Research Article

Molecular Structure and Vibrational Spectra of 2-Ethylhexyl Acrylate by Density Functional Theory Calculations

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The Fourier transform infrared spectra (FTIR) of 2-ethylhexyl acrylate have been measured in liquid phase. The molecular geometry, vibrational frequencies, and infrared intensities have been calculated by using density functional theory. We found two local minima representing *s*-cis and *s*-trans conformations for 2-ethylhexyl acrylate molecule. The optimized geometries at DFT//B3LYP/6-311+G** are in good agreement with electron diffraction data of methyl acrylate for the acrylic group. The two conformers were used for the interpretation of the experimental infrared spectrum of title compound. PED calculations are represented for a more complete and concise assignment. There is one band in the infrared spectrum at 1646 cm^{-1} that definitely indicates the conformer with *s*-trans arrangement of acrylic moiety to be present or not in the liquid 2-ethylhexyl acrylate.

1. Introduction

Alkyl acrylates are important monomers used in the manufacture of polymers and copolymers. Acrylates give polymers exhibiting outstanding transparency and aging proprieties which have made them of interest in a wide variety of applications [1–4]. The structural data and the preferred molecular conformation of these acrylates molecules would be important for basic understanding of these polymers [5].

2-Ethylhexyl acrylate is used for production of paint, adhesive, and paper coating trade. This monomer imparts flexibility and water resistance to the polymers [1, 6]. It is also used for curing polymeric materials [7–15].

To our best knowledge no structural data or detailed interpretation of the vibrational spectra of 2-ethylhexyl acrylate is presented in the literature. This prompted us to look into the vibrational spectroscopy of 2-ethylhexyl acrylate more carefully.

Many reports, experimental [16–21] and theoretical [20, 22], show that acrylates and related compounds exhibit rotational isomerism with the planar *s*-trans and *s*-cis heavy-atom structures being the energetically most stable conformations. However, uncertainty continues to exist regarding

the relative stability of the two conformers. Gas electron diffraction studies on methyl methacrylate [20] suggested the *cis*/*trans* ratios to be equal to 2:1. On the other hand, the IR spectrum of methyl methacrylate in Ar low temperature matrix suggested an inverse ratio [23]. Many experimental and theoretical studies on methyl acrylate reported that the *s*-cis conformer is more stable than the *s*-trans conformer [24–29]. However, Bowles et al. [30] assumed that the *s*-trans conformer is more stable.

2. Experimental

2-Ethylhexyl acrylate (purity greater than 99%) was purchased from Sigma-Aldrich and it was used as it is without further purification. The infrared spectra of liquid films placed between the KBR windows were recorded within $4000\text{--}700\text{ cm}^{-1}$ range with a Perkin Elmer FTIR System-2000 model.

3. Computational

The optimizations of the stable conformers were conducted with the density functional theory using 6-311+G** basis

FIGURE 1: 2-Ethylhexyl acrylate molecule s-cis and s-trans conformations.

sets. The DFT calculations were performed using Becke's 3-parameter (local, nonlocal, Hartree-Fock) hybrid exchange functionals with Lee-Yang-Parr correlational functionals (B3LYP) [31, 32].

The harmonic vibrational frequencies of the stable conformations were calculated at the same level of theories used for the calculated optimized geometries. The calculated frequencies were scaled down by the wavenumber linear scaling procedure (WLS) of Yoshida et al. [33, 34] using the following equation:

$$\frac{\nu_{\text{obs}}}{\nu_{\text{calc}}} = 1.0087 - 0.0000163\nu_{\text{calc}}. \quad (1)$$

All the calculations were carried out with the Gaussian 03 program [35]. The vibrational assignments of the normal modes were provided on the basis of the calculated PEDs by using the program GAR2PED [36].

4. Geometry Optimizations and Energies

The geometries optimizations were conducted at the B3LYP/6-311+G** assuming the s-cis and s-trans conformations. All the optimized geometries are recognized as true minima due to the lack of imaginary harmonic frequencies. The results are given in Table 1 for s-cis and s-trans conformers, respectively. For atoms numbering, see Figure 1.

In Table 1, the calculated bond lengths, bond angles, and dihedral angles have approximately the same values for the s-cis and s-trans conformers. However, some changes occur in going from the s-cis to the s-trans conformation. The bond angles $C_1C_4C_6$ and $C_4C_6O_8$ increase by 3.8° and 2.7° , respectively, while $C_4C_6O_7$ decreases by 2.5° .

The X ray structural data of s-cis methyl acrylate reported by Egawa et al. [21] and ab initio structure of s-trans methyl acrylate reported by Tsuji et al. [20] are very close to those we found for 2-ethylhexyl acrylate molecule.

The zero-point corrected energy of the s-cis conformation is 365.102×10^6 cal/mol showing more stability than the calculated one for the s-trans conformation. The energy for the latter conformation is 365.101×10^6 cal/mol.

5. Vibrational Analysis

The most stable conformers, s-cis and s-trans 2-ethylhexyl acrylate, belong to the C_1 point group. Each conformer represents 93 normal vibrational modes. We juxtaposed the experimental IR spectrum with the computed ones for both conformers and we checked whether we can recognize them or not. Tables 2 and 3 represent the calculated and scaled fundamental wavenumbers, intensities of vibrational peaks, and potential energy distribution along the internal coordinates obtained by DFT//B3LYP/6-311+G** level of theory. The corresponding experimental wavenumbers together with assignments are also reported in these tables. The potential energy distributions are given as per the internal coordinate system recommended by Pulay et al. using DFT [37].

5.1. The CH Stretching Vibrations Region ($3200\text{--}2800\text{ cm}^{-1}$, Figure 2). In this region, the calculations reveal the existence of 20 vibrational normal modes for both the s-cis and s-trans conformers. These normal modes are of approximately the same energies and intensities for both conformers. In the IR spectrum in this region (Figure 2(a)) there are three groups of bands, two groups of strong bands and one group of a very weak band. In the latter there are three bands of very weak intensity at 3104 , 3069 , and 3038 cm^{-1} which are well reproduced by the theoretical bands 3093 , 3047 , and 3012 cm^{-1} , respectively. These bands are ascribed to the C_1H and C_4H stretching modes of vibrations of the vinyl group. The second group is composed of the strongest peaks at 2961 and 2931 cm^{-1} . These two bands are well reproduced by the theoretical bands 2963 and 2953 cm^{-1} , respectively. The third group is composed of one peak slightly asymmetric at 2875 cm^{-1} in the experimental IR spectrum; this band is reproduced at 2903 cm^{-1} in the theoretical calculations. The remaining bands below 2900 cm^{-1} with higher intensity in these series of CH stretching vibrational modes may be assigned to reproduce the broad shoulder at 2861 cm^{-1} . All the theoretical peaks located between 3000 and 2860 cm^{-1} are ascribed to CH stretching of the methylene groups in

TABLE 1: Optimized geometries of s-cis and s-trans 2-ethylhexyl acrylate conformations by DFT//B3LYP/6-311+G**.

Internal coordinates	Level of theory DFT/6-311+G** s-cis EHA	s-cis methyl acrylate ^a	DFT/6-311+G** s-trans EHA	s-trans methyl acrylate ^b
Bond lengths (Å)				
C ₁ H ₂	1.084		1.083	1.074
C ₁ H ₃	1.083		1.084	1.075
C ₁ C ₄	1.331	1.341(7)	1.332	1.319
C ₄ H ₅	1.084		1.084	1.075
C ₄ C ₆	1.486	1.484(6)	1.484	1.484
C ₆ O ₇	1.210	1.211(2)	1.211	1.191
C ₆ O ₈	1.351	1.349(3)	1.348	1.325
O ₈ C ₉	1.448	1.439(3)	1.448	1.417
C ₉ H ₁₀	1.093		1.093	
C ₉ H ₁₁	1.093		1.092	
C ₉ C ₁₂	1.526		1.526	
C ₁₂ H ₁₃	1.098		1.098	
C ₁₂ C ₁₄	1.543		1.543	
C ₁₄ H ₁₅	1.097		1.097	
C ₁₄ H ₁₆	1.096		1.096	
C ₁₄ C ₁₇	1.531		1.531	
C ₁₇ C ₁₈	1.094		1.094	
C ₁₇ H ₁₉	1.093		1.093	
C ₁₇ H ₂₀	1.092		1.092	
C ₁₂ C ₂₁	1.549		1.549	
C ₂₁ H ₂₂	1.097		1.097	
C ₂₁ H ₂₃	1.094		1.094	
C ₂₁ C ₂₄	1.534		1.534	
C ₂₄ H ₂₅	1.097		1.097	
C ₂₄ H ₂₆	1.095		1.095	
C ₂₄ C ₂₇	1.533		1.533	
C ₂₇ H ₂₈	1.097		1.097	
C ₂₇ H ₂₉	1.097		1.096	
C ₂₇ C ₃₀	1.531		1.531	
C ₃₀ H ₃₁	1.094		1.093	
C ₃₀ H ₃₂	1.094		1.094	
C ₃₀ H ₃₃	1.094		1.094	
Bond angles (°)				
H ₂ C ₁ H ₃	118.049		117.591	
H ₂ C ₁ C ₄	120.479		121.432	121.7
C ₁ C ₄ H ₅	122.220		121.739	122.1
C ₁ C ₄ C ₆	121.072	120.3(8)	124.970	124.2
C ₄ C ₆ O ₇	125.710	126.1(5)	123.066	122.9
C ₄ C ₆ O ₈	110.564	110.3(3)	113.320	113.7
C ₆ O ₈ C ₉	116.570	116.4(5)	116.493	116.8
O ₈ C ₉ H ₁₀	108.658		108.697	
O ₈ C ₉ H ₁₁	108.313		108.339	
O ₈ C ₉ C ₁₂	108.522		108.488	

TABLE I: Continued.

Internal coordinates	Level of theory DFT/6-311+G** s-cis EHA	s-cis methyl acrylate ^a	DFT/6-311+G** s-trans EHA	s-trans methyl acrylate ^b
C ₉ C ₁₂ C ₁₄	108.099		108.115	
C ₁₂ C ₁₄ H ₁₅	108.729		108.720	
C ₁₂ C ₁₄ H ₁₆	108.539		108.544	
C ₁₂ C ₁₄ C ₁₇	115.410		115.400	
C ₁₄ C ₁₇ H ₁₈	111.304		111.345	
C ₁₄ C ₁₇ H ₁₉	110.477		110.478	
C ₁₄ C ₁₇ H ₂₀	112.028		112.001	
C ₉ C ₁₂ C ₂₁	111.382		111.384	
C ₁₂ C ₂₁ H ₂₂	109.228		109.231	
C ₁₂ C ₂₁ H ₂₃	109.005		109.019	
C ₁₂ C ₂₁ C ₂₄	114.775		114.824	
C ₂₁ C ₂₄ H ₂₅	108.695		108.731	
C ₂₁ C ₂₄ H ₂₆	110.286		110.291	
C ₂₁ C ₂₄ C ₂₇	113.287		113.308	
C ₂₄ C ₂₇ H ₂₈	109.207		109.229	
C ₂₄ C ₂₇ H ₂₉	109.217		109.208	
C ₂₄ C ₂₇ C ₃₀	113.280		109.208	
C ₂₇ C ₃₀ H ₃₁	111.428		111.428	
C ₂₇ C ₃₀ H ₃₂	111.218		111.209	
C ₂₇ C ₃₀ H ₃₃	111.189		111.202	
Dihedral angles (°)				
H ₃ H ₂ C ₁ C ₄	180		-179.908	
H ₂ C ₁ C ₄ H ₅	-179.977		179.808	
H ₂ C ₁ C ₄ C ₆	0.037		0.106	
C ₁ C ₄ C ₆ O ₇	-0.166		178.652	
C ₁ C ₄ C ₆ O ₈	179.844		-1.298	
C ₄ C ₆ O ₈ C ₉	179.896		179.515	
C ₆ O ₈ C ₉ H ₁₀	55.606		55.506	
C ₆ O ₈ C ₉ H ₁₁	-61.282		-61.454	
C ₆ O ₈ C ₉ C ₁₂	177.303		177.169	
O ₈ C ₉ C ₁₂ H ₁₃	55.024		54.463	
O ₈ C ₉ C ₁₂ C ₁₄	171.114		170.547	
C ₉ C ₁₂ C ₁₄ H ₁₅	61.844		61.568	
C ₉ C ₁₂ C ₁₄ H ₁₆	-53.102		-53.378	
C ₉ C ₁₂ C ₁₄ C ₁₇	-175.215		-175.516	
C ₁₂ C ₁₄ C ₁₇ H ₁₈	56.957		57.249	
C ₁₂ C ₁₄ C ₁₇ H ₁₉	176.491		176.782	
C ₁₂ C ₁₄ C ₁₇ H ₂₀	-63.865		-63.596	
O ₈ C ₉ C ₁₂ C ₂₁	-63.322		-63.915	
C ₉ C ₁₂ C ₂₁ H ₂₂	-96.883		-97.147	
C ₉ C ₁₂ C ₂₁ H ₂₃	18.587		18.279	
C ₉ C ₁₂ C ₂₁ C ₂₄	139.536		139.298	
C ₁₂ C ₂₁ C ₂₄ H ₂₅	-59.615		-59.061	
C ₁₂ C ₂₁ C ₂₄ H ₂₆	56.214		56.717	

TABLE I: Continued.

Internal coordinates	Level of theory DFT/6-311+G** s-cis EHA	s-cis methyl acrylate ^a	DFT/6-311+G** s-trans EHA	s-trans methyl acrylate ^b
C ₁₂ C ₂₁ C ₂₄ C ₂₇	178.823		179.360	
C ₂₁ C ₂₄ C ₂₇ H ₂₈	-58.771		-58.768	
C ₂₁ C ₂₄ C ₂₇ H ₂₉	56.758		56.753	
C ₂₁ C ₂₄ C ₂₇ C ₃₀	179.033		179.029	
C ₂₄ C ₂₇ C ₃₀ H ₃₁	179.693		-179.983	
C ₂₄ C ₂₇ C ₃₀ H ₃₂	-60.205		-59.888	
C ₂₄ C ₂₇ C ₃₀ H ₃₃	59.599		59.917	

^a Determined by a joint analysis of electron diffraction data and rotational constants [21].

^b Determined by ab initio calculation at HF/6-31G** [20].

FIGURE 2: Comparison of the experimental IR (a) CH stretching region (3200–2800 cm⁻¹) with the appropriate theoretical DFT//B3LYP/6-311+G** spectra ((b) and (c)) for s-cis and s-trans 2-ethylhexyl acrylate, respectively.

the butyl and the ethyl sides of the 2-ethylhexyl acrylate molecule.

5.2. The C=O and C=C Stretching and CH Bending Vibrations (1800–1200 cm⁻¹, Figure 3). In the IR spectrum (Figure 3(a)), a very strong peak at 1727 cm⁻¹ represents the C=O stretching

band. The simulated peaks are at 1735 and 1731 cm⁻¹ for the s-cis and s-trans conformations; these two frequencies contribute to the experimental C=O stretching band.

There are two C=C stretching bands in the experimental spectra located at 1637 and 1619 cm⁻¹, of medium intensity. These bands are well reproduced by the theoretical bands at

TABLE 2: Frequencies and PEDs of s-cis 2-ethylhexyl acrylate.

Number ^b	Observed (cm ⁻¹)	DFT/6-311+G** Unscaled (cm ⁻¹)	Scaled (cm ⁻¹)	Intensity (km·mol ⁻¹)	Assignment (%PED) ^a
1	—	30.5017	30,7519	0.1860	τ (O ₈ C ₉) (63); τ (C ₉ C ₁₂) (35);
2	—	36.7273	37,02484	1.9384	τ (C ₉ C ₁₂) (83); τ (O ₈ C ₉) (17)
3	—	48.2766	48,65862	1.2435	τ (C ₉ C ₁₂) (98)
4	—	74.7391	75,29828	0.0096	ρ (C ₃₀ H ₃) (62); τ (C ₉ C ₁₂) (17); τ (O ₈ C ₉) (7); ρ (C ₁₄ H ₂) (7)
5	—	93.1493	93,81827	0.7602	τ (C ₉ C ₁₂) (84); ρ (C ₁₄ H ₂) (15)
6	—	99.6177	100,32262	0.6102	τ (C ₉ C ₁₂) (76); τ (C ₉ C ₁₂) (21)
7	—	115.9962	116,78605	0.2949	τ (C ₉ C ₁₂) (94)
8	—	133.8201	134,69244	0.7707	τ (C ₉ C ₁₂) (43); ρ (C ₂₇ H ₃) (31); ρ (C ₉ H ₂) (15)
9	—	146.1924	147,11591	0.0469	τ (C ₉ C ₁₂) (58); ρ (C ₉ H ₂) (17); ρ (C ₁₄ H ₂) (16)
10	—	201.0708	202,16112	1.8808	τ (C ₉ C ₁₂) (89); δ (C ₆ O ₈ C ₉) (5)
11	—	213.9423	215,05753	2.7336	τ (C ₉ C ₁₂) (98)
12	—	234.1345	235,27792	0.6986	ρ (C ₃₀ H ₃) (94)
13	—	253.7618	254,91989	1.2866	ρ (C ₃₀ H ₃) (99)
14	—	265.4468	266,60766	0.7334	τ (C ₉ C ₁₂) (83); ρ (C ₃₀ H ₃) (14)
15	—	285.1163	286,27176	3.5548	ρ (C ₃₀ H ₃) (78); τ (C ₉ C ₁₂) (18)
16	—	315.7568	316,87874	0.5814	ρ (C ₉ H ₂) (89); ρ (C ₁₇ H ₃) (6)
17	—	355.1126	356,14657	0.2263	ρ (C ₁₇ H ₃) (36); ρ (C ₉ C ₁₂ C ₁₄) (31); ρ (C ₉ H ₂) (19)
18	—	375.9666	376,93349	4.3994	ρ (C ₂₄ C ₂₇ C ₃₀) (27); ρ (C ₉ C ₁₂ C ₁₄) (23); ρ (C ₁₇ H ₃) (17); δ (C ₂₁ C ₂₄ C ₂₇) (10); ρ (C ₉ C ₁₂ H ₁₃) (10); δ (C ₂₁ H ₂) (8)
19	—	470.318	470,80422	0.6863	ρ (C ₉ C ₁₂ C ₂₁) (72); ρ (C ₁₇ H ₃) (11); ρ (C ₉ H ₂) (5);
20	—	512.0856	512,26637	6.2054	ρ (C ₉ C ₁₂ C ₁₄) (80); ρ (C ₉ H ₂) (7); δ (C ₂₁ C ₁₂ C ₁₄) (6)
21	—	527.3488	527,40376	0.1504	ρ (C ₉ H ₂) (87); O (C ₆ O ₇) (9)
22	—	533.9978	533,99558	1.1100	ρ (C ₉ C ₁₂ C ₁₄) (77); ρ (C ₆ O ₈ C ₉) (8)
23	—	681.189	679,55184	3.1928	ρ (C ₉ C ₁₂ C ₁₄) (42); δ (O ₇ C ₆ C ₄) (42); ρ (C ₆ O ₈ C ₉) (5)
24	731 (m)	731.2122	728,8586	4.5137	ρ (C ₂₁ C ₂₄ C ₂₇) (99)
25	748 (sh)	779.5982	776,474	1.0039	ρ (C ₂₇ H ₂) (65); ρ (C ₉ C ₁₂ C ₁₄) (18); ρ (C ₁₄ H ₂) (12)
26	770 (m)	786.3101	783,07298	1.6507	ρ (C ₂₇ H ₂) (36); ρ (C ₂₁ H ₂) (32); ρ (C ₁₄ H ₂) (23); ρ (C ₁₇ H ₃) (8)
27	811 (m)	829.5925	825,59191	24.9487	ρ (C ₉ H ₂) (73); O (C ₆ O ₇) (21); γ (C ₁ H ₂) (8)
28	852 (w)	852.3514	847,92486	3.0736	ρ (C ₉ C ₁₂ C ₂₁) (82); ρ (C ₉ H ₂) (16)
29	896 (w)	901.6472	896,24016	1.0870	ρ (C ₉ C ₁₂ H ₂₁) (62); ω (C ₂₄ H ₂) (16); γ (C ₂₁ H ₂) (9); δ (C ₃₀ H ₃) (8)
30	—	906.8585	901,34317	1.0553	ρ (C ₉ C ₁₂ H ₂₁) (86); ρ (C ₉ H ₂) (10)
31	909 (w)	917.2167	911,48352	7.2928	ρ (C ₉ H ₂) (58); ω (C ₂₇ H ₂) (27); ρ (O ₇ C ₆ O ₈) (12)
32	933 (sh)	947.8927	941,49381	5.9570	δ (C ₁₄ C ₁₂ H ₃) (50); ω (C ₂₇ H ₂) (46)
33	962 (m)	983.6705	976,45643	25.1442	ρ (C ₉ C ₁₂ H ₁₃) (83); δ (C ₆ O ₈ C ₉) (21); γ (C ₂₁ H ₂) (14); γ (C ₂₇ H ₂) (11); γ (C ₁₄ H ₂) (11)
34	984 (m)	1006.9955	999,22751	25.5334	ω (C ₁ H ₂) (84); γ (C ₁₄ H ₂) (10)
35	—	1016.9241	1008,91495	5.1103	ρ (C ₁₄ H ₂) (41); ρ (C ₉ C ₁₂ C ₂₁) (24); δ (C ₁₂ C ₂₁ C ₂₄) (23); ρ (C ₁₇ H ₃) (7)
36	1015 (sh)	1023.2765	1015,11136	26.0306	o (C ₄ H ₅) (99)
37	—	1025.8451	1017,61651	1.9504	δ (C ₉ C ₁₂ C ₁₄) (98); ν (C ₉ O ₈) (5)
38	1025 (sh)	1045.9956	1037,26182	27.8636	γ (C ₂₄ H ₂) (42); ν (C ₉ C ₁₂) (42); ν (O ₈ C ₉) (6)
39	—	1062.1068	1052,95957	0.4109	ρ (C ₁₄ C ₁₂ H ₁₃) (83); ν (C ₂₇ C ₃₀) (12)
40	—	1065.9864	1056,73835	0.4863	ν (C ₁₄ C ₁₇) (83); ν (C ₂₄ C ₂₇) (11)
41	—	1083.5238	1073,81387	1.6531	ω (C ₉ H ₂) (83); ω (C ₂₁ H ₂) (15)
42	1057 (m)	1089.4787	1079,60965	2.2238	ρ (C ₉ H ₂) (84); ω (C ₂₇ H ₂) (14)

TABLE 2: Continued.

Number ^b	Observed (cm ⁻¹)	DFT/6-311+G** Unscaled (cm ⁻¹)	Scaled (cm ⁻¹)	Intensity (km·mol ⁻¹)	Assignment (%PED) ^a
43	—	1150.5508	1138,98319	1.9252	ρ (C ₉ C ₁₂ H ₁₃) (96)
44	1116 (w)	1168.5589	1156,46723	11.8316	δ (C ₁₂ C ₂₁ C ₂₄) (67); ρ (C ₁₄ C ₁₂ H ₁₃) (9); ρ (O ₈ C ₉ C ₁₂) (7); δ (C ₁₄ C ₁₂ C ₂₁) (67)
45	1060 (sh)	1185.6606	1173,06145	0.0857	δ (C ₉ C ₁₂ C ₁₄) (63); ρ (C ₃₀ H ₃) (26); δ (C ₁₂ C ₁₄ C ₁₇) (6)
46	1191	1205.1044	1191,9167	626.1232	ρ (C ₆ C ₄ H ₅) (87)
47	—	1243.7853	1229,3901	0.3621	γ (C ₂₁ H ₂) (94); γ (C ₂₇ H ₂) (5)
48	—	1258.6429	1243,77093	1.0505	ρ (C ₉ H ₂) (76); ω (C ₂₁ H ₂) (23)
49	—	1281.7118	1266,0853	0.7178	γ (C ₁₄ H ₂) (55); ω (C ₂₁ H ₂) (44)
50	—	1300.3301	1284,08198	1.3337	ω (C ₂₁ H ₂) (93)
51	—	1317.9028	1301,05761	11.1581	ω (C ₂₄ H ₂) (24); ρ (C ₉ C ₁₂ H ₁₃) (17); γ (C ₁₄ H ₂) (13); ω (C ₂₇ H ₂) (7); ρ (C ₆ O ₈ C ₉) (5)
52	1272	1324.5992	1307,52384	68.3227	γ (C ₂₇ H ₂) (37); ρ (C ₉ C ₁₂ H ₁₃) (29); γ (C ₂₁ H ₂) (22); γ (C ₁₄ H ₂) (6)
53	1295	1328.2386	1311,03753	6.0034	γ (C ₂₇ H ₂) (93)
54	—	1338.1682	1320,62195	0.5711	γ (C ₂₄ H ₂) (70); γ (C ₂₇ H ₂) (28)
55	1340	1361.0156	1342,66291	1.3124	ω (C ₂₁ H ₂) (78); ω (C ₉ H ₂) (21)
56	—	1381.2224	1362,1423	0.4732	ρ (C ₉ C ₁₂ C ₂₁) (78); ω (C ₂₁ H ₂) (21)
57	1357	1394.2309	1374,67547	3.3349	ω (C ₉ H ₂) (95)
58	—	1404.5719	1384,63467	4.5032	ω (C ₂₄ H ₂) (95); ω (C ₂₁ H ₂) (5)
59	1381	1410.9338	1390,75996	7.3272	ω (C ₂₁ H ₂) (97)
60	—	1414.1585	1393,86422	2.3703	ω (C ₂₁ H ₂) (99)
61	—	1418.0649	1397,62426	0.4645	ω (C ₂₁ H ₂) (93); ω (C ₁₄ H ₂) (6)
62	1408	1437.761	1416,57487	83.1633	ω (C ₉ H ₂) (49); ω (C ₂₁ H ₂) (26); δ (CH ₂) (20)
63	—	1486.1635	1463,09161	1.0310	δ (C ₂₁ H ₂) (40); δ (C ₂₄ H ₂) (20); δ (C ₁₂ C ₂₁ C ₂₄) (12); δ (C ₁₄ H ₂) (7)
64	—	1488.3957	1465,235	1.0310	δ (C ₂₇ H ₂) (29); δ (C ₂₁ H ₂) (28); δ (C ₂₄ H ₂) (18); δ (C ₁₂ C ₂₁ C ₂₄) (14); δ (C ₁₄ H ₂) (10); δ (C ₂₇ H ₂) (10)
65	—	1492.293	1468,97685	1.3617	δ (C ₂₁ H ₂) (67); δ (C ₂₇ H ₂) (11); δ (C ₁₄ H ₂) (7)
66	—	1499.9113	1476,28987	8.3925	δ (C ₃₀ H ₃) (88); δ (C ₂₇ H ₂) (10)
67	—	1501.7672	1478,07111	4.3738	δ (C ₂₁ H ₂) (29); δ (C ₃₀ H ₃) (28); δ (C ₂₄ H ₂) (15); δ (C ₂₁ C ₁₂ H ₁₃) (11); δ (C ₁₄ H ₂) (6)
68	—	1503.707	1479,93276	3.5078	δ (C ₂₇ H ₂) (31); δ (C ₂₁ H ₂) (29); δ (C ₉ H ₂) (18)
69	1464	1509.3473	1485,34511	9.9123	δ (C ₁₇ H ₃) (27); δ (C ₂₇ H ₂) (26); δ (C ₂₁ H ₂) (10); δ (C ₁₂ C ₂₁ C ₂₄) (8); δ (C ₂₄ H ₂) (7); δ (C ₁₂ C ₁₄ C ₂₁) (6)
70	—	1510.6836	1486,62726	10.8575	δ (C ₂₁ H ₂) (83); δ (C ₂₇ H ₂) (10)
71	—	1515.4657	1491,21508	6.0184	δ (C ₂₄ H ₂) (42); δ (C ₂₁ C ₂₄ C ₂₇) (25); δ (C ₂₇ H ₂) (13); δ (C ₂₁ H ₂) (10)
72	1637	1687.5503	1655,81242	26.9151	ν (C ₁ C ₄) (87); δ (C ₁ H ₂) (7)
73	1727	1770.955	1735,24092	243.4946	ν (C ₆ O ₇) (80); δ (O ₈ C ₉ H ₁₂) (7); δ (C ₂₁ H ₂) (5); ν (C ₄ C ₆) (5)
74	—	2997.3914	2877,02371	2.7860	ν (C ₂₁ H ₂₂) (45); ν (C ₁₄ H ₂) (33); ν (C ₁₂ H ₁₃) (14)
75	—	2999.8142	2879,23075	1.7988	ν (C ₂₁ H ₂) (76); ν (C ₂₄ H ₂) (14)
76	—	3002.0159	2881,23622	13.8469	ν (C ₂₇ H ₂) (33); ν (C ₂₄ H ₂) (32); ν (C ₃₀ H ₃₁) (22); ν (C ₂₁ H ₂) (6)
77	—	3005.8916	2884,76609	14.6381	ν (C ₂₁ H ₂) (74); ν (C ₁₄ H ₂) (14); ν (C ₁₂ H ₁₃) (5)
78	2861	3014.5745	2892,67245	45.7319	ν (C ₁₂ H ₁₃) (63); ν (C ₃₀ H ₃₁) (31)
79	2875	3018.0275	2895,81595	55.9324	ν (C ₃₀ H ₃₁) (98)
80	—	3023.8407	2901,10723	22.2942	ν (C ₁₇ H ₁₉) (58); ν (C ₁₇ H ₁₈) (29)
81	—	3026.1436	2903,20306	16.4278	ν (C ₁₇ H ₁₉) (32); ν (C ₁₄ H ₂) (29); ν (C ₁₇ H ₁₈) (15); ν (C ₃₀ C ₃₁) (8); ν (C ₂₁ H ₂) (6)
82	—	3034.8324	2911,10906	35.1134	ν (C ₁₄ H ₂) (96)

TABLE 2: Continued.

Number ^b	Observed (cm ⁻¹)	DFT/6-311+G** Unscaled (cm ⁻¹)	Scaled (cm ⁻¹)	Intensity (km·mol ⁻¹)	Assignment (%PED) ^a
83	—	3041.9158	2917,55246	16.0910	ν (C ₂₇ H ₂) (38); ν (C ₉ H ₂) (20); ν (C ₁₄ H ₂) (19); ν (C ₂₁ H ₂) (6); ν (C ₂₄ H) (6)
84	—	3043.1697	2918,6929	14.5616	ν (C ₂₇ H ₂) (47); ν (C ₉ H ₂) (26); ν (C ₂₄ H ₂) (10); ν (C ₁₄ H ₂) (7)
85	—	3062.906	2936,63657	46.5673	ν (C ₂₁ H ₂) (55); ν (C ₂₇ H ₂) (25); ν (C ₂₄ H ₂) (9); ν (C ₁₂ H ₁₃) (5)
86	2931	3078.8255	2951,10087	85.8987	ν (C ₂₇ H ₂) (62); ν (C ₂₇ H ₃₀) (10); ν 2955,03236 (C ₃₀ H ₃) (9); ν (C ₉ H ₂) (6); ν (C ₁₇ H ₁₉) (6)
87	—	3083.1541	2955,03236	45.5349	ν (C ₃₀ H ₃₁) (99)
88	—	3084.5244	2956,27682	35.1235	ν (C ₁₇ H ₁₉) (67); ν (C ₁₇ C ₁₉) (67); ν (C ₁₇ C ₁₈) (17); ν (C ₃₀ H ₃₁) (15)
89	—	3087.9105	2959,3517	19.5239	ν (C ₉ H ₂) (63); ν (O ₈ C ₉) (16); ν -(C ₁₂ H ₁₃) (11); ν (C ₁₇ C ₁₉) (6)
90	2961	3093.1423	2964,10191	56.1433	ν (C ₁₇ H ₁₉) (38); ν (C ₉ H ₂) (26); ν (C ₁₇ H ₂₀) (12); ν (C ₁₄ H ₂) (10); ν (C ₁₇ H ₁₈) (9)
91	3038	3142.8663	3009,20422	5.1952	ν (C ₁ C ₄) (45); ν (C ₁ H ₂) (38); ν (C ₁ H ₃) (9)
92	—	3185.092	3047,44188	3.2650	ν (C ₁ H ₂) (95)
93	3104	3235.9105	3093,38372	2.3617	ν (C ₄ H ₅) (67); ν (C ₁ H ₂) (22); ν (C ₁ H ₃) (6)

^a Assignments and potential energy distribution (PED) (contributing $\geq 5\%$) for vibrational normal mode. Types of vibration: ν : stretching; δ : deformation; ω : out-of-plane bending; ω : wagging; γ : twisting; ρ : rocking; τ : torsion; w: weak; m: medium; sh: shoulder.

^b Normal mode number.

1655 cm⁻¹ for s-cis conformer (Figure 3(b)) and 1647 cm⁻¹ for the s-trans conformer (Figure 3(c)). The band at 1637 cm⁻¹ may be used to definitely indicate that conformer with s-trans arrangement of acrylic moiety is present or not in the liquid 2-ethylhexyl acrylate.

In the region from 1500 to 1200 cm⁻¹, in the experimental spectrum (Figure 3), there are four bands of medium intensity located at 1464, 1408, 1295, and 1272 cm⁻¹. The bands of weak intensity of account of three are located at 1381, 1357, and 1340 cm⁻¹. The calculated frequencies in this region for the s-cis and s-trans conformations have close energies for each normal mode, and the differences do not exceed 5 cm⁻¹. Based on the assignments reported by Dulce et al. [28] and our PED calculations, we have ascribed the theoretical frequencies 1485 cm⁻¹ (s-cis) and 1484 cm⁻¹ (s-trans) to the experimental band at 1464 cm⁻¹ and they are representing a C₁₇H₃ symmetric bending. The calculated frequencies at 1479, 1478, and 1476 cm⁻¹ may be contributed to the experimental band at 1464 cm⁻¹ due to its relatively large middle width of about 75 cm⁻¹. Mishra et al. [38] have reported the experimental and the theoretical IR spectra of γ form of oleic acid, many peaks reported in the region 1370 to 1220 cm⁻¹ for the CH₂ carboxyl-sided chain correspond approximately to those we found in our spectrum from 1400 to 1200 cm⁻¹, and all of them may be assigned to CH₂ deformation. The assignment is based on the bands intensities; we found a good correlation between the experimental and the theoretical spectra. One should point out that the very intense bands predicted at 1267 and

1264 cm⁻¹ for s-trans form reproduce well the asymmetric shape of the experimental band at 1272 cm⁻¹. For bands assignment, see Tables 2 and 3.

5.3. The CO Stretching and CH Bending Vibrations (1200–700 cm⁻¹, Figure 4). In this region, in the IR spectrum, there is one very strong band at 1192 cm⁻¹ with weak shoulder at 1160 cm⁻¹ and four medium intensity bands 1057, 984, 962, shoulder at 933 and 811 cm⁻¹. The bands at 1116, 1025, 909, 896, 852, 770, and 727 cm⁻¹ (shoulder at 748 cm⁻¹) are of weak intensity (Figure 4). Based on PEDs and intensities of the calculated frequencies, we correlate the two intense bands at 1192 and 1156 cm⁻¹ for the more stable and the less stable conformers to the band at 1191 cm⁻¹ in the experimental IR spectrum. The medium bands in IR spectrum are well reproduced by the calculated peaks at 1079, 999, 976, 941, and 811 cm⁻¹ for the s-cis conformer and 1067, 993, 940, 911, and 828 cm⁻¹ for the s-trans conformer. They may be ascribed to CH₂ rocking, C₁H₂ wagging, CCH rocking O₈C₉, and C₁H₂ twisting. The peaks predicted by DFT at 728 and 783 cm⁻¹ in s-cis form and the peaks at 726 and 782 cm⁻¹ in the s-trans form may be correlated to the bands at 727 and 770 cm⁻¹ and they are assigned to the CH₂ deformations of the alkyl sides of the title molecule.

In the IR spectra of 2-ethylhexyl acrylate, reported in this work, there are a few bands with weak to very weak intensity which do not appear in the IR spectra of methyl acrylate reported by Dulce et al. [28] and George et al. [39]. These bands appear at 1157, 1120, 1052, and 1022 cm⁻¹, and they

TABLE 3: Frequencies and PEDs of s-trans 2-ethylhexyl acrylate.

Number ^b	Observed (cm ⁻¹)	DFT/6-311+G** Unscaled (cm ⁻¹)	Scaled (cm ⁻¹)	Intensity (km·mol ⁻¹)	Assignment (%PED) ^a
1	—	29.5569	29,79981	1.3888	τ (C ₂₁ C ₂₄) (95)
2	—	31.2922	31,54848	1.2915	τ (C ₂₁ C ₂₄) (100)
3	—	45.3002	45,66086	0.0227	τ (C ₂₁ C ₂₄) (91); τ (O ₈ C ₉) (6)
4	—	69.075	69,59818	0.0113	τ (C ₂₁ C ₂₄) (98)
5	—	91.6561	92,31657	0.7304	ρ (C ₁₄ H ₂) (64); τ (C ₉ C ₁₂) (19); τ (C ₂₄ C ₂₁) (15)
6	—	106.795	107,53821	0.0788	τ (C ₁₂ C ₁₄) (92)
7	—	116.406	117,19786	0.4606	τ (O ₈ C ₉) (90); τ (C ₂₁ C ₂₄) (7)
8	—	128.002	128,84855	0.7652	τ (C ₂₁ C ₂₄) (99)
9	—	137.7311	138,62015	0.0737	τ (C ₂₄ C ₂₁) (94)
10	—	188.6176	189,67867	2.4795	τ (C ₂₄ C ₂₁) (53); O (O ₈ C ₉) (44)
11	—	196.4898	197,56995	2.2280	ρ (C ₉ H ₂) (82); τ (C ₉ C ₁₂) (13)
12	—	234.6	235,74391	1.7535	ρ (C ₃₀ H ₃) (90); τ (C ₂₁ C ₂₄) (7)
13	—	249.5865	250,74252	3.2507	ρ (C ₃₀ H ₃) (78); τ (C ₁₂ C ₂₁) (19)
14	—	262.3636	263,52416	1.2259	ρ (C ₉ H ₂) (72); ρ (C ₁₇ H ₃) (22)
15	—	274.1636	275,32362	0.5126	τ (C ₁₂ C ₂₁) (96)
16	—	335.2283	336,31302	0.4554	δ (C ₂₁ C ₁₂ C ₁₄) (93)
17	—	354.6136	355,649	0.1655	δ (C ₂₁ C ₁₂ C ₂₄) (95)
18	—	406.411	407,25451	2.5402	δ (C ₉ C ₁₂ C ₁₄) (92)
19	—	471.3032	471,78287	1.0320	ρ (C ₉ C ₁₂ C ₁₄) (70); δ (C ₉ C ₁₂ C ₂₁) (12); ρ (C ₁₄ H ₂) (11)
20	—	509.8943	510,09251	0.4733	γ (C ₁ H ₂) (86); O (C ₆ O ₈) (12)
21	—	514.0157	514,18098	7.3067	ρ (C ₁₂ C ₁₄ C ₁₇) (38); ρ (C ₉ C ₁₂ C ₂₁) (15); ρ (C ₁₂ C ₂₁) (14); ρ (C ₁₄ C ₁₂ H ₁₃) (13); ρ (C ₁ H ₂) (8); δ (C ₁₂ C ₂₁ C ₂₄) (7);
22	—	550.859	550,70531	2.2808	ρ (C ₉ C ₁₂ C ₁₄) (78); ρ (C ₆ O ₈ C ₉) (9); ρ (C ₁ H ₂) (6);
23	—	636.0175	634,9572	1.9146	ρ (O ₈ C ₉ C ₁₂) (97);
24	727 (m)	728.4338	726,12214	4.3677	ρ (C ₉ C ₁₂ C ₂₁) (92);
25	—	778.027	774,92902	0.6843	ρ (C ₉ C ₁₂ C ₂₁) (98);
26	770 (m)	785.397	782,17532	1.8732	ρ (C ₂₁ H ₂) (59); ρ (C ₁₄ H ₂) (36);
27	811 (m)	832.1364	828,08904	21.5147	γ (C ₁ H ₂) (94); ρ (C ₉ H ₂) (5);
28	852 (w)	850.1904	845,80503	3.4731	ρ (C ₉ C ₁₂ C ₂₁) (47); ρ (C ₉ H ₂) (27); ρ (C ₁ H ₂) (15); ν (C ₁₄ C ₁₇) (5);
29	896 (w)	901.7561	896,3468	0.9206	ρ (C ₉ C ₁₂ C ₂₁) (73); ρ (C ₂₁ C ₂₄ C ₂₇) (14);
30	909 (w)	906.5632	901,05403	1.3451	ρ (C ₉ C ₁₂ C ₂₁) (46); ρ (C ₉ H ₂) (35); ρ (C ₁₂ C ₁₄ C ₁₇) (9);
31	933 (sh)	917.0283	911,29911	7.6343	ρ (O ₇ C ₆ O ₈) (86); ρ (C ₉ H ₂) (10);
32	962 (m)	947.0255	940,64585	6.0649	ρ (C ₆ O ₈ C ₉) (99);
33	—	972.6775	965,71834	7.0484	ρ (C ₆ O ₈ C ₉) (99);
34	984 (m)	1001.2212	993,59199	34.4957	ω (C ₁ H ₂) (52); ν (C ₁ C ₄) (15); δ (C ₄ C ₆ O ₈) (15); ν (C ₁₂ C ₂₁) (15)
35	1015 (sh)	1017.1676	1009,15249	7.0006	ν (C ₁₂ C ₂₁) (92)
36	—	1021.9635	1013,83071	3.5045	ν (C ₂₁ C ₂₄) (85); δ (C ₉ C ₁₂ O ₁₄) (9)
37	1025 (sh)	1029.9052	1021,57589	18.5130	γ (C ₁ H ₂) (97)
38	—	1040.755	1032,15388	0.3554	ν (C ₂₁ C ₂₄) (70); ν (C ₉ C ₁₂) (14); γ (C ₂₁ H ₂) (5)
39	—	1060.8287	1051,71458	5.5936	γ (C ₂₁ H ₂) (58); ρ (C ₁₄ C ₁₂ H ₁₃) (29); ρ (C ₁₄ H ₂) (7)
40	—	1064.0573	1054,85945	18.8097	ν (C ₂₁ C ₂₄) (88); ν (C ₁₄ C ₁₇) (8)
41	1057 (m)	1076.7989	1067,26727	192.6571	ν (C ₉ O ₈) (82); ν (C ₁₄ C ₁₇) (13)
42	1060 (sh)	1089.5069	1079,6371	4.6500	ρ (C ₉ H ₂) (40); δ (C ₉ C ₁₂ C ₂₁) (30); ω (C ₂₇ H ₂) (25)
43	1116 (w)	1150.6075	1139,03825	1.4631	ρ (C ₉ C ₁₂ H ₁₃) (51); δ (C ₉ C ₁₂ C ₂₁) (42)
44	1191	1168.2621	1156,17915	3.2253	ρ (C ₁₄ C ₁₂ H ₁₃) (72); ω (C ₂₁ H ₂) (16); ρ (O ₈ C ₉ C ₁₂) (9)
45	—	1185.0265	1172,44634	0.1695	δ (C ₉ C ₁₂ C ₁₄) (94)

TABLE 3: Continued.

Number ^b	Observed (cm ⁻¹)	DFT/6-311+G** Unscaled (cm ⁻¹)	Scaled (cm ⁻¹)	Intensity (km·mol ⁻¹)	Assignment (%PED) ^a
46	—	1242.923	1228,55525	1.7298	γ (C ₂₁ H ₂) (89)
47	—	1258.238	1243,37912	1.1546	ρ (C ₉ C ₁₂ C ₂₁) (35); ω (C ₂₁ H ₂) (35); ω (C ₉ H ₂) (27)
48	—	1280.1017	1264,52842	77.9146	ω (C ₂₁ H ₂) (47); ρ (C ₉ C ₁₂ C ₂₁) (37); ρ (C ₉ H ₂) (27);
49	1272	1283.202	1267,52616	351.6365	ω (C ₂₁ H ₂) (60); γ (C ₁₄ H ₂) (27); γ (C ₉ H ₂) (10)
50	—	1299.1286	1282,92094	4.4292	γ (C ₉ H ₂) (72); γ (C ₂₁ H ₂) (26);
51	1295	1311.7811	1295,14505	7.2842	γ (C ₁₄ H ₂) (99)
52	—	1318.75	1301,87577	6.8204	γ (C ₁₄ H ₂) (100)
53	—	1326.4691	1309,3292	0.1479	γ (C ₂₁ H ₂) (97)
54	—	1336.2199	1318,74163	0.4090	γ (C ₂₄ H ₂) (94); γ (C ₂₁ H ₂) (5)
55	1340	1359.997	1341,68063	1.0793	ω (C ₂₁ H ₂) (86); ρ (C ₂₁ C ₁₂ C ₁₄) (7); ω (C ₉ H ₂) (5)
56	—	1380.0145	1360,97825	0.4801	ρ (C ₉ C ₁₂ C ₂₁) (43); δ (C ₉ H ₁₂) (28); ω (C ₂₁ H ₂) (25)
57	1357	1393.1134	1373,59902	2.8872	ω (C ₉ H ₂) (50); ω (C ₁₄ H ₂) (23); δ (C ₂₁ C ₁₂ H ₁₃) (12); ω (C ₂₁ H ₂) (86)
58	—	1404.3849	1384,45461	0.9476	ω (C ₂₁ H ₂) (86); ω (C ₉ H ₂) (12)
59	—	1411.9509	1391,73911	0.8054	ω (C ₉ H ₂) (85); ω (C ₂₁ H ₂) (14)
60	1381	1414.5333	1394,225	5.0233	ω (C ₂₁ H ₂) (54); ω (C ₉ H ₂) (45)
61	—	1417.3104	1396,89807	0.8100	ω (C ₂₁ H ₂) (89); ω (C ₉ H ₂) (8)
62	1408	1441.4398	1420,11302	30.5726	ω (C ₉ H ₂) (93); ω (C ₂₁ H ₂) (5)
63	—	1483.1028	1460,15241	2.0326	δ (C ₉ H ₂) (38); δ (C ₂₁ C ₁₂ H ₁₃) (18); δ (C ₂₄ C ₂₁ C ₁₂) (15); δ (C ₁₄ H ₂) (13); δ (C ₂₄ H ₂) (7); δ (C ₂₁ H ₂) (6)
64	—	1487.6468	1464,51591	0.4300	δ (C ₂₁ C ₁₂ H ₁₃) (33); δ (C ₂₇ H ₂) (28); δ (C ₂₄ H ₂) (20); δ (C ₂₁ H ₂) (10)
65	—	1491.6884	1468,3964	1.2432	δ (C ₂₁ H ₂) (54); δ (C ₉ H ₂) (21); δ (C ₂₇ H ₂) (11)
66	—	1500.0764	1476,44833	2.4692	δ (C ₂₄ H ₂) (32); δ (C ₂₁ C ₁₂ H ₁₃) (24); δ (C ₂₇ H ₂) (8); δ (C ₃₀ H ₃) (8); δ (C ₂₁ H ₂) (6)
67	—	1500.718	1477,06413	7.0795	δ (C ₃₀ H ₃) (75); δ (C ₉ H ₂) (11); δ (C ₂₇ H ₂) (6)
68	—	1502.5266	1478,79993	8.9950	δ (C ₉ H ₂) (74); δ (C ₁₇ H ₃) (21)
69	1464	1508.1671	1484,21269	9.8400	δ (C ₂₇ H ₂) (26); δ (C ₃₀ H ₃) (22); δ (C ₂₁ H ₂) (14); δ (C ₁₇ H ₃) (14); δ (C ₂₄ H ₂) (11)
70	—	1511.6225	1487,52807	10.5533	δ (C ₂₁ H ₂) (73); δ (C ₂₁ C ₁₂ H ₁₃) (6); δ (C ₂₄ H ₂) (5); δ (C ₁₇ H ₃) (5)
71	—	1514.069	1489,8752	5.6625	δ (C ₂₄ H ₂) (30); δ (C ₂₁ H ₂) (29); δ (C ₂₁ C ₂₄ C ₂₇) (20); δ (C ₂₇ H ₂) (9)
72	1619	1678.7098	1647,38009	28.7096	ν (C ₁ C ₄) (52); ν (C ₄ C ₆) (22); δ (C ₉ C ₁₂ H ₁₃) (11); δ (C ₂₁ H ₂) (8)
73	1727	1766.8533	1731,34006	315.5882	δ (C ₉ C ₁₂ C ₂₁) (63); ν (C ₄ C ₆) (16); δ (C ₂₁ H ₂) (6); ν (C ₆ O ₇) (6)
74	—	2995.932	2875,69419	2.0873	ν (C ₂₄ H ₂) (35); ν (C ₁₄ H ₂) (34); ν (C ₂₁ H ₂) (25)
75	—	2998.467	2878,00355	0.6759	ν (C ₂₄ H ₂) (40); ν (C ₁₂ H ₁₃) (29); ν (C ₂₁ H ₂) (12); ν (C ₁₄ H ₂) (10)
76	—	3001.649	2880,90203	13.5187	ν (C ₂₁ H ₂) (92)
77	—	3005.3152	2884,24116	13.2101	ν (C ₂₄ H ₂) (87); ν (C ₂₄ H ₂) (8)
78	2861	3013.385	2891,58948	58.5964	ν (C ₂₁ H ₂) (45); ν (C ₃₀ C ₃₂) (36); ν (C ₁₂ H ₁₃) (12)
79	2875	3017.8939	2895,69433	47.2871	ν (C ₃₀ C ₃₂) (96)
80	—	3023.6248	2900,91073	21.1397	ν (C ₁₄ H ₁₂) (46); ν (C ₁₇ H ₁₉) (32); ν (C ₁₇ H ₁₈) (17)
81	—	3026.0401	2903,10887	15.9088	ν (C ₁₂ H ₁₃) (30); ν (C ₁₇ H ₁₉) (27); ν (C ₁₇ H ₁₈) (13); ν (C ₃₀ C ₃₂) (12)
82	—	3034.55	2910,85214	32.9164	ν (C ₂₁ H ₂) (66); ν (C ₁₄ H ₂) (28)
83	—	3040.4085	2916,18149	4.0314	ν (C ₂₁ H ₂) (55); ν (C ₃₀ C ₃₂) (27); ν (C ₁₂ H ₁₃) (7)
84	—	3043.7899	2919,25696	26.3738	ν (C ₂₁ H ₂) (98)
85	—	3060.9167	2934,82854	50.3404	ν (C ₂₁ H ₂) (85); ν (C ₃₀ C ₃₂) (12)
86	2931	3078.6333	2950,92629	82.4131	ν (C ₃₀ C ₃₂) (95)

TABLE 3: Continued.

Number ^b	Observed (cm ⁻¹)	DFT/6-311+G** Unscaled (cm ⁻¹)	Scaled (cm ⁻¹)	Intensity (km·mol ⁻¹)	Assignment (%PED) ^a
87	—	3083.3975	2955,25341	44.1245	ν (C ₃₀ C ₃₂) (93)
88	—	3084.2781	2956,05315	36.9537	ν (C ₁₇ H ₁₉) (67); ν (C ₁₇ H ₁₈) (18); ν (C ₂₁ H ₂) (9)
89	—	3088.9498	2960,29541	15.1201	ν (C ₂₁ H ₂) (52); ν (C ₉ H ₂) (14); ν (C ₁₂ H ₁₃) (14); ν (C ₁₄ H ₂) (8); ν (C ₁₇ H ₁₉) (7)
90	2961	3093.0704	2964,03663	59.5099	ν (C ₁₇ H ₁₉) (36); ν (C ₁₄ H ₂) (28); ν (C ₁₇ H ₂₀) (10); ν (C ₂₁ H ₂) (10); ν (C ₁₇ H ₁₈) (8); ν (C ₉ H ₂) (6)
91	3038	3146.2567	3012,27655	5.2018	ν (C ₁ C ₄) (50); ν (C ₁ H ₂) (31); ν (C ₁ H ₃) (10)
92	3069	3185.7999	3048,08243	3.4136	ν (C ₄ H ₅) (57); ν (C ₄ C ₆) (23); ν (C ₁ C ₄) (14)
93	3104	3237.707	3095,00628	4.4771	ν (C ₁ H ₂) (70); ν (C ₁ H ₃) (11); ν (C ₄ H ₅) (7)

^a Assignments and potential energy distribution (PED) (contributing $\geq 5\%$) for vibrational normal mode. Types of vibration: ν : stretching; δ : deformation; ρ : out-of-plane bending; ω : wagging; γ : twisting; ρ : rocking; τ : torsion; w: weak; m: medium; sh: shoulder.

^b Normal mode number.

FIGURE 3: Comparison of the experimental IR (a) C=O and C=C stretching and CH bending region (1800–1200 cm⁻¹) with the appropriate theoretical B3LYP/6-311+G** spectra ((b) and (c)) for s-cis and s-trans 2-ethylhexyl acrylate, respectively.

are well correlated to the calculated peaks in DFT for both conformers; see Tables 2 and 3.

The shoulders in the infrared spectrum at 1025, 1015 cm⁻¹ of weak to medium intensities may be correlated to the bands 1037, 1015 cm⁻¹ for s-cis and 1015, 988 cm⁻¹ for the s-trans

conformer. These bands are ascribed to the CH out-of-plane bending modes of the vinyl group.

The remaining bands of weak intensity in the experimental IR spectrum are 909, 896, and 852 cm⁻¹. These bands are close to the ones at 911, 996, and 847 cm⁻¹ for the s-cis

FIGURE 4: Comparison of the experimental IR (a) CO stretching and CH bending region ($1200\text{--}700\text{ cm}^{-1}$) with the appropriate theoretical B3LYP/6-311+G** spectra ((b) and (c)) for s-cis and s-trans 2-ethylhexyl acrylate, respectively.

conformation of the title molecule. All the vibrational normal modes in this region are not pure and the majority of them were ascribed according to PED calculations to CH bending (for more details see Tables 2 and 3).

5.4. Region below 700 cm^{-1} . This spectral region includes the bands associated with C=C-C, C-O-C, O=C-O, O-C-C, C-C-C, and C-C-C bending and torsion modes about the single bonds O-C and C-C. The frequencies and PED calculations are presented in Tables 2 and 3. Comparing the 23 first normal modes for the two conformers, we notice that they have the same type of vibrational modes. However, the normal modes 16, 17, and 18 represent CCC bending in the s-trans and CH and CCC rocking modes in the s-cis conformer.

Due to the lack of experimental data on this region, we compare our calculated frequencies to some experimental IR bands of related molecules presented in the literature. The bands at 356 , 254 , 116 , and 100 cm^{-1} are close to the bands at $349(\text{A}')$, $244(\text{A}'')$, $114(\text{A}'')$, and $114\text{ cm}^{-1}(\text{A}'')$ reported by Dulce et al. [28]. From the same work the bands at 530 , 244 , 114 , and 114 cm^{-1} belonging to A'' symmetry, for the s-trans

methyl acrylate in liquid state, are close to our calculated bands in DFT at 542 , 244 , 116 , and 106 cm^{-1} .

6. Conclusions

The mid-IR spectrum of 2-ethylhexyl acrylate was measured and interpreted with support of the DFT//B3LYP/6-311+G** calculated vibrational spectra followed by potential energy distribution analysis. Assuming the s-cis and s-trans conformations, we found two stable conformations, close in their energies. The fully optimized geometries of s-cis and s-trans conformations by DFT//B3LYP/6-311+G** were compared with the experimental and theoretical data presented in the literature on the methyl acrylate molecule. The comparison shows a good agreement. The experimental vibrational spectrum is in good agreement with the theoretical spectra calculated for the two conformations. Two neighbor bands in the IR spectrum at 1619 and 1637 cm^{-1} may be used as characteristic bands to locate and distinguish the existence of one or both conformations.

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