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VIBRATIONAL FREQUENCIES AND STRUCTURE OF ESTRAGOLE USING SEMIEMPIRICAL CALCULATIONS

ORAWAN SIRICHOTE, KANIDTHA HANSONGNERN AND PRAVIT SUDKEAW
Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkla 90112, Thailand.

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ABSTRACT

The vibrational spectrum of liquid estragole (4-methoxy-1-allylbenzene) was obtained from FT-IR spectroscopy. Comparison among experimental fundamental vibrational frequencies and fundamental vibrations calculated using five semiempirical methods (CNDO, INDO, MNDO, AM1 and PM3) indicate PM3 method gives the best agreement of vibrational description. Ab initio calculations using 3-21G, 3-21G and 6-31G* basis sets were performed for comparison. It was found that 6-31G* gave the best frequency results but it was only 1 % more reliable than PM3 method. Since estragole is one of the significant attractants for the American western corn rootworm (WCR),* Diabrotica virgifera virgifera *Leconte, the study of molecular structure of estragole from PM3 method was then used to probe for some information about the WCR active site.*

INTRODUCTION

Estragole (4-methoxy-1-allylbenzene) is one of the naturally occuring phenylpropanoids and recognized as the significant attractant for the American western corn rootworm (WCR)[1], *Diabrotica virgifera virgifera* LeConte. The insect antenna is usually the focal point of the receptive phase of insect and plant kairomone communication.[2,3] There are receptor cells inside the antenna segment. The active site of the receptor is a membrane-bound macromolecule that is complementary in size, shape, and stereochemical configuration to the stimulating chemical and to the position, number, and nature of its functional groups. Binding between the kairomonal molecule and the membrane receptor leads to a conformational change of the receptor into an active stage by opening of ion channels. This results in the depolarization of the cell membrane and the receptor potential produced is transmitted to the brain. WCR attractant to estragole is characterized by a highly specific structure-activity relationship.[4] The position of the double bond and the methoxy ring substituent are critical for activity.

Studies of the molecular geometry of estragole will give some useful information about the types of chemical bonds between the estragole molecule and the receptor active sites including the locations of each active site. Then, theoretical calculations are needed to obtain the molecular geometry of estragole. There are many levels of theory such as semiempirical models, Hartree-Fock (HF) theory and density functional theory (DFT). Semiempirical models are chosen for this work because the computational cost of such method is much less expensive than the other two models. Moreover, there are several methods of semiempirical calculations such as CNDO (complete neglect of differential overlap), INDO (intermediate neglect of differential overlap), MNDO (modified neglect of diatomic overlap), AM1 (Austin Model 1) and PM3 (parametric method 3).[5-7] We also examine the utility of Hartree-Fock (HF) level calculations[8,9] in obtaining the molecular geometry of estragole. In order to find the most reliable methods for calculated geometry, the accuracy of those methods in predicting vibrational frequencies of estragole are determined by comparison with the corresponding experimental fundamental frequencies.

MATERIALS AND METHODS

Experimental Spectrum

Sample of neat liquid estragole obtained from Aldrich Co. The liquid phase spectrum of estragole was recorded on BioRad FT-IR spectrometer model FTS165 from 400 to 3500 cm^{-1} as shown in Fig. 1.

Quantum Chemical Calculations

Semiempirical calculations Semiempirical calculations have been carried out using the HyperChem software package. Studies were done using personal computer ATEC Pentium 120 MHz. Geometry optimizations of estragole were performed first, followed by computations of the fundamental vibrational frequencies using CNDO, INDO, MNDO, AM1 and PM3 methods, respectively. The molecule of estragole was assumed to be isolated within an absolute vacuum.

Ab initio calculations Calculations were performed using GAUSSIAN 94[10] running on Sun workstation. Fully optimized geometry without constraint and vibrational frequencies of estragole molecule were carried out at Hartree-Fock level using the following basis sets: 3-21G, 3-21G* and 6-31G*. For 3-21G and 3-21G* frequencies were scaled by 0.9085 while the scale factor 0.8929 was used for 6-31G* frequencies.

RESULTS AND DISCUSSION

Experimental Spectrum

Fig. 1 shows the experimental FT-IR spectrum of estragole from 400 to 3500 cm^{-1}. Assignments for experimental fundamental vibrational frequencies are listed in Table 1. The band at 761.0 cm^{-1} is observed in the region expected for C-H out of plane bending in *cis*-RCH=CHR.[11,12] The absorption band at 812.7 cm^{-1} is detected in the region expected for C-H out of plane bending in *p*-disubstituted benzene. For the band at 995.2 cm^{-1} is expected belong to C-H out of plane bending in $RCH=CH_2$. Stronger absorption at 1248.3 cm^{-1} is assigned to be C-O stretching in $-OCH_3$. The band at 1640.0 cm^{-1} is assigned to C=C stretching in $RCH=CH_2$. The absorption at 2836.4 cm^{-1} is attributed to C-H stretching in methyl ether. In addition, the band at 3033.8 cm^{-1} and 3078.3 cm^{-1} appear in the region expected for sp^2 C-H asymmetric stretching and $=CH_2$ asymmetric stretching, respectively.

Quantum Chemical Calculations

Semiempirical calculations

The calculated fundamental frequencies of estragole from all five methods of semiempirical models compare with the observed fundamental vibrations are listed in Table 1. PM3 method gives the best agreement among those five methods with 7.4% mean absolute percentage deviation. The computed frequencies and integrated infrared band intensities using PM3 method of estragole is shown in Fig. 1. Some important geometrical parameters of optimized geometry of estragole with PM3 method are listed in Table 2. The value of the torsional angle C(11)-O(10)-C(1)-C(2) is 179.1° which means that the methoxy group is in the same plane of

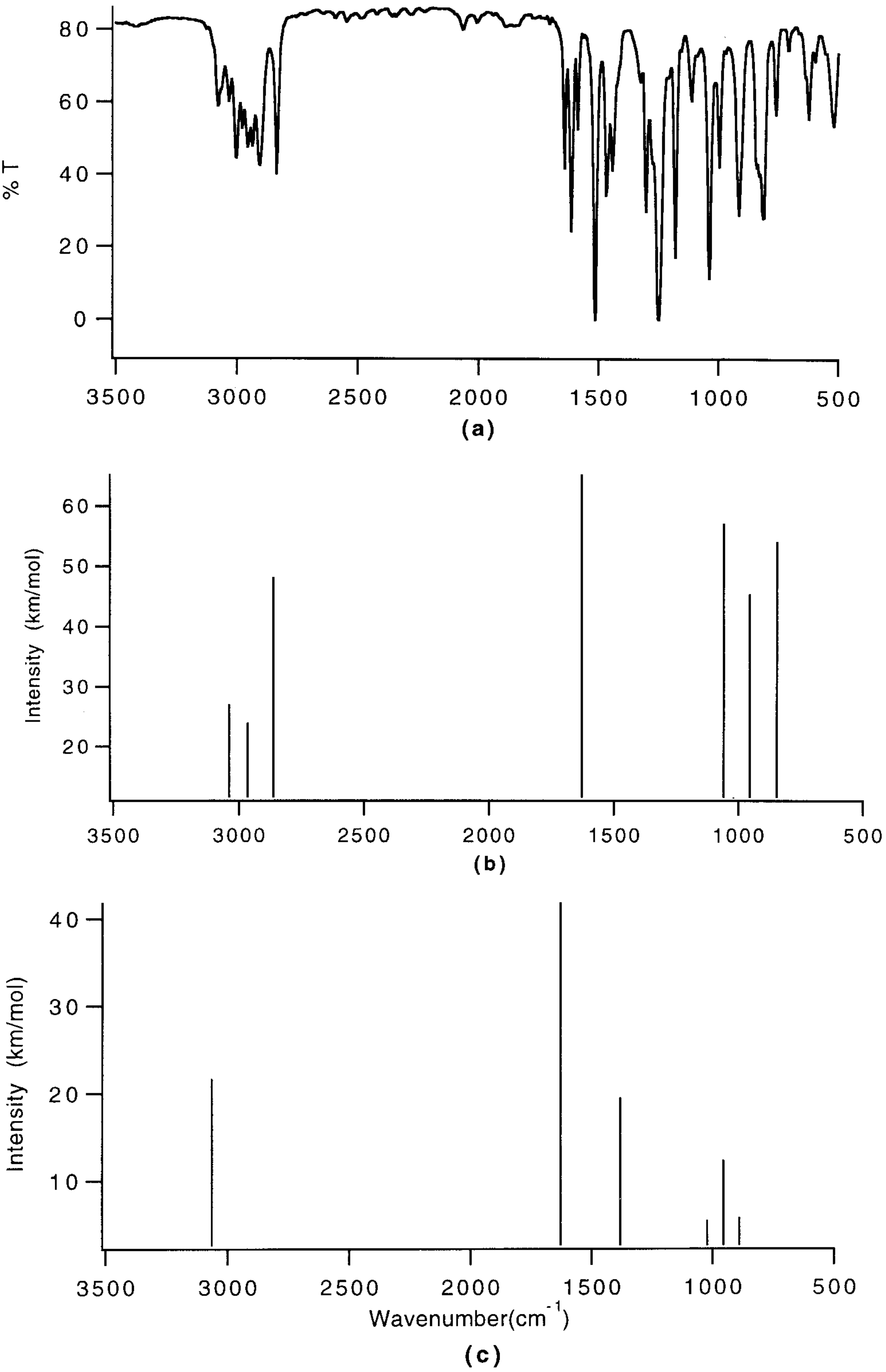

Fig. 1. Comparison of experimental FT-IR transmission spectrum of liquid estragole (a) with calculated vibrational spectra using 6-31G* ab initio calculation (b) and PM3 semiempirical calculation (c).

Table 1. Comparison of experimental and semiempirical calculated fundamental vibrational frequencies of estragole

Description of Mode	Experimental Frequency (cm^{-1})	Theoretical Frequency (cm^{-1})							
		Semiempirical Calculations					Ab initio Calculations		
		CNDO	INDO	MNDO	AM1	PM3	3-21G*	3-21G*	6-31G*
C-H out of plane bend in *cis*-RCH=CHR	761.0	690.5	710.6	1106.4	-	890.4	889.4	889.4	845.3
C-H out of plane bend in *p*-disubstituted benzene	812.7	1011.3	1170.2	-	915.8	954.7	931.1	931.1	955.9
C-H out of plane bend in $RCH=CH_2$	995.2	-	-	-	1052.2	1021.6	1009.6	1009.6	1020.8
C-O stretch in $O\text{-}CH_3$	1248.3	2058.8	2228.0	1677.0	1345.4	1381.2	1036.2	1036.2	1058.9
C=C stretch in $RCH=CH_2$	1640.0	2576.1	2379.2	1753.8	1786.8	1627.0	1625.9	1625.9	1628.3
C-H stretch in methyl ether	2836.4	4499.8	4468.4	3300.1	3149.0	-	2905.1	2905.1	2862.5
sp^2-C-H asymmetric stretch	3033.8	4614.1	4593.5	3397.5	3181.4	3064.6	3005.6	3005.6	2965.1
$=CH_2$ asymmetric stretch	3078.3	4703.1	4679.2	3412.0	3199.0	3136.2	3076.6	3076.6	3039.3
*Mean absolute percentage deviation (%)	45.6	47.9	21.0	7.8	7.4		6.8	6.8	6.4

*mean absolute percentage deviation = $100 \times (1/8) \times \sum_{i=1}^{8} (|observed - predicted|/observed)$

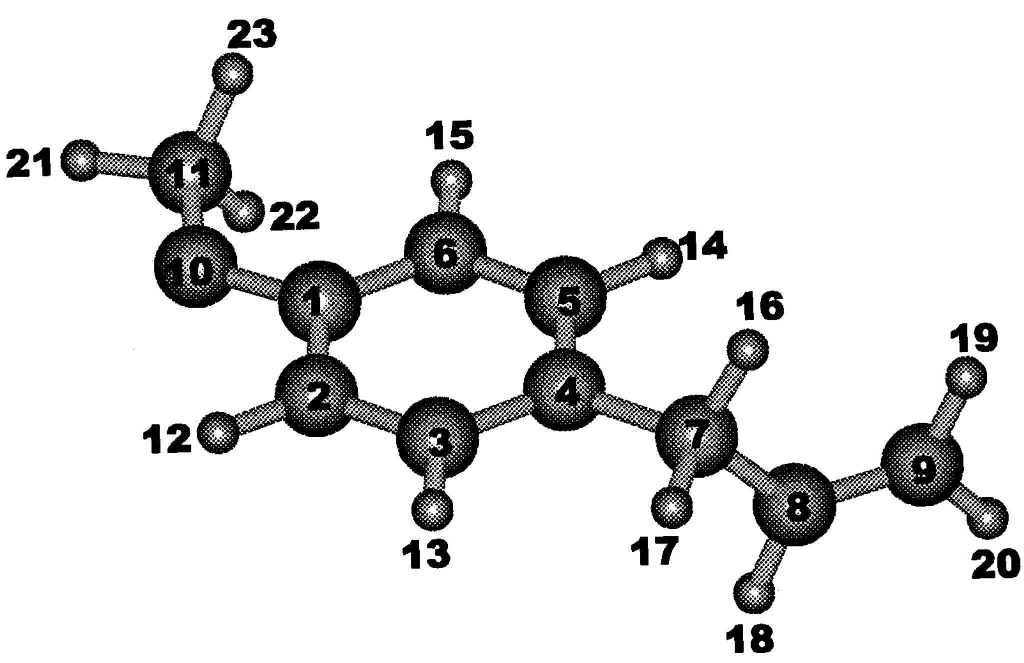

Fig. 2. The 6-31G* optimized structure of estragole.

Table 2. Comparison of some interesting geometrical parameters for estragole with PM3 and 6-31G* calculations (bond lengths in Å, bond angles and torsional angles in deg)

Parameter	PM3	6-31G*
C(2)-C(3)	1.3857	1.3797
C(1)-O(10)	1.3813	1.3502
C(8)-C(9)	1.3276	1.3190
< C(3)-C(4)-C(7)	120.0	121.4
< C(5)-C(4)-C(7)	120.4	121.1
Torsional angle C(3)-C(4)-C(7)-C(8)	76.5	120.8
Torsional angle C(4)-C(7)-C(8)-C(9)	135.4	122.6
Torsional angle C(11)-O(10)-C(1)-C(2)	179.1	-180.0

benzene ring. In contrast, unsaturated C=C of allyl side chain is not in the same plane of benzene ring since the value of torsional angles C(3)-C(4)-C(7)-C(8) is 76.5° and C(4)-C(7)-C(8)-C(9) is 135.4°, respectively.

Ab initio calculations

The computed vibrational frequencies of estragole at Hatree-Fock level with 3-21G, 3-21G* and 6-31G* basis sets are compared to the experimental results in Table 1. All frequency calculations from these three basis sets are in better agreement with experiments than semiempirical calculations. The 6-31G* calculation approaches the best accuracy with 6.4 % of minimum mean absolute percentage deviation. The 6-31G* calculated spectrum of estragole is displayed in Fig. 1. The optimized structure using 6-31G* calculation is shown in Fig. 2 and some interesting geometrical parameters of 6-31G* optimized geometry of estragole are listed in Table 2. The mean absolute percentage deviations of 3-21G and 6-31G* frequencies are 0.6 % and 1 % less than the mean absolute percentage deviation of PM3 frequencies, respectively. These results lead to the conclusion that high level ab initio calculations give better values of geometry optimization and vibrational frequencies of estragole than low-level semiempirical calculations.

R.L. Metcalf and his coworkers pointed out that the interaction of estragole with the WCR antennal receptor was quite specific.[1] They indicated the strong receptor binding of both the *para*-CH_3O group and the position of the C=C bond of side chain. The first active site was proposed to form hydrogen bonding with the electronegative oxygen atom, O(10). The second active site had the interaction with the benzene ring and the third active site was suggested to interact with the unsaturated C=C of allyl side chain.[2] The work reported herein presents the idea of using the optimized structure of estragole to probe for some information about the active site in WCR receptor. The 6-31G* optimized geometry of estragole from this study can be used to estimate the distance between the first and the second active site of WCR receptor which is equal to C(1)-O(10) bond with 1.3502 Å. The value of torsional angle C(11)-O(10)-C(1)-C(2) of estragole in Table 2 is -180.0° which means that the methoxy is in the same plane of benzene ring therefore, the first and second active site must be in the same plane of benzene ring for the best interaction. The values of torsional angle C(3)-C(4)-C(7)-C(8) and C(4)-C(7)-C(8)-C(9) are 120.8° and 122.6°, respectively which mean that the allyl side chain is not in the same plane of benzene ring. Then, the third active site is proposed to be in different plane of the first and second active site.

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บทคัดย่อ

ในการศึกษาค่าความถี่ของการสั่นของ estragole (4-methoxy-1-allylbenzene) โดยวิธีสเปกโทรสโกปีชนิด FT-IR เมื่อเปรียบเทียบระหว่างค่าความถี่ของการสั่นแบบพื้นฐานที่ได้จากการทดลองกับค่าความถี่ของการสั่นแบบพื้นฐานจากการคำนวณแบบเซมิเอมพิริคัลทั้งหมด 5 แบบ (CNDO, INDO, MNDO, AM1 และ PM3) พบว่าวิธีของ PM3 ให้ค่าความถี่การสั่นพื้นฐานที่ใกล้เคียงกับผลการทดลองมากที่สุด เมื่อเปรียบเทียบกับผลการคำนวณแบบแอป อินนิชิโอ ด้วย basis sets 3-21G, 3-21G* และ 6-31G* พบว่าการคำนวณด้วย 6-31G* ให้ค่าที่เชื่อถือมากที่สุด แต่ดีกว่าวิธีของ PM3 เพียง 1% เนื่องจาก estragole เป็นสารดึงดูดด้วงเจาะรากข้าวโพดทางตะวันตกของประเทศสหรัฐอเมริกา (WCR), *Diabrotica virgifera virgifera* LeConte ดังนั้น การศึกษาโครงสร้างโมเลกุลของ estragole จากวิธีของ 6-31G* สามารถใช้เป็นแม่แบบของการหาตำแหน่งในการออกฤทธิ์ของ WCR