

EXPERIMENTAL AND THEORETICAL STUDIES OF VIBRATIONAL FREQUENCIES OF TRANS-CINNAMALDEHYDE

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(Received September 16, 1996)

ABSTRACT

The vibrational frequencies of trans-cinnamaldehyde in liquid phase were measured by using FT-IR spectroscopy. Five semiempirical calculations were used to assign the bands. When comparing the calculated frequencies, the heat of formation and the dipole moment of trans-cinnamaldehyde with the experimental results, it is concluded that PM3 provides the best fit between experimental and theoretical vibrational frequencies.

INTRODUCTION

Semiempirical refers to a type of quantum mechanical calculation that used parameters derived from experiments to simplify the calculation process. Semiempirical models have the Roothan-Hall equation¹ as a starting point. Restrictions and additional approximations are then applied in order to reduce the computation. The performance of semiempirical methods can be assessed by comparison with experimental equilibrium geometries, vibrational frequencies, relative energies, electric dipole moments, thermodynamic property values, etc., for stable molecules. The semiempirical methods are much less costly than Ab initio and density functional methods.

The semiempirical here is confined to closed shell molecules and to the valence electrons in them, these being assume to move in the field of a fixed core composed of the nuclei and inner shell electrons (core approximation). The valence shell molecular orbitals (Ψ_i) are represented by linear combinations of a minimum basis set of valence shell atomic orbitals (ϕ_μ);

$$\Psi_i = \sum_{\mu=1}^N c_{\mu i} \phi_\mu \quad (1)$$

in which the atomic orbitals are Slater orbitals² of the form

$$\phi_\mu = N e^{-\zeta r} Y_l^m(\theta, \phi) \quad (2)$$

where ζ is the orbital exponent and Y_l^m are the real spherical harmonics. The exponent represented the effective nuclear charge experienced by an electron in the atomic orbital. The Roothan-Hall equations are

$$\sum_{\nu=1}^N (F_{\mu\nu} - \epsilon_\nu S_{\mu\nu}) c_{\nu i} = 0, \quad \mu = 1, 2, \dots, N \quad (3)$$

with the normalization conditions

$$\sum_{\mu=1}^N \sum_{\nu=1}^N c_{\mu}^* S_{\mu\nu} c_{\nu} = 1 \quad (4)$$

ϵ_i is the one-electron energy of molecular orbital, ψ_i ; $S_{\mu\nu}$ are the elements of an $N \times N$ matrix termed the overlap matrix,

$$S_{\mu\nu} = \int \phi_{\mu}^*(1) \phi_{\nu}(1) dx_1 dy_1 dz_1 \quad (5)$$

where ϕ_{μ} is an atomic orbital of atom A and ϕ_{ν} of atom B. $F_{\mu\nu}$ are the elements of another $N \times N$ matrix, the Fock matrix,

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^N \sum_{\sigma=1}^N P_{\lambda\sigma} [\langle \mu\nu|\lambda\sigma \rangle - \frac{1}{2} \langle \mu\lambda|\nu\sigma \rangle] \quad (6)$$

where $H_{\mu\nu}^{core}$ is a matrix representing the energy of a single electron in a field of "bare" nuclei. Its elements are

$$H_{\mu\nu}^{core} = \int \phi_{\mu}^*(1) \bar{H}^{core}(1) \phi_{\nu}(1) dx_1 dy_1 dz_1,$$

$$H^{core}(1) = -\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \sum_{A=1}^M \frac{Z_A}{R_{1A}} \quad (7)$$

Here Z_A is the atomic number of atom A and summation is carried out over all atoms. The term $\langle \mu\nu|\lambda\sigma \rangle$ in (6) are two-electron repulsion integrals,

$$\langle \mu\nu|\lambda\sigma \rangle = \iint \phi_{\mu}^*(1) \phi_{\nu}(1) \left(\frac{1}{R_{12}} \right) \phi_{\lambda}^*(2) \phi_{\sigma}(2) dx_1 dy_1 dz_1 \quad (8)$$

They are multiplied by the elements of the one-electron density matrix, $P_{\lambda\sigma}$,

$$P_{\lambda\sigma} = 2 \sum_{i=1}^{occ} c_{\lambda}^* c_{\sigma i} \quad (9)$$

The summation is over occupied molecular orbitals only. The factor of two indicates that two electrons occupy each molecular orbital, and the asterisk denotes complex conjugation (required if the molecular orbitals are not real functions). The total energy E_{tot}^{mol} of the molecule is the sum of the electronic energy E_{el} and the repulsions E_{AB}^{core} between the cores of atoms A and B

$$E_{tot}^{mol} = E_{el} + \sum_A \sum_B E_{AB}^{core} \quad (10)$$

In this study attempts had been made to calculate the vibrational frequencies of *trans*-cinnamaldehyde by different methods of semiempirical calculations. The five semiempirical methods³ used to obtain the vibrational frequencies of *trans*-cinnamaldehyde were 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), respectively.

The CNDO Equations. HyperChem implements the CNDO/2 developed by Pople, Segal and Santry^{4,6}. The form of CNDO/2 equations for the Fock matrix in equation (3) based upon a complete neglect of differential overlap approximation. All approximations⁷ used in CNDO are

1. All overlap integrals involving different atomic orbitals in equation (5) are set to zero.
2. All charge clouds arising from different atomic orbitals, ϕ_μ , are ignored. This eliminated most multicenter two-electron integrals since

$$\langle \mu\nu | \lambda\sigma \rangle = \delta(\mu,\nu)\delta(\lambda,\sigma) \langle \mu\nu | \lambda\sigma \rangle \quad (11)$$

where $\delta(\mu,\nu) = 1$ if μ is equal to ν , zero otherwise.

3. All two-center two-electron integrals between a pair of atoms are set equal, i.e.,

$$\langle \mu\nu | \lambda\sigma \rangle = \gamma_{AB} \quad (12)$$

where γ_{AB} is a function of atom A and B and the interatomic distance R_{AB} only.

4. All electron-core interactions for a given pair of atoms are set equal, i.e.,

$$\langle \mu | v_b | \nu \rangle = \delta(\mu,\nu) V_{AB} \quad (13)$$

V_{AB} is the interaction energy of an electron in any valence orbital of A with the core (nucleus + inner shells) of B. V_{AB} is corrected in CNDO/2 by including the inequality of the electron-core attraction and the electron-core repulsion.

$$V_{AB} = Z_B \gamma_{AB} \quad (14)$$

γ_{AB} is an average interaction energy between an electron in any valence atomic orbital of A with another in an orbital B.

5. The off-diagonal one-electron or resonance integrals are set proportional to the overlap integral.

$$H_{\mu\nu} = \beta_{AB} S_{\mu\nu} \quad (15)$$

β_{AB} is a parameter which depends on the nature of atom A and B only. The core-core interaction in CNDO and CNDO/2 was

$$E_{AB} = Z_A Z_B / R_{AB} \quad (16)$$

where Z_A , Z_B are the charges of the nuclei with collapsed inner shell electrons.

In CNDO/2, the one-electron one-center integral, $U_{\mu\mu}$ is the average of the energy required to remove an electron from atomic orbital in the fully ionized atom and the energy released when a full ionized atom gained an electron.

$$U_{\mu\mu} = -\frac{1}{2}(I_{\mu} + A_{\mu}) - (Z_A - \frac{1}{2})\gamma_{AA} \quad (17)$$

The diagonal element of Fock matrix in CNDO/2 is

$$F_{\mu\mu} = -\frac{1}{2}(I_{\mu} + A_{\mu}) - (Z_A - \frac{1}{2})\gamma_{AA} - \sum_{B \neq A} Z_B \gamma_{AB} \quad (\text{One - electron})$$

$$+ (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} P_{BB} \gamma_{AB} \quad (\text{Two - electron}) \quad (18)$$

and the off-diagonal term becoming

$$F_{\mu\nu} = \beta_{AB} S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \quad (19)$$

The INDO Equations. In the method of complete neglecting differential overlap, differences in spin states for radicals, e.g., the $^3\Sigma$ and $^1\Delta$ states of NH, cannot be represented. This was rectified by the intermediate neglect of differential overlap (INDO) method⁸. The INDO method improves on the CNDO by neglecting the differential overlap in all electron-interaction integrals except those involving one-center repulsions between electrons on the same atom. The evaluation of the elements of the Fock matrices is simplified by a set of approximations which are parallel to those used in CNDO method, the principal difference being that all one-center exchange integrals are retained. The two-, three-, and four-center integrals of type $\langle \mu\lambda|\nu\sigma \rangle$ are set equal to zero unless $\mu = \lambda$ and $\nu = \sigma$. The diagonal Fock matrix element in INDO is

$$F_{\mu\mu} = U_{\mu\mu} \quad (\text{One - electron})$$

$$+ \sum_{\lambda} [P_{\lambda\lambda} \langle \mu\mu|\lambda\lambda \rangle - P_{\lambda\lambda}^{\alpha} \langle \mu\lambda|\mu\lambda \rangle] \quad (\text{Two - electron})$$

$$+ \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB} \quad (20)$$

where P^{α} is the density matrix element computed from orbitals of spin α , and the off-diagonal monocentric Fock matrix element is

$$F_{\mu\nu}^{\alpha} = (2P_{\mu\nu} - P_{\mu\nu}^{\alpha}) \langle \mu\nu|\mu\nu \rangle - P_{\mu\nu}^{\alpha} \langle \mu\mu|\nu\nu \rangle \quad (21)$$

The off-diagonal two-center Fock matrix element has a similar form as that in CNDO/2. In INDO the resonance integral is a function of the average β terms for the two contributing atomic orbitals.

$$F_{\mu\nu}^{\alpha} = -\frac{1}{2}(\beta_{\mu} + \beta_{\nu}) S_{\mu\nu} - P_{\mu\nu}^{\alpha} \langle \mu\mu|\nu\nu \rangle \quad (22)$$

The MNDO Equations. INDO approximation has difficulty with systems which contained lone pairs and cannot represent lone-pair lone-pair interactions. To rectify this Dewar and co-workers⁹⁻¹² proposed and developed MNDO method based on the neglect of diatomic differential overlap (NDDO) approximation. The Fock matrix in MNDO has the following form:

1. Diagonal terms

$$\begin{aligned}
 F_{\mu\mu} = & U_{\mu\mu} - \sum_{B \neq A} Z_B \langle \mu\mu | s s \rangle && \text{(One - electron)} \\
 & + \sum_{\nu} P_{\nu\nu} [\langle \mu\mu | \nu\nu \rangle - \frac{1}{2} \langle \mu\nu | \mu\nu \rangle] && \text{(Two -electron)} \\
 & + \sum_B \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \langle \mu\mu | \lambda\sigma \rangle
 \end{aligned} \tag{23}$$

2. Off-diagonal terms on the same atom

$$\begin{aligned}
 F_{\mu\nu} = & - \sum_{B \neq A} Z_B \langle \mu\nu | s s \rangle && \text{(One - electron)} \\
 & + \frac{1}{2} P_{\mu\nu} [3 \langle \mu\nu | \mu\nu \rangle - \langle \mu\mu | \nu\nu \rangle] && \text{(Two - electron)} \\
 & + \sum_B \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle
 \end{aligned} \tag{24}$$

3. Terms between orbitals on different atoms

$$F_{\mu\nu} = \frac{1}{2} (\beta_{\mu} + \beta_{\nu}) S_{\mu\nu} - \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\lambda\nu} \langle \mu\lambda | \nu\sigma \rangle \tag{25}$$

The core-core repulsion term was made a function of the electron-electron repulsion integral:

$$E_{AB} = Z_A Z_B \langle s_A s_A | s_B s_B \rangle \tag{26}$$

The AM1 Method. Since the inability to reproduce hydrogen bonding was fatal to the application of MNDO to the study of biologically interesting systems then Dewar and co-workers¹³⁻¹⁵ immediately started work on correcting this problem. Reparameterization was not the answer because no terms existed within MNDO that could correct for the excessive repulsions at van der Waals' distances. Instead, each atom was assigned a number of spherical Gaussians that were intended to mimic the correlation effects. The core-core term in AM1 became

$$\begin{aligned}
 E_{AB} = & Z_A Z_B \langle s_A s_A | s_B s_B \rangle \\
 & + Z_A Z_B / R_{AB} \sum_I^4 [a_i(A) e^{-b_i(A)(R_{AB} - c_i(A))^2} + a_i(B) e^{-b_i(B)(R_{AB} - c_i(B))^2}]
 \end{aligned} \tag{27}$$

in which the $a_i(A)$, $b_i(A)$ and $c_i(A)$ were parameters and $\langle s_A s_A | s_B s_B \rangle$ is two-center two-electron integral.

The PM3 Method. PM3 is a variant of the AM1 method^{16,17}. It uses the same algorithms but an alternative parameter set. In many cases, it improves on the performance of AM1.

MATERIALS AND METHODS

Experimental Spectrum

The *trans*-cinnamaldehyde was a Chemical Dynamics Corporation product. Spectrum was recorded on Perkin Elmer 1600 Series FT-IR spectrometer from 450 to 4400 cm^{-1} . The spectrum is shown in Fig.1.

Semiempirical calculations

Semiempirical calculations were carried out, using the HyperChem software package. The geometrical optimization calculations were performed using CNDO, INDO, MNDO, AM1 and PM3 methods, respectively. Fundamental frequencies were obtained after geometry optimization for each method. These calculations were assumed that the molecule was isolated and in an absolute vacuum.

RESULTS AND DISCUSSION

Experimental Spectrum

The experimental FT-IR spectrum of *trans*-cinnamaldehyde are illustrated in Fig.1. The spectrum exhibited bands which were the characteristic vibrational frequencies of monosubstitution benzene. The two bands at 689.1 and 749.1 cm^{-1} correspond to C-H out of plane bend monosubstitution benzene¹⁸. The band at 974.5 cm^{-1} associated with the C-H out of plane bend in *trans*-RCH=CHR. The characteristic vibrational frequencies at 1627.2 and 1675.1 cm^{-1} correspond to C=C stretch and C=O stretch in carbonyl, respectively. Bands observed at 2743 and 2817.5 cm^{-1} are C-H stretch in aldehyde.

Semiempirical calculations

The calculated fundamental frequencies of *trans*-cinnamaldehyde obtained using HyperChem are listed in Table 1. All of the calculated frequencies are higher than the experimentally observed frequencies. PM3 method gave the lowest mean absolute percentage deviation of theoretical frequencies from experimental values as in Table 2. The calculated frequencies and integrated Infrared band intensities using PM3 semiempirical calculation is shown in Fig. 2.

The least-squares fit of the experimental frequencies to the calculated ones are listed in Table 2. All the fits give good correlation coefficients except for the MNDO methods. The best fit between experiment and PM3 semiempirical calculation is shown in Fig. 3. In this regard, PM3 calculation provides the most unambiguous guidance in assigning spectra. The AM1 calculation is nearly as good in this respect.

The standard enthalpy of formation of *trans*-cinnamaldehyde from CRC Handbook¹⁹ is -10.64 kcal mol^{-1} . The calculated standard enthalpy of formation of *trans*-cinnamaldehyde in Table 3 deviate significantly from the handbook. However, the PM3 calculated standard enthalpy of formation gives the smallest difference.

The experimental value of dipole moment of *trans*-cinnamaldehyde is 3.63 D²⁰. The

Table 1 Comparison of experimental and calculated fundamental vibrational frequencies of *trans*-cinnamaldehyde.

Description of Mode (cm ⁻¹)	Experimental Frequency	Theoretical Frequency (cm ⁻¹)				
		CNDO	INDO	MNDO	AM1	PM3
C-H out of plane bend monosubstitution benzene	689.1	913.0	912.2	817.8	792.4	765.8
	749.1	1146.8	1142.2	1229.4	989.0	958.4
C-H out of plane bend in <i>trans</i> -RCH=CHR	974.5	1799.0	1788.0	1446.2	1257.6	1257.4
C=C stretch	1627.2	2656.7	2639.0	1816.1	1873.9	1863.1
C=O stretch in carbonyl	1675.1	2847.6	2809.5	2106.5	2046.2	1971.7
C-H stretch in aldehyde	2743.0	4519.9	4471.3	3247.0	3083.6	2924.1
	2817.5	4550.3	4521.9	3344.7	3128.9	2988.9

Table 2 Results of least-squares fits of observed and calculated vibrational frequencies (cm⁻¹) for *trans*-cinnamaldehyde^a

Calculated Methods	Slope	Intercept (cm ⁻¹)	r	Mean Absolute Percentage Deviation ^b (%)
CNDO	0.5980	36.1	0.992	61.4
INDO	0.6044	32.1	0.992	60.1
MNDO	0.9015	-193.1	0.979	29.3
AM1	0.9345	-147.7	0.995	19.4
PM3	0.9922	-193.5	0.993	16.0

^a Equation: observed = intercept + slope x calculated; r = correlation coefficient;

^b mean absolute percentage deviation = $100 \times (1/7) \times \sum_{i=1}^7 (|\text{observed} - \text{predicted}| / \text{observed})$

Table 3 The calculated standard enthalpy of formation and dipole moment of *trans*-cinnamaldehyde.

Method	Standard Enthalpy of Formation (kcal mol ⁻¹)	Dipole Moment (D)
CNDO	-3980.66	3.64
MNDO	5.99	3.46
INDO	-3813.22	4.00
AM1	5.24	3.64
PM3	3.59	3.22

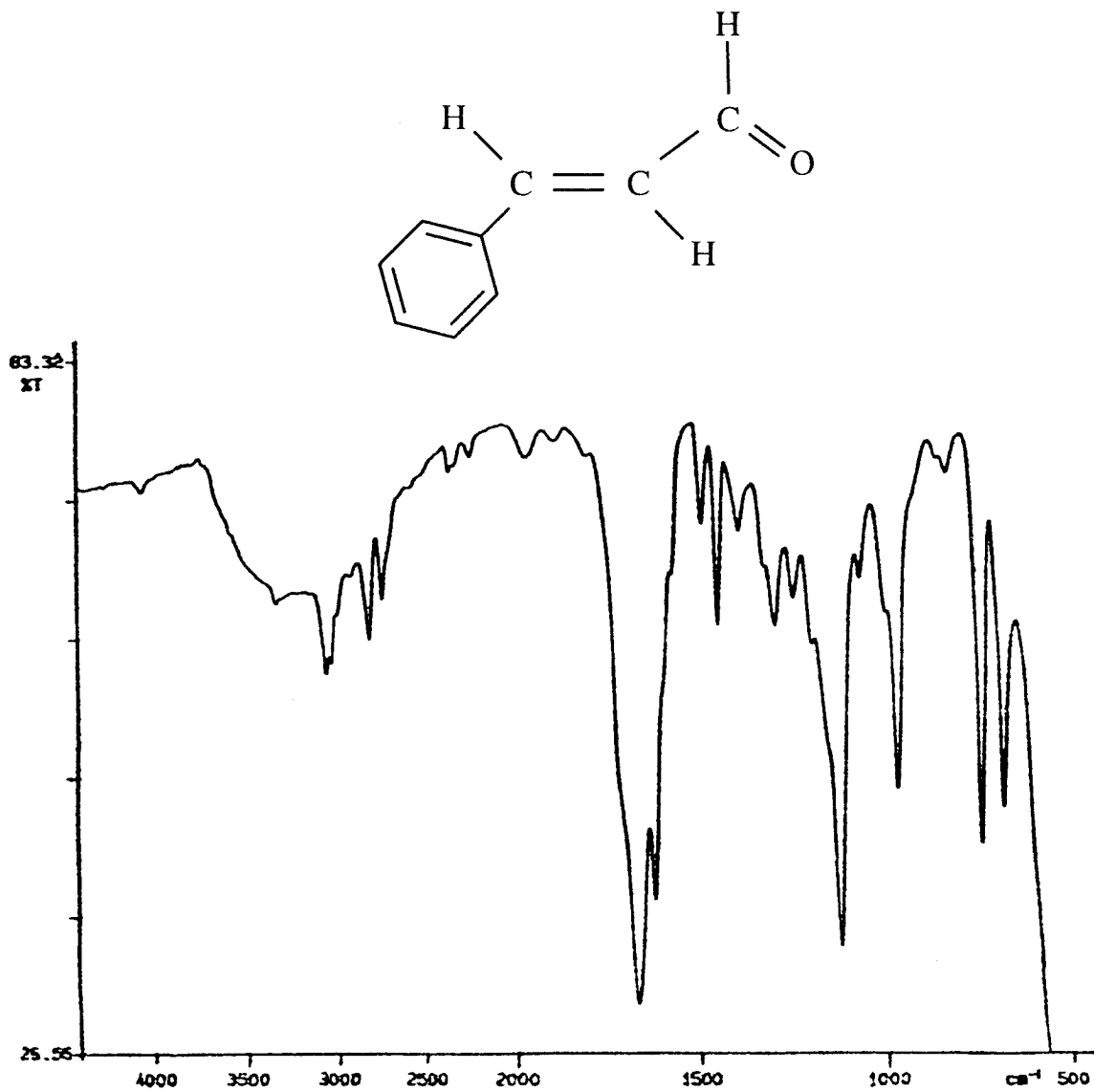


Fig. 1. Experimental FT-IR transmission spectrum of liquid *trans*-cinnamaldehyde.

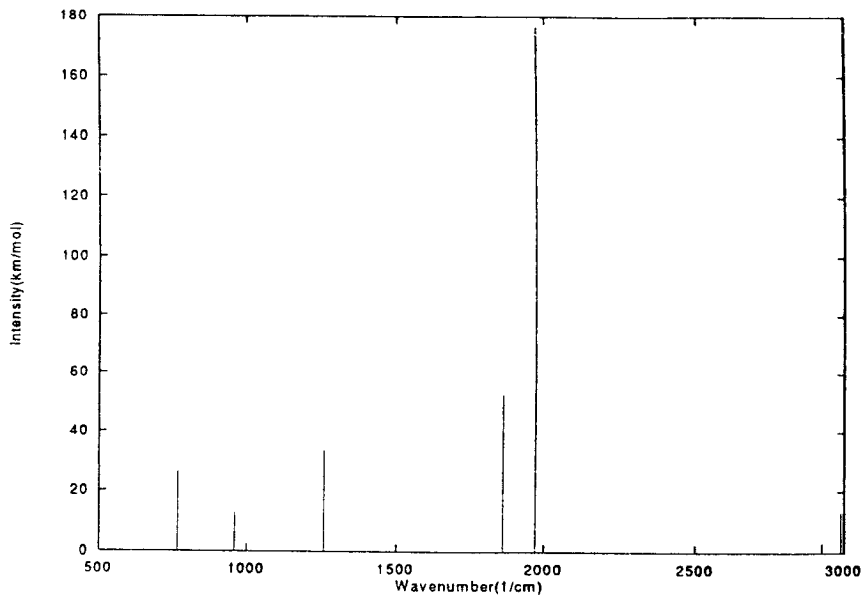


Fig. 2. Calculated wavenumber and integrated band intensity of *trans*-cinnamaldehyde with PM3 semiempirical calculation.

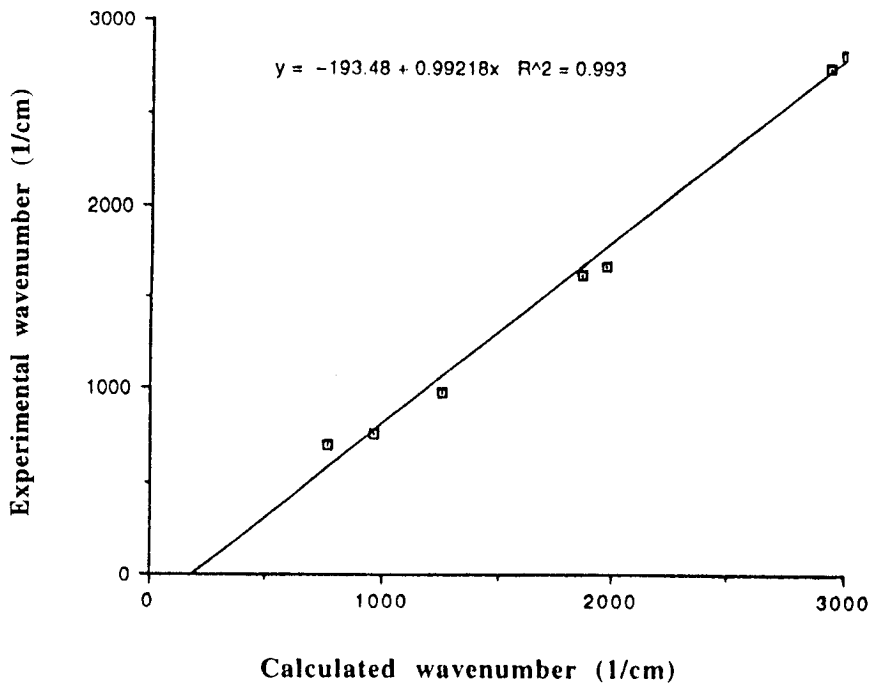


Fig. 3. Plot of experimental vs calculated wavenumber (semiempirical PM3) for all fundamental vibration of *trans*-cinnamaldehyde.

percentage deviations of theoretical dipole moment from the literature value are 0.3 %, 4.7 %, 4.7 %, 10.2 % and 11.3 % for AM1, CNDO, MNDO, INDO and PM3 methods, respectively, which are not significantly different. Thus, the PM3 method provide a reasonable means for assigning fundamental vibrational frequencies of *trans*-cinnamaldehyde, since it gave the minimum mean absolute percentage deviation from the experimental vibrational frequencies as in Table 2.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Vimom Tantishaiyakul, Department of Pharmaceutical Chemistry, Faculty of Pharmaceutical Science, Prince of Songkla University, Hat -Yai, Songkla for assistance in obtaining FT-IR spectrum. We also thank Dr. Pravit Sudkeaw, Department of Chemistry, Faculty of Science, Khon Kaen University for some helpful calculations.

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บทคัดย่อ

จากการทดลองวัดค่าความถี่ของการสั่นของ *trans*-cinnamaldehyde ในสถานะของเหลวโดยวิธีสเปกโทรสโกปีชนิด FT-IR ได้ใช้การคำนวณแบบเซมิเอมพิริคัล 5 แบบช่วยอธิบายสเปกตรัมของ *trans*-cinnamaldehyde เมื่อเปรียบเทียบกับค่าความถี่ของการสั่นแบบพื้นฐาน, ค่าความร้อนของการก่อเกิดและค่าโมเมนต์ขั้วคู่ที่ได้จากการคำนวณทั้ง 5 แบบกับค่าจากการทดลองสรุปว่าการคำนวณด้วยวิธี PM3 ให้ค่าความถี่ของการสั่นแบบพื้นฐานที่ใกล้เคียงกับค่าการทดลองมากที่สุด