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Density functional study and the vibrational spectra of 4-chloro-5-fluoro-1,2-phenylenediamine

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Abstract

The solid phase FTIR and FT-Raman spectra of 4-chloro-5-fluoro-1,2-phenylenediamine ($C_6H_6ClFN_2$) have been recorded in the region 4000–400 and 3500–100 cm^{-1}, respectively. The spectra were interpreted with the aid of normal coordinate analysis following a full structure optimization and force field calculations based on the density functional theory (DFT) using the standard B3LYP/6-31G* method and basis set combination. A close agreement was achieved between the observed and calculated frequencies by refinement of the scale factors.
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1. Introduction

Aromatic amines are very important in biological as well as in materials science [1,2]. Particularly, aniline was studied because of its technological application in a vast amount of industrial processes [3,4]. In fact, it was used as a precursor for the synthesis of dye and sensitizer molecules and also for the synthesis of molecules having potential large non linear optical responses [5,6].

The inclusion of a substituent group in aromatic amines leads to the variation of charge distribution in molecules, and consequently this greatly affects the structural, electronic and vibrational parameters. The methyl and amino groups are generally referred as electron donating substituents in aromatic ring systems [7]. The CH_3 interacts with nearby π-systems via hyper conjugation, while the NH_2 share its lone pair of electrons with the p-electrons in a ring. Both mechanisms imply electronic delocalization and are taken into account by the molecular orbital approach [8,9]. In addition to the amino groups, the fluorine and chlorine substituents present in the title compound at the fourth and fifth positions of the ring are highly electronegative and hence

they withdraw the electrons from the ring which results into the change in ionization potential, electronic affinity and excitation energies of the system.

In order to understand the vibrational properties and structural characteristics of 4-chloro-5-fluoro-1,2-phenylenediamine ($C_6H_6ClFN_2$), the density functional theory (DFT) calculations with B3LYP/6-31G* basis set was carried out and the observed bands are assigned based on the results of normal coordinate analysis.

2. Experimental

The fine polycrystalline sample of 4-chloro-5-fluoro-1,2-phenylenediamine was kindly provided by the Lancaster chemical company (UK) and used as such for the spectral measurements. The room temperature fourier transform infrared spectrum of the title compound was measured with KBr pellet technique in the 4000–400 cm^{-1} region at a resolution of 1 cm^{-1} using BRUKER IFS 66 V FTIR spectrometer equipped with a cooled MCT detector for the mid-IR range. Boxcar apodization was used for the 250 averaged interferograms collected for the sample and background.

The FT-Raman spectrum was recorded on a BRUCKER IFS-66 V model interferometer equipped with an FRA-106 FT-Raman accessory. The spectrum was recorded in the

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3500–100 cm^{-1} stokes region using 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within ±1 cm^{-1}.

3. Computational details

Quantum chemical density functional calculations were carried out with the 1998 version of the Gaussian suite of program [10] using the Becke3-Lee-Yang-Parr (B3LYP) functionals [11,12] supplemented with the standard 6-31G* basis set (referred to as DFT calculations). The normal grid (50, 194) was used for numerical integration. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming C$_s$ point group symmetry. The multiple scaling of the force constants was performed by the SQM method [13,14], with selective scaling in the natural internal coordinate representation [13,15] using transferable scale factors available in the literature [16]. The transformation of force field from Cartesian to internal coordinate, the scaling, the subsequent normal coordinate analysis, calculation of potential energy distribution (PED) and IR and Raman intensities were done on a PC with the version V7.0-G77 of the Molvib program written by Sundius [17,18]. To achieve a close agreement between the observed and calculated frequencies, the least square fit refinement algorithm was used. The force field obtained this way was then used to recalculate the normal modes, PED's and the corresponding theoretically expected IR and Raman intensities to predict the full IR and Raman spectra. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHH) of 10 cm^{-1}.

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (S_i) calculated by the Gaussian-98 program and adjusted during the scaling procedure with Molvib were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [19,20]

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\nu_i/kT)]}$$

where ν_0 is the exciting frequency (in cm^{-1} units), ν_i is the vibrational wave number of the ith normal mode, hc and k are the universal constants, and f is the suitably chosen common scaling factor for all the peak intensities.

4. Results and discussion

4.1. Structural properties

The confirmation of 4-chloro-5-fluoro-1,2-phenylenediamine is related to different rotamers with respect to
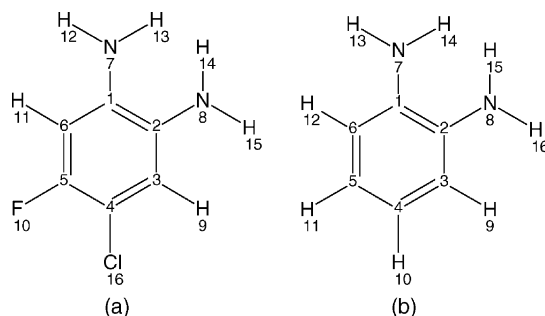

Fig. 1. (a) Molecular structure of 4-chloro-5-fluoro-1,2-phenylenediamine along with numbering of atoms. (b) Molecular structure of o-phenylenediamine along with numbering of atoms.

torsion around C-NH$_2$ bonds. The most optimized geometry of the title compound is shown in Fig. 1(a). The optimized values obtained for bond lengths and bond angles are reported in Table 1. The theoretical results show that the aromatic ring of the title compound is distorted from the regular hexagon due to the steric and electronic effects of electron donating NH$_2$ groups. The global minimum energy obtained by DFT structure optimization (Fig. 1(a)) is found to be −901.7804 Hartrees. In the vibrational studies of phenylenediamine (PDA) isomers, Rosina Noto et al. [21] observed the global minimum energy of o-PDA, m-PDA, p-PDA conformers as −340.7811, −340.7829, −340.7770 Hartrees, respectively. When compared to these energies, the energy obtained for 4-chloro-5-fluoro-1,2-phenylenediamine whose geometry is close to o-PDA as given in Fig. 1(b) is found to be less. The difference in energy between these two systems is found to be $\Delta E = -560.9993$ Hartrees. The drift observed in the energy calculations between o-PDA and the title compound is due to the halogen atoms (F and Cl) substitutions at the fourth and fifth positions of the o-PDA ring. Subsequently, all vibrational frequencies have been calculated and it is found to be positive for the lowest energy configuration of the title compound shown in Fig. 1(a).

Table 1
Optimized geometrical parameters of 4-chloro-5-fluoro-1,2-phenylenediamine obtained by B3LYP/6-31G* density functional calculations

| Bond length	Value (Å)	Bond angles	Value (Å)
C1–C2	1.4161	C1–C2–C3	119.42
C2–C3	1.3945	C2–C3–C4	120.81
C3–C4	1.3977	C3–C4–C5	119.29
C4–C5	1.3898	C4–C5–C6	120.79
C5–C6	1.3915	C2–C1–N7	117.67
C1–N7	1.406	C2–C3–H9	120.094
C2–N8	1.4093	C4–C3–F10	120.816
C3–H9	1.086	C1–C6–H11	121.1185
C5–F10	1.3461	C1–N7–H12	113.38
C6–H11	1.086	C1–N7–H13	112.113
N7–H12	1.0141	C2–N8–H14	112.044
N7–H13	1.0174	C2–N8–H15	113.334
N8–H14	1.0173	C3–C4–Cl14	120.516
N8–H15	1.014		
C4–Cl16	1.7503		
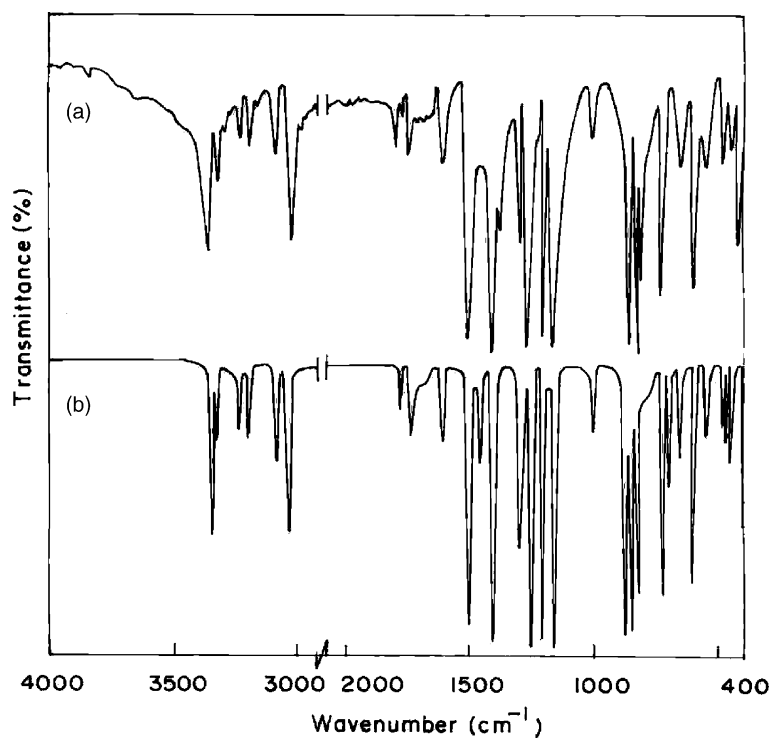
Fig. 2. FTIR spectra of 4-chloro-5-fluoro-1,2-phenylenediamine (a) observed (b) calculated.

4.2. Vibrational force constants

The output files of the quantum chemical calculations contain the force constant matrix in Cartesian coordinates and in hartrees/bohr^2 units. These force constants were transformed into internal coordinates using the usual $10^2 \, \mathrm{Nm}^{-1}$, $10^{-8} \, \mathrm{N}$ and $10^{-18} \, \mathrm{Nm}$ units for stretching–stretching, stretching–deformation and deformation–deformation ele-
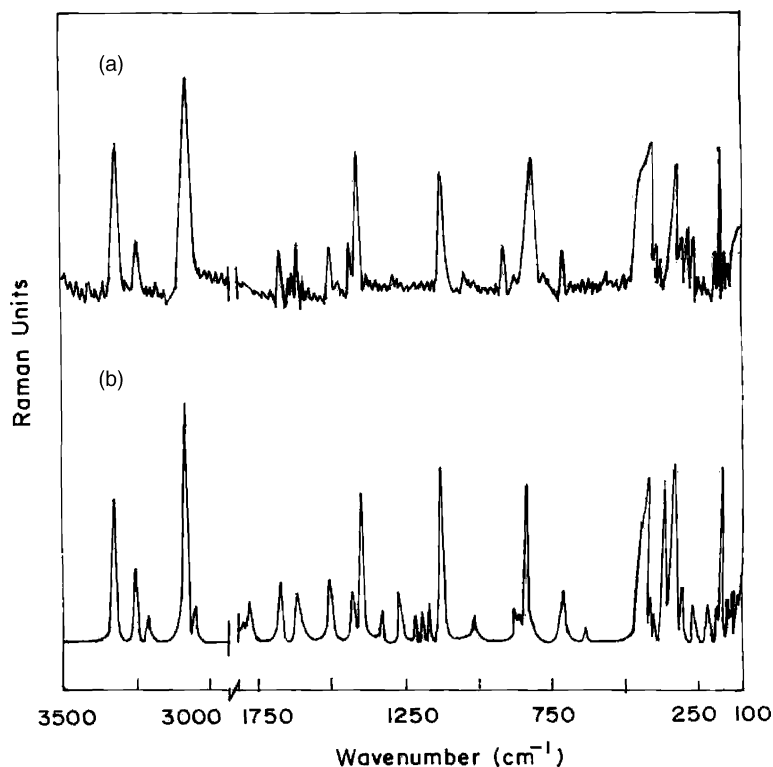

Fig. 3. FT-Raman Spectra of 4-chloro-5-fluoro-1,2-phenylenediamine (a) observed (b) calculated.

Table 2
Diagonal force constants, scale factors and internal coordinates of 4-chloro-5-fluoro-1,2-phenylenediamine

Internal coordinates[a]	Diagonal force constants	Optimized scale factors
$R39$	5.101	0.9051
$R611$	5.111	0.9051
$R17$	4.972	0.7984
$R28$	4.980	0.7984
$R12$	6.435	0.9551
$R23$	6.944	0.9551
$R34$	6.615	0.9551
$R45$	6.983	0.9551
$R56$	6.821	0.9551
$R16$	6.822	0.9551
$R416$	3.334	0.9017
$R510$	5.960	0.8952
$R712$	6.087	0.8537
$R713$	5.908	0.8537
$R814$	5.906	0.8537
$R815$	6.089	0.8537
$\Phi493-\Phi293$	0.529	0.9916
$\Phi5116-\Phi1116$	0.508	0.9916
$\Phi271-\Phi671$	1.006	0.9578
$\Phi382-\Phi182$	0.971	0.9578
$2\Phi12713-\Phi1317-\Phi1217$	0.653	1.0414
$2\Phi14815-\Phi1528-\Phi1428$	0.649	1.0414
$\Phi1712$	0.727	1.0175
$\Phi1713$	0.734	1.0175
$\Phi2814$	0.736	1.0175
$\Phi2815$	0.714	1.0175
$\Phi5416-\Phi3416$	0.604	0.6893
$\Phi6510-\Phi4510$	0.706	0.7057
$\theta9324$	0.402	1.0000
$\theta11615$	0.389	1.0000
$\theta7162$	0.884	1.0000
$\theta8213$	0.725	1.0000
$\theta1643$	0.451	0.8999
$\theta10564$	0.727	1.1549
$\Phi612-\Phi123+\Phi234-\Phi345-\Phi456-\Phi561$	1.639	1.2387
$2\Phi612-\Phi123-\Phi234+2\Phi345-\Phi456-\Phi561$	1.606	1.2387
$\Phi123-\Phi234+\Phi456-\Phi561$	1.768	1.2387
$\tau1234-\tau2345+\tau3456-\tau4561+\tau5612-\tau6123$	0.388	1.0000
$\tau1234-\tau3456+\tau4561-\tau6123$	0.360	1.0000
$-\tau1234-2\tau2345+\tau3456-\tau4561+2\tau5612-\tau6123$	0.389	1.0000
$\tau1428+\tau1528$	0.321	0.9870
$\tau1217+\tau1317$	0.290	0.9870

[a] R: change in bond lengths, Φ: change in valance angles, θ: change in dihedral angles, τ: change in torsional angles, for numbering of atoms see Fig. 1(a).

ments, respectively. Internal coordinates of the rings were chosen according to Pulay's recommendation [13]. The diagonal force constants and the optimised scale factors together with the definition of the internal coordinates are listed in Table 2. These results are in good agreement with the changes in the geometrical parameters.

4.3. Analysis of vibrational spectra

The title compound, 4-chloro-5-fluoro-1,2-phenylenediamine has C_s symmetry and its 42 normal modes are distributed among the symmetry species as

$$\Gamma_{\text{vib}} = 29A'\{\text{IR}(x, y), R(p)\} + 13A''\{\text{IR}(z), R(\text{d}p)\}$$

i.e., all the vibrations are active both in infrared absorption and Raman scattering. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A'') to depolarized band (if measured in liquid or solution state). The observed and calculated infrared and Raman spectra of the title compound are shown in Figs. 2 and 3 respectively. The assignments of the normal modes of vibrations of the investigated molecule along with the observed fundamentals, unscaled frequencies obtained by B3LYP/6-31G* calculations and scaled frequencies,

Table 3
Detailed assignment of fundamental vibrations of 4-chloro-5-fluoro-1,2-phenylenediamine by normal mode analysis based on SQM force field calculations.

Symmetry species	Observed frequency[a]		Calculated using B3LYP/6-31G*force field				Characterisation of normal modes with PED%[b]
	Infrared	Raman	Frequency (cm⁻¹)		IR intensity	Raman activity	
			Unscaled	Scaled			
A''	3358ms	3326m	3338	3342	1.343	98.327	νNH(100)
	3338m	–	3336	3336	21.506	34.238	νNH(100)
	3248w	3250w	3236	3243	10.460	265.616	νNH(100)
		–	3233	3209	7.500	83.528	νNH(100)
		3070ms	3059	3089	2.958	141.247	νCH(99)
	3045m	–	3055	3051	5.765	30.569	νCH(99)
	3200w	–	1785	1786	27.624	12.581	βHNH(69), βCNH(30)
	3090w	–	1764	1765	76.091	16.484	βHNH(65), βCNH(29)
	1666sh	1656w	1660	1661	4.968	41.145	νCC(64)
	1624w	1620w	1646	1627	3.861	10.554	νCC(70)
	1513vs	1500w	1528	1516	212.328	2.197	νCC(43), βCH(39)
	–	1453w	1468	1459	15.347	0.482	νCC(41), βCNH(33)
	1424vs	1427m	1395	1411	5.977	6.525	νCC(75), βCNH(17)
	1300m	–	1313	1313	20.952	1.161	βCNH(24), βCH(23), νCC(19)
	1271vs	–	1267	1269	16.577	17.478	νCC(49), νCN(17)
	1242sh	–	1230	1239	37.843	1.631	βCH(31), νCN(19), βRing(18)
	1220vs	–	1203	1216	22.595	7.041	βCNH(46), νCC(46)
	1177vs	–	1169	1169	52.565	1.456	βCH(50), νCC(18)
	–	1163m	1147	1165	30.618	0.603	βRing(37), νCC(24)
	1018w	–	1011	1014	24.380	1.909	βRing(24), νCN(19), νCF(17), νCCl(17)
	865vs	–	888	867	286.881	13.097	βCNH(45), βHNH(15)
A''	853vs	915w	857	858	153.930	3.173	γCH(57)
A''	821s	–	822	822	33.633	4.696	γCH(57), τRing(15)
A''	–	818m	810	809	70.135	5.726	γCH(42), βCNH(22)
	751sh	–	768	758	152.616	7.235	νCN(42), νCC(19)
	734s	–	736	738	53.997	13.618	βRing(35), νCC(17)
A''	–	704w	710	706	40.573	3.121	τRing(54), γCN(34)
A''	652w	–	663	659	20.935	1.431	τRing(43), γCF(27), γCCl(17)
	601s	–	614	609	56.942	0.804	νCN(31), βRing(28), νCCl(17)
	558w	–	559	552	2.982	2.045	βCF(38), βCN(36)
A''	475w	–	471	481	5.238	1.644	τNH₂(83)
	–	465sh	456	470	3.178	9.521	βRing(35)
A''	456w	–	440	462	5.014	1.119	τRing(55), γCN(22)
A''	411m	–	403	401	9.221	1.000	γCN(52), γCCl(19), γCF(18)
	–	394m	383	388	0.412	5.521	βRing(44), νCCl(21), βCN(17)
A''	–	319m	296	304	0.044	1.109	γCN(40), βCF(30)
A''	–	301w	292	289	1.283	0.637	τRing(47)
	–	267w	271	268	0.392	0.766	βCN(84)
A''	–	224w	219	214	21.538	1.922	τNH₂(84)
	–	186w	197	185	0.122	1.381	βCCl(82)
A''	–	169m	171	179	5.415	0.359	τRing(29), τNH₂(23), γCN(15)
A''	–	112sh	107	113	0.179	0.735	τRing(84)

[a] s: strong; vs: very strong; m: medium; w: weak; sh: shoulder.
[b] ν: stretching; β: in-plane deformation; γ: out-of-plane deformation; τ: torsion.

as well as the PED descriptions are reported in Table 3. Expressed in root mean square (RMS) values

$$\text{RMS} = \sqrt{\frac{1}{(n-1)}\sum_i^n (\nu_i^{\text{calcu}} - \nu_i^{\text{exp}})^2}$$

deviations are found to be $13.2\,\text{cm}^{-1}$ between the unscaled and experimental frequencies for all modes. This is quite

obvious, since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from the observed frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, a multiple scale factors are applied in the normal coordinate analysis and the subsequent least

square fit refinement, results into the very close agreement between the observed fundamentals and the scaled frequencies (Table 3). Refinement of the scaling factor applied in this study achieved a weighted mean deviation of $5.76\,cm^{-1}$ between the experimental and SQM frequencies.

The asymmetric and symmetric NH_2 stretching vibrations arising from the amino groups of the title compound are well found within the characteristic region. The strong infrared bands observed at 1220 and $1300\,cm^{-1}$ are assigned to CNH in-plane bending vibration in agreement with the high PED contribution. The bands at 224 and $475\,cm^{-1}$ are assigned to NH_2 torsion vibrations.

5. Conclusion

Based on the SQM force field obtained by DFT calculations at B3LYP/6-31G* level, a complete vibrational analysis of 4-chloro-5-fluoro-1,2-phenylenediamine was performed.

The chlorine and fluorine substitutions in the phenylenediamine(*o*-PDA) ring produced a remarkable effect on the geometric and spectroscopic properties of the title compound. The $-I > +M$ effect of the chlorine and fluorine acted not only on the close environment of the place of the substitution but also on other parts of the ring through π-electron system. As a result of the halogen atoms substituents in the phenylenediamine ring, remarkable changes were observed in the ring breathing modes, in-plane bending modes and out-of-plane bending modes of the title compound.

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