



Ab initio and DFT studies of the molecular structures and vibrational spectra of succinonitrile

Yunusa Umar*, M.A. Morsy

Department of Chemistry, King Fahd University of Petroleum and Minerals, KFUPM Box 5048, Dhahran 31261, Saudi Arabia

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Abstract

The Molecular structure, conformational stability and vibrational frequencies of succinonitrile $\text{NCCH}_2\text{CH}_2\text{CN}$ have been investigated with ab initio and density functional theory (DFT) methods implementing the standard 6–311++G* basis set. The potential energy surfaces (PES) have been explored at DFT-B3LYP, HF and MP2 levels of theory. In agreements with previous experimental results, the molecule was predicted to exist in equilibrium mixture of *trans* and *gauche* conformers with the *trans* form being slightly lower in energy. The vibrational frequencies and the corresponding vibrational assignments of succinonitrile in both C_{2h} and C_2 symmetry were examined theoretically and the calculated Infrared and Raman spectra of the molecule were plotted. Observed frequencies for normal modes were compared with those calculated from normal mode coordinate analysis carried out on the basis of ab initio and DFT force fields using the standard 6–311++G* basis set of the theoretical optimized geometry. Theoretical IR intensities and Raman activities are reported.

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1. Introduction

It is well established [1–5] that 1,2 di-substituted ethanes consist of equilibrium mixtures of two rotational isomers, *trans* and *gauche*. The symmetrical di-substituted ethane, 1,2-dicyanoethane (succinonitrile) was also reported to exist as an equilibrium mixture of two rotational isomers. Fitzgerald and Jantz [6], as well as Fujiyama et al. [7] reported the existence of both the *trans* and *gauche* forms of succinonitrile, $\text{NCCH}_2\text{CH}_2\text{CN}$ in liquid and solid states from infrared and Raman spectra measurements, but only the *gauche* form remains to exist when the solid is cooled to -50°C . Fernolt and Kveseth [8], studied gaseous succinonitrile by electron diffraction and concluded the more stable conformer in the vapor is *trans*, contributing with about 74% at 170°C . The X-ray analysis [9] and the infrared spectra [10] of the coordination compounds bis(succinonitrile)copper(1)-nitrate, $[\text{Cu}(\text{NCCH}_2\text{CH}_2\text{CN})_2]\text{NO}_3$, and succinonitrile silver nitrate, $[\text{Ag}(\text{NCCH}_2\text{CH}_2\text{CN})]\text{NO}_3$ show that the ligand succinonitrile takes the *gauche* and *trans* form, respectively.

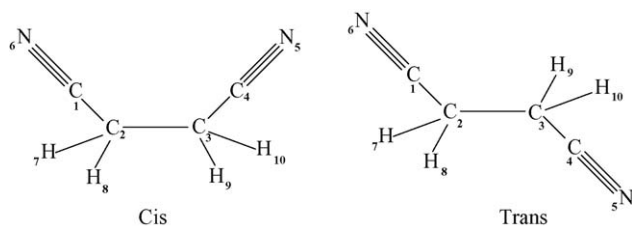
The infrared spectra of succinonitrile molecule have been investigated in some details [6,10,11]. However, the measured vibration and individual assignments are partially in disagreement. In order to get clear and unequivocal assignments, Fenger and Ruoff [12] recently reported a detailed discussion of the infrared and Raman spectra of succinonitrile along with three succinonitrile isotopomers at both room temperature and liquid nitrogen temperature. A detailed quantum chemical calculation of the structure and vibrational modes of succinonitrile will aid making definitive assignments to the fundamental normal modes and in clarifying the available experimental data for this important molecule. In this study, molecular geometry, infrared and Raman spectra of succinonitrile $\text{NCCH}_2\text{CH}_2\text{CN}$ are investigated using the Gaussian 03 program package [13] and compared against available experimental geometry and vibrational data. The vibrational frequencies of $\text{NCCH}_2\text{CH}_2\text{CN}$ were calculated using ab initio and DFT methods. In DFT method, Becke's three-parameter exchange functional [14] combined with Lee–Yang–Parr [15] correlation functional (B3LYP) methods were employed using the standard 6–311++G* basis set [16,17]. The same basis set was used for Hatree Fock (HF) and second-order Møller–Plesset (MP2) perturbation theory [18]. A complete assignment of the fundamental vibrational modes was done on the

* Corresponding author. Tel.: +966 5 02045518; fax: +966 3 8604277.
E-mail address: uyunusa@kfupm.edu.sa (Y. Umar).

basis of comparison between the calculated and experimental results.

2. Computational methods

Gaussian 03 program package was used to optimize the structure, predict dipole moment and calculate the vibrational frequencies for succinonitrile, $\text{NCCH}_2\text{CH}_2\text{CN}$ (Scheme 1). Calculations were performed at DFT-B3LYP, HF and MP2 levels of theory. The standard 6-311++G* basis set was used to carry out the calculations utilizing the C_{2h} and C_2 symmetry of $\text{NCCH}_2\text{CH}_2\text{CN}$. Some of the optimized bond lengths and bond angles of succinonitrile are listed in Table 1. Generation of potential energy functions from the experimental data is a difficult task, since only conformations near the minima are appreciably populated. The alternative is to carry out accurate ab initio calculations for an appropriate numbers of rotational angles. Therefore, to study different conformations of the molecule, potential energy surface (PES) for the internal rotation about the C–C single bond was performed at all the three levels of theory. Torsional angle ϕ (CC–CC) was varied over a range of 180° at an increment 15° . The saddle points were determined and full geometry optimization was carried out at the transition state. In addition, full geometry optimization at each of the fixed CC–CC torsional angle (ϕ) of 15° , 30° , 45° , 60° , 75° , 90° , 105° , 120° ,



Scheme 1. Atom numbering for succinonitrile in the *cis* and *trans* form.

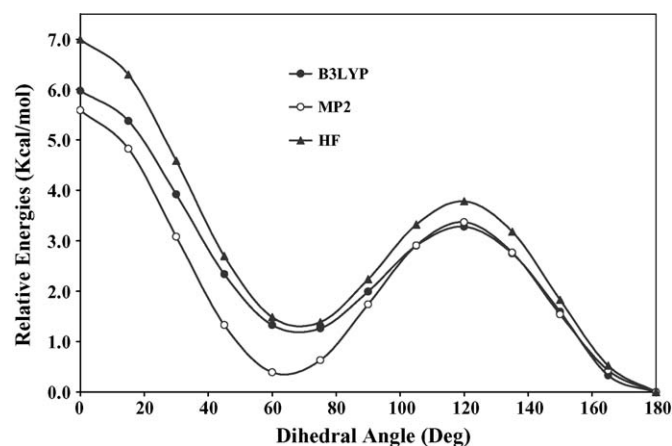


Fig. 1. Potential energy surface of succinonitrile as a function of dihedral angle (ϕ) computed at B3LYP/6-311++G*, MP2/6-311++G* and HF/6-311++G* levels of theory.

135° , 150° , and 165° were carried out at B3LYP/6-311++G*, HF/6-311++G* and MP2/6-311++G* levels of calculations.

Fig. 1 shows the potential energy surface of succinonitrile as a function of the dihedral angle (ϕ). All the reported minima along the potential energy surface were subjected to full geometry optimizations. The minima were confirmed using frequency calculations. The infrared data are reported, and each of the vibrational modes was reliably confirmed by Gaussian view program. The vibrational infrared and Raman spectra were calculated as described previously [19,20]. The frequencies ν_j , the scattering activities S_j , and the depolarization ratios ρ_j obtained from B3LYP/6-311++G*, HF/6-311++G* and MP2/6-311++G* calculations were used to calculate infrared and Raman spectra at all the three levels of theory respectively. The calculated vibrational Raman and infrared spectra are shown in Figs. 2–7.

Table 1
Optimized parameters for the stable conformers of succinonitrile at DFT-B3LYP, MP2 and HF levels using 6-311++G* basis set

| Parameter | B3LYP/6-311++G* | | MP2/6-311++G* | | HF/6-311++G* | | Expt ^a |
|--------------------------------|-----------------|--------|---------------|--------|--------------|--------|-------------------|
| | <i>Trans</i> | Gauge | <i>Trans</i> | Gauge | <i>Trans</i> | Gauge | |
| Bond lengths (Å) | | | | | | | |
| C ₁ –C ₂ | 1.460 | 1.461 | 1.464 | 1.465 | 1.469 | 1.469 | 1.465 |
| C ₂ –C ₃ | 1.549 | 1.547 | 1.542 | 1.540 | 1.537 | 1.536 | 1.561 |
| C ₃ –C ₄ | 1.460 | 1.461 | 1.464 | 1.465 | 1.469 | 1.469 | 1.465 |
| C≡N | 1.153 | 1.152 | 1.175 | 1.175 | 1.129 | 1.129 | 1.161 |
| C–H | 1.093 | 1.093 | 1.093 | 1.094 | 1.082 | 1.082 | 1.092 |
| Bond angles (°) | | | | | | | |
| CCC | 111.4 | 113.3 | 110.6 | 111.8 | 110.9 | 113.0 | 110.4 |
| CCN | 179.1 | 179.3 | 178.4 | 178.9 | 179.4 | 179.2 | |
| CCCC | 180.0 | 68.3 | 180.0 | 64.3 | 180.0 | 68.7 | |
| Dipole moment (Debye) | 0.180 | 5.703 | 0.177 | 5.754 | 0.0 | 5.969 | |
| Rotational constants (GHz) | | | | | | | |
| A | 25.6878 | 7.1974 | 25.2067 | 6.7022 | 26.0354 | 7.2765 | |
| B | 1.4802 | 2.2658 | 1.4770 | 2.4057 | 1.4968 | 2.2964 | |
| C | 1.4241 | 1.8461 | 1.4198 | 1.9003 | 1.4402 | 1.8709 | |

^a Experimental values taken from Ref. [8].

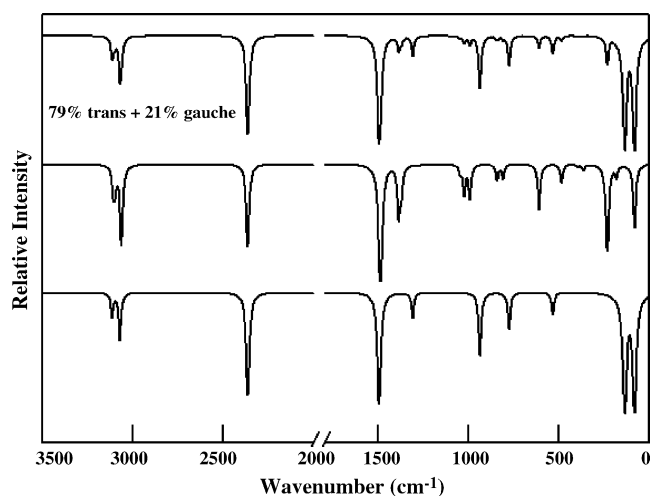


Fig. 2. Calculated vibrational infrared spectra of succinonitrile for the *trans* and *gauche* mixture (top), pure *trans* (middle) and pure *gauche* (bottom) at 300 °C by the DFT-B3LYP/6-311++G*.

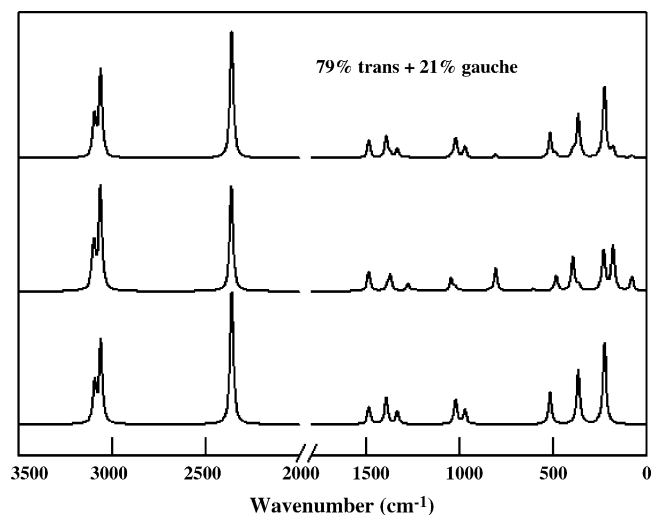


Fig. 3. Calculated vibrational Raman spectra of succinonitrile for the *trans* and *gauche* mixture (top), pure *trans* (middle) and pure *gauche* (bottom) at 300 °C by the DFT-B3LYP/6-311++G*.

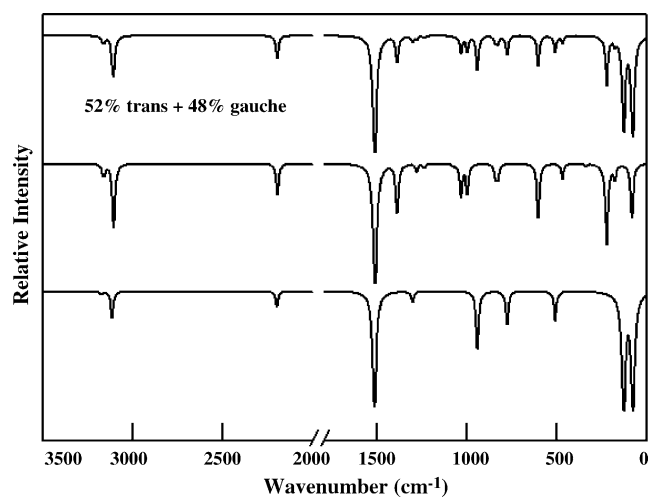


Fig. 4. Calculated vibrational infrared spectra of succinonitrile for the *trans* and *gauche* mixture (top), pure *trans* (middle) and pure *gauche* (bottom) at 300 °C by the MP2/6-311++G*.

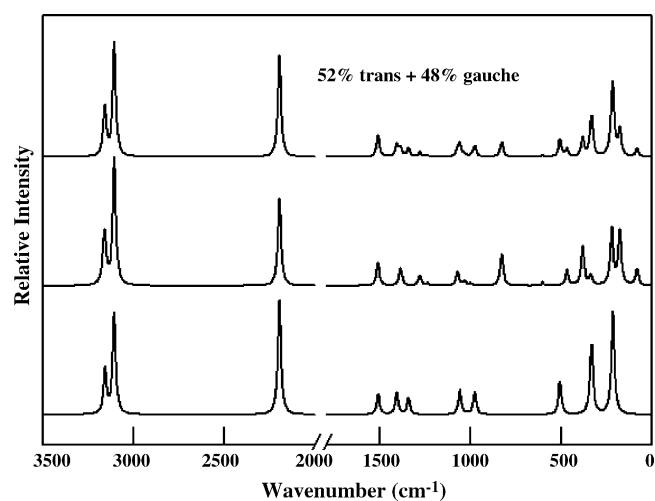


Fig. 5. Calculated vibrational Raman spectra of succinonitrile for the *trans* and *gauche* mixture (top), pure *trans* (middle) and pure *gauche* (bottom) at 300 °C by the MP2/6-311++G*.

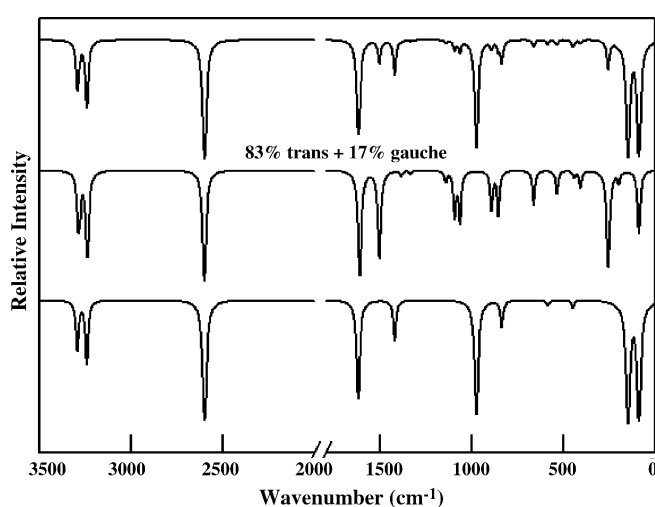


Fig. 6. Calculated vibrational infrared spectra of succinonitrile for the *trans* and *gauche* mixture (top), pure *trans* (middle) and pure *gauche* (bottom) at 300 °C by the HF/6-311++G*.

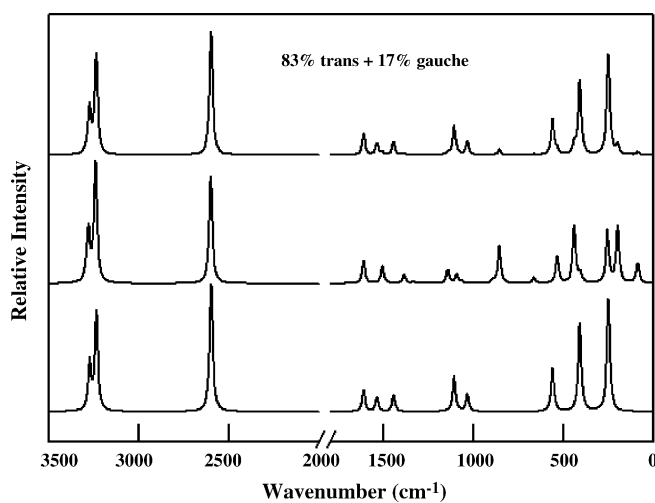


Fig. 7. Calculated vibrational Raman spectra of succinonitrile for the *trans* and *gauche* mixture (top), pure *trans* (middle) and pure *gauche* (bottom) at 300 °C by the HF/6-311++G*.

3. Results and discussion

The geometry parameters optimized at DFT-B3LYP, MP2 and HF levels of theory for succinonitrile are presented in Table 1 along with reported electron diffraction data reported by Fernolt and Kveseth [8]. Computed total dipole moments and rotational constants are also presented therein. The standard basis set 6–311++G** was utilized in all calculations. The calculated rotational constants R_A , R_B , and R_C for the two stable conformers are summarized in Table 1. The computed geometry parameters fairly agree well with the reported main experimental structural parameters obtained by electron diffraction [8]. The structural data suggests a repulsive interactions in the gauche forms, i.e. NC–C–C–CN torsional angles larger than 60° and C–C–CN angles are larger in gauche than *trans* conformers. The molecular symmetries of succinonitrile are C_{2v} and C_{2h} for the conformations corresponding to the C–C–C–C dihedral angles $\phi = 0^\circ$ and $\phi = 180^\circ$, respectively. The symmetry becomes C_2 for the intermediate angles. From steric considerations, and the polar nature of the cyano groups, the eclipsed conformers are predicted the least likely of the possible configurations. Total dipole moments obtained from geometry optimization of *trans* conformer at all the three levels of calculations were found to be smaller than those predicted from geometry optimization of gauche conformer. While the gauche conformer possesses a large dipole moment of about 5.7 Debye, the dipole moment of the *trans* conformer vanishes owing to its center of inversion.

The potential energy surface (PES) of succinonitrile have been explored at the B3LYP/6–311++G*, HF/6–311++G* and MP2/6–311++G* levels of theory. At a fixed value of torsional angle (ϕ), the other geometrical parameters were relaxed to their equilibrium values. Fig. 1 shows the potential energy curves of succinonitrile as a function of the dihedral angle (ϕ). The calculated PESs have the same skeleton, which clearly show two distinct minima at $\phi \approx 60^\circ$ and $\phi = 180^\circ$ at all levels of theory. All the reported minima along the potential energy surface were subjected to full geometry optimizations and the minimum was verified by calculating the vibrational frequencies that result in the absence of imaginary frequencies. The B3LYP and HF calculations gave the *trans*/gauche energy differences of 1.20 and 1.34 kcal/mol, respectively, but when electron correlation was included (MP2), the difference was found to be 0.47 kcal/mol favoring *trans* conformer. These results are in agreement with the reported electron diffraction experiment [8], where the *trans* was found to be more stable than the gauche conformer by 1.5(3) kcal/mol. Based on reaction field theory of Osernger, Fitzgerald et al. predicted vapor state of succinonitrile to be a mixture of the gauche and *trans* isomeric form with the energy difference of about 1 kcal/mol in favor of the *trans* conformer. Computed total energies of the two conformers and the transition state of the molecules calculated at MP2, B3LYP and BLYP are presented in Table 2. Relative energies, corrected relative energies and rotational barriers are also presented therein. The gauche–*trans* internal rotational barrier was predicted to be about 2.0–2.4 kcal/mol depending on the level of theory applied.

Table 2

Computed total energies (hartree) and/or zero-point corrections (kcal/mol), and relative energy and rotational barriers (kcal/mol) in succinonitrile at DFT-B3LYP, MP2 and HF levels using 6–311++G* basis set

| Level/parameter | B3LYP | MP2 | HF |
|--|-------------|-------------|-------------|
| Total energy | | | |
| <i>Trans</i> | –264.373341 | –263.607974 | –262.750313 |
| Gauche | –264.371495 | –263.607447 | –262.748261 |
| TS ^a | –264.368119 | –263.602623 | –262.744279 |
| Relative energy | 1.158 | 0.330 | 1.288 |
| <i>Trans</i> –gauche barrier | 3.277 | 3.357 | 3.786 |
| Gauche– <i>trans</i> barrier | 2.119 | 3.027 | 2.499 |
| Zero-point correction | | | |
| <i>Trans</i> | 0.073561 | 0.073233 | 0.079174 |
| Gauche | 0.07362 | 0.073451 | 0.079259 |
| TS ^a | 0.073407 | 0.073226 | 0.079093 |
| Corrected relative energy | 1.195 | 0.467 | 1.341 |
| Corrected <i>trans</i> –gauche barrier | 3.180 | 3.353 | 3.736 |
| Corrected gauche– <i>trans</i> barrier | 1.985 | 2.886 | 2.395 |

^a Transition state energy, dihedral angle at the transition state was found to be 118.2°, 120.3° and 120.0° at B3LYP, MP2 and HF levels, respectively.

The optimized structural parameters were used to compute the vibrational frequencies of succinonitrile at, DFT-B3LYP, HF and MP2 levels of theory. Standard basis set 6–311++G* was utilized in all calculations. Tables 3–8 present the calculated vibrational frequencies for the two stable conformers of succinonitrile computed at the DFT-B3LYP, HF and MP2 levels of theory respectively. These calculations result in 24 fundamental vibrations which span irreducible representations $\Gamma_{\text{vib}} = 8A_g + 5A_u + 4B_g + 7B_u$ and $\Gamma_{\text{vib}} = 13A + 11B$ of the C_{2h} point group of the *trans* and C_2 point group of the gauche, respectively. For the C_2 (gauche) isomer all the 24 fundamental modes are both Raman and infrared active while the C_{2h} (*trans*) form, the fundamental modes are mutually exclusive due to the C_{2h} symmetry. Thus the C_{2h} isomer has approximately half as many infrared active fundamental as the C_2 form. The assignment of each normal mode is also given in each table. The high degree of the symmetry of the molecule was helpful in making vibrational assignments. The symmetry of each vibrational has been determined by using the standard procedures [21] where the traces of the symmetry operations for each vibrational mode were translated to into an irreducible representation under the C_{2h} and C_2 point groups. The normal modes associated with individual vibrations are graphically displayed using GaussView program. Combining the motions observed using the GaussView program, Infrared band intensities and Raman line activities, with the experimental reported results, complete vibrational frequency assignments were made with high degree of confidence. Each vibrational mode was assigned to one of eleven types of motion (C–H stretch, C≡N stretch, CH₂ bend, CH₂ wag, C–C stretch, C–CN stretch, C–C–C bend, C–C≡N bend, CH₂ twist, CH₂ rock, torsion).

Comparison of the results of the calculated vibrational frequencies presented in Tables 3–8 with the experimental values reflects a reasonable agreement for the vibrational frequencies.

Table 3

Calculated vibrational frequencies^a of *trans* succinonitrile (cm⁻¹) at the DFT (B3LYP) level of theory using the standard 6–311++G** basis set

| Symmetry | No. | Frequency | IR intensity | Raman activity | Expt ^b | $\nu_{\text{expt}}/\nu_{\text{calc}}$ | Assignment |
|----------------|------------|-----------|--------------|----------------|-------------------|---------------------------------------|-----------------------|
| A _g | ν_1 | 3060 | Inactive | 207.8 | 2947 | 0.96 | C–H stretch |
| | ν_2 | 2359 | Inactive | 216.6 | 2254 | 0.96 | C≡N stretch |
| | ν_3 | 1485 | Inactive | 14.0 | 1425 | 0.96 | CH ₂ bend |
| | ν_4 | 1392 | Inactive | 20.5 | 1359 | 0.98 | CH ₂ wag |
| | ν_5 | 1020 | Inactive | 12.7 | 1025 | 1.00 | C–C stretch |
| | ν_6 | 971 | Inactive | 7.2 | 951 | 0.98 | C–CN stretch |
| | ν_7 | 515 | Inactive | 6.9 | 508 | 0.99 | C–C–C bend |
| | ν_8 | 224 | Inactive | 5.2 | 240 | 1.07 | C–C≡N bend |
| A _u | ν_9 | 3112 | 1.7 | Inactive | 2985 | 0.96 | C–H stretch |
| | ν_{10} | 1231 | 0.0 | Inactive | 1232 | 1.00 | CH ₂ twist |
| | ν_{11} | 773 | 2.8 | Inactive | 762 | 0.98 | CH ₂ rock |
| | ν_{12} | 402 | 0.0 | Inactive | 388 | 0.97 | C–C≡N bend |
| | ν_{13} | 79 | 22.8 | Inactive | – | – | Torsion |
| B _g | ν_{14} | 3093 | Inactive | 101.1 | 2982 | 0.96 | C–H stretch |
| | ν_{15} | 1333 | Inactive | 9.2 | 1178 | 0.88 | CH ₂ twist |
| | ν_{16} | 1045 | Inactive | 0.1 | 1005 | 0.96 | CH ₂ rock |
| | ν_{17} | 364 | Inactive | 7.4 | 357 | 0.98 | C–C≡N bend |
| B _u | ν_{18} | 3670 | 3.9 | Inactive | 2965 | 0.81 | C–H stretch |
| | ν_{19} | 2361 | 13.5 | Inactive | 2255 | 0.96 | C–N stretch |
| | ν_{20} | 1494 | 17.2 | Inactive | 1431 | 0.96 | CH ₂ bend |
| | ν_{21} | 1307 | 1.7 | Inactive | 1272 | 0.97 | CH ₂ wag |
| | ν_{22} | 934 | 5.7 | Inactive | 917 | 0.98 | C–C stretch |
| | ν_{23} | 531 | 1.6 | Inactive | 529 | 1.00 | C–C–C bend |
| | ν_{24} | 132 | 23.4 | Inactive | 180 | 1.36 | C–C≡N bend |

^a IR intensities and Raman activities are calculated in km mol⁻¹ and Å⁴ amu⁻¹, respectively.^b Experimental values taken from Ref. [7].

Table 4

Calculated vibrational frequencies^a of *trans* succinonitrile (cm⁻¹) at the HF level of theory using the standard 6–311++G** basis set

| Symmetry | No. | Frequency | IR intensity | Raman activity | Expt ^b | $\nu_{\text{expt}}/\nu_{\text{calc}}$ | Assignment |
|----------------|------------|-----------|--------------|----------------|-------------------|---------------------------------------|-----------------------|
| A _g | ν_1 | 3234 | Inactive | 190.0 | 2947 | 0.91 | C–H stretch |
| | ν_2 | 2596 | Inactive | 169.0 | 2254 | 0.87 | C≡N stretch |
| | ν_3 | 1609 | Inactive | 14.0 | 1425 | 0.89 | CH ₂ bend |
| | ν_4 | 1535 | Inactive | 8.8 | 1359 | 0.89 | CH ₂ wag |
| | ν_5 | 1105 | Inactive | 14.5 | 1025 | 0.93 | C–C stretch |
| | ν_6 | 1032 | Inactive | 6.2 | 951 | 0.92 | C–CN stretch |
| | ν_7 | 559 | Inactive | 7.3 | 508 | 0.91 | C–C–C bend |
| | ν_8 | 249 | Inactive | 5.9 | 240 | 0.96 | C–C≡N bend |
| A _u | ν_9 | 3292 | 4.8 | Inactive | 2985 | 0.91 | C–H stretch |
| | ν_{10} | 1331 | 0.1 | Inactive | 1232 | 0.93 | CH ₂ twist |
| | ν_{11} | 835 | 2.2 | Inactive | 762 | 0.91 | CH ₂ rock |
| | ν_{12} | 447 | 0.6 | Inactive | 388 | 0.87 | C–C≡N bend |
| | ν_{13} | 86 | 25.7 | Inactive | – | – | Torsion |
| B _g | ν_{14} | 3271 | Inactive | 94.9 | 2982 | 0.91 | C–H stretch |
| | ν_{15} | 1442 | Inactive | 9.4 | 1178 | 0.82 | CH ₂ twist |
| | ν_{16} | 1144 | Inactive | 0.2 | 1005 | 0.88 | CH ₂ rock |
| | ν_{17} | 408 | Inactive | 9.7 | 357 | 0.88 | C–C≡N bend |
| B _u | ν_{18} | 3241 | 6.8 | Inactive | 2965 | 0.91 | C–H stretch |
| | ν_{19} | 2597 | 25.3 | Inactive | 2255 | 0.87 | C≡N stretch |
| | ν_{20} | 1618 | 14.0 | Inactive | 1431 | 0.88 | CH ₂ bend |
| | ν_{21} | 1419 | 3.7 | Inactive | 1272 | 0.90 | CH ₂ wag |
| | ν_{22} | 973 | 20.9 | Inactive | 917 | 0.94 | C–C stretch |
| | ν_{23} | 584 | 0.4 | Inactive | 529 | 0.91 | C–C–C bend |
| | ν_{24} | 145 | 27.7 | Inactive | 180 | 1.24 | C–C≡N bend |

^a IR intensities and Raman activities are calculated in km mol⁻¹ and Å⁴ amu⁻¹, respectively.^b Experimental values taken from Ref. [7].

Table 5
Calculated vibrational frequencies^a of trans succinonitrile (cm⁻¹) at the MP2 level of theory using the standard 6-311++G** basis set

| Symmetry | No. | Frequency | IR intensity | Raman activity | Expt ^b | $\nu_{\text{expt}}/\nu_{\text{calc}}$ | Assignment |
|----------------|------------|-----------|--------------|----------------|-------------------|---------------------------------------|-----------------------|
| A _g | ν_1 | 3104 | Inactive | 197.3 | 2947 | 0.95 | C–H stretch |
| | ν_2 | 2192 | Inactive | 126.6 | 2254 | 1.03 | C≡N stretch |
| | ν_3 | 1508 | Inactive | 13.5 | 1425 | 0.94 | CH ₂ bend |
| | ν_4 | 1405 | Inactive | 13.1 | 1359 | 0.97 | CH ₂ wag |
| | ν_5 | 1057 | Inactive | 10.1 | 1025 | 0.97 | C–C stretch |
| | ν_6 | 976 | Inactive | 8.4 | 951 | 0.97 | C–CN stretch |
| | ν_7 | 505 | Inactive | 5.4 | 508 | 1.01 | C–C–C bend |
| | ν_8 | 214 | Inactive | 4.6 | 240 | 1.12 | C–C≡N bend |
| A _u | ν_9 | 3172 | 0.2 | Inactive | 2985 | 0.94 | C–H stretch |
| | ν_{10} | 1227 | 0.0 | Inactive | 1232 | 1.00 | CH ₂ twist |
| | ν_{11} | 775 | 2.4 | Inactive | 762 | 0.98 | CH ₂ rock |
| | ν_{12} | 365 | 0.0 | Inactive | 388 | 1.06 | C–C≡N bend |
| | ν_{13} | 76 | 21.1 | Inactive | – | – | Torsion |
| B _g | ν_{14} | 3154 | Inactive | 90.5 | 2982 | 0.95 | C–H stretch |
| | ν_{15} | 1340 | Inactive | 9.1 | 1178 | 0.88 | CH ₂ twist |
| | ν_{16} | 1048 | Inactive | 0.1 | 1005 | 0.96 | CH ₂ rock |
| | ν_{17} | 332 | Inactive | 6.1 | 357 | 1.08 | C–C≡N bend |
| B _u | ν_{18} | 3112 | 1.9 | Inactive | 2965 | 0.95 | C–H stretch |
| | ν_{19} | 2196 | 1.0 | Inactive | 2255 | 1.03 | C≡N stretch |
| | ν_{20} | 1512 | 18.7 | Inactive | 1431 | 0.95 | CH ₂ bend |
| | ν_{21} | 1301 | 0.7 | Inactive | 1272 | 0.98 | CH ₂ wag |
| | ν_{22} | 940 | 4.8 | Inactive | 917 | 0.98 | C–C stretch |
| | ν_{23} | 507 | 2.1 | Inactive | 529 | 1.04 | C–C–C bend |
| | ν_{24} | 126 | 21.2 | Inactive | 180 | 1.43 | C–C≡N bend |

^a IR intensities and Raman activities are calculated in km mol⁻¹ and Å⁴ amu⁻¹, respectively.

^b Experimental values taken from Ref. [7].

Table 6
Calculated vibrational frequencies^a of gauche succinonitrile (cm⁻¹) at the DFT (B3LYP) level of theory using the standard 6-311++G* basis set

| Symmetry | No. | Frequency | IR intensity | Raman activity | Expt ^b | $\nu_{\text{expt}}/\nu_{\text{calc}}$ | Assignment |
|----------|------------|-----------|--------------|----------------|-------------------|---------------------------------------|-------------------------|
| A | ν_1 | 3105 | 2.1 | 27.7 | 2985 | 0.96 | C–H stretch |
| | ν_2 | 3060 | 2.6 | 16.1 | 2965 | 0.97 | C–H stretch |
| | ν_3 | 2362 | 3.3 | 124.7 | 2254 | 0.95 | C≡N stretch |
| | ν_4 | 1484 | 7.4 | 5.3 | 1420 | 0.96 | CH ₂ scissor |
| | ν_5 | 1384 | 4.5 | 3.8 | 1322 | 0.96 | CH ₂ wag |
| | ν_6 | 1234 | 0.1 | 1.1 | 1200 | 0.97 | CH ₂ twist |
| | ν_7 | 1022 | 2.3 | 2.0 | 1026 | 1.00 | C–C stretch |
| | ν_8 | 990 | 2.6 | 0.5 | 963 | 0.97 | CH ₂ rock |
| | ν_9 | 807 | 1.0 | 9.1 | 818 | 1.01 | C–CN stretch |
| | ν_{10} | 483 | 1.3 | 3.2 | 480 | 0.99 | C–C–C bend |
| | ν_{11} | 393 | 0.1 | 5.1 | 387 | 0.98 | C–C≡N bend |
| | ν_{12} | 230 | 9.7 | 2.7 | 230 | 1.00 | C–C≡N bend |
| | ν_{13} | 78 | 5.7 | 4.0 | – | – | Torsion |
| B | ν_{14} | 3096 | 1.6 | 103.0 | 2985 | 0.96 | C–H stretch |
| | ν_{15} | 3062 | 5.9 | 243.1 | 2965 | 0.97 | C–H stretch |
| | ν_{16} | 2361 | 5.4 | 47.1 | 2255 | 0.95 | C≡N stretch |
| | ν_{17} | 1486 | 13.4 | 11.3 | 1431 | 0.96 | CH ₂ scissor |
| | ν_{18} | 1370 | 2.2 | 11.9 | 1339 | 0.98 | CH ₂ wag |
| | ν_{19} | 1276 | 0.1 | 5.6 | 1232 | 0.97 | CH ₂ twist |
| | ν_{20} | 1044 | 0.5 | 6.9 | 975 | 0.93 | C–CN stretch |
| | ν_{21} | 839 | 1.1 | 0.4 | 813 | 0.97 | CH ₂ rock |
| | ν_{22} | 607 | 3.8 | 0.9 | 604 | 1.00 | C–C–C bend |
| | ν_{23} | 361 | 0.4 | 0.8 | 358 | 0.99 | C–C≡N bend |
| | ν_{24} | 179 | 0.8 | 2.0 | 247 | 1.38 | C–C≡N bend |

^a IR intensities and Raman activities are calculated in km mol⁻¹ and Å⁴ amu⁻¹, respectively.

^b Experimental values taken from Ref. [7].

Table 7
Calculated vibrational frequencies^a of gauche succinonitrile (cm⁻¹) at the HF level of theory using the standard 6-311++G* basis set

| Symmetry | No. | Frequency | IR intensity | Raman activity | Expt ^b | $\nu_{\text{expt}}/\nu_{\text{calc}}$ | Assignment |
|----------|------------|-----------|--------------|----------------|-------------------|---------------------------------------|-------------------------|
| A | ν_1 | 3287 | 5.1 | 23.7 | 2985 | 0.91 | C–H stretch |
| | ν_2 | 3233 | 3.7 | 18.9 | 2965 | 0.92 | C–H stretch |
| | ν_3 | 2598 | 11.0 | 35.3 | 2254 | 0.87 | C≡N stretch |
| | ν_4 | 1609 | 4.7 | 4.6 | 1420 | 0.88 | CH ₂ scissor |
| | ν_5 | 1505 | 3.5 | 8.0 | 1322 | 0.88 | CH ₂ wag |
| | ν_6 | 1332 | 0.2 | 1.0 | 1200 | 0.90 | CH ₂ twist |
| | ν_7 | 1091 | 4.4 | 3.7 | 1026 | 0.94 | C–C stretch |
| | ν_8 | 1063 | 5.1 | 0.7 | 963 | 0.91 | CH ₂ rock |
| | ν_9 | 854 | 4.3 | 10.8 | 818 | 0.96 | C–CN stretch |
| | ν_{10} | 533 | 2.0 | 4.2 | 480 | 0.90 | C–C–C bend |
| | ν_{11} | 439 | 0.5 | 6.9 | 387 | 0.88 | C–C≡N bend |
| | ν_{12} | 254 | 13.8 | 2.8 | 230 | 0.91 | C–C≡N bend |
| | ν_{13} | 86 | 6.6 | 3.3 | – | – | Torsion |
| B | ν_{14} | 3277 | 3.1 | 92.3 | 2985 | 0.91 | C–H stretch |
| | ν_{15} | 3239 | 8.5 | 215.3 | 2965 | 0.92 | C–H stretch |
| | ν_{16} | 2599 | 7.9 | 107.9 | 2255 | 0.87 | C≡N stretch |
| | ν_{17} | 1610 | 11.9 | 10.2 | 1431 | 0.89 | CH ₂ scissor |
| | ν_{18} | 1501 | 8.2 | 2.6 | 1339 | 0.89 | CH ₂ wag |
| | ν_{19} | 1384 | 0.4 | 4.9 | 1232 | 0.89 | CH ₂ twist |
| | ν_{20} | 1141 | 0.8 | 5.9 | 975 | 0.85 | C–CN stretch |
| | ν_{21} | 891 | 3.6 | 1.0 | 813 | 0.91 | CH ₂ rock |
| | ν_{22} | 661 | 3.1 | 1.4 | 604 | 0.91 | C–C–C bend |
| | ν_{23} | 405 | 1.4 | 1.0 | 358 | 0.88 | C–C≡N bend |
| | ν_{24} | 197 | 0.9 | 2.0 | 247 | 1.25 | C–C≡N bend |

^a IR intensities and Raman activities are calculated in km mol⁻¹ and Å⁴ amu⁻¹, respectively.

^b Experimental values taken from Ref. [7].

Table 8
Calculated vibrational frequencies^a of gauche succinonitrile (cm⁻¹) at the MP2 level of theory using the standard 6-311++G* basis set

| Symmetry | No. | Frequency | IR intensity | Raman activity | Expt ^b | $\nu_{\text{expt}}/\nu_{\text{calc}}$ | Assignment |
|----------|------------|-----------|--------------|----------------|-------------------|---------------------------------------|-------------------------|
| A | ν_1 | 3165 | 0.5 | 30.0 | 2985 | 0.94 | C–H stretch |
| | ν_2 | 3104 | 1.3 | 15.3 | 2965 | 0.96 | C–H stretch |
| | ν_3 | 2192 | 1.5 | 72.1 | 2254 | 1.03 | C≡N stretch |
| | ν_4 | 1509 | 8.1 | 5.2 | 1420 | 0.94 | CH ₂ scissor |
| | ν_5 | 1388 | 2.8 | 2.6 | 1322 | 0.95 | CH ₂ wag |
| | ν_6 | 1235 | 0.3 | 1.2 | 1200 | 0.97 | CH ₂ twist |
| | ν_7 | 1031 | 2.5 | 2.1 | 1026 | 1.00 | C–C stretch |
| | ν_8 | 996 | 2.1 | 0.9 | 963 | 0.97 | CH ₂ rock |
| | ν_9 | 826 | 1.0 | 9.4 | 818 | 0.99 | C–CN stretch |
| | ν_{10} | 467 | 1.0 | 2.3 | 480 | 1.03 | C–C–C bend |
| | ν_{11} | 380 | 0.0 | 4.2 | 387 | 1.02 | C–C≡N bend |
| | ν_{12} | 220 | 8.1 | 2.6 | 230 | 1.05 | C–C≡N bend |
| | ν_{13} | 80 | 4.4 | 3.3 | – | – | Torsion |
| B | ν_{14} | 3156 | 0.5 | 88.0 | 2985 | 0.95 | C–H stretch |
| | ν_{15} | 3104 | 4.2 | 230.4 | 2965 | 0.96 | C–H stretch |
| | ν_{16} | 2195 | 0.8 | 26.2 | 2255 | 1.03 | C≡N stretch |
| | ν_{17} | 1509 | 14.5 | 10.2 | 1431 | 0.95 | CH ₂ scissor |
| | ν_{18} | 1383 | 1.4 | 8.2 | 1339 | 0.97 | CH ₂ wag |
| | ν_{19} | 1278 | 0.5 | 5.6 | 1232 | 0.96 | CH ₂ twist |
| | ν_{20} | 1071 | 0.1 | 5.7 | 975 | 0.91 | C–CN stretch |
| | ν_{21} | 839 | 0.9 | 0.4 | 813 | 0.97 | CH ₂ rock |
| | ν_{22} | 601 | 4.4 | 0.7 | 604 | 1.00 | C–C–C bend |
| | ν_{23} | 335 | 0.1 | 0.8 | 358 | 1.07 | C–C≡N bend |
| | ν_{24} | 175 | 0.9 | 1.7 | 247 | 1.41 | C–C≡N bend |

^a IR intensities and Raman activities are calculated in km mol⁻¹ and Å⁴ amu⁻¹, respectively.

^b Experimental values taken from Ref. [7].

The calculated frequencies are usually higher than their experimental counterparts and the difference can be accounted for by including scale factor for each level of theory. There are different ways of finding scaling factor but this has not been considered in this paper. However, the ratios of the experimental and calculated vibrational frequencies were computed and presented in Tables 3–8. These ratios reflect the highly level of conformity between the harmonic frequencies obtained from all the three levels of calculation and the observed fundamental frequencies. The vibrational infrared and Raman spectra were calculated as described previously [19,20]. The frequencies ν_j , the scattering activities S_j , and the depolarization ratios ρ_j obtained from B3LYP/6–311++G*, HF/6–311++G* and MP2/6–311++G* calculations were used to calculate infrared and Raman spectra at all the three levels of theory, respectively. The calculated vibrational Raman and infrared spectra are shown in Figs. 2–7.

4. Summary and conclusion

Ab initio and DFT theoretical studies were performed to obtain the molecular structures of *trans* and *gauche* rotational isomers of succinonitrile. The molecular geometries were optimized at the B3LYP/6–311++G*, HF/6–311++G* and MP2/6–311++G* levels of theory. The potential energy surfaces were obtained for the internal rotation about the C–C single bond at all the three levels of theory. The normal modes and corresponding vibrational assignment of succinonitrile were theoretically examined using Gaussian 03 package. A complete assignment of the fundamental vibrational modes is proposed based on the GaussView visualization program and experimental results. Theoretical infrared and Raman spectra are reported. Symmetry of the molecule, Infrared and Raman intensities were helpful in making the assignments of the fundamental vibrational modes.

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