Molecular structure and vibrational analysis of 2-vinyl furan

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Abstract

Infrared and vibrational Raman spectra have been recorded in the liquid phase and interpreted using semiempirical calculations (PM3, AMI and MNDO). Molecular properties and relative conformational energies have been calculated and compared with literature data, when available. The *trans* conformer of the molecule seems to be the conformation of lowest energy and its computed structural parameters are reported.

1. Introduction

The 2-vinyl furan molecule (Fig. 1) is important as a synthetic reagent in polymer chemistry, being used to produce resins and polymers [1]. It belongs to a group of monomers, incorporating the furan moiety, that may be produced from biomass. This family thus represents a possible alternative to petroleum-based monomers [2],
Despite its interest, little work has been reported on the molecular properties of 2-vinyl fu-ran. A single microwave investigation [3] has been published but, as far as we are aware, no information is available on its vibrational spectrum.
We have been concerned with the spectroscopic properties of furan derivatives [4-7]. Pertinent to this is the investigation of the Infrared (IR) and vibrational Raman spectra of the 2-vinyl furan reported here.

2. Experimental methods

The Fourier transform infrared (FT-IR) spectrum was recorded on a Bruker IFS66 machine using KBr windows in the 3500—400 cm^{-1} region. The accuracy on the FR-IR measurements is estimated to be ± 5 cm^{-1}. Vibrational Raman spectra were recorded on a Jobin Yvon Lab Ram spectrometer using an Argon ion laser (514.5 nm). Samples were placed in glass cuvette. The Stokes' region was recorded from 3300 to the notch filter cut off at ~100 cm^{-1}. The accuracy on the Raman spectra is estimated to be ± 4 cm^{-1}.
The sample was prepared according to the method described by Fabian and Tchelitcheff [8] and modified by Schmidt and Werner [9] Briefly, thermal decarboxylation, catalyzed by copper(I) oxide, of furyl acrylic acid in quinoline under argon produced 2-vinyl furan. The crude material
was dried over magnesium sulfate and rectified on a 40 cm Vigreux column. The purity, as determined by GC-MS, was better than 99%. One ppm butylated hydroxytoluene (BHT) was added as stabilizing agent. Overall yield was 65%.
Boiling point 98—99 °C (Litt. 99—100 °C [8], 98-99 °C [10], ^{1}H-NMR (250 MHz in $CDCl_3$, RT): δ = 5.17 ppm [dd, 1H, $^2J_{\beta\gamma}$ = 1.20 Hz, $^3J_{\alpha\gamma}$ = 11.34 Hz, H_γ], δ = 5.67 ppm [dd, 1H, $^2J_{\beta\gamma}$ = 1.20 Hz, $^3J_{\alpha\beta}$ = 17.44 Hez, H_β], δ = 6.27 ppm [d, 1H, V_{34}=3.24 Hz, H_3], ,δ = 6.38 pm [dd, 1H, $^3J_{45}$ = 1-78 Hz, $^3J_{34}$ = 3.16 Hz, H_4], δ = 6.51 ppm [dd, 1H. $^3J_{\alpha\gamma}$ = 11.28 Hz, $^3J_{\alpha\beta}$ = 17.49 Hz, H_α], δ = 7.37 ppm [s, 1H, H_5].
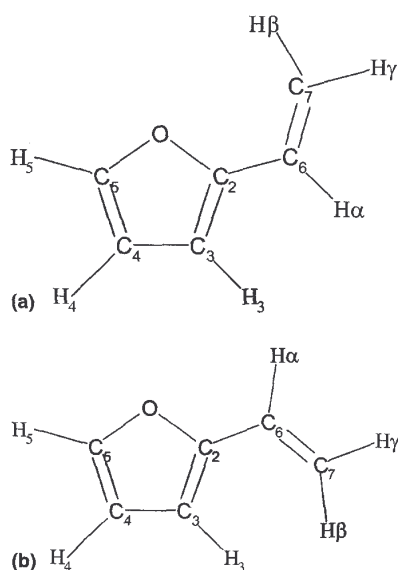
Fig. 1. 2-Vinyl furan molecule with atom numbering: (a) trans conformer; (b) cis conformer.

3. Theoretical methods

The semiempirical calculations were performed with the software package MOPAC 2000 [11]. All calculations were made at the RHF SCF level of theory with configuration interactions (SDCI) and using the MNDO, [12] AM1 [13] and PM3[14] semiempirical methods. Those last are based on the neglect of diatomic differential overlap (NDDO) approximation. They contain sets of parameters, which come either from experimental data (not optimized) or are optimized. In contrast with the other, the PM3 method uses only optimized parameters. In addition, AM1 and PM3 have a modified expression for the core-core repulsion integral compared to MNDO.

Table 1 Relative conformational energies for different conformations of 2-vinyl furan

	E (kJ/mol)[11]		
	trans	*cis*	$90°$[b]
PM3[C]	3.26	0.00	14.74
AM1[C]	0.00	0.10	16.15
MNDO[c]	0.00	0.88	6.42
STO-3G[d]	0.00	2.58	25.70
INDO[d]	0.65	0.00	13.55
CNDO/2[d]	0.00	0.72	12.20
STO-3G[e]	0.00	3.04	24.83

[a]*Conformational energies are given relatively to the most stable conformation.* [b] *Conformation for which the dihedral angle $C_3C_2C_6C_7$ is 90°.* [c]*This work.* [d]*Ref. [17].* [e]*Ref. [18].*

This explains the different numerical values for the relative conformational energies reported in Table 1. Although the PM3 method has been found to be usually in better agreement with experiment than AMI and MNDO [15], this is not always the case. Therefore comparison of the three methods turns out to be useful and agreements in the outcome of several methods are believed to indicate more secure results. The equilibrium structures were fully optimized using the eigenvector following routine (EF) [16].

4. Results and discussion

4.1. Equilibrium structure - conformational energies - molecular properties

The equilibrium structure of the molecule has been theoretically investigated by others. Parr et al. [17] calculated the relative energies of *cis, trans* and 90° conformers of 2-vinyl furan by both ab inito (STO-3G) and semiempirical methods (INDO, CNDO/2 and MINDO/3). Their calculations give conflicting results; the STO-3G method finds the *trans* conformer to be the most stable, whereas the semiempirical methods favour the *cis* form. INDO and STO-3G methods concur in predicting only small energy differences between *cis* and *trans* conformations.

Table 2 Calculated molecular properties for cis and trans 2-vinyl furan and comparison with experimental data

Method	Property μ_{total} (D)					
Microwave [a]	0.69(7)[e]					
	trans			*cis*		
PM3[b]	0.27			0.36		
AM1[b]	0.45			0.61		
MNDO[b]	**0.45**			**0.63**		
STO-3G[c]	0.33			**0.39**		
INDO[c]	0.82			0.64		
CNDO/2[c]	0.88			**0.69**		
STO-3G[d]	0.45			—		
Rotational constant (MHz)						
Microwave [a]	*A*		*B*		*C*	
	7828.385(4)[e]		2112.551(4)[e]		1667.170(3)[e]	
	trans			*cis*		
	A	*B*	*C*	*A*	*B*	*C*
PM3[b]	7639.822	2084.487	1637.647	7681.044	2041.557	1612.854
AM1[b]	7550.184	2086.856	1634.948	7635.895	2018.383	1596.395
MNDO[b]	7707.905	2018.053	1599.333	7726.4022	1979.680	1575.919
Moments of inertia (10^{-40} g cm^{-2})						
Microwave [a]	I_A		I_B		I_C	
	107.199258(5)[e] =		397.243590(7)*		504.27363(9) [e]	
	trans			*cis*		
	I_A	I_B	*lc*	I_A	I_B	*lc*
PM3[b]	109.8460	402.5941	512.4400	109.2562	411.0626	520.3183
AM1[b]	111.1498	402.1379	513.2877	109.9022	415.7791	525.6812
MNDO[b]	108.8756	415.8459	524.7215	108.6149	423.9054	532.5200

[a]Ref. [3].

[b]This work.

[c]Ref. [17].

[d]Ref. [18].

eRM**S** values given in parenthesis refer to the last digit. For example 0.69(7) is equivalent to 0.69 ±0.007.

John and Radom [18] subsequently reconsidered the equilibrium structure of the molecule. They used ab initio MO calculations with the minimal STO-3G basis set, finding the trans conformation to be the most stable. Rotational barriers computed by Parr et al. [17] and John and Radom [18] agree well (Table 1).

We are aware of a single microwave experiment on 2-vinyl furan [3]. From this, the authors determined the molecule to be planar. On the basis of an estimation of the dipole moment for each conformer and its projection along two axes, they concluded that the observed rotational spectrum was due to the *trans* conformation. Signal due to the *cis* form was detected but the intensity was too low for analysis. Hence, one conformer is predominant in the vapor phase [3].

We have computed formation enthalpies for the *cis, trans* and 90° conformers. AMI and MNDO methods concur in finding the *trans* form as the most stable in contrast to the PM3 methods. All three procedures give small differences in energies between the two conformers. The rotational barrier, as estimated from the relative conformation energies (Table 1), ranges from ~6.4 to 16.2 kJ/ mol, which is not much in disagreement with the STO-3G predictions [17,18]. From the Boltzman population, a rotational barrier of 10 kJ/mol would result around 1% *cis* conformer. This is consistent with the low intensity microwave spectrum for the *cis* form reported by Latypova et al. [3] since 10 kJ/mol is very likely an inferior limit for the rotational barrier (Table 1).

In Table 2, computed dipole moments, rotational constants and moments of inertia are listed for *cis* and *trans* conformers and the values compared with the available literature data. From the computed dipole moments, it is not possible to choose which relates better to experimental data [3]. However, comparison of the calculated rotational constants and moments of intertia with those experimentally measured (Table 2) shows that the best agreement with experiment is obtained for the *trans* rotamer; the computed values of I_c are much closer to experiment than those obtained for the *cis* conformation.

Table 3 Molecular structure for trans 2-vinyl furan. Atom labeling is given at Fig. 1

	PM3
Bond length (A)	
OC_5	1.374
OC_4	1.388
C_4C_5	1.384
C_3C_4	1.437
C_2C_3	1.391
C_2C_6	1.443
C_6C_7	1.344
C_5H	1.085
C_4H	1.086
C_3H	1.086
C_6H	1.097
C_7H	1.086
Angle (°)	
OC_5C_4	110.7
OC_2C_3	109.8
$C_2C_3C_4$	106.4
$C_5C_4C_3$	106.2
$C_3C_2C_6$	130.0
$C_2C_6C_7$	124.9
HC_5C_4	133.9
HC_4C_3	127.5
HC_3C_4	126.3
HC_6C_2	114.1
$H_\gamma C_7C_6$	121.9
$H_\beta C_\gamma C_6$	123.7

Indeed, as the I_c moment of inertia is perpendicular to the molecular plane, it is very sensitive to the relative position of the vinyl group to the cycle. In addition it has the same direction in both *cis* and *trans* vinyl furan which allows direct comparison between the two conformations. This observation adds credence to the findings of Latypova et al. [3] that the *trans* conformational isomer predominates in the vapor phase.

From the above considerations, we suppose that the *trans* conformation is the equilibrium structure and report PM3 computed structural parameters for only this one (Table 3).

4.2. Normal vibrational modes

The molecule possesses 33 normal vibrational modes distributed through 10a" and 23a'; the *a*" modes are anti-symmetric and the a' ones are symmetric with respect to the molecular symmetry plane. In Table 4, the symmetric vibrations are labeled v_1-v_{23} in order of increasing wavenumber and the antisymmetric modes, likewise, v_{24}-v_{33}.

Assignations of the normal vibrational modes were made by comparison with PM3, AM1 and MNDO calculations. In correlating calculated vibrational frequencies with those observed in the IR spectrum, consideration was given to absorption intensities. In most cases, calculated frequencies having large transition dipoles were identified with the more intense absorption bands in the IR spectrum. The results are gathered in Table 4.

Normal modes of energy higher than 3000 cm^{-1} can be described as mainly CH stretch vibrations. For these, all three parameterizations agree on the relative ordering of both frequencies and infrared transition dipoles. The best agreement with experiment is achieved for PM3 with an average deviation of ~32 cm^{-1}, which is of the order of 1%. AMI and MNDO differ by ~5% and ~10%, respectively, from the measured data.

Between 3150 and 991 cm^{-1}, the average difference between theory and experiment is ~25, ~60 and ~90 cm^{-1}, for, respectively, PM3, AM1 and MNDO. However, for those modes whose measured frequency is above about 1000 cm^{-1}, all computations find the same energy ordering, leading to straightforward assignments. In contrast, differences appear between the different methodologies for lower frequency vibrations. This is not surprising given the relatively small energy differences between some of the modes. In assigning the measured spectrum, we have followed the PM3 results, but assignments cannot be considered definitive for closely spaced vibrational modes.

The three vibrations of lowest frequency were detected in only the Raman spectrum. It is clear that one of these is of a' symmetry, which from the PM3 and AMI results, we assign to the 215 cm^{-1} band. Latypova et al. [3] detected two vibration-ally excited levels whose reported wavenumbers are 119 ±27 and 232 ±20 cm^{-1}. These values are in excellent agreement with our present data of 129±4 and 215±4 cm^{-1} for modes la" and la'.

Table 4 Normal vibrational modes for trans 2-vinyl furan (wavenumbers are given in cm^l)

Sym.^{a}	Label	Nature^a	Ram.^{c}	IR^d	PM3		AM1		MNDO	
					E	TD^e	E	TD^e	E	TD^e
1a"	v_{24}	γ_{cc}	129	-	95	0.14	83	0.20	69	0.15
1a'	V_1	δ_{CC}	215	-	207	0.17	206	0.25	242	0.14
2a"	v_{25}	γ_{cc}	257	-	216	0.46	221	0.53	219	0.40
2a"	v_2	δ_{cc}	461	467	479	0.24	509	0.18	494	0.28
3a"	V_{26}	$\gamma_{ec} + \gamma_{ea}$	478	483	505	0.09	512	0.22	497	0.37
4a"	V_{27}	$(\gamma_{cc} + \gamma_{co})$ ring	595	600	522	0.50	533	0.55	513	0.28
5a"	v_{28}	γ_{CH}	652	659	672	0.10	678	0.07	684	0.13
3a"	v_3	$V_{CC} + V_{CH}$	717	724	695	0.22	727	0.25	692	0.44
6a"	V_{29}	$y_{cc} + \Gamma_{CH}$	739	744	745	1.52	792	1.53	852	1.13
7a"	V_{30}	V_{CH}	807	814	832	0.52	840	0.87	902	0.05
4a"	V_4	v_{cc} ring	883	890	891	0.41	935	0.54	847	0.64
8a"	$V_{3[}$	Γ_{CH}	903	910	901	0.30	887	0.20	947	0.54
9a"	V_{32}	γ_{CH}	923	929	912	1.12	918	0.86	959	0.40
5a"	v_5	$\gamma_{co} + \Delta_{CH}$	991	988	952	0.52	1012	0.30	998	0.56
10a"	V_{33}	Γ_{CH}	998	1004	960	0.88	998	1.39	1051	0.67
6a"	V_6	Δ_{CH}	1011	1016	976	0.28	1061	0.53	1110	0.35
7a"	V_7	δ_{CH}	1025	1032	1041	0.28	1121	0.58	1143	0.25
8a'	v_8	δ_{CH}	1078	1085	1077	0.41	1199	0.50	1206	0.25
9a'	V_9	δ_{CH}	1152	1158	1123	0.30	1242	0.36	1283	0.19
10a'	V_{lO}	$\delta_{CH} + \delta_{CC}$	1213	1220	1203	0.35	1288	0.30	1356	0.32
11a'	V_{11}	$V_{cc} + V_{co}$	1253	1260	1300	0.83	1364	1.6	1409	1.10
12a'	V_{12}	δ_{CH}	1290	1296	1316	0.44	1393	0.60	1458	0.20
13a'	V_{13}	v_{cc}	1385	1392	1390	0.98	1405	0.32	1503	1.6
14a'	V_{14}	v_{cc} ring	1489	1496	1488	0.86	1506	0.84	1573	0.74
15a'	V_{15}	v_{cc} ring	1574	1586	1612	0.75	1609	0.55	1586	0.19
16a'	V_{16}	v_{cc}	1638	1646	1672	0.40	1682	0.25	1639	1.30
17a'	V_{17}	v_{cc}	-	1820	1791	1.29	1815	1.27	1750	0.95
18a'	V_{18}	V_{CH}	3020	3026	3034	0.56	3105	0.43	3375	0.13
19a'	v_{19}	V_{CH}	3059	3064	3127	1.00	3170	0.79	3414	0.32
20a'	V_{20}	V_{CH}	3101	3106	3136	0.81	3214	0.86	3441	0.25
21a'	V_{21}	V_{CH}	3120	3124	3142	0.82	3309	1.29	3480	0.74
22a'	V_{21}	V_{CH}	3129	3133	3163	0.77	3326	1.64	3492	0.62
23a'	V_{23}	V_{CH}	3150	3154	3172	1.13	3389	1.19	3499	0.66

^{a} Symmetry.
^{b} Nature of the modes, v: stretching vibration, δ: symmetric bending deformation, y: out-of-plane bending deformation.
^{c} Raman.
^{d} FT-IR.
^{e} IR transition dipole.

Acknowledgements

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