3LYP and HF method with 6-31G(d) and 6-31 + G(d) basis sets. In particular, the results of the B3LYP/6-31 + G(d) level has shown better fit to experimental data than the HF/6-31 + G(d) level in evaluating ^{13}C chemical shift values. Likewise, the B3LYP method seems to be more appropriate than the HF method for the calculation of geometric parameters of molecules. As well as being very economical with respect to computational resources, density functional calculations would be more suitable for studying typical chemical molecules, especially taking into account that large basis sets are required for NMR properties prediction.[26]

To test the different theoretical approaches (HF, DFT/B3LYP) reported here, computed and experimental[16] ^{1}H and ^{13}C chemical shifts in the DMSO-d$_6$ solution and in the solid state of ethene-1,1,2,2-tetrayltetramethylene tetrathiocyanate were compared. More commonly, however, the NMR spectrum is used in conjunction with other forms of spectroscopy and chemical analysis to determine the structures of complicated organic molecules.

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