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Synthesis, structure, photo-responsive properties of 4-(2-fluorobenzylideneamino) antipyrine: A combined experimental and theoretical study

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HIGHLIGHTS

- The title compound was synthesized in one step by an amine-anhydride reaction.
- ► The structural characteristic is revealed by an X-ray diffraction technique.
- The vibrational spectra have been precisely ascribed to the molecular structure.
- The theoretical first-order hyperpolarizabilitie is nearly fortyfive times magnitude of urea.
- The UV-vis spectrum is revealed by the TD-DFT calculation and FMO analysis.

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ABSTRACT

In this work, 4-(2-fluorobenzylideneamino)antipyrine (FBIAAP) was synthesized and characterized by elemental analysis, XRD, FT-IR, FT-Raman and UV–Vis techniques as well as density functional calculations. The studied molecule adopts a *trans* configuration about the imine C=N bond, and adjacent molecules are linked through two kinds of weak hydrogen bonds to form supramolecular layered structures along the *ab* plane. Vibrational spectral analyses show that the benzene moiety directly attached to the central pyrazoline shows good vibrational isolation from the other moiety of pyrazole-imino-benzene presenting good vibrational resonances. UV–vis absorption bands mainly belong to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ according to the electron transfer orbital assignments for the electron absorption spectrum of FBIAAP. The first-order hyperpolarizability of FBIAAP is 44.9 times that of urea theoretically. In addition, the thermodynamic properties were also obtained theoretically from the harmonic frequencies of the optimized structure.

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Introduction

Antipyrine and its derivatives have been widely used as pharmaceuticals due to broad bioactivities, such as antitumor [1-3], antimicrobial [4-6], antiviral [7,8], and analgesic [9] etc., and the antipyrine derivatives (APDs) have been accepted as a

important kind of biomodel compounds in the biological and medical fields for many years [10]. Recently, ADPs have exhibited many attractive functional properties, such as coordinate [11], antioxidant [12] antiputrefactive [13] and optical [14,15] characteristics, in chemical and material fields. As a result, APDs have been used widely as model compounds in biological, medial, material and chemical fields.

With the social needs of photo-responsive materials, such as bioelectrics [16,17], photovoltaics [18–20], photoluminescence

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[21,22], nonlinear optics [23–25], etc., the photo-responsive characteristics of substances have gradually become the focus of researchers.

Considering the above-mentioned and as an extension of our work [25–33], our group is interested in the continuous investigation on APDs. In this work, we report the synthesis, molecular and crystal structure of 4-(2-fluorobenzylideneamino)antipyrine (FBIAAP), together with photo-responsive properties revealed by vibrational spectra, UV-vis electron absorption and nonlinear optics. The results are helpful to promote the further application for the studied compound by presenting the relatively systematical characteristics in this work.

Experimental and theoretical methods

Experimental

General

Elemental analysis for carbon, hydrogen and nitrogen were performed by a Perkin-Elmer 240C elemental instrument. The melting point was determined on a Yanaco MP-500 melting point apparatus. Electronic absorption spectra in MeOH solution were measured on a Shimadzu UV3100 spectrophotometer. The FT-IR spectrum of the solid compound was recorded in the region $4000-400 \text{ cm}^{-1}$ in evacuation mode with a scanning speed of $30 \text{ cm}^{-1} \min^{-1}$ and the spectral width of 2.0 cm^{-1} on Bruker IFS 66V spectrophotometer using KBr pellet. The FT-Raman spectrum of the solid samples was measured in the region $3500-100 \text{ cm}^{-1}$ with a spectral resolution of 1.0 cm^{-1} in the backscattering configuration on a RENISHAW inVia Raman microscope with a counter current detector and a 785 nm diode laser excitation.

Synthetic

All chemicals (reagent grade) were purchased from commercial sources and used without further purification. The title compound was synthesized according to the classical condensation of aldehydes with ammonia [34]. 4-Aminoantipyrine and 2-fluorobenzaldehyde with 1:1 stoichiometric ratio were dissolved in MeOH solvent with stirring for about 1 h at room temperature to give a clear yellow solution. After the solution had been kept in air at room temperature for several days, yellow prism-shaped crystals were formed. M.p. 189–190 °C. Yield: 94%. Calculated for C₁₈H₁₆FN₃O: C 69.87, H 5.22, N 13.59%. Analysis found: C 69.77, H 5.15, N 13.54%.

The synthetic route is shown in Scheme 1.

Crystallographic

A suitable single crystal was attached to a glass fiber. Data were collected at 295(2) K on a Bruker AXS SMART APEX area-detector diffractometer (MoKa radiation, $\lambda = 0.71073$ Å) with SMART [35] as the driving software; data integration was performed with SAINTPlus [36]and multiscan absorption correction applied using SADABS [37]. The structure was solved by direct method and difference Fourier and refined by least squares on F^2 with anisotropic displacement parameters for non-H atoms. H atoms attached to C

Table 1

Crystal data and refinement parameters for the studied compound.

Empirical formula	C ₁₈ H ₁₆ FN ₃ O
Formula weight	309.34
Crystal system	Orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
a (Å)	6.917 (2)
b (Å)	13.577 (3)
c (Å)	17.148 (4)
V (Å ³)	1610.4 (6)
Ζ	4
$D_c (Mg/m^3)$	1.276
μ mm ⁻¹)	0.09
Absorpt. Corr. T _{min} /T _{max}	0.980/0.983
Crystal shape/color	Prism, yellow
Crystal size (mm ³)	$0.23\times0.20\times0.19$
Measured reflections	17596
Independent reflections	1933
Observed reflections $(I > 2\sigma(I))$	1715
R _{int}	0.026
Ranges of h, k, l	-8/8, -17/17, -21/21
R, $wR[(I > 2\sigma(I))]$	0.039, 0.098
R, wR (all data)	0.044, 0.101
Goodness-of-fit on F^2	1.12
Reflections/parameters	1933/210
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (e/Å)	0.12, -0.17
CCDC	721322

Note. $R = \sum ||F_0| - |F_c|| / \sum |F_0|$, $wR = \left[\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2 \right]^{1/2} w = 1 / [\sigma^2(F_0^2) + (0.01897(F_o^2 + 2F_c^2))^2 + 0.02630(F_o^2 + 2F_c^2)]$.

were placed in calculated positions [aromatic C–H = 0.93 Å and with $U_{iso}(H) = 1.2$ $U_{eq}(C)$, methyl C–H = 0.96 Å and with $U_{iso}(H) = 1.5$ $U_{eq}(C)$]. All calculations to solve the structure, refine the model proposed, and obtain derived result were carried out with the computer programs SHELXS-97 and SHELX-L97 [38] and SHELXTL [39]. Full use of the CCDC package was also made for searching in the CSD database. The crystallographic data and experimental details for the structural analysis are listed in Table 1.

Theoretical

For meeting the requirements of both accuracy and computing economy, theoretical methods and basis sets should be considered. Density functional theory (DFT) has been proved to be extremely useful in treating electronic structures of molecules. The basis set 6-31G(d) was used as a very effective and economical level to study fairly large organic molecules [40]. Basing on the points, the density functional three-parameter hybrid model (DFT/B3LYP) at the 6-31G(d) basis set level was adopted to calculate the properties of the studied molecule in this work. All the calculations were performed using Gaussian 09W program package [41] with the default convergence criteria.

As the first step of our DFT calculations for the studied compound, the initial geometrical configuration directly taken from their X-ray crystallographic data was optimized without any constraints. Secondly, the harmonic vibrational frequencies were performed to convince the optimized structure in a stable ground state. Thirdly, the calculated IR and Raman spectra were assigned



Scheme 1. The schematic diagram of the studied compound.

to its molecular structure basing on the fundamental normal vibrational mode analysis with the aid of the GaussView program [42]. Fourthly, the statistical thermodynamic properties were theoretically predicted by the harmonic frequencies of the optimized structure. Fifthly, the molecular dipole moment, linear polarizability, and first hyperpolarizability properties of the molecular system were obtained from the molecular polarizabilities basing on the theoretical calculation. Finally, the UV–Vis spectra and electronic absorption properties were explained effectively and illustrated visually from the orientation of frontier molecular orbitals of FBIAAP.

Results and discussion

Crystal structure

The asymmetric unit of the compound consists of one independent molecule, which is shown in Fig. 1 by the displacement ellipsoid plot with atomic numbering. The atomic coordinates and thermal parameters of the molecule can be obtained from the supplementary material. All the bond lengths and angles in the compound were comparable to the corresponding values observed in other similar antipyrine Schiff bases cited above. The selected bond lengths and angles were listed in Table 2. In the compound, the C12=N3 bond length 1.280(2) Å is as expected for a normal imine double bond. The bond length between N3 and C8 [1.388(2)Å] is intermediate between classical C–N (1.43 Å) and C=N (1.28 Å) bond lengths because of the molecular conjugated effect. Basing on the reason, the dihedral angle of $14.5(2)^{\circ}$ formed by the substituted 2-fluorophenyl ring and the pyrazoline ring is less than the one of 55.8 (2)° formed by the No. 1 benzene ring and the pyrazoline ring. As expected, the molecule adopts a trans configuration about the imine C12=N3 bond.

An intramolecular weak hydrogen bonding of C12–H12···O1 (Table 3) can be found in the compound, which is helpful to strengthen the molecule stability (Fig. 2(a)). In the crystal structure of FBIAAP, adjacent molecules are linked through weak hydrogen bonding of C10–H10A An intramolecular weak hydrogen bonding of O1ⁱ (i: -1 + x, y, z) and C15–H15···O1ⁱⁱ (ii: 1 - x, -1/2 + y, 1/2 - z) (Table 3), forming supramolecular layered structures along the *ab* plane (Fig. 2(b)).

Optimized structure

The first task for the computational work is to determine the optimized geometry of the studied compound. In order to compare

with experimental results, the theoretically optimized parameters were also listed in Table 2.

As seen from Table 2, the calculated geometric parameters represent good approximations to the XRD data on the whole. Most of the optimized bond lengths are slightly longer than the experimental values agreeing within 0.032 (2) Å and the bond angles are slightly different from the experimental ones agreeing within 6.6 (2)°, because the molecular states are different in the experimental and theoretical processes. One isolated molecule is considered in gas phase in the theoretical calculation, while many packing molecules are treated in condensed phase in the experimental measurement.

The same structural characteristics in the theoretical results can be found as experimental ones, such as, the distances of C8–N3 and N3–C12 show single–double and double bonds characteristics, respectively, and the fairly large *pi*-electronic conjugated system has been formed between the pyrazoline and No. 3 benzene rings due to the imine bridging. As important geometrical characteristics for FBIAAP, the theoretical bond distances of C=O, C=N show absolute errors of -0.008 Å, +0.011 Å, respectively.

Although theoretical results are not exactly close to the experimental values of the compound, they are generally accepted that bond lengths and bond angles depend upon the method and the basis set used in the calculation, and they can be used as foundation to compute the molecular properties for the compound.

Vibrational spectra

It is well known that the harmonic frequencies obtained by DFT calculation are usually higher than the corresponding experimental quantities due to the facts of the electron correlation approximate treatment, anharmonicity effect and basis set deficiency etc.[43,44]. The theoretical frequencies corrected by empirical factors will match well with experimental ones. Basing on the point, the theoretical harmonic frequencies were scaled by the empirical factor of 0.9614 in this work referring to previous literatures [44,45].

The experimental FT-IR and FT-Raman spectra along with the corresponding theoretically simulated IR and Raman spectra are shown in Figs. 3 and 4, respectively, where the experimental and theoretical intensities are plotted against the vibrational wavenumbers. In Raman spectra, the Raman scattering activities calculated by Gaussian 09W program have been suitably converted to relative Raman intensities using the following relationship derived



Fig. 1. Molecular structure with atomic numbering for FBIAAP.

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20	letteu	2COMCUNC.	Dalameters	IOI LITE	Studieu	compound.

	Experimental	Theoretical		Experimental	Theoretical
Bond lengths/Å					
C1-C2	1.379 (3)	1.401	C9-C10	1.478 (3)	1.491
C2-C3	1.368 (3)	1.394	N2-C11	1.457 (2)	1.469
C3-C4	1.378 (4)	1.397	N3-C8	1.388 (2)	1.383
C4–C5	1.380 (3)	1.395	N3-C12	1.280 (2)	1.291
C5–C6	1.386 (3)	1.395	C12-C13	1.468 (3)	1.466
C1-C6	1.388 (3)	1.401	C13-C14	1.381 (3)	1.402
N1-C1	1.421 (2)	1.421	C14-C15	1.365 (3)	1.389
N1-N2	1.405 (2)	1.414	C15-C16	1.368 (4)	1.394
N1-C7	1.396 (2)	1.417	C16-C17	1.380 (4)	1.400
C7–C8	1.437 (2)	1.469	C17-C18	1.383 (3)	1.390
C8–C9	1.371 (2)	1.372	C13-C18	1.390 (3)	1.407
N2-C9	1.355 (2)	1.387	F1-C14	1.367 (3)	1.351
01–C7	1.234 (2)	1.226			
Bond angles/°					
C2-C1-C6	120.8 (2)	120.1	N3-C8-C9	123.1 (1)	123.1
C1-C2-C3	119.5 (2)	119.4	C7-C8-C9	107.7 (1)	107.7
C2-C3-C4	120.7 (2)	120.8	N2-C9-C8	110.3 (1)	110.9
C3-C4-C5	119.8 (2)	119.5	N2-C9-C10	121.6 (1)	121.6
C4-C5-C6	120.3 (2)	120.5	C8-C9-C10	128.1 (2)	127.5
C1-C6-C5	118.8 (2)	119.7	C8-N3-C12	119.3 (1)	120.6
N2-N1-C1	120.0 (1)	119.0	N3-C12-C13	120.4 (2)	120.6
N2-N1-C7	109.0 (1)	109.8	C12-C13-C14	120.6 (2)	120.3
C1-N1-C7	121.5 (1)	123.9	C12-C13-C18	122.8 (2)	122.7
N1-N2-C9	107.2 (1)	106.6	C14-C13-C18	116.6 (2)	117.0
N1-N2-C11	117.7 (1)	114.1	C13-C14-C15	123.9 (2)	122.9
C9-N2-C11	125.7 (1)	119.1	C14-C15-C16	118.3 (2)	118.8
N1-C1-C2	118.1 (2)	118.8	C15-C16-C17	120.4 (2)	120.1
N1-C1-C6	121.1 (2)	121.1	C16-C17-C18	120.1 (2)	120.1
01-C7-N1	123.3 (2)	124.4	C13-C18-C17	120.7 (2)	121.2
01-C7-C8	131.3 (2)	130.9	F1-C14-C13	118.2 (2)	118.9
N1-C7-C8	105.3 (1)	104.6	F1-C14-C15	117.9 (2)	118.2
N3-C8-C7	128.8 (1)	129.1			

Table 3			
Distances (Å) and angles (°) invol	ving hydrogen bondin	g of the studied co	mpound. ^a

C12-H12···O1 0.930 2.300 2.974 (2) 129.0 C10-H10A···O1 ⁱ 0.960 2.520 3.457 (3) 167.0	Hydrogen bonding	D-H	$H{\cdots}A$	$D{\cdots}A$	$D{-}H{\cdot}{\cdot}{\cdot}A$
C15-H15O1 ⁱⁱ 0.930 2.300 3.200 (3) 162.0	C12-H12···01	0.930	2.300	2.974 (2)	129.0
	C10-H10A···01 ⁱ	0.960	2.520	3.457 (3)	167.0
	C15-H15···01 ⁱⁱ	0.930	2.300	3.200 (3)	162.0

^a Symmetry codes: (i) -1 + x, y, z; (ii) 1 - x, -1/2 + y, 1/2 - z.

from the intensity theory of Raman scattering stated in previous references [46,47]:

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}S_{i}}{v_{i}\left[1 - \exp\left(\frac{-hcv_{i}}{kT}\right)\right]}$$
(1)

where v_0 is the exciting frequency (in cm⁻¹ units), v_i is the vibrational wavenumber of the *i*th normal mode, *h*, *c* and *k* are universal constants, and *f* is the suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra have been plotted using pure Lorentzian band shapes with a bandwidth of 10 cm⁻¹.

The present molecule has C_1 point group symmetry, 39 atoms and 111 normal vibrational modes. For comparative purpose, the observed experimental wavenumbers together with the corresponding theoretical frequencies were tabulated in Table 4, where the theoretical frequencies were given along with corresponding theoretical IR and Raman intensities as well as the proposed vibrational assignments for the optimized structure. Mode numbers are extracted from the output results of the B3LYP calculation. The selected vibrational modes were numbered from small to big frequency in Table 4. The proposed vibrational assignments were made on the basis of the relative intensities, magnitude of the frequencies and the normal coordinate analysis with the aid of the GaussView program [42].

As a whole, the theoretically scaled wavenumbers of the DFT calculation are close to the experimental data, and the DFT/6-31G(d) level can effectively predict the vibrational frequencies for the compound. Owing to the fact that the detailed spectral assignments have been given in the Table 4 and Figs. 3 and 4, we decided to discuss the characteristics or strong peaks for these spectral bands below.

As seen from the Table 4 and Fig. 3, the C=O stretching vibration is characterized by very strong peak appearing at 1653 cm^{-1} in the FT-IR spectra, while the same vibrational mode is shown at the theoretical wavenumber of 1702 cm^{-1} giving a positive deviation. The error is caused by the fact that the theoretically calculated C=O bond distance is shorter than experimental one, which indicate that the electrons of C=O bond have a great contribution to the pyrazole moiety leading to show shorter bond lengths than theoretical ones (Table 2), and the C=O stretching vibration is infected with intermolecular hydrogen bonding interactions in the crystal packing structure (Table 3).

The identification of pyrazoline ring vibrations is a difficult task since the mixing of vibrations in this region. However, with the help of theoretical calculations, the heterocyclic vibrations were identified and assigned in this work. The pyrazole puckering modes partly mixing adjacent phenyl ring are characterized by weak peaks observed at 415, 450, 750 cm⁻¹ and found at 407, 437, 722 cm⁻¹ in IR of FBIAAP. The wavenumber at 569(observed)/ 560(found) cm⁻¹ is assigned to the mixing angle bending of C7C8C9 and No. 3 phenyl ring. The wavenumber at 623 cm⁻¹ is ascribed to the mixing angle bending of C7N1N2 and No. 1 phenyl ring. The medium infrared peak appearing at 1305(observed)/ 1276(found) cm⁻¹ is designated to the mixing mode of C1–N1 and N8–N3 stretching vibrations. All the theoretically computed



(a) The trimolecular structure linked through intermolecular hydrogen bonding of C10-H10A...Olⁱ (i: -1+x, y, z) and C15-H15...Olⁱⁱ (ii: 1-x, -1/2+y, 1/2-z).



(b) The supramolecular layered structures, viewed along the a axis.

Fig. 2. Neighboring molecular structural diagrams of FBIAAP (the dashed lines indicate hydrogen bonds).

wavenumbers for pyrazole ring show very good agreements with the experimental results.

The phenyl puckering vibrations are found theoretically as weak peaks at 480 cm^{-1} for No. 3 ring and at 497 cm^{-1} for No. 1 ring, and observed at 483 and 503 cm⁻¹ respectively. The angle bending vibration appears in the band of 530–839 cm⁻¹, and the same theoretical mode band of 519–827 cm⁻¹ shows good agreements with the experimental results. The breathing vibrations of No. 1 phenyl ring can be exhibited by weak peaks at the 997(observed)/ 978(found) cm^{-1} in Raman spectrum and 1017(observed)/ 1006(found) cm^{-1} in IR spectrum. However, the 2-fluoro substituted No. 3 phenyl ring is sensitive to the substituent group, and exhibits hardly the breathing vibrations in IR and Raman spectra, which is different from the similar compounds cited above. The medium peak at 761(observed)/745(found) is assigned to the C-H out-of-plane wagging vibrations of phenyl rings in the IR spectra. The C-H out-of-plane and in-plane wagging for benzene rings are in the bands of 483-952 cm⁻¹ and 1019-1338 cm⁻¹, respectively. Apparently, the phenyl puckering and angle bending vibrations are described as mixed modes as there are partial contributions mainly from the C-H out-of-plane and in-plane wagging vibrations, respectively. The C=C stretching vibrations are displayed by medium peak at 1451 cm⁻¹, and by strong peaks at 1568, 1596, 1613 cm^{-1} in FT-Raman spectrum and in the band of 1560–1595 cm⁻¹ in FT-IR spectrum, which the corresponding theoretical results show excellent agreements with the experimental ones.

The imine C–H in-plane bending can be observed experimentally at 1361, 1381 cm⁻¹ and found theoretically at 1361, 1375 cm⁻¹ in IR spectra. The peak observed at 966 cm⁻¹ is ascribed to the C–H out-of-plane wagging of imine, and the corresponding theoretical wavenumber is at 985 cm⁻¹. The observed peaks at 878 cm⁻¹ in FT-IR and 876 cm⁻¹ in FT-Raman are assigned to the imine in-plane wagging. The C=N stretching modes are coupled with the adjacent C=C vibrations in the conjugated system linked through the Schiff base imine, which are displayed at the theoretical wavenumbers of 1578, 1596 and 1610 cm⁻¹.

The observed medium peaks at 1041 and 1131 cm^{-1} in FT-IR spectrum are designated to the CH₃ rocking vibrations. The theoretical values of 1031 and 1122 cm⁻¹ are in accordance with the ones. The methyl C–H in-plane wagging vibrations are found in the band of 1362–1421 cm⁻¹ and observed at 1361, 1412 and 1431 cm⁻¹. The wavenumbers found in the band of 1448–1485 cm⁻¹ and observed at 1453 and 1485 cm⁻¹ in the IR spectra are ascribed to the scissoring vibrations of CH₃. The peak observed at 2933 cm⁻¹ and the bands found in 2926–3055 cm⁻¹ are assigned to the methyl C–H stretching vibrations.

In low frequency region, these bands are mainly ascribed to the molecular skeleton wagging, rocking and torsion vibrations. In high frequency region, the band of 2926–3127 cm⁻¹ is assigned to the C–H stretching vibration of different moleties including the methyl, phenyl and imine groups. The stretching vibrations for the methyl and imine groups have been stated above. The band of 3063–3127 cm⁻¹ is corresponding to the phenyl C–H stretching vibrations theoretically.

In addition, the C=N bond exhibits hardly its own characteristic peak in IR spectra, but it is tightly relative to the strongest Raman scattering activities of the molecule. As seen in Table 4 and Fig. 4, the stronger Raman intensities of the compound are closely related to the molecular conjugative moiety linked through the Schiff base imine.

By the vibrational analyses, we can find that the pyrazole-imino-benzene moiety presents good vibrational resonances, while the No. 1 benzene ring shows good vibrational isolation from the imino-bridged moiety.

Thermodynamic properties

On the basis of vibrational analysis at B3LYP/6-31G(d) level for the compound, the standard statistical thermodynamic functions, viz., heat capacity at constant pressure $(C_{p,m}^{\Theta})$, entropy (S_{m}^{Θ}) , and enthalpy change $(\Delta H_{m}^{\Theta}(0 \rightarrow T))$ were obtained from the theoretically scaled frequencies of the optimized structure (the scaling factor is also 0.9614), and the corresponding values were listed in Table 5.

As seen from Table 5, we can find that all the values of $C_{p,m}^{\Theta}$, S_m^{Θ} and ΔH_m^{Θ} are increasing with temperature ranging from 200 to 600 K due to the fact that the vibrational intensities of molecule increase with the enhancement of temperature. The correlation equations between these thermodynamic properties and temperatures were fitted by quadratic, linear and quadratic formulas, respectively, and the corresponding correlation coefficients are all beyond 0.999. The corresponding fitting equations are as follows:

$$C_{nm}^{\Theta} = -13.2038 + 1.3897T - 6.5218 \times 10^{-4} T^2$$
⁽²⁾

$$S_m^{\Theta} = 307.65 + 1.0930T \tag{3}$$

$$\Delta H_m^\Theta = -6.4620 + 0.0822T + 4.3717 \times 10^{-4} T^2 \tag{4}$$





Fig. 4. Raman spectra of FBIAAP: (a) observed, (b) simulated.

All the thermodynamic data and equations may be used to further study on the compound, especially, they can be used to compute the other thermodynamic energies basing on relationships of thermodynamic functions and to estimate directions of chemical reactions basing on the second law of thermodynamics in thermochemical research field.

Nonlinear optical effects

It is an important and inexpensive way to evaluate the nonlinear optical (NLO) properties of materials by theoretical calculations. Nowadays, density functional theory has been extensively used as an effective method to investigate the organic NLO materials [48],

Table 4

Comparison of the observed and calculated vibrational spectra of FBIAAP.^a

Mode	Experimenta	rimental Theoretical			Approximate assignments	
	IR	Raman	Freq.	I _{IR}	I _{Raman}	
23	415		407	10.5	2.7	vR _{2.3}
24	450		437	28.0	1.2	vR_2
26	483		480	14.5	2.0	vR ₃
27	503		497	7.9	0.6	vR ₁
28	530		519	8.4	1.2	αR_1
30	569		560	35.6	2.7	$\alpha C7C8C9 + \alpha R_3$
32	595		601	12.7	2.1	αR _{1.3}
34	623		623	35.0	1.5	$\alpha R_1 + \alpha C7N1N2$
35	665		664	9.3	0.9	$\alpha R_1 + \tau R_2$
36	679		673	5.6	0.1	$vR_1 + \alpha N3C12C13$
37	696		686	24.9	0.2	$vR_1 + \gamma CH \text{ of } R_1$
39	750		722	12.1	0.3	$\gamma CH \text{ of } R_1 + \nu R_2$
40	761		745	78.5	0.3	γCH of R _{1.3}
42	800	800	790	11.5	5.9	α C8N3C12 + α R ₃
44	839		827	10.0	3.1	αR_3
46	878	876	856	6.5	10.7	βimine
48	909		912	11.7	0.3	υC7C8 + υC9N2 + ρCH ₃
53		997	978	0.1	5.0	θR_1
54	966		985	7.7	1.1	γCH of imine
55	1017		1006	11.2	1.7	$\theta R_1 + \upsilon N1N2$
58	1041	1034	1031	16.6	5.1	ρCH ₃
60	1068	1091	1063	23.6	6.2	β CH of R ₁ + ν C7N1
61	1093		1079	18.6	4.2	βCH of R _{1,3} + υC7N1
63	1131		1122	127.7	1.8	ρCH ₃
64		1151	1134	41.8	17.2	ρ CH ₃ + β CH of R ₃ + ν C7N1 + ν C8N3
70	1229	1231	1227	67.8	45.7	βCH of R ₃ + υC14F1
71	1277	1278	1261	67.6	35.3	βCH of R ₃
72	1305		1276	179.0	2.4	υC1N1 + υC8N3
76	1338	1313	1316	35.2	5.4	υ C7N1 + υ C9N2 + υ C8N3 + β CH of R ₁
77	1361		1362	24.3	7.7	β CH of CH ₃ + β CH of imine
78	1381		1375	119.6	0.3	βCH of imine
79	1412	1411	1398	75.8	12.4	υ C9C10 + β CH of CH ₃
80	1431		1421	15.3	4.0	β CH of CH ₃
81		1451	1444	16.5	21.9	$\upsilon C = C \text{ of } R_3 + \beta CH \text{ of } R_3$
84	1453		1454	22.0	1.5	δCH ₃
88	1485		1485	75.9	0.9	$\delta CH_3 + \beta CH \text{ of } R_1$
90	1560	1568	1578	41.9	98.9	υC8C9 + υN3C12 + υC=C of R _{1,3}
93	1574	1596	1600	96.7	41.9	υC8C9 + υN3C12 + υC=C of R ₃
94	1595	1613	1610	10.9	15.5	υ N3C12 + υ C=C of R ₃
95	1653		1702	228.9	2.3	υ C= 0
97	2933		2929	42.1	3.2	υCH of CH ₃
107	3060		3086	37.4	1.6	υ CH of R ₁

^a Mode numbers are extracted from the output result of the B3LYP calculation. Observed wavenumbers (IR and Raman) and vibrational frequencies are in cm⁻¹; theoretical vibrational frequencies (Freq.) are in cm⁻¹; the calculated IR intensities are in km.mol⁻¹; the calculated Raman scattering intensities (I_{Raman}) are in arbitrary units by Eq. (1). R, ring; subscripting numbers followed by R represent ring numbering modes shown in Scheme 1. α , angle bending; β , in-plane bending; γ , out-of-plane bending; ω , wagging; ν , puckering; θ , breathing; δ , scissoring; τ , torsion; ρ , rocking; ν , stretching.

Table 5

Thermodynamic properties of FBIAAP at different temperatures.

T (K)	$C^{\Theta}_{p,m}$	S_m^{Θ}	ΔH_m^{Θ}
200.00	240.77	520.17	27.91
250.00	291.90	579.37	41.22
298.15	341.27	635.01	56.47
350.00	392.66	693.77	75.51
400.00	439.00	749.27	96.32
450.00	481.38	803.46	119.34
500.00	519.65	856.20	144.39
550.00	553.98	907.36	171.24
600.00	584.73	956.91	199.72

Temperatures (*T*) are in K; standard heat capacities $(C_{p,m}^{\Theta})$ are in $J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; standard entropies (S_m^{Θ}) are in $J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; standard enthalpy changes (ΔH_m^{Θ}) are in $kJ \cdot \text{mol}^{-1}$.

and the calculations of the molecular dipole moment (μ), linear polarizability (α) and first hyperpolarizability (β) from the Gaussian output have been explained in detail previously [49,50].

In this work, the NLO related properties of the studied molecule were calculated at the B3LYP/6-31G(d) level using Gaussian 09W

Table 6

The calculated electric dipole moments (Debye), static polarizability components (a.u.) and first hyperpolarizability components (a.u.) of FBIAAP.

1.7033 -0.0979 386.37 228.61 106.74
-0.0979 386.37 228.61 106.74
386.37 228.61 106.74
228.61 106.74
106.74
2221.68
-263.30
-223.66
159.28
254.35
-22.03
-67.56
60.09

program package. The calculated electric dipole moments, linear polarizabilities and first hyperpolarizabilitis were listed in Table 6. And the values of the μ_0 , α_0 and β_0 of the investigated molecule

are 1.8136 Debye, 35.6134 Å³ and 1,6755 × 10⁻²⁹ cm⁵/esu, respectively, which are greater than those of urea (the μ_0 , α_0 and β_0 of urea are 1.3732 Debye, 3.8312 Å³ and 3.7289 × 10⁻³¹ cm⁵/esu calculated with the same method), especially, the β_0 of FBIAAP is 44.9 times that of urea theoretically, which is greater than those of reported compounds [29,48–51], therefore, the compound is a promising organic NLO material.

In quest of the NLO structural characteristics, the molecular orbital surfaces of the compound basing on the B3LYP/6-31G(d) calculation have been shown in Fig. 5. Natural population analysis is to invest on the frontier molecular orbitals (FMOs), which indicate that the FMOs are mainly composed of atomic *p*-electron orbitals, as shown by the surfaces of FMOs in Fig. 5. Obviously, the NLO properties of the compound are caused easily by the transferring effect of the *p*-electrons and inapparent FMO level gaps of the molecule.

UV-vis spectra

The UV–vis absorption spectrum of the studied compound was measured in MeOH solvent on a Shimadzu UV3100 spectrophotometer. Fig. 6 shows the experimental bands with fitted bands. There are four broad absorption bands exhibited at 331.9, 251.8, 233.7 and 204.8 nm seemingly. In facts, there are six fitted peaks as a minimum corresponding to the experimental spectral bands. As we know that a common absorption band in UV–vis spectra is associated to electronic transitions between the corresponding frontier molecular orbitals involved in the photoabsorption response of a molecule. When a molecule absorb or emit light from one energy state to another, the wavelength of the light is related to the energies of the two states by the Eq. (7).

$$E_{\text{final}} - E_{\text{initial}} = hc/\lambda \tag{5}$$

Where *h* is Planck's constant, *c* is the velocity of light and λ is the light wavelength.

A molecule can move from one electronic energy state to another by absorbing or emitting a photon of energy. If it absorbs a photon of energy, hc/λ , it moves from a lower to a higher energy state, and its energy increases by hc/λ .

Therefore, the photoabsorption equation is as follows:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{high}} - E_{\text{low}} = hc/\lambda \tag{6}$$

Actually, the time-dependent density functional theory (TD-DFT) has been successfully used to present the most promising scheme for evaluating the low-lying excited spectrum of conjugated molecules, and has been the subject of countless applications even allowing for bulk solvent effects [52,53]. So, in this work, the vertical electronic transition energies of the studied molecule are determined by means of a TD-B3LYP/6-31G(d) calculation, and the theoretical excitation wavelengths with oscillator strengths calcu-



Fig. 5. Surfaces of FMOs of FBIAAP.



Fig. 6. Experimental UV-vis spectrum with fitted bands as well as the theoretical excitation wavelengths with oscillator strengths of FBIAAP.

lated are also shown in Fig. 6. The higher oscillator strength bands including the mainly involved orbitals are listed in Table 7. Thus, the experimental bands of the investigated compound are further ascribed to the molecular electron transfer orbitals.

As seen from Table 7 and Fig. 6, an experimental band is generally consisted of several electron transitions for the bigger π -conjugated molecule, and the fitted bands except the band of 226.9 nm show excellent agreements with theoretical results. The oscillator strengths are higher if the moieties involved in the relatively adjacent orbitals are closer each other due to matching rule of orbitals symmetry.

Natural population analysis indicates that these FMOs are mainly composed of atomic *p* orbitals, so above electronic transitions are mainly derived from the contributions of bands $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. As seen from Fig. 5, the HOMO-1 and LUMO+1 orbitals are principally delocalized among the atoms of antipyrine moiety, while HOMO, LUMO and LUMO+5 are principally delocalized

Table 7UV-vis absorption spectral wavenumbers of FBIAAP.^a

Experimental Theoretical						
λ_E^A/nm	λ_E^F/nm	λ_T/nm	λ_T/eV	I_T	Main involved	orbitals (%)
331.9	341.5	343.48 322.86	3.610 3.840	0.6741 0.0951	81→82(92%) 79→82(64%)	80→82(31%)
	302.6	300.38 275.85	4.128 4.495	0.2354 0.0643	$80 \rightarrow 82(61\%)$ $81 \rightarrow 83(92\%)$	79→82(32%)
	260.2	262.07	4.731	0.1035	79→83(53%)	80→83(37%)
251.8	249.2	251.17	4.936	0.2167	80→83(58%)	79→83(36%)
		244.01	5.081	0.1299	76→82(38%)	81→85(38%)
		238.13	5.207	0.0270	81→85(49%)	76→82(36%)
		219.98	5.636	0.0237	80→85(77%)	
233.7	226.9	214.40	5.783	0.0634	79→84(47%)	75→82(29%)
		212.32	5.839	0.0337	77→83(65%)	
		211.71	5.856	0.0582	75→82(30%)	79→84(26%)
		204.07	6.076	0.0222	76→83(70%)	79→86(15%)
204.8	204.8	201.58	6.151	0.0375	81→87(64%)	

^a λ_E^A are the apparent maximum absorption wavelengths experimentally measured in methanol solvent; λ_E^F are the fitted absorption wavelengths for experimental bands. λ_T are the theoretical excitation energies considering solvent effects, I_T are the theoretical oscillator strengths considering solvent. Orbital numbers are extracted from the output result of the B3LYP calculation.

among the atoms of the biggest π -electron conjugated moiety linked by the imine bond. HOMO-5 and HOMO-6 are almost populated among the whole molecule. However, the LUMO+2 and HOMO-4 orbitals are only delocalized among the terminal No. 1 phenyl ring, and LUMO+3 is occupied by the the π -electrons of the terminal No. 3 benzene ring, and HOMO-2 gives vital distribution in the lone electron pairs of O1 and N3 atoms of the molecule. The electron transfers among the FMOs mentioned above lead to the photoabsorption characteristics of the compound. The first band of 331.9(observed)/343.48 (calculated) nm is related to the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), and the frontier molecular orbitals (FMOs) ranged from HOMO-6 to LUMO+5 are responsible for the other bands as seen in Table 7 in details.

Concluding remarks

The title compound has been synthesized by the condensation of 2-fluorobenzaldehyde and 4-aminoantipyrine in MeOH solution in one step. The compound was characterized by elemental analysis, FT-IR, FT-Raman, UV-vis absorption and X-ray single crystal diffraction techniques. Density functional theory calculations at B3LYP/6-31G(d) were performed to further study on the molecular structure, vibrational spectra, thermodynamic properties, NLO effects, and photoabsorption properties. The results show that the optimized geometries closely resemble the crystal structure and the theoretical vibrational frequencies agree with experimental data. The thermodynamic properties of $C_{p,m}^{\Theta}, S_m^{\Theta}, \Delta H_m^{\Theta}$ and these correlations with temperatures were obtained on the basis of theoretical vibrations of the optimized structure. Furthermore, the Raman spectrum analysis indicates the strongest Raman activities of the molecule are tightly relative to the molecular conjugative mojety linked through the Schiff base imine bond. The predicted electronic absorption spectra show good agreements with experimental values and molecular orbital coefficients analysis suggests that the electronic spectra are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions. NLO calculation indicates that the compound may be a promising optical material. We hope the results are of assistance in the quest of experimental and theoretical evidences for the title compound.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.07.117.

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