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Synthesis, conformational and spectroscopic characterization of monomeric styrene derivatives having pendant *p*-substituted benzylic ether groups

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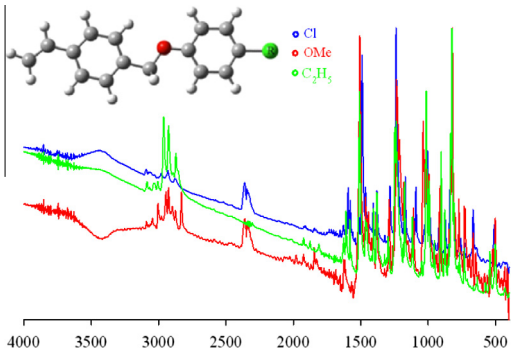
HIGHLIGHTS

- Monomeric styrene derivatives having pendant p-substituted benzylic ether groups were synthesized.
- Vibrational spectra were examined via FT-IR and DFT calculations.
- Electronic transitions were investigated in solution environment.
- Chemical shift were determined depending on predicted and recorded NMR spectra.
- The substituent effect on the spectroscopic behavior was carried out.

GRAPHICAL ABSTRACT



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ABSTRACT

Three derivatives of styrene monomer, 4-chlorophenyl-4-vinylbenzyl ether (I), 4-methoxyphenyl-4-vinylbenzyl ether (II) and 4-ethylphenyl-4-vinylbenzyl ether (III) were synthesized. The synthesized two novel compounds (I and III) and one with undefined structural features were identified by experimental spectroscopic techniques and density functional approach. The optimized geometrical structure, vibrational and electronic transitions along with chemical shifts of those compounds were presented in this study. The vibrational spectra of investigated compounds were recorded in solid state with FT-IR spectrometry in the range of 4000–400 cm^{-1}. The computational vibrational wavenumbers and also ground state equilibrium conformations were carried out by using density functional method with 6-311++G(d,p) basis set. Assignments of the fundamental vibrational modes were examined on the basis of the measured data and total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanical (SQM) method. Isotropic chemical shift of hydrogen and carbon nuclei were investigated via observed ^{1}H and ^{13}C NMR spectra in deuterated DMSO solution and predicted data applied with gauge–invariant atomic orbitals (GIAOs) method. The UV absorption spectra of monomers were observed in the range of 200–800 nm in ethanol, and time dependent DFT method was used to obtain the electronic properties. A detailed description of spectroscopic behaviors of compound was given based on the comparison of experimental measurements and theoretical computations.

Introduction

Styrene is used industrial monomer and its polymers are used in many different areas such as; plastics, latex paints and coatings, synthetic rubbers, polyesters and styrene alkyd coatings [1]. 20–30 Million tons styrene produced each year for industrial usage. Moreover, it is known that styrene is the second most widely used monomer for production of food-contact packaging polymers.

In the present study, the derivatives of styrene monomer that having pendant *p*-substituted benzylic ether groups namely, 4-chlorophenyl-4-vinylbenzyl ether (I), 4-methoxyphenyl-4-vinylb-

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enzyl ether (II) and 4-ethylphenyl-4-vinylbenzyl ether (III) were synthesized. The ground state conformations of synthesized compounds were determined using quantum chemical calculations. Based on measured spectra, the vibrational and electronic transitions and the chemical shifts of steady compounds were identified. All spectroscopic features were computed by using density functional theory (DFT) approach, and compared with recorded data.

Materials and methods

The synthesis of compounds and characterization techniques

The details of used chemicals, synthesis of investigated monomeric compounds and experimental characterization techniques were given our earlier reported study [2].

Quantum chemical calculations

The Becke's three parameter functional of DFT (B3LYP) method was applied to provide optimized ground state geometry and vibrational modes with a fairly large and flexible basis set 6-311++G(d,p) level. In order to improve the agreement with the experimental data, the calculated harmonic wavenumbers were scaled with two different scale factors; i.e. 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1} [3,4]. The assignments of the vibrations were performed on the basis of TED that calculated with SQM method [5,6].

The calculated Raman scattering activities were converted to relative Raman intensities using the relationship derived from the intensity theory of Raman scattering [7,8]. Gauge–invariant atomic orbital (GIAO) [9,10] approach was carried out to determine the isotropic chemical shifts of carbon and hydrogen nuclei applied with B3LYP/6-311++G(d,p). The chemical shifts were taken into account with reference to tetramethlsilane (TMS); thus, the reference data of isolated TMS were determined using the same method. Time dependent-DFT (TD-DFT) [11–14] level employing B3LYP functional with standard Pople basis set that includes diffuse functions on all atoms was applied to compute the lowest 15 singlet → singlet spin-allowed electronic vertical excitation energies. Since the experimental NMR and UV spectra were measured in solutions, beside the vacuum phase, the solution environment were taken into account for calculations. The vibrational modes were assigned on the basis of TED analysis using PQS program [15], and the structural and spectroscopic features of steady molecules were characterized using Gaussian 09 program package on the personal computer [16].

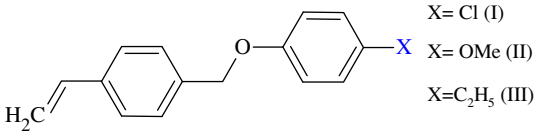
Results and discussions

Molecular geometry

The chemical structures of synthesized monomers are shown in Scheme 1. The compound I and III were synthesized for the first time while the compound II was synthesized in 1976 by Kamogawa et al. with several polymerizable hydroquinone derivatives [17]. However, the conformational structure of this compound has not been defined by any experimental methods yet. Thus, in this study, the ground state geometric parameters of synthesized compounds were obtained using quantum chemical calculations in gas phase. The optimized structures and geometric parameters are given in Fig. S1 (Supplementary materials) and Table 1, respectively. Our calculations show that the molecule I has a planer structure where the O and central C atom of the substituted functional group of molecule II is also planer with the system of the vinylphenyl-CH_2-bridge-phenyl. On the other hand, when the C_2H_5 substituted to phenyl ring, the planarity was broken with the dihedral angle ($C_2C_3C_9O_{16}$) of −48.2°. Therefore, the predicted bond distances and bond angles of III slightly deviate from data obtained for I and II.

Vibrational wavenumbers and assignments

The recorded FT-IR and computed vibrational wavenumbers along with their relative intensities and tentative assignments with TED of studied molecules are presented in Table S1a–c (Supplementary materials). The recorded FT-IR spectra are given in



Scheme 1. General chemical structures of synthesized monomers.

Table 1
The ground state optimized (B3LYP/6-311++G(d,p)) geometric parameters of investigated compounds in vacuum phase, bond lengths in angstrom (Å), bond angles and dihedral angles in degree (°).

Bond lengths	I	II	III	Bond angles	I	II	III	Bond angles	I	II	III
C1—C2	1.386	1.386	1.390	C2—C1—6	120.9	120.9	120.9	C6—C7—C8	127.6	127.7	127.6
C1—C6	1.406	1.406	1.403	C1—C2—C3	121.0	121.1	121.1	C11—C12— (Cl/O/C)17	119.8	125.0	121.4
C2—C3	1.402	1.402	1.398	C2—C3—C4	118.6	118.6	118.5	C13—C12— (Cl/O/C)17	119.6	115.8	121.1
C3—C4	1.393	1.393	1.397	C2—C3—C9	118.7	118.8	120.6	C12—O17—C18	–	118.3	113.3
C3—C9	1.510	1.511	1.507	C4—C3—C9	122.7	122.6	121.0	$CCH_{average}$	118.4	118.3	116.1
C4—C5	1.394	1.394	1.390	C3—C4—C5	120.2	120.3	120.5	$OCH_{average}$	109.7	109.7	109.7
C5—C6	1.401	1.401	1.404	C4—C5—C6	121.7	121.7	121.5	$C{=}CH_{average}$	120.5	120.5	120.5
C6—C7	1.471	1.471	1.471	C1—C6—C5	117.5	117.5	117.6	$HCH_{average}$	112.0	110.0	109.1
C7=C8	1.337	1.337	1.337	C1—C6—C7	123.3	123.3	123.3	Selected dihedral angles			
C10—C11	1.397	1.403	1.398	C5—C6—C7	119.2	119.2	119.0	C2—C3—C9—O16	−180.0	179.9	133.6
C10—C15	1.397	1.391	1.396	C11—C10—C15	119.9	120.2	119.5	C4—C3—C9—O16	−0.1	−0.1	−48.2
C11—C12	1.387	1.391	1.394	C10—C11—C12	119.9	120.3	122.0	C1—C6—C7—C8	0.0	0.0	2.8
C12—C13	1.394	1.403	1.403	C11—C12—C13	120.6	119.2	117.4	C5—C6—C7—C8	180.0	−180.0	−177.4
C13—C14	1.387	1.382	1.387	C12—C13—C14	119.5	120.5	121.6	C10—C11—C12— (Cl/O/C)17	−180.0	−180.0	178.3
C14—C15	1.400	1.402	1.400	C13—C14—C15	120.5	120.5	120.1	(Cl/O/C)17—C12—C13—C14	−180.0	180.0	−178.2
C15—O16	1.365	1.372	1.369	C10—C15—C14	119.6	119.3	119.4	C11—C12—C17— (—/O/C)18	–	0.0	−92.5
C9—O16	1.422	1.418	1.428	C10—C15—O16	124.7	125.0	124.8	C13—C12—C17—C18	–	−180.0	86.0
C12— (Cl/O/C)17	1.761	1.369	1.513	C14—C15—O16	115.7	115.7	115.8				
(O/C)17—C18	–	1.419	1.419	C9—O16—C15	118.8	118.5	118.6				
$C{-}H_{average}$	1.086	1.088	1.089	C3—C9—O16	110.0	110.0	109.0				