Supramolecular self-assembly of a new multi-conformational Schiff base through hydrogen bonds: Crystal structure, spectroscopic and theoretical investigation

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Abstract
The compound 4-(4-dimethylaminobenzylidene)aminoacetophenone was synthesized by condensation of 4-aminoacetophenone and 4-(dimethylamino) benzaldehyde in ethanol. This compound was characterized by CG-MS, infrared, Raman, UV−Vis, 1H and 13C NMR spectroscopy. The crystal structure was solved by single-crystal X-ray diffraction methods. The crystallographic data reveals that there are four independent molecules per asymmetric unit, that mainly differ from one another in rotations around the σ-bond of the azomethine N-atom with the phenyl ring. A detailed analysis of the intermolecular interactions in the four conformers of the compound has been performed using Hirshfeld surfaces and their associated two-dimensional fingerprint plots. The optimized geometrical parameters and calculated spectroscopic features obtained by quantum chemical calculations at B3LYP method show a very good agreement with the experimental data. Moreover, Natural Bond Orbital (NBO) analysis confirms the strong hyper-conjugative LP N(n1) → σ* (C(n9))−H interaction between the lone pair located in the N-atom of the azomethine group and the C−H bond. Liquid crystalline properties of the Schiff base were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and Powder X-ray diffraction techniques. Mesomorphic behaviour was observed in this unsymmetrical azomethine. Based on POM and DSC measurements, the hexatic Smectic B phase was detected.

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1. Introduction

Azomethines, generally known as Schiff bases, were first reported in 1864 by Hugo Schiff [1]. They can be obtained by condensation of primary amines with carbonyl compounds (aldehydes or ketones). The common structural feature of these compounds is the azomethine functional group with the general formula RHC = N-R, where R and R1 are alkyl, aryl, cycloalkyl or heterocyclic groups. Benzylidene anilines are an important class of Schiff bases which have been widely used in coordination, medicinal and biological chemistry and therefore experimental and theoretical studies on their molecular and crystal structure have been of considerable interest. Generally, Schiff bases exhibit a wide array of biological activities, including anti-fungal, anti-bacterial, anti-malarial, anti-proliferative, anti-inflammatory, anti-viral and anti-pyretic properties [2,3]. Furthermore, imine or azomethine group is present in various natural, naturally derived and non-natural compounds, and the −C=NH moiety has proved to be critical for biological activity [4−6]. Schiff bases are also of interest...
as corrosion inhibitors, catalyst carriers, thermo-stable materials, metal complexation agents and in biological systems they have a wide range of applications, such as dyes and pigments [7–11]. A large number of Schiff bases and their metal complexes have been investigated because their ability to bind reversibly to oxygen [12], catalytic activity in the hydrogenation of olefins [13,14], photo-chromic properties [15] and complexing ability towards some toxic metals [16].

Schiff bases containing 4-(dimethylamino)benzaldehyde, as precursor, are reported in literature [17–22] and some were used as ligand in coordination compounds [17] and as novel third order non-linear optical materials [18–21]. Recently, Fang et al. have reported the relationship between the molecular conformation and spectroscopic properties of unsymmetrical 4,4’-disubstituted benzyldiene anilines [23]. The Schiff bases are also used in the design of liquid crystals and prompted research in establishing structure property relationships, which are elemental in selecting molecular interactions on the crystal packing was evaluated using Hirshfeld surface analysis. The stability of the different observed conformations was estimated by means of the NBO analysis. The liquid crystalline properties were also evaluated.

2. Materials and methods

2.1. Synthesis of 4-(4-dimethylaminobenzylidene) aminocacetophenone

A solution of 4-(dimethylamino) benzaldehyde (1) and 4-aminoacetophenone (2) in absolute ethanol in molar ratio 1:1 was heated under reflux for 12 h. The reaction mixture was then cooled and the obtained yellow solid was isolated by filtration and washed with cold ethanol. The solid was re-crystallized from hot ethanol to give yellow crystals. The purity of the substance was checked by 1H and 13C NMR, IR and Raman spectroscopy and GC-Mass spectrometry. Single crystals of suitable quality for X-ray diffraction analysis were obtained by slow evaporation of the solution in methanol.

Scheme 1 shows the mentioned reaction.

2.1.1. 4-(4-dimethylaminobenzylidene)aminocacetophenone (3)

Yield: 70%; MP: 178 °C; 1H NMR (200 MHz, CDCl3): δ = 8.35 (s, H—C=N), 8.02 (d, H-8, H-9), 7.82 (d, H-24, H-26), 7.26 (d, H-7, H-10), 6.78 (d, H-28, H-29), 3.12 (s, N(CH3)2), 2.65 (s, COCH3). 13C NMR (50.3 MHz, CDCl3): δ = 197 (C-11), 161 (C-17), 157 (C-27), 153 (C-6), 134 (C-3), 130 (C-22, C-21, C-2, C-4), 129 (C-20), 121 (C-1, C-5), 112 (C-23, C-25), 40 (C-31,C-35), 27 (C-13) ppm (For atoms numbering scheme see Fig. 1). EIMS: m/z (rel. int.) [M+]+ 266 (90), 251 (75), 223 (40), 145 (15), 120 (5). Experimental spectra are presented in Supplementary Information.

2.2. Instrumentation

2.2.1. NMR spectra

The 1H (200 MHz) and 13C (50.3 MHz) NMR spectra were recorded on a Varian Unity 200 spectrometer. The sample was dissolved in CDCl3 in a 5 mm NMR tube. Chemical shifts (δ) for 1H and 13C NMR spectra are given in ppm relative to TMS (δ = 0 ppm) and are referenced by using the residual non-deuterated solvent signal. Coupling constants, J, are reported in Hz, being the singlet and doublet identified as s and d, respectively.

2.2.2. GC-MS spectrometry

The analysis was carried out using a Model Trace GC Ultra gas chromatography Thermo electron coupled to a Polaris Q mass spectrometer with an ion-trap analyzer using a DB-5 capillary column. Split-less injection (10 μL) was used for this study, the initial temperature of 60 °C was kept for 4 min, and then was increased at a rate of 15 °C/min to reach 200 °C. The final temperature was maintained for 6 min and the total run time was 13.8 min, using Helium as carrier gas. The mass spectrometer was operated in the electronic ionization scan mode (range, m/z: 40–450). Quantification of the peaks was based on peak area.

2.2.3. UV-visible spectroscopy

The spectra of the substance in dimethylformamide (DMF) and chloroform (10–5 M) were recorded on a Beckman/DU 7500 spectrophotometer in the spectral region of 200–800 nm using a quartz cell (10 mm optical path length).

2.2.4. Fluorescence spectra

Fluorescence measurements were recorded on a Perkin-Elmer LS-50B luminescence spectrometer (Beaconsfield, England) equipped with a quartz cell of 1 cm path length, a pulsed xenon lamp (half peak height < 10 m s, 60 Hz), an R928 photomultiplier tube. Both excitation and emission slits were 10 nm wide.

2.2.5. IR and Raman spectroscopy

The IR absorption spectra of the solid were recorded in KBr pellets, with a resolution of 2 cm−1 on a FTIR Perkin Elmer GX1 in the 4000 and 400 cm−1 range. The Raman spectrum of the solid was measured in the 3500–50 cm−1 interval with a Thermo-scientific DXR Raman microscope. The Raman dispersion data were collected using a diode-pump, solid state laser of 352 nm (at 5 cm−1 spectral resolution), a confocal aperture of 25 μm pinhole and 10 × objective. The sample was placed on gold-coated sample slide. To improve the signal to noise ratio, 30 spectral scans of 2 s each were accumulated during the measurements with the laser power maintained at 10 mW.

2.2.6. Thermal analysis

Thermo-gravimetric (TGA) and differential thermal analysis (DTA) measurements were performed with a Shimadzu DTG-60 thermo-balance in the temperature range of 25–800 °C at a heating rate of 5 °C/min under air flow.
2.2.7. Mesomorphic studies

Mesomorphic properties have been studied by means of variable temperature polarizing optical microscopy (POM), Differential Scanning Calorimetry (DSC) and room temperature powder X-ray diffraction (PXRD) techniques. POM measurements have been carried out between crossed polarizers using a Leitz DMRX microscope equipped with a Leitz 1350 hot-stage. DSC experiments have been performed either on a Shimadzu DSC-50 calorimeter or a Perkin Elmer Pyris DSC 6 calorimeter, with heating and cooling rates of 2 or 10 °C/min, respectively. PXRD measurements on powdered samples were performed on a Siemens D5000 apparatus using the Cu-Kα line (λ = 1.5418 Å) source radiation; the samples were contained on planar glass sample holders.

2.3. X-ray diffraction data

The measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated CuKα (λ = 1.5418 Å) radiation. X-ray diffraction intensities were collected (ω scans with θ and k-offsets), integrated and scaled with CrysAlisPro [29] suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro.

In a first attempt, it was intended to solve the structure in P-1 space group with a standard run of direct methods implemented in SHELXS of the SHELX suite of programs [30]. Though it provided an electron density map which could be interpreted in terms of the expected molecule, however the appearance of spurious peaks mainly at the centers of a honey comb-like structure make it difficult the interpretation of the map in terms of four molecules per asymmetric unit. It is well known that frequently direct methods works better by referring the cell to a non center-symmetric triclinic space group. In fact, a standard run in P1 cell revealed all eight molecules in the unit cell though still showing the honey-comb centering mentioned above. At variance with the P-1 run, now the map can be easily interpreted in terms of the molecules atomic constituents and the structural problem reduced to find the shift of the constellation of atoms to refer them to one inversion center of P-1 group, then eliminate one of the inversion related set of molecules and finally proceed with the refinement of the remaining ones in the correct center-symmetric space group. The above problems were easily overcome with the recently available SHELXT program (see Ref. [31] and references therein). The new development is a radical departure of standard structure determination procedures where normally the space group is determined first and the crystal structure afterward. Now, with the only prior knowledge (besides cell constants) of the Laue group and the atom species present in the solid:

1) The X-ray diffraction data set is expanded to the subgroup P1 of all space groups where the structure is solved from an initial trial constellation of peaks provided by Patterson superposition methods. This is followed by dual-space recycling to obtain optimal electron density and phases.
2) The phases are first subjected to a center-symmetric test and a measure of the phase error (σ0) is calculated. This should be small for a constellation of atoms that possess an inversion center.
3) The phases are then employed to determine both the correct space group and the translation necessary to refer the electron density to the proper unit cell origin.

4) The phases are then averaged in every possible space group compatible with the known Laue group and used to calculate improved maps.

5) The integrated electron density around the peaks of the maps is assigned to atomic species and thus the chemical formula is determined.

6) The correct space group and structure solution is selected among the trials on the basis of several figures of merit, including the standard agreement R1-factor, Rweak (average of calculated F2 for the 10% of unique reflections with the smallest observed normalized structure factors Eobs), and the phase error (Δ), all of which should be the smallest for the right choice.

Assuming the Laue group P-1 (C1) and the presence in the solid of O, N, and C atomic species, the structure now yielded easily to the above procedure producing a clear and complete electron density map (no spurious peaks) with an essentially correct interpretation of its maxima in terms of the expected non-H atoms except for the miss assignment of a nitrogen as a carbon atom, a minor problem that probably arises because the closeness in the number of atomic electrons for both elements.

The initial molecular model was refined by full-matrix least-squares procedure with SHELXL of the SHELX package [30]. Most H-atoms were found in a Fourier difference map phased on the heavier atoms. However, they were positions on stereo-chemical basis and refined with the riding model. The methyl H-atoms were refined as rigid groups allowed to rotate around their corresponding C-C and N-C bonds such as to maximize the sum of the observed residual electron density at their calculated positions. As a result all –CH3 groups converged to staggered conformations. Crystal data and structure refinement results are summarized in Table 1. Crystallographic structural data have been deposited at the Cambridge Crystallographic Data Center (CCDC). Any request to the Cambridge Crystallographic Data Center for this material should quote the full literature citation and the reference number CCDC 1411260.

2.4. Quantum chemical calculations

Theoretical calculations were performed using the Gaussian 03 program [32]. The employed methods are based on the gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [33] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [34]. Scans of the potential energy curves were carried out by the B3LYP/6-31G(d,p) approximation. Final optimizations and vibrational frequencies were computed employing the 6-311++G(d,p) basis set. The calculated vibrational properties correspond, in all cases, to potential energy minima with no imaginary values for the frequencies. The Potential Energy Distribution (PED) analysis has been calculated using the VEDA4 program [35,36]. Electronic transitions were calculated within the Time-Dependent Density Functional Theory (TD-DFT) [37] in gas phase and taking into account implicitly the solvent effect (DMF and CHCl3) at B3LYP/6-311+G(2d,p) approximation. The 1H and 13C NMR chemical shifts were calculated at the B3LYP/6-311+G(2d,p) level by the Gauge-including atomic orbital (GIAO) method [38] using the corresponding TMS shielding calculated at the same level of theory. The Natural Bond Orbital (NBO) analysis for the molecule was performed at B3LYP/6-311+G(d,p) approximation by means the NBO 3.1 program implemented in the Gaussian 03 package.

| Table 1 Crystal data and structure refinement results for the Schiff base 4-(4-dimethylaminobenzylidene)aminoacetophenone. |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| **Compound (3)**  | Empirical formula  | C17H18N2O2        | Molecular weight   | 266.33            |
|                   | Formula weight     | 266.33            |                   |                   |
|                   | Temperature        | 293(2) K          |                   |                   |
|                   | Wavelength         | 1.54184 Å         |                   |                   |
|                   | Crystal system     | Triclinic         |                   |                   |
|                   | Space group        | P-1               |                   |                   |
|                   | Unit cell dimensions | $a = 9.9357(4)$ Å| $b = 7.8347(4)$ Å| $c = 14.9145(9)$ Å| $\alpha = 76.996(4)$ Å| $\beta = 77.169(4)$ Å| $\gamma = 76.996(4)$ Å|
|                   | Volume             | 2896.2(2) Å$^3$   |                   |                   |
|                   | Z, density (calculated) | 8.1220 Mg/m$^3$  |                   |                   |
|                   | Absorption coefficient | 0.604 mm$^{-1}$  |                   |                   |
|                   | F(000)             | 1116              |                   |                   |
|                   | Crystal size       | 0.354 x 0.154 x 0.109 mm$^3$ |       |                   |
|                   | $\beta$-range for data collection | 3.38–71.0° |                   |                   |
|                   | Index ranges       | $-6 \leq h \leq 12$, $-20 \leq l \leq 20$, $-19 \leq k \leq 22$ |       |                   |
|                   | Reflections collected | 23254             |                   |                   |
|                   | Independent reflections | 11154             | ($R_{int} = 0.0290$) |                   |
|                   | Observed reflection | 7116              |                   |                   |
|                   | Completeness to $\tilde{I} = 71.00\%$ | 99.6%              |                   |                   |
|                   | Refinement method  | Full-matrix least-squares on F$^2$ |       |                   |
|                   | Data/restraints/parameters | 11154/0/733       |                   |                   |
|                   | Goodness-of-fit on F$^2$ | 1.019             |                   |                   |
|                   | Final R indices ($I$ > 2$\sigma$(I)) | R1 = 0.0557, wR2 = 0.1423 |                   |                   |
|                   | R indices (all data)$^*$ | R1 = 0.0889, wR2 = 0.1715 |                   |                   |
|                   | Largest diff. peak and hole | 0.220 and $-0.165$ eÅ$^{-3}$ |       |                   |

$^*$ $R_1 = \sum||F_o|| - \sum||F_c||/\sum||F_o||$, $wR_2 = \sum[w||F_o^2 - F_c^2||^2]/\sum[wF_c^2]^2$.$^{1/2}$.

2.5. Hirshfeld surface analysis

Hirshfeld surfaces and their associated 2D fingerprints for all conformers of the Schiff base were generated using CrystalExplorer3.1 program [39]. The $d_{norm}$ (normalized contact distance) surface and the breakdown of 2D fingerprint plots [40–42] are a novel visual simultaneously representation of all the intermolecular interactions, and they are unique for a given crystal structure and polymorph. Fingerprints provide numerous applications to a wide variety of molecular crystals and intermolecular interactions, including polymorphs systems, as well as crystals with more than one molecule in the asymmetric unit (Z > 1). Distances from points on the surface to a nucleus (atom) inside ($d_i$) and outside ($d_o$) the mean surface are determined by the differing van der Waals (vdW) radii of atoms, whereby the contact distances $d_c$ and $d_o$ can be normalized ($d_{norm}$). Therefore, intermolecular interactions (short, moderate, long) in the crystal structure resulting from hydrogen bond donors/acceptors can be visually represented by Hirshfeld surfaces. The 3D $d_{norm}$ surfaces are mapped over a fixed color scale of –0.08 au (red) to 0.6 au (blue). The 2D fingerprint plots are displayed by using the standard 0.57–2.7 Å view and including reciprocal contacts, with the $d_c$ and $d_o$ distance scales showed on the graph axes.

3. Results and discussion

3.1. Crystallographic structural results

Crystal data and structure refinement results are summarized in Table 1. The compound 4-(4-dimethylaminobenzylidene)aminoacetophenone crystallizes in the triclinic P-1 space group with $a = 9.9357(4)$ Å, $b = 7.8347(4)$ Å, $c = 14.9145(9)$ Å, $\alpha = 76.996(4)$ Å, $\beta = 77.169(4)$ Å, $\gamma = 76.996(4)$ Å, and Z = 8 molecules per unit cell. Fig. 1 shows the molecular structure of the four independent conformers as asymmetric unit observed in the solid state structure of the compound which have an E conformation about the central
–C=–N bonding. These molecules differ from each other mainly in rotations around the σ-bond of the azomethine N-atom with the phenyl ring (C5–C9–C11–C15 torsion angles of 42.1(3)°, –37.7(3)°, 130.3(2)°, and –140.2(2)° for n = 1(C1), 2(C2), 3(C3), and 4(C4) conformers, respectively), a fact that reflects the conformational freedom of the molecule around this single bond [N–C(phen)] in distances in the 1.403(3)–1.406(3) Å range. This link contrasts with the much shorter and partially double N(azo)=CH bond [N–C distances in the 1.265(3)–1.275(3) Å interval], which is part of an extended π-de-localization that renders N–(CH–(ph)–N(CH3)2 skeleton nearly planar. The (ph)–N(CH3)2 N–CH3 and carbonyl C=O bond lengths are in the range of 1.358(3)–1.370(3) Å, 1.436(4)–1.452(3) Å and 1.212(3)–1.221(3) Å, respectively. Bond distances within the phenyl rings vary from 1.364(3) to 1.415(3) Å, as expected for the resonant bond structures of these aromatic groups. The corresponding bond lengths, angles and selected dihedral angles for each conformer found in the crystal are given in Table 2, where they are compared with the corresponding computed values at B3LYP/6-311++G(d,p) approximation. All geometrical parameters determined experimentally are presented in the Supporting Information. The above bond distances are in general agreement with the corresponding reported ones for the same compound.

Furthermore, the geometry of the four conformers detected experimentally by X-ray diffraction methods were fully optimized minimizing the potential energy in all geometrical parameters by varying the torsion angle around the C–N bond, in steps of 10°, in the range of 0–360°. The potential energy curve (see Supplementary Information) shows four minima, two of them located approximately at 40° and 140° (global). From the curve, two stable conformations are predicted for the compound, the CI conformer possesses the lowest energy corresponding to the most stable conformation. The relative energy difference between CI and C4 conformers is predicted to be 0.5 kJ mol⁻¹. The minima located at 220 and 325° correspond to mirror images (enantiomers) of CI and C4, respectively.

### 3.2. Structural properties

The conformational properties of the Schiff base have been investigated through quantum chemical calculations using B3LYP/6-31G(d,p) level of approximation. The scan was obtained by minimizing the potential energy in all geometrical parameters by varying the torsion angle around the C–N bond, in steps of 10°, in the range of 0–360°. The potential energy curve (see Supplementary Information) shows four minima, two of them located approximately at 40° and 140° (global). From the curve, two stable conformations are predicted for the compound, the CI conformer possesses the lowest energy corresponding to the most stable conformation. The relative energy difference between CI and C4 conformers is predicted to be 0.5 kJ mol⁻¹. The minima located at 220 and 325° correspond to mirror images (enantiomers) of CI and C4, respectively.

Furthermore, the geometry of the four conformers detected experimentally by X-ray diffraction methods were fully optimized including frequency calculations at the B3LYP/6-311++G(d,p) level of theory.
approximation (see Supplementary Information). The molecule possesses an E conformation determined both experimental and calculated. The 4-(dimethylamino)benzylidene ring is nearly coplanar with the C–C=N chain, whereas the acetonaphone ring is twisted significantly. Some conformational discrepancies between the crystal structure and the optimized counterpart were observed in conformer CIII. The most significant structural differences are found in the orientation of the 4-aminoacetophenone ring (Ring 2). This structural disparity is defined by the following torsion angles C(39)–N(31)–C(34)–C(33) and C(39)–N(31)–C(34)–C(35) with experimental values 130.3(2)° and −51.5(3)°, respectively for CIII. The computed values at B3LYP/6-311++G(d,p) level were 141.1° and −42.0°, respectively. The angles C(n3)–C(n5)–N(n1) and N(n1)–C(n10)–C(n9) are in the range 118.2–123.4° and 123.2–123.5°, respectively for all conformers. The increase respect to the usual values (122.3 Å) [22] should reduce steric repulsions between the azomethine group and the phenyl ring. The observed bond lengths C(n9)–N(n1) are between 1.265 and 1.275 Å, indicating a double bond character (calculated values: 1.282–1.287 Å).

The Natural Bond Orbital (NBO) analysis is an efficient method to evaluate the intra- and intermolecular bonding and interactions. Some relevant interactions between Lewis and non-Lewis orbitals along with their stabilization energies are listed in Table 3. For the Schiff base, the most important interaction is LP N(n1) → σ*(C(n9)) → H (between the C=N azomethine and the C–H bond). The stabilization energy associated with this hyper-conjugative interaction is in the range 12.27–12.71 kcal mol⁻¹ for all conformers, and increases the electron population of the σ* C(n9)–H orbital (0.043e).

The calculated energy values for the LP N(n2) → σ*(C(n13)–C(n12)) interactions between 42.81 and 46.66 kcal mol⁻¹ as shown in Table 3. This strong donor-acceptor overlap can be associated with a resonance structure with a partial double bond character for the N(n2)–C(n13) bond.

### 3.3 Hirshfeld surface analyses

The Hirshfeld surface in the crystal is representative of the region in space where molecules come into contact. Therefore, its analysis gives the possibility of obtaining quantitative insights into the nature of intermolecular interactions in the crystalline state. In order to understand the nature of intermolecular contacts and their quantitative contributions to the crystal packing of the Schiff base, the Hirshfeld surfaces and the associated 2D fingerprint plot were calculated. Fig. 2 shows the surfaces mapped over \(d_{\text{norm}}\) for the four conformers observed in the crystal lattice. As expected, they reveal the close contacts between donors hydrogen bonds and some acceptors, but other close contacts are also evident. For conformer I, the two red regions labeled 1 and 2 in the \(d_{\text{norm}}\) map are attributed to C–H···O hydrogen bonds. The remaining visible red region on \(d_{\text{norm}}\) surface of CII is assigned to N···H–C interactions (labeled 3) involving the N atom from the azomethine group and the hydrogen at the meta position on dimethylaminophenyl ring of conformer CIV. The pale blue to white spots (labeled 4) represent C–H···π interactions (labeled 5 in the \(d_{\text{norm}}\) map) involving the H18 atom of the methyl group bounded to the carbonyl of C1 and the C36–C35 benzene ring (centroid Cg(3); symmetry: 1-x,1-y,-z). The shorter interaction H18···Cg(3) found was 2.90 Å. C–H···O hydrogen bonds are also present in CII conformer where the deep-red regions labeled 1 and 2 are attributed to C–H···O interactions. The red area marked as 1 on the CIV conformer surface is associated to C–H···O interactions.

Fingerprint plots [40–42] of the main intermolecular contacts for all conformers are shown in Fig. 3. The shortest interactions labeled 1 correspond to the close H···H contacts. The O···H (labeled 2) and N···H (labeled 3) interactions, with sharp pairs of spike centered near a \([d_e-d_i]\) sum of 2.5 and 2.8 Å, respectively, correspond to O···H–C and N···H–C hydrogen bonds. A pair of broad wings labeled 4 at around \([d_e-d_i]\) of 2.8 Å is evidence of C–H contacts. In accordance with the fingerprint plots, no π···π stacking interactions were observed. These results are in accordance with reported values for the hydrogen bonding parameters (Supplementary Information). This study emphasizes the importance of Hirshfeld surface and fingerprint plots for a full understanding of non-classical hydrogen bonds and short intermolecular contacts in Schiff bases.

The relative contributions of the intermolecular interactions to the Hirshfeld surface area for all conformers are shown as a histogram (see Supplementary Information). For CII conformer, the H···H interactions have the major contribution to the crystal packing (51.4%) and the C···H interactions comprise the 34% of total Hirshfeld surface area. Some interactions such as O···H and N···H are also observed with contributions of 8.7% and 5.1%, respectively. For CII and CIV conformers, the O···H interactions have higher values of contribution compared with those CII and CIII conformers.

### 3.4 Vibrational analysis

The experimental IR and Raman spectra of the compound (solid) are shown in Fig. 4. The assignment of the observed bands was performed based on theoretical calculations (B3LYP/6-311++G(d,p)) and values reported for related molecules [44–52]. Table 4 displays experimental and calculated frequencies and a tentative assignment of the most important vibration modes. In order to approximate the theoretical values to experimental ones, the scale factor of 0.9608 was used, in accordance with results previously reported [44,45]. The simulated IR and Raman spectra are presented in the Supporting Information. Only some characteristic vibration modes of the Schiff base will be discussed.

#### 3.4.1 Methyl vibrations

The molecule possesses one methyl group linked to the C=O group and two others connected to the amino group. The bands located at 2993, 2946 and 2847 cm⁻¹ in the IR spectrum are assigned to the CH₃ symmetric stretching modes of the methyl groups attached to the nitrogen atom, in good agreement with the computed values (3005, 2966 and 2872 cm⁻¹), whereas the Raman spectrum shows only a weak band at 2926 cm⁻¹. The low intensity band located at 2821 cm⁻¹ in the IR spectrum can be attributed to the CH₃ symmetric stretching mode (computed value 2866 cm⁻¹), while the CH₃ stretching modes of the acetyl group

| Interaction (donor → acceptor)\(^{a}\) | \(E(2)^{b}\), kcal mol⁻¹ |
|-----------------------------------------|------------------|
| LP O(n1) → σ*(C(n1))–C(n7)             | 20.33            |
| LP O(n1) → σ*(C(n7))–C(n8)             | 21.41            |
| LP N(n2) → σ*(C(n13))–C(n12)          | 46.66            |
| LP N(n1) → σ*(C(n13))–C(n5)           | 6.32             |
| LP N(n1) → σ*(C(n1))–C(n2)            | 6.10             |
| LP N(n1) → σ*(C(n9))–H                | 12.71            |
| Total                                  | 113.5            |

\(^{a}\) LP indicates the lone pair on the specified atom. See Fig. 1 for atom numbering scheme. n = 1, 2, 3, 4 for CII, CIII, CIV and CIV, respectively.

\(^{b}\) \(E(2)\) is the energy of hyper-conjugative interactions.
were not observed.

The weak bands located at 1485 and 1447 cm\(^{-1}\) in the IR spectrum (1447 cm\(^{-1}\) in Raman) are assigned to the CH\(_3\) asymmetric and symmetric bending modes of the N(CH\(_3\))\(_2\) group, respectively, whereas those for the CH\(_3\) linked to the carbonyl group are observed at 1416 and 1365 cm\(^{-1}\), respectively. These values are in accordance with calculated (See Table 4) and previously reported results [44,46].

3.4.2. C=O vibrations

The strong IR band located at 1670 cm\(^{-1}\) (1668 cm\(^{-1}\) in Raman) is assigned to the C=O stretching mode, while the predicted value is 1665 cm\(^{-1}\). The red shift, relative to other ketones, can be due to the conjugation effect of the C=O bond with the aromatic ring. The frequency of the carbonyl stretching mode is not particularly influenced by the ring substituents [47–49]. For the parent Schiff base, 1-(4-((4-bromo-benzylidene)amino)phenyl)ethanone, the C=O vibration is observed as a strong IR band at 1668 cm\(^{-1}\) [47].

The medium-intense bands located at 600 and 592 cm\(^{-1}\) in the IR spectrum are assigned to the out-of-plane and in-plane C=O bending modes, respectively, and are in good agreement with the calculated values (see Table 4).

3.4.3. Phenyl ring vibrations

The very weak IR bands located at 3053 and 3031 cm\(^{-1}\) are assigned to the C–H stretching modes of both aromatic rings. The C–H in-plane bending modes of both rings are attributed to the IR bands at 1316, 1208, 1175 and 1165 cm\(^{-1}\) (1317, 1208, 1177 and 1166 cm\(^{-1}\) in Raman). The C–H out-of-plane bending modes are observed at 956, 819 and 720 cm\(^{-1}\) in IR and in Raman at 959, 952, 941, 825, 818 and 724 cm\(^{-1}\), in accordance with reported [44,50] and calculated values (See Table 4). PED calculations show clearly that these vibrations are coupled with C–C stretching modes of the aromatic rings and with other vibration modes of the substituents.

The C–C ring stretching modes are prominent in the vibrational spectra of benzene and its derivatives and are assigned in the range of 1650–1200 cm\(^{-1}\) [44,51]. For the title molecule, they are attributed to the medium and strong IR bands located at 1607, 1578, 1550, 1436 and 1408 cm\(^{-1}\) (1578, 1553, 1434 and 1411 cm\(^{-1}\) in Raman), most of them are coupled. This spectral region is well

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**Fig. 2.** Views of Hirshfeld surfaces of the four Schiff base conformers with thermal ellipsoids plotted at the 50% level of probability. For Conformer I, the surface in column 2 is rotated 180° around the horizontal axis of the plot.
reproduced with quantum chemical calculations with the corresponding frequencies computed to occur at 1649, 1616, 1581, 1471 and 1441 cm$^{-1}$.

3.4.4. C=N vibrations

The azomethine bond is very sensitive to the charge transfer between donor and acceptor groups, and therefore, the C=N stretching mode becomes relevant in the synthesis and study of Schiff bases and coordination compounds. The weak band located at 1623 cm$^{-1}$ in the IR spectrum (1624 cm$^{-1}$ in Raman) is assigned to the C=N stretching mode. The calculated value for this mode is predicted at 1679 cm$^{-1}$ with a contribution of 63%. For related compounds this vibration was reported at 1609 cm$^{-1}$ and 1582 cm$^{-1}$ [47,52].

The H–C=N in-plane bending mode appears as a strong band located at 1268 cm$^{-1}$ in the IR spectrum (1269 cm$^{-1}$ in Raman), and the weak IR band at 956 cm$^{-1}$ with a Raman counterpart at 959 cm$^{-1}$ can be assigned to the out-of-plane bending of the H–C=N group.

3.5. $^1$H and $^{13}$C NMR analysis

Chemical shifts are recognized as an imperative part of the information contained in NMR spectra. They are valuable for structural interpretation due to their sensitivity to conformational variations. The combined use of NMR experimental spectra and computational simulation methods offers a powerful way to interpret and predict the structure of a large organic molecules and biomolecules. The observed and calculated $^1$H and $^{13}$C NMR chemical shifts for 4-(4-dimethylaminobenzylidene)
Table 4
Experimental and calculated wavenumbers of the Schiff base and tentative assignment of main fundamental vibrational modes.

| IR (solid) | Raman (solid) | Calculated<sup>b</sup> B3LYP/6-311++G(d,p) | Approximate description of modes, PED (%)<sup>de</sup> |
|------------|---------------|--------------------------------------------|--------------------------------------------------|
| 3053 vww   | –             | 3210                                       | v C23–H (75) + v C21–H(13) + v C25-H (11)        |
| 3031 vww   | –             | 3180                                       | v C2–H (76) + v C5–H (18)                        |
| –          | –             | 3157                                       | v C22–H (97)                                     |
| 2939 vw    | –             | 3134                                       | νCH3(N)(96)                                      |
| 2946 sh    | –             | 3090                                       | νCH3(N) (100)                                    |
| –          | –             | 3048                                       | νCH3(N) (86)                                     |
| 2898 w     | –             | 2999                                       | v C17–H (97)                                     |
| 2847 w     | –             | 2992                                       | νCH3 (N) (83)                                    |
| 2821 w     | –             | 2985                                       | νCH3(N) (83)                                     |
| 1670 s     | 1668 (4)      | 1734                                       | ν C=N=O (87)                                     |
| 1623 w     | 1624 (9)      | 1679                                       | ν C17–N19 (63)                                   |
| 1607 m     | –             | 1649                                       | νC21-23 + v C22-25 (53) + δ CCH (11)             |
| 1578 vs    | 1578 (100)    | 1616                                       | v C4–C5 (58)                                     |
| 1550 s     | 1553 (38)     | 1581                                       | ν C20–C21 + v C20–C22 (50)                      |
| 1528 m     | –             | 1599                                       | ν C27–N30 (20) + δ CCH (26)                      |
| 1447 w     | –             | 1532                                       | δ CH3(N)(59) + δ ν CH3(N)(21)                    |
| 1436 m     | 1434 (3)      | 1488                                       | δ CH3(N) (75)                                    |
| 1416 vw    | 1417 (3)      | 1471                                       | v C22-25 + v C21-23 (40) + δ CCH (27) + δ ν CH3(N)(11) |
| 1408 m     | 1411 (2)      | 1383                                       | ν C2–C1 + ν C5–C4(47) + δ δ CCH (29)             |
| 1365 s     | 1365 (7)      | 1384                                       | δ CH3(N)(83)                                     |
| 1316 m     | 1317 (1)      | 1342                                       | δ CCH (40) + δ C–C4 + ν C1–C6 (21)               |
| 1208 s     | 1269 (6)      | 1280                                       | δ N19–C17–H (16) + ν C20–C17 (13) + ν C6–N19(11) |
| 1208 w     | 1208 (5)      | 1234                                       | ν C6–N19 (24) + δ CCH (R2)(60) + v C4–C5 (11)   |
| 1175 sh    | 1177 (9)      | 1200                                       | δ CCH (R1)(54)                                   |
| 1105 s     | 1166 (48)     | 1184                                       | δ CCH (56)                                       |
| 1123 w     | 1126 (3)      | 1138                                       | δ CH3 (N) (62) + δ δ CH3(N)(27)                   |
| –          | 1075 (5)      | 1089                                       | v C=C (R2)(31)+ v C13–C11 (10) + δ CH3(CO)(22)   |
| 1070 w     | –             | 1079                                       | ν N30–C35 + ν N30–C31(28) + ν CH3(N)(67)          |
| –          | –             | 987 (5)                                    | 984                                            |
| 956 w      | 959 (2)       | 1006                                       | 966                                            |
| –          | –             | 952 (2)                                    | 956                                            |
| –          | –             | 941 (2)                                    | 945                                            |
| 887 w      | 888 (<1)      | 900                                        | 864                                            |
| –          | –             | 843 (4)                                    | 813                                            |
| 825 (2)    | –             | 841                                        | 807                                            |
| 819 m      | 818 (3)       | 832                                        | 799                                            |
| 747 ww     | 748 (4)       | 759                                        | 729                                            |
| –          | –             | 732 (v)                                    | 717                                            |
| 720 wv     | 724 (<1)      | 738                                        | 709                                            |
| 695 w      | 697 (<1)      | 704                                        | 676                                            |
| –          | –             | 634 (1)                                    | 647                                            |
| 600 m      | 600 (<1)      | 605                                        | 581                                            |
| –          | –             | 592 (m)                                    | 576                                            |
| –          | –             | 546 (1)                                    | 513                                            |
| 532 w      | 528 (2)       | 539                                        | 518                                            |
| 495 vv     | 492 (<1)      | 498                                        | 478                                            |
| 485 (<1)   | –             | 487                                        | 468                                            |
| 453 vww    | 458 (<1)      | 460                                        | 442                                            |
| 426 vww    | 427 (<1)      | 436                                        | 419                                            |
| –          | 409 (3)       | 423                                        | 406                                            |
| –          | 333 (1)       | 331                                        | 318                                            |
| –          | 290 (2)       | 288                                        | 276                                            |
| –          | 232 (3)       | 250                                        | 240                                            |
| –          | 210 (3)       | 198                                        | 190                                            |
| –          | 163 (10)      | 160                                        | 154                                            |
| –          | 131 (6)       | 110                                        | 106                                            |
| –          | 90 (4)        | 87                                         | 84                                             |
| –          | –             | 70                                         | 73                                             |

<sup>a</sup> sh, shoulder; s, strong; w, weak; m, medium; v, very weak; vw, extremely weak.
<sup>b</sup> Relative band heights in parentheses.
<sup>c</sup> Calculated at B3LYP/6-311++G(d,p) level of theory. Scale factor: 0.9608.
<sup>d</sup> α: stretching, δ: in-plane deformation, γ: out-of-plane deformation, ρ: rocking, ω: wagging, τ: twisting, τ: torsion modes.
<sup>e</sup> See Fig. 57 for the atom numbering. R1: Dimethylamino phenyl ring; R2: Acetophenone ring.
The chemical shifts calculation (δ) of 1H and 13C was performed with the GIAO method [38], after full geometry optimization with the GAUSSIAN 03 program. Comparing the experimental and theoretical data for protons, a good agreement is observed with Δ = δexp - δcalc deviation ranging from 0.29 to -0.09 in gas phase and from 0.36 to -0.22 in CHCl3.

The Δ-values found for carbon atoms rise up to 12.0 ppm. The greatest discrepancy was found in the prediction of the C=–N–C chemical shift; Δ = -12.0 ppm (–11.0 in CHCl3). This fact can be explained taking into account that calculations only consider the inductive effect (-I) that is negative for the corresponding carbon atom, excluding the resonance effect, and consequently the shielding contribution of the nitrogen atom.

3.6. Thermo-gravimetric and differential thermal analysis (TG-DTA)

The thermal behaviour of the title compound was evaluated by means of TG and DT analysis (Supplementary Information). The experiment was carried out under air atmosphere at a heating rate of 5°C/min. The molecule resulted stable up to 250 °C and then thermal decomposition takes place. The high thermal stability of this compound probably arises because the chains are further stabilized in the crystal packing by hydrogen bonds between adjacent molecules as was deduced from the X-ray structure discussed previously. The first step finished at 400 °C with a decrease in mass of 60.2% (theoretical value: 58%), which is associated with the loss of the phenyl groups. From the DT analysis (see Supplementary Information), two endothermic peaks were observed at 153 and 179 °C, corresponding to the complete degradation of the sample into volatile compounds. The DTA curve shows an exothermic peak located at 608 °C, corresponding to the complete degradation of the sample into volatile compounds.

3.7. Electronic spectra

The experimental and calculated electronic spectra of the Schiff base in chloroform and dimethylformamide are shown in Table 5 (TMS was used as internal reference). The experimental 1H and 13C NMR spectra are shown in Supplementary Information.

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3.7. Electronic spectra

The experimental and calculated electronic spectra of the Schiff base in chloroform and dimethylformamide are shown in Fig. 5. The transitions with major contribution are shown in Table 6, and only the dominant excitations (chosen in accordance with their oscillator strength) are used to assign the observed bands. Based on these results, it can be concluded that the correlation between them is a good.

The electronic spectrum in CHCl3 presents a band located at 375 nm (calculated: 403 nm) attributed to a dominant one-electron transition, with π → π* character (see Supplementary Information), from HOMO to LUMO orbitals (98% of contribution). The absorption observed at 335 nm is assigned to the HOMO—1 → LUMO transition, with minor contribution of HOMO—2 → LUMO—1 transition and the band at 323 nm corresponds to the HOMO—1 → LUMO excitation. The behaviour of the Schiff base in DMF resulted similar and these results are in accordance with the computed values reported in Table 6.

The frontier molecular orbitals mainly involved in the electronic transitions used to assign the observed bands are depicted in Supplementary Information. The HOMO corresponds to a π bonding system localized over phenyl groups and the non-bonding character of the oxygen and both nitrogen atoms. The HOMO—1 involves a π* bonding system localized over both phenyl rings and a p-type orbital strongly located on the N atoms. HOMO—2 contains π bonding electronic density located in the phenyl ring (R2) and a p system over acetyl group. Both LUMO and LUMO—1 orbitals exhibit π anti-bonding character delocalized over both phenyl rings and non-bonding character of nitrogen, oxygen and carbon atoms of methyl groups.

### Table 5

|     | Exp. | J' | B3LYP/6-311+G(2d,p) |
|-----|------|----|---------------------|
|     |      |    | Gas Phase CHCl3     |
| N–CH3 | 3.12 (s) | – | 3.01 (0.11) 3.08 (0.04) |
| C(=O)–CH3 | 2.65 (d) | – | 2.46 (0.19) 2.58 (0.07) |
| H2B,H29 | 6.78 (d) | 8.39 | 6.17 (0.03) 6.84 (0.06) |
| H7,H10 | 7.26 (d) | – | 7.27 (-0.01) 7.38 (-0.12) |
| H24,H26 | 7.82 (d) | – | 7.88 (-0.06) 8.1 (-0.28) |
| H8 | 8.02 (d) | – | 8.02 (0.00) 8.24 (-0.22) |
| H18 | 8.35 (s) | – | 8.44 (-0.09) 8.53 (-0.18) |
| H9 | 8.82 (d) | – | 8.53 (-0.29) 8.46 (0.36) |
| N=CH3 | 27 | – | 27 (0.00) 28 (-1.00) |
| N–CH3 | 40 | – | 41 (-1.00) 41 (-1.00) |

a Multiplicity between parentheses; s: singlet; d: doublet.
b Δ = δexp - δcalc values in parentheses predicted in vacuo and taking into account implicitly the solvent. The standard numbering scheme adopted for atoms labeling is presented in Supplementary Information.
c Coupling constants in Hz.
3.8. Fluorescence spectra

4-(4-dimethylaminobenzylidene)aminoacetophenone was found to be fluorescent, even though some information was found in the literature [53] and the emission spectrum excited at 430 nm ($\lambda_{exc}$) is shown in Fig. 6. The broad fluorescence band extends from 450 to 650 nm with the maximum located at 507 nm. Taking into account the UV absorption spectrum, the emission takes place in a region (red-shifted) where there is no absorption, and accordingly no overlapping between both signals was observed. This could be due, probably, to differences in the geometry of the excited and ground states.

To determine the influence of concentration on the fluorescence, moles of the Schiff base were added to the initial solution in CH$_3$CN (8.25 $\times$ 10$^{-4}$ M). As observed, the fluorescence raised to the third addition (3 $\times$ 16.3 nmoles added), then began to go down up to (5 $\times$ 16.3 nmoles added) and subsequently an erratic behaviour was noted. In principle, the auto-absorption could be discarded since the negligible UV absorption cross-section at the wavelength of fluorescence. Therefore, it could be inferred, at least at an early stage, that the most probable process would be intermolecular interaction to form dimers. This is supported by the observed crystal packing, (see, Fig. 1), in which the molecules are linked through hydrogen bonds as was discussed previously.

### Table 6

| Wavelength (nm) | Oscillator strength | Assignment                  |
|-----------------|---------------------|-----------------------------|
| Chloroform      |                     |                             |
| 375 403         | 1.0869              | HOMO $\rightarrow$ LUMO (98%) |
| 335 328         | 0.0248              | HOMO $\rightarrow$ LUMO (74%) |
| 323 325         | 0.1755              | HOMO $\rightarrow$ LUMO (16%) |
| 290 294         | 0.104               | HOMO $\rightarrow$ LUMO (16%) |
| Dimethylformamide (DMF) |         |                             |
| 378 415         | 1.0461              | HOMO $\rightarrow$ LUMO (98%) |
| 320 330         | 0.2004              | HOMO $\rightarrow$ LUMO (48%) |
|                  |                     | HOMO $\rightarrow$ LUMO (27%) |

*D Calculated at B3LYP/6-311+G(2d,p) approximation.*

3.9. Mesomorphic behaviour

DSC experiments performed at 2 $^\circ$C/min (see Fig. 7) showed two endothermic peaks on heating: the first one from 149 to 153 $^\circ$C ($\Delta H = 3$ kJ mol$^{-1}$); the second one from 175 to 177 $^\circ$C ($\Delta H = 27$ kJ mol$^{-1}$). On cooling, their exothermic counterparts were observed at lower temperatures: 134 to 131 $^\circ$C ($\Delta H = -27$ kJ mol$^{-1}$) and 36 to 32 $^\circ$C ($\Delta H = -1$ kJ mol$^{-1}$). The same values have been obtained in subsequent heating/cooling cycles; moreover, the powder XRD pattern recorded at room temperature on a sample heated in the DSC up to the end of the second endothermic peak agreed (except for the relative intensities of some peaks) with that corresponding to a virgin sample.

POM observations showed subtle texture changes at ca. 150 $^\circ$C; at 180 $^\circ$C the sample cleared to the isotropic state (fluid opaque texture). On cooling, a well defined fan-shaped + focal-conic texture has been detected below 135 $^\circ$C. This texture, characteristic of smectic phases, is displayed in Fig. 7. Mosaic textures have been observed in other cooling cycles. Fan-shaped textures are often associated to SmA, SmC or SmB mesophases; mosaic textures are more typical of SmB phases. Moreover, transformations from fan-shaped into mosaic textures after annealing for long time have been reported as characteristic of SmB phases [54]. The relative values of the enthalpy changes associated to both phase transitions ($\Delta H$ for the crystal to Sm transition lower than that of the Sm to isotropic transition) also point to an ordered (hexatic) SmB phase.

Schiff bases have been widely used in the field of liquid crystals. A search in the LiquCrystal database [55] retrieved 10184 entries for the specific core under study ($\text{Ph} = \text{CH} = \text{N} = \text{Ph} = \text{Ph} = \text{Ph} = \text{Ph}$) from approx. 100000 total cases. In most cases, mesogenic compounds involve long aliphatic chains in at least one of the two terminal positions. Most of the compounds exhibiting the $\text{Ph} = \text{CH} = \text{N} = \text{Ph} = \text{Ph} = \text{Ph} = \text{Ph}$ core and “small” substituents in the terminal positions (i.e. halogen atoms groups, nitro groups, alkoxy groups with no more than 2 carbon atoms) are not mesogenic. Among the few examples of mesogenic compounds inside this group, O$_2$N$\text{Ph} = \text{CH} = \text{N} = \text{Ph} = \text{OCH}_3$ (N monotropic) and CH$_3$O$\text{Ph} = \text{CH} = \text{N} = \text{Ph} = \text{CONH}_2$ (Sm enanthyotropic) deserve to be mentioned. A search restricted to derivatives exhibiting one terminal group identical to those of the compound under study in this work (excluding long-chain compounds) retrieved less than 15 cases of $\text{Ph} = \text{Ph} = \text{Ph} = \text{Ph} = \text{Ph} = \text{Ph} = \text{Ph}$ compounds and about 20 cases of (CH$_3$)$_2$N$\text{Ph} = \text{Ph} = \text{Ph} = \text{Ph} = \text{Ph}$ compounds. Among the first group, the only mesogenic compounds were those with R = Ph-, NC-, CH$_3$CH$_2$S- (unidentified phases), CH$_2$=CH$\text{COO} = \text{(N)}$, CH$_3$COOO$ = \text{(N)}$, CH$_3$CH$_2$COO$ = \text{(N)}$. 

*Fig. 6. Fluorescence spectra of the Schiff base in CH$_3$CN excited at 430 nm.*

*Fig. 7. DSC measurements for the Schiff base with the corresponding POM images.*
CH3COO– (N), CH3O– (N) and CH2CH2O– (N). Among the second group, only those in which –R = –OCH3 (N), –OCH2CH3 (N), –CH=CH–COOCH2CH2CH(3) (Sm), –COO–Ph–X for X = Br, CN, and CH3 (N) were mesogenic.

The absence of a mesogenic character for most of this kind of compounds deprived from long terminal chains agrees with the ordered character of the SmB mesophase detected for our compound. It bears very short aliphatic groups in both extremes, but the number of terminal methyl groups and the nature of the functional groups they are attached to, seem to be just enough to warrant its mesogenic character—very likely as a delicate balance of geometry anisotropy [56], axial and lateral interactions [27,57] which manifest in a hextactic SmB phase.

4. Conclusions

The synthesis of the Schiff base 4-(4-dimethylaminobenzylidene) aminoacetophenone was achieved by the reaction between 4-(dimethylamino) benzaldehyde and 4-aminoacetophenone in ethanol. The product was characterized by IR, Raman, UV–Vis, 1H, and 13C NMR and fluorescence spectroscopy. To support the interpretation of the experimental results, the analysis was complemented with quantum chemical calculations at B3LYP method and different basis sets. The crystal structure was determined by means of single-crystal X-ray diffraction methods. This compound crystallizes in the triclinic P-1 space group with α = 9.9357(4)Å, b = 17.1016(9)Å, c = 18.1945(9)Å, α = 78.347(4)°, β = 77.169(4)°, γ = 76.996(4)°, and Z = 8 molecules per unit cell. The crystallographic data reveals that there are four independent molecules per asymmetric unit that mainly differ from one another in rotations around the α-bond of the azomethine N-atom with the phenyl ring, hence reflecting the conformational degree of freedom of the molecule. The Hirshfeld surfaces and fingerprint plots were an important tool in the analysis of the intermolecular interactions and their quantitative contributions to the crystal packing of the Schiff base. These results indicate that the H···H contributions are more remarkable than other contacts. The crystal packing showed noticeably stabilized by non-conventional C–H···O, C–H···N and C–H···C hydrogen bonds and π–π stacking interactions were observed. The substance is thermally stable up to 250 °C, and the vibration and electronic properties of the substance were fully determined and supported by quantum chemical calculations. The Fluorescence spectrum of the molecule provided measurable signals when irradiated with λexc. = 430 nm. The formation of dimers proposed due to intermolecular interactions, when Schiff base concentration was increased, is consistent with the short contacts found in the crystal packing, and seems also in line with the detected hextactic SmB mesophase.

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Appendix A. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.11.071.

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