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Experimental and DFT studies on the vibrational, electronic spectra and NBO analysis of thiamethoxam

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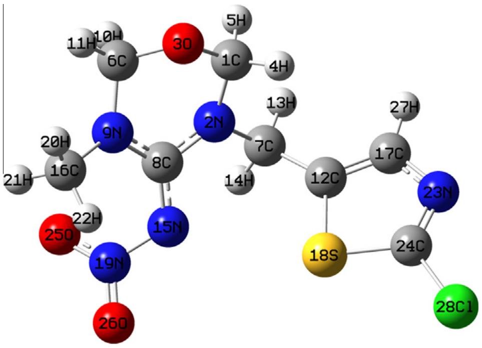
HIGHLIGHTS

- The FT-IR, FT-Raman spectra and UV–vis of the title compound have been recorded experimentally.
- Optimized geometry, vibrational frequencies are obtained with six DFT methods.
- The complete assignments of the experimental spectra are performed on the basis of PED.
- The HOMO and LUMO energies have been calculated.
- The absorption spectra of the compound were computed both in gas-phase and in H_2O solution.

GRAPHICAL ABSTRACT

DFT study of the structural and spectroscopic properties of thiamethoxam has been reported



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ABSTRACT

Vibrational and electronic spectral measurements were performed for 3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene(nitro) amine (thiamethoxam). Optimized geometrical structure and harmonic vibrational frequencies were calculated with *ab initio* RHF and DFT (B3LYP, CAM-B3LYP, M06 and PBE1PBE) methods with 6-311++G (d, p) basis set. Complete assignments of the observed spectra were proposed. The absorption spectra of the compound were computed in gas-phase using TD-B3LYP/6-311++G (d, p) approach and H_2O solution using PCM-TD-B3LYP/6-311++G (d, p) approach. The calculated results matched well with the experimental values. Temperature dependence of thermodynamic parameters in the range of 100–1000 K were determined. The bond orbital occupancies, contribution from parent natural bond orbital (NBO), the natural atomic hybrids was discussed.

Introduction

Neonicotinoids are a class of neuro-active insecticides developed in 1972 by Shell and in 1990s by Bayer [1]. The neonicotinoids were developed in large part because they showed reduced toxicity compared to organophosphate and carbamate insecticides used previously. Because of the different binding affinities with the acetylcholine receptor (nAChR) of insect's neurosystem, they afforded broad spectrum activity and high selectivity [2–4] and much lower toxicity against mammals, birds, aquatic life than insects [5]. Neonicotinoid pesticide is a new group of insecticide class with novel mechanisms of action, which includes the commercial products imidacloprid, acetamiprid, nitenpyram and thiamethoxam [6–8]. Since they became commercially available in 1990s, they were receipted considerable interests from both

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agricultural chemistry and medicinal fields [9–11]. Thiamethoxam is a representative product of the second-generation neonicotinoid pesticide [12,13]. The compound was introduced to the market in 1991 and has become the world's second largest marketing neonicotinoid with sales of $627 million in at least 65 countries for 115 crops in 2009 [14]. Thiamethoxam affects selectively on the insect nervous system by acting as an agonist at the nicotinic acetylcholine receptors and then blocks the nicotinergic neuronal pathways and attracts amassing of the neurotransmitter acetylcholine [15–19]. It is a very useful insecticide for control of a broad range of sucking insect pests of various crops, such as aphids, plant-hoppers, leaf-hopper and whitefly [20,21]. The unique capabilities of thiamethoxam, such as broad spectrum activity, systemic activity, flexible application methods and low acute mammalian toxicity have resulted in taking place of the organophosphates, carbamates and synthetic pyrethroids [22–24].

Many experimental studies of the toxicities of thiamethoxam have been reported, however, theoretical studies of this compound are scarce, and the mechanisms are still unclear, thus additional studies are required in order to understand the mechanisms involved, which will then facilitate the design of new compound for applications in the biochemical and biophysical fields. In this present work, the efforts have been taken to predict a complete description of the molecular geometry, vibrational frequencies, and natural bond orbital (NBO) analysis. To calculate the absorption spectra, the time-dependent density functional theory (TD-DFT) at B3LYP/6-311++G (d, p) level associated with the polarized continuum model (PCM) was performed. Thermodynamic properties of the title compound at different temperatures have also been calculated and they reveal the correlation between heat capacity, entropy, enthalpy changes, Gibbs free energy and temperatures.

Experimental and computational

Experimental

3-Methyl-4-nitroimino-tetrahydro-1,3,5-oxadiazine (0.1 mol, 16.0 g), 2-chloro-5- (chloromethyl) thiazole (0.12 mol, 20.16 g) and potassium carbonate (0.25 mol, 34.5 g) were dissolved in DMF (100 ml). The mixture was heated for 16 h at 50 °C, then cooled, filtered, and concentrated under vacuum. The product was recrystallized from toluene, giving 21.12 g, yield 72.6%, m.p. 138.5–138.8 °C. ^{1}H NMR (solvent-$CDCl_3$): 7.84 (s, 1H), 4.88 (s, 4H), 4.75 (S, 2H), 3.04 (S, 3H).

The FT-IR of the compound was measured on AVATAR360 spectrophotometer in the range of 400–3500 cm^{-1} at room temperature using KBr pellet technique. The Raman spectra was recorded on Bruker RFS 100/S FT-Raman spectrometer in the 400–3500 cm^{-1} region with diode-pumped air-cooled cw Nd-YAG laser source giving 1064 nm as exciting line at 75 mW power. The UV–vis spectrum was recorded on UV–vis 916 spectrophotometer in the region 200–400 nm using H_2O as solvent.

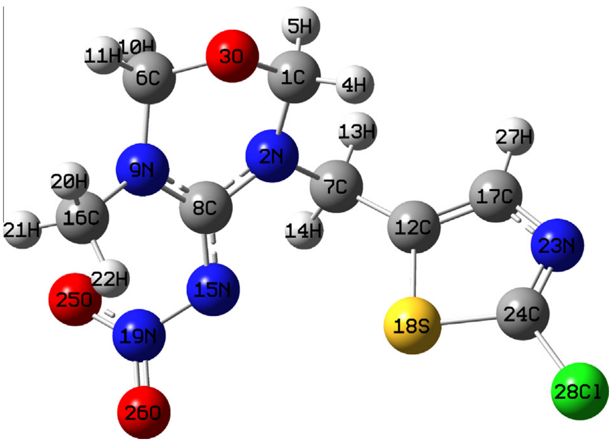

Fig. 1. Optimized geometry with atomic numbering of the title compound.

Methods of calculation

The original geometry of thiamethoxam was optimized using the MM$^+$ molecular modeling in Hyperchem 6.0 package [25]. This equilibrium geometry was then re-optimized at DFT methods B3LYP [26], CAMB3LYP [27], M06 [28], PBE1PBE [29] and *ab initio* RHF method [30] with 6-311++G (d, p) basis set. Time-dependent density functional theory (TD-DFT) [31] excited-state calculation was performed at B3LYP/6-311++G (d, p) level of theory in gas phase. A polarizable continuum model (PCM) [32] including solvent effect was chosen in excitation energy calculations in H_2O solution. All calculations were performed using Gaussian 09W program package [33].

Table 1
Optimized and experimental bond distances (Å) and bond angles (°) for the title compound.

	RHF	B3LYP	CAM-B3LYP	M06	PBE1PBE	Exp[a]
R(1,2)	1.462	1.473	1.466	1.463	1.462	1.471
R(1,3)	1.379	1.402	1.395	1.387	1.392	1.396
R(2,7)	1.459	1.468	1.460	1.457	1.456	1.475
R(2,8)	1.349	1.365	1.358	1.359	1.358	1.337
R(3,6)	1.389	1.419	1.410	1.404	1.408	1.411
R(6,9)	1.442	1.449	1.444	1.442	1.440	1.448
R(7,12)	1.504	1.502	1.498	1.491	1.495	1.495
R(8,9)	1.340	1.358	1.350	1.354	1.351	1.372
R(8,15)	1.313	1.327	1.320	1.318	1.321	1.362
R(9,16)	1.459	1.463	1.457	1.453	1.452	1.462
R(12,17)	1.342	1.365	1.357	1.360	1.364	1.349
R(12,18)	1.743	1.752	1.740	1.742	1.736	1.723
R(15,19)	1.353	1.385	1.375	1.383	1.373	1.330
R(17,23)	1.378	1.375	1.372	1.367	1.367	1.375
R(18,24)	1.728	1.749	1.734	1.742	1.734	1.713
R(19,25)	1.201	1.237	1.228	1.222	1.226	1.254
R(19,26)	1.185	1.222	1.214	1.210	1.213	1.229
R(23,24)	1.264	1.289	1.283	1.285	1.289	1.280
R(24,28)	1.719	1.731	1.722	1.721	1.714	1.717
A(2,1,3)	111.4	111.7	111.5	111.5	111.6	110.8
A(1,2,7)	115.3	115.6	115.6	115.2	115.6	115.3
A(1,2,8)	123.2	122.8	122.9	122.9	122.8	123.1
A(1,3,6)	111.7	110.5	110.4	110.1	110.0	109.0
A(3,6,9)	109.3	109.4	109.3	109.5	109.4	108.7
A(2,7,12)	114.6	114.8	114.4	113.7	114.4	112.4
A(2,8,9)	116.3	115.8	116.0	115.6	115.7	116.9
A(2,8,15)	115.8	116.3	116.2	116.6	116.3	117.3
A(9,8,15)	127.8	127.7	127.7	127.7	127.9	125.3
A(6,9,8)	116.0	115.5	115.4	115.3	115.1	117.9
A(6,9,16)	119.5	120.4	120.4	120.6	120.7	118.5
A(7,12,18)	124.4	123.9	124.0	123.8	123.8	123.6
A(17,12,18)	108.9	109.0	109.2	109.3	109.0	108.8
A(8,15,19)	118.4	118.2	118.0	117.5	117.9	114.9
A(12,17,23)	116.8	116.9	116.7	117.0	116.9	117.1
A(12,18,24)	87.8	87.8	87.9	87.4	88.0	88.4
A(15,19,25)	119.7	119.9	119.7	119.4	119.7	121.0
A(15,19,26)	116.1	115.7	116.0	115.7	115.7	117.7
A(17,23,24)	109.6	109.6	109.6	109.3	109.3	108.5
A(18,24,23)	116.9	116.6	116.7	117.0	116.7	117.1
A(23,24,28)	123.0	123.3	123.2	123.4	123.2	122.9
D(3,1,2,7)	−175.4	−175.7	−174.0	−172.1	−173.6	−169.7
D(1,2,7,12)	77.6	74.8	76.0	74.9	74.4	78.6
D(1,2,8,9)	18.6	23.9	23.0	24.1	24.9	14.7
D(1,3,6,9)	65.2	66.1	66.6	67.3	67.1	66.7
D(2,7,12,18)	67.8	69.4	68.9	68.7	68.9	84.3
D(8,15,19,25)	31.5	30.2	31.8	36.0	30.1	15.9

[a] Ref. [34]