

# Optical and nonlinear optical properties of new Schiff's bases: experimental versus theoretical study of inclusion interactions

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Received: 24 June 2011 / Accepted: 27 April 2012 / Published online: 10 June 2012  
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**Abstract** Experimentally and theoretically were studied the physical properties of 19 new Schiff's bases and their different protonated forms, depending on reaction conditions. It was elucidated the correlation between the type of molecular architecture, substituents and pH of the medium on first hyperpolarizability ( $\beta$ ) with regard to the potential application of these compounds as organic nonlinear optical materials. The structure and optical properties were also studied, comparing quantum chemical data and experimental results from the mass spectrometry, electronic absorption, diffuse reflectance, and fluorescence spectroscopy, vibrational spectroscopy in condense phase, nuclear magnetic resonance, as well as thermal methods.

**Keywords** Schiff's bases · Optical and NLO properties · Quantum chemistry · Spectroscopy

## Introduction

Great potential relevance of the organic materials in the electro-optical (EO), nonlinear optical (NLO) and THz-technologies, doing the research in this area innovative and dynamic [1–31]. The possibilities of THz-spectroscopy opens up new areas of interdisciplinary application such as security, environmental inspection, biomedical analysis [32–43]. The Schiff's bases are among the most exploited in the design of organic and the metal–organic NLO materials, enabling the design and tuning of the molecular

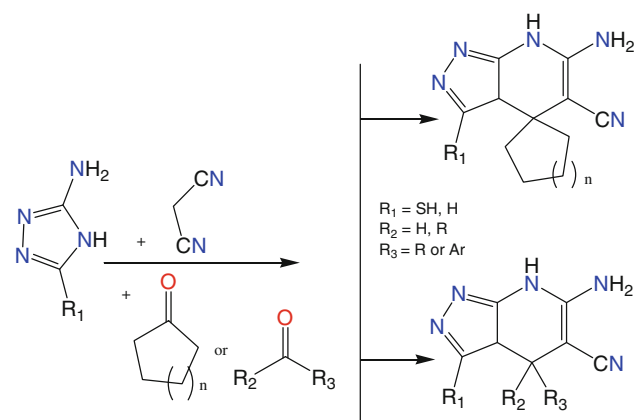
architecture for organic, the coordination ability and no covalently interactions [44–59]. In this context it was presented new derivatives (Scheme 1), designed towards the large first hyperpolarizability  $\beta$  that translates into  $\chi^{(2)}$  in the crystals, where the noncentrosymmetric structures were essential. Advanced have been investigated both experimentally and theoretically the effect of the substituents in the molecular skeleton, and the pH of the medium in view of subsequent receipt of organic salts. The last objects have been shown great potential, by analogy with (*E*)-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST) [1–31]. The important role of the organic salts is that depending of the counter ion was used to modify crystal packing, solubility, stability and higher chromophore number densities. Based on our previous studies on organic dyes [60–63] have been selected 19 new compounds (Scheme 1) in which it studied the relationship between structure, spectroscopic and NLO properties.

## Experimental

### Physical measurements

The UV–VIS–NIR spectra between 190 and 1,190 nm, using solvent acetonitrile (Uvasol, Merck product) at a concentration of  $2.5 \times 10^{-5}$  M in 0.921 cm quartz cells were recorded on Tecan Safire Absorbance/Fluorescence XFluor 4 V 4.40 spectrophotometer. The thermogravimetric study was carried out using a Perkin-Elmer TGS2 instrument. The calorimetric measurements were performed on a DSC-2C Perkin Elmer apparatus under argon. Diffuse reflectance (Ds) spectra were measured on a PerkinElmer Lambda 750 in reflectance mode. The reflection spectra were automatically converted to

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**Scheme 1** Synthetic pathway of the heterocyclic fragments in (13)–(19)

absorbance spectra using Kubelka–Munk theory. The mass spectrometric measurements were made, using TSQ Quantum AM ULTRA (Thermo Electron Corporation) instrument. Two eluents were used A—H<sub>2</sub>O with 0.1 % HCOOH and B—CH<sub>3</sub>CN with 0.1 % HCOOH. ESI mass spectrometry: a triple quadrupole mass spectrometer (TSQ 7000 Thermo Electron, Dreieich, Germany) equipped with an ESI 2 source was used for detection and operated under the following conditions: capillary temperature 120 °C; sheath gas 60 psi and spray voltage 4.5 kV. The samples were injected into the ion source by an auto sampler (Surveyor) with a flow rate of 0.2 ml/min pure acetonitrile. 1 mg/ml of the sample will be dissolved in acetonitrile. The data obtained were processed using Xcalibur 1.3 software. <sup>1</sup>H- and <sup>13</sup>C-NMR measurements, referenced to sodium 3-(trimethylsilyl)-tetradeuteriopropionate, were made at 298 K with a Bruker DRX-400 spectrometer using 5 mm tubes and D<sub>2</sub>O as solvent. The thermal analyses were performing in the 300–500 K range on a Differential Scanning Calorimeter Perkin-Elmer DSC-7, and a Differential Thermal Analyzer DTA/TG (Seiko Instrument, model TG/DTA 300). The experiments were carried out with a scanning rate of 10 K min<sup>-1</sup> under an argon atmosphere.

#### Computational details

Quantum chemical calculations are performed with GAUSSIAN 98, 09 and Dalton 2.0 program packages [64–66]. The result files are visualized by means of the GaussView03 [67]. The geometries of the studied species were optimized at density functional theory (DFT) using the 6-31 + G(d,p) basis set. The DFT method employed is B3LYP [68–70]. Molecular geometries of the studied species were fully optimized by the force gradient method using Bernys' algorithm. For every structure the stationary

points found on the molecule potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. The absence of the imaginary frequencies, as well as of negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to minima of the potential energy hypersurfaces. The molecular properties of the studied species in acetonitrile solution were obtained at CAM-B3PW91 and M06-2X level of theory, using the 6-31 + G(d) basis set. The protonation ability of the molecules was evaluated by the NBO analysis. The theoretical calculations of the molecular hyperpolarizability were performed, using the diffuse and polarization functions. As far as it has been shown that the B3LYP method give unreliable results for these calculations in some conjugated organic NLO materials, the CAM-B3PW91 and M06-2X functionals were used also for calculation of the hyperpolarizability, providing better agreement with experiments, as well as close results in the property to predict the molecular properties of organic, metal–organic and no covalently interaction systems [71–81]. The NBO analysis were performed at the same theoretical levels.

The  $\beta$  total values are calculated according the Eq. 1, where are  $\beta_x$ ,  $\beta_y$  and  $\beta_z$  are described with the Eqs. 2–4, respectively.

$$\|\beta_{tot}\| = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (1)$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (2)$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \quad (3)$$

and

$$\beta_z = \beta_{zzz} + \beta_{yyz} + \beta_{xxz} \quad (4)$$

The experimental and theoretical spectroscopic patterns were processed by R4Cal OpenOffice STATISTICS for Windows 7 program package [82]. Baseline corrections and curve-fitting procedures were applied. For the interpretation of the CD and fluorescence spectra [83–96], the Gaussian function best fits to the experimental data set, thus giving in our cases the  $r^2$  values within the range 0.9793<sub>3</sub>–0.9908<sub>3</sub>, respectively. The statistical significance of each regression coefficient was checked by the use of  $t$  test (calculation of the number of significance using data from the experimental error, usually higher than 0.100). The model fit was determined by  $F$  test (comparison of calculated by the model and experimentally obtained signal values).

#### Synthesis

Equimolar amounts of the aldehydes and aromatic amines were mixed in 50 ml toluene under stirring at heating

(40–100 °C) for 1–6 h, according the classical synthetic scheme [97–99]. To the reaction mixtures were added 10 ml CH<sub>3</sub>COOH. The obtained dark colored powders were filtered off and recrystallized from methanol. Yields of (1)–(19) are within 90–95 %. The modeled heterocyclic structural fragments in (13)–(19) structural fragment was obtained according [100, 101], by mixing of the equimolar amounts of the starting compounds in 50 ml methanol, under stirring at heating reflux (50 °C) for 2 h.

(4-Dimethylamine-benzylidene)-pyridin-4-yl-amine (1): Found, C, 74.5<sub>8</sub>; H, 6.7<sub>0</sub>; N, 18.6<sub>6</sub>; Calc. [C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>], C, 74.6<sub>4</sub>; H, 6.7<sub>1</sub>; N, 18.6<sub>5</sub> %; <sup>1</sup>H-NMR: 3.24 (3H, –NCH<sub>3</sub>, s), 3.27 (3H, –NCH<sub>3</sub>, s), 5.00 (1H, s), 7.26–7.88 ppm (8H, m), <sup>13</sup>C-NMR: 27.8, 28.8 (NCH<sub>3</sub>), 77.6 (NCH), 127.8–135.8 ppm (CH<sub>Ar</sub>); (4-diethylamine-benzylidene)-pyridin-4-yl-amine (2): Found, C, 75.8<sub>8</sub>; H, 7.5<sub>2</sub>; N, 16.5<sub>9</sub> %; Calc. [C<sub>16</sub>H<sub>19</sub>N<sub>3</sub>], C, 75.8<sub>6</sub>; H, 7.5<sub>6</sub>; N, 16.5<sub>9</sub> %; <sup>1</sup>H-NMR: 3.22 (3H, –NCH<sub>2</sub>, t), 3.2<sub>9</sub> (3H, –NCH<sub>2</sub>, t), 3.33, 3.41 (2× CH<sub>2</sub>, q, *J* = 7.0 Hz), 5.02 (1H, s), 7.22–7.90 ppm (8H, m), <sup>13</sup>C-NMR: 27.7, 28.2 (NCH<sub>3</sub>), 32.7, 32.2 (2× CH<sub>2</sub>) 77.0 (NCH), 128.1–136.6 ppm (CH<sub>Ar</sub>); *N,N*-diethyl-*N'*-(4-pyrrolidin-1-yl-benzylidene)-benzene-1,4-diamine (3): Found, C, 78.5<sub>5</sub>; H, 8.4<sub>7</sub>; N, 13.0<sub>7</sub> %; Calc. [C<sub>21</sub>H<sub>27</sub>N<sub>3</sub>], C, 78.4<sub>6</sub>; H, 8.4<sub>7</sub>; N, 13.0<sub>7</sub> %; <sup>1</sup>H-NMR: 3.21 (3H, –NCH<sub>3</sub>, t), 3.30 (3H, –NCH<sub>3</sub>, t), 3.21, 3.40 (2× CH<sub>2</sub>, q, *J* = 7.1 Hz), 3.12, 3.16 (8H, t, m, *J* = 6.2 Hz), 5.01 (1H, s), 7.20–7.85 ppm (8H, m), <sup>13</sup>C-NMR: 27.2, 28.0 (NCH<sub>3</sub>), 32.5, 32.1 (2× CH<sub>2</sub>), 29.7, 28.9, 30.1, 34.4 (4× CH<sub>2</sub>), 77.2 (NCH), 128.0–135.0 ppm (CH<sub>Ar</sub>); *N,N*-Diethyl-*N'*-(4-morpholin-1-yl-benzylidene)-benzene-1,4-diamine (4): Found, C, 74.7<sub>7</sub>; H, 8.1<sub>0</sub>; N, 12.5<sub>5</sub>; Calc. [C<sub>21</sub>H<sub>27</sub>N<sub>3</sub>O], C, 74.7<sub>4</sub>; H, 8.0<sub>6</sub>; N, 12.4<sub>5</sub> %; <sup>1</sup>H-NMR: 3.20 (3H, –NCH<sub>3</sub>, t), 3.28 (3H, –NCH<sub>3</sub>, t), 3.20, 3.42 (2× CH<sub>2</sub>, q, *J* = 7.1 Hz), 4.22, 4.19 (8H, t, m, *J* = 7.7 Hz), 5.00 (1H, s), 7.25–7.66 ppm (8H, m), <sup>13</sup>C-NMR: 27.3, 28.2 (NCH<sub>3</sub>), 32.2, 32.0 (2× CH<sub>2</sub>), 30.2, 30.8, 38.3, 39.1 (4× CH<sub>2</sub>), 77.0 (NCH), 128.0–136.2 ppm (CH<sub>Ar</sub>); *N,N*-diethyl-*N'*-(4-piperidin-1-yl-benzylidene)-benzene-1,4-diamine (5): Found, C, 57.1<sub>1</sub>; H, 6.5<sub>0</sub>; N, 9.1<sub>0</sub>; Calc. [C<sub>22</sub>H<sub>30</sub>N<sub>3</sub>], C, 57.0<sub>2</sub>; H, 6.5<sub>2</sub>; N, 9.0<sub>7</sub> %; <sup>1</sup>H-NMR: 3.22 (3H, –NCH<sub>3</sub>, t), 3.30 (3H, –NCH<sub>3</sub>, t), 3.29, 3.40 (2× CH<sub>2</sub>, q, *J* = 7.0 Hz), 4.30, 4.20, 4.88 (10H, t, m, m, *J* = 7.2–8.3 Hz), 4.77 (1H, m), 5.02 (1H, s), 7.30–7.70 ppm (8H, m), <sup>13</sup>C-NMR: 27.2, 28.1 (NCH<sub>3</sub>), 30.6 (CH), 32.0, 32.2 (2× CH<sub>2</sub>), 29.7, 30.2, 30.2, 33.1, 34.1 (5× CH<sub>2</sub>), 77.3 (NCH), 128.2–135.7 ppm (CH<sub>Ar</sub>); 2-[(4-dimethylamino-benzylidene)-amino]-4-methyl-benzoic acid (6): Found, C, 72.1<sub>1</sub>; H, 6.6<sub>2</sub>; N, 9.9<sub>0</sub> %; Calc. [C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>], C, 72.3<sub>3</sub>; H, 6.4<sub>4</sub>; N, 9.9<sub>2</sub> %; <sup>1</sup>H-NMR: 2.23 (3H, –CH<sub>3</sub>, s), 3.25 (3H, –NCH<sub>3</sub>, s), 3.30 (3H, –NCH<sub>3</sub>, s), 5.11 (1H, s), 7.30–7.90 (7H, m), 9.88 ppm (OH, s, broad), <sup>13</sup>C-NMR: 27.0, 28.2 (NCH<sub>3</sub>), 77.1 (NCH), 125.5–134.4 (CH<sub>Ar</sub>), 178.2 ppm (COOH); 4-[(4-diethylamino-phenylimino)-

methyl]-2,6-dimethoxy-phenol (7): Found, C, 69.5<sub>0</sub>, H, 7.3<sub>5</sub>, N, 8.5<sub>5</sub>; Calc. [C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>], C, 69.4<sub>9</sub>, H, 7.3<sub>7</sub>, N, 8.5<sub>5</sub> %; <sup>1</sup>H-NMR: 3.33 (3H, –NCH<sub>2</sub>, t), 3.31 (3H, –NCH<sub>2</sub>, t), 4.11, 4.15 (2× OCH<sub>3</sub>, s), 5.04 (1H, s), 7.12–7.55 ppm (6H, m), 11.3 (OH, s, broad), <sup>13</sup>C-NMR: 27.8, 28.5 (NCH<sub>2</sub>), 32.5, 32.4 (2× CH<sub>3</sub>) 75.1 (NCH), 86.4, 86.7 (–OCH<sub>3</sub>), 130.0–144.0 ppm (CH<sub>Ar</sub>); 4-methyl-2-[(4-morpholin-4-yl-benzylidene)-amino]-benzoic acid (8): Found, C, 70.3<sub>3</sub>; H, 6.2<sub>0</sub>; N, 8.6<sub>6</sub>; Calc. [C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>], C, 70.3<sub>5</sub>, H, 6.2<sub>1</sub>, N, 8.6<sub>4</sub>; <sup>1</sup>H-NMR: 2.25 (3H, –CH<sub>3</sub>, s), 3.30 (2H, –NCH<sub>2</sub>, t), 3.32 (2H, –NCH<sub>2</sub>, t), 4.12 (2H, –NCH<sub>2</sub>CH<sub>2</sub>, t), 4.12 (2H, –NCH<sub>2</sub>CH<sub>2</sub>, t), 5.11 (1H, s), 7.22–7.76 (7H, m), 8.45 ppm (OH, s, broad), <sup>13</sup>C-NMR: 27.3, 28.1, 29.30, 29.45 (NCH<sub>2</sub>CH<sub>2</sub>), 77.0 (NCH), 126.0–135.5 (CH<sub>Ar</sub>), 177.7 ppm (COOH); 4-methyl-2-[(4-pyrrolidin-4-yl-benzylidene)-amino]-benzoic acid (9): Found, C, 74.1<sub>0</sub>; H, 6.5<sub>5</sub>; N, 9.1<sub>0</sub>; Calc. [C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>], C, 74.0<sub>0</sub>, H, 6.5<sub>4</sub>, N, 9.0<sub>8</sub>; <sup>1</sup>H-NMR: 2.26 (3H, –CH<sub>3</sub>, s), 3.32 (2H, –NCH<sub>2</sub>, t), 3.34 (2H, –NCH<sub>2</sub>, t), 3.21 (2H, –NCH<sub>2</sub>CH<sub>2</sub>, t), 3.12 (2H, –NCH<sub>2</sub>CH<sub>2</sub>, t), 5.06 (1H, s), 7.20–7.88 (7H, m), 8.59 ppm (OH, s, broad), <sup>13</sup>C-NMR: 28.1, 29.5, 29.7, 29.9 (NCH<sub>2</sub>CH<sub>2</sub>), 79.0 (NCH), 125.1–133.7 (CH<sub>Ar</sub>), 180.1 ppm (COOH); 4-[(4-hydroxy-benzylidene)-amino]-benzene-1,3-diol (10): Found, C, 68.1<sub>0</sub>; H, 4.8<sub>5</sub>; N, 6.1<sub>5</sub>; Calc. [C<sub>13</sub>H<sub>11</sub>O<sub>3</sub>N], C, 68.1<sub>1</sub>; H, 4.8<sub>4</sub>; N, 6.1<sub>1</sub> %; 4-[(3,4-dihydroxy-benzylidene)-amino]-benzene-1,3-diol (11): Found, C, 59.7<sub>5</sub>; H, 5.0<sub>0</sub>; N, 6.3<sub>4</sub> %; Calc. [C<sub>13</sub>H<sub>11</sub>O<sub>4</sub>N], C, 59.7<sub>3</sub>; H, 5.0<sub>1</sub>; N, 6.3<sub>3</sub> %; <sup>1</sup>H-NMR: 5.30 (1H, s), 7.80–7.95 (6H, m), 10.4, 8.59, 8.20, 8.18 ppm (4× OH, s, broads), <sup>13</sup>C-NMR: 81.5 (NCH), 136.8–140.5 ppm (CH<sub>Ar</sub>); 4-[(3,5-dimethoxy-4-hydroxy-benzylidene)-amino]-benzene-1,3-diol (12): Found, C, 62.3<sub>0</sub>, H, 5.2<sub>3</sub>, N, 4.8<sub>4</sub>; Calc. [C<sub>15</sub>H<sub>15</sub>O<sub>5</sub>N], C, 62.2<sub>8</sub>, H, 5.2<sub>3</sub>, N, 4.8<sub>4</sub> %; <sup>1</sup>H-NMR: 4.46, 4.50 (3H, –OCH<sub>3</sub>, s), 5.22 (1H, s), 7.56–7.90 (5H, m), 10.4, 8.59, 8.18 ppm (3× OH, s, broads), <sup>13</sup>C-NMR: 33.3, 34.2 (OCH<sub>3</sub>), 80.0 (NCH), 135.7–139.2 ppm (CH<sub>Ar</sub>). The quinoide forms of (10)–(12), were obtained by mixing of corresponding compounds (10)–(12), by mixing of the preliminary dissolved substances in 25 ml methanol and adding the the equimolar amount of KOH dissolved in same solvent. 3-Hydroxy-4-(4-oxo-cyclohexa-2,5-dienylidenemethylimino)-cyclohexa-2,5-dienone (10a): Found, C, 68.7<sub>7</sub>, H, 3.9<sub>9</sub>, N, 6.1<sub>5</sub> %; Calc. [C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>N], C, 68.1<sub>0</sub>; H, 4.8<sub>2</sub>; N, 6.1<sub>0</sub> %; 4-[(2-hydroxy-4-oxo-cyclohexa-2,5-dienylideneamino)-methylene]-2-hydroxy-cyclohexa-2,5-dienone (11a): Found, C, 64.2<sub>0</sub>; H, 3.7<sub>5</sub>, N, 5.7<sub>7</sub>; Calc. [C<sub>13</sub>H<sub>10</sub>O<sub>4</sub>N], C, 59.7<sub>2</sub>; H, 5.0<sub>0</sub>; N, 6.3<sub>2</sub> %; 4-[(2-hydroxy-4-oxo-cyclohexa-2,5-dienylideneamino)-methylene]-2,6-dimethoxy-cyclohexa-2,5-dienone (12a): Found, C, 62.7<sub>5</sub>, H, 4.5<sub>5</sub>; N, 4.9<sub>0</sub> %; Calc. [C<sub>15</sub>H<sub>14</sub>O<sub>5</sub>N], C, 62.2<sub>2</sub>, H, 5.2<sub>2</sub>, N, 4.8<sub>3</sub> %; 3-amino-5-phenyl-7-[(4-pyrrolidin-1-yl-benzylidene)-amino]-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (13): Found, C, 67.2<sub>2</sub>, H, 5.6<sub>6</sub>, N, 27.2<sub>5</sub> %; Calc.

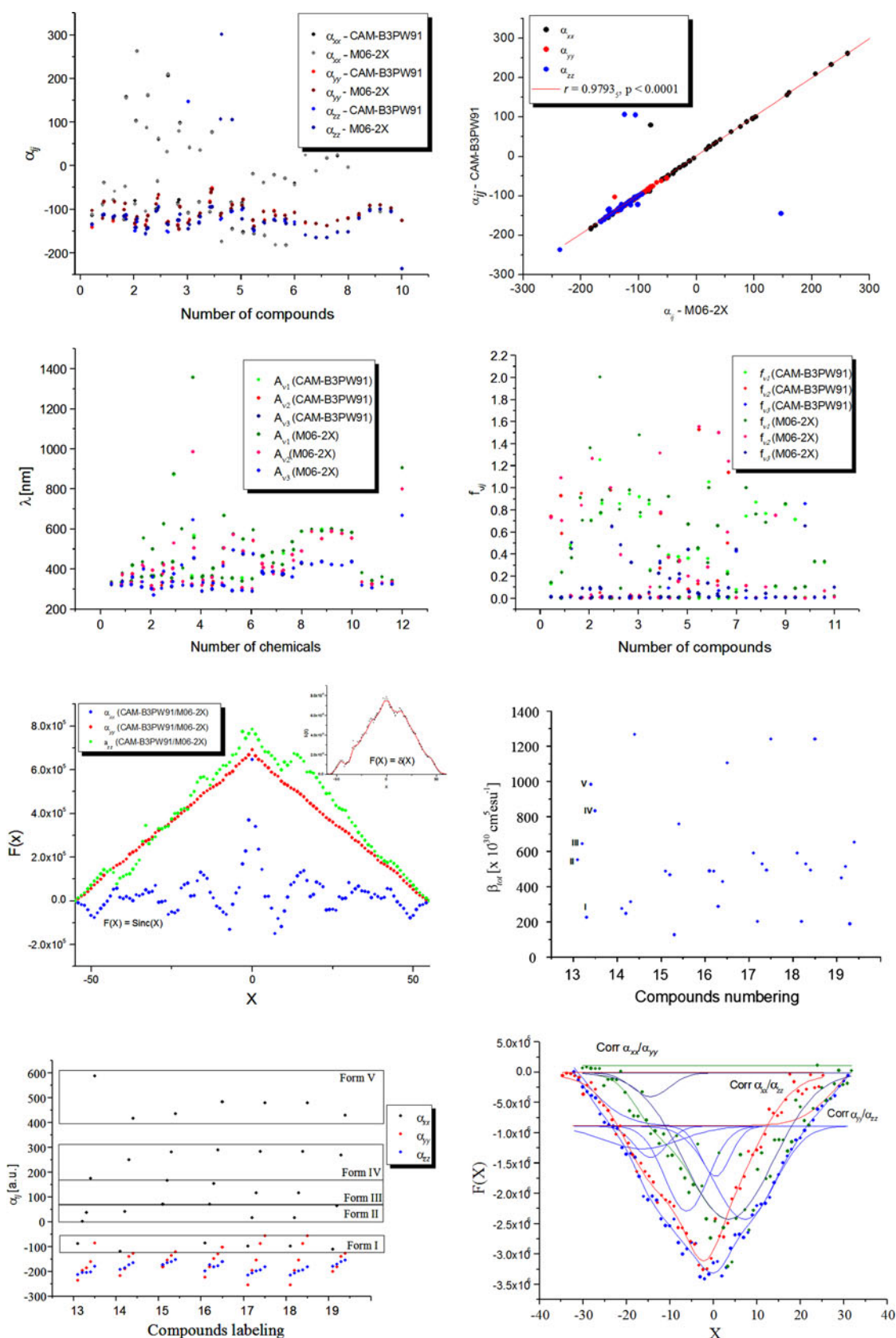
[C<sub>23</sub>H<sub>23</sub>N<sub>8</sub>], C, 67.1<sub>4</sub>, H, 5.6<sub>3</sub>, N, 27.2<sub>3</sub> %; 3-amino-5-(4-dimethylamino-phenyl)-7-[(4-pyrrolidin-1-yl-benzylidene)-amino]-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (**14**): Found, C, 66.1<sub>0</sub>; H, 6.2<sub>0</sub>, N, 27.7<sub>5</sub>; Calc. [C<sub>25</sub>H<sub>28</sub>N<sub>9</sub>], C, 66.0<sub>6</sub>, H, 6.2<sub>1</sub>, N, 27.7<sub>3</sub> %; 3-amino-7-[(4-pyrrolidin-1-yl-benzylidene)-amino]-5-(4-pyrrolidin-1-yl-phenyl)-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (**15**): Found, C, 67.50; H, 6.30, N, 26.25; Calc. [C<sub>27</sub>H<sub>30</sub>N<sub>9</sub>], C, 67.48, H, 6.29, N, 26.23; 3-amino-5-(4-morpholin-4-yl-phenyl)-7-[(4-pyrrolidin-1-yl-benzylidene)-amino]-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (**16**): Found, C, 65.3<sub>2</sub>, H, 6.1<sub>0</sub>, N, 25.4<sub>0</sub>; Calc. [C<sub>27</sub>H<sub>30</sub>N<sub>9</sub>O], C, 65.3<sub>0</sub>, H, 6.0<sub>9</sub>, N, 25.3<sub>8</sub> %; 3-amino-5-cyclohexyl-7-[(4-pyrrolidin-1-yl-benzylidene)-amino]-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (**17**): Found, C, 65.6<sub>6</sub>, H, 6.5<sub>0</sub>, 27.8<sub>5</sub> %; Calc. [C<sub>22</sub>H<sub>26</sub>N<sub>8</sub>], C, 65.6<sub>5</sub>, H, 6.5<sub>1</sub>, N, 27.8<sub>4</sub>; 3-amino-5-cyclooctyl-7-[(4-pyrrolidin-1-yl-benzylidene)-amino]-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (**18**): Found, C, 66.9<sub>8</sub>, H, 7.0<sub>1</sub>, N, 26.0<sub>5</sub> %; Calc. [C<sub>24</sub>H<sub>30</sub>N<sub>8</sub>], C, 66.9<sub>5</sub>, H, 7.0<sub>2</sub>, N, 26.0<sub>3</sub>; 3-amino-7-[(4-morpholin-4-yl-benzylidene)-amino]-5-(4-morpholin-4-yl-phenyl)-5,8-dihydro-[1, 2, 4]triazolo[4,3-a]pyrimidine-6-carbonitrile (**19**): Found, C, 63.3<sub>0</sub>, H, 5.9<sub>2</sub>, N, 24.6<sub>0</sub>; Calc. [C<sub>27</sub>H<sub>30</sub>N<sub>9</sub>O<sub>2</sub>], C, 63.2<sub>7</sub>, H, 5.9<sub>0</sub>, N, 24.5<sub>9</sub> %, respectively.

## Results and discussion

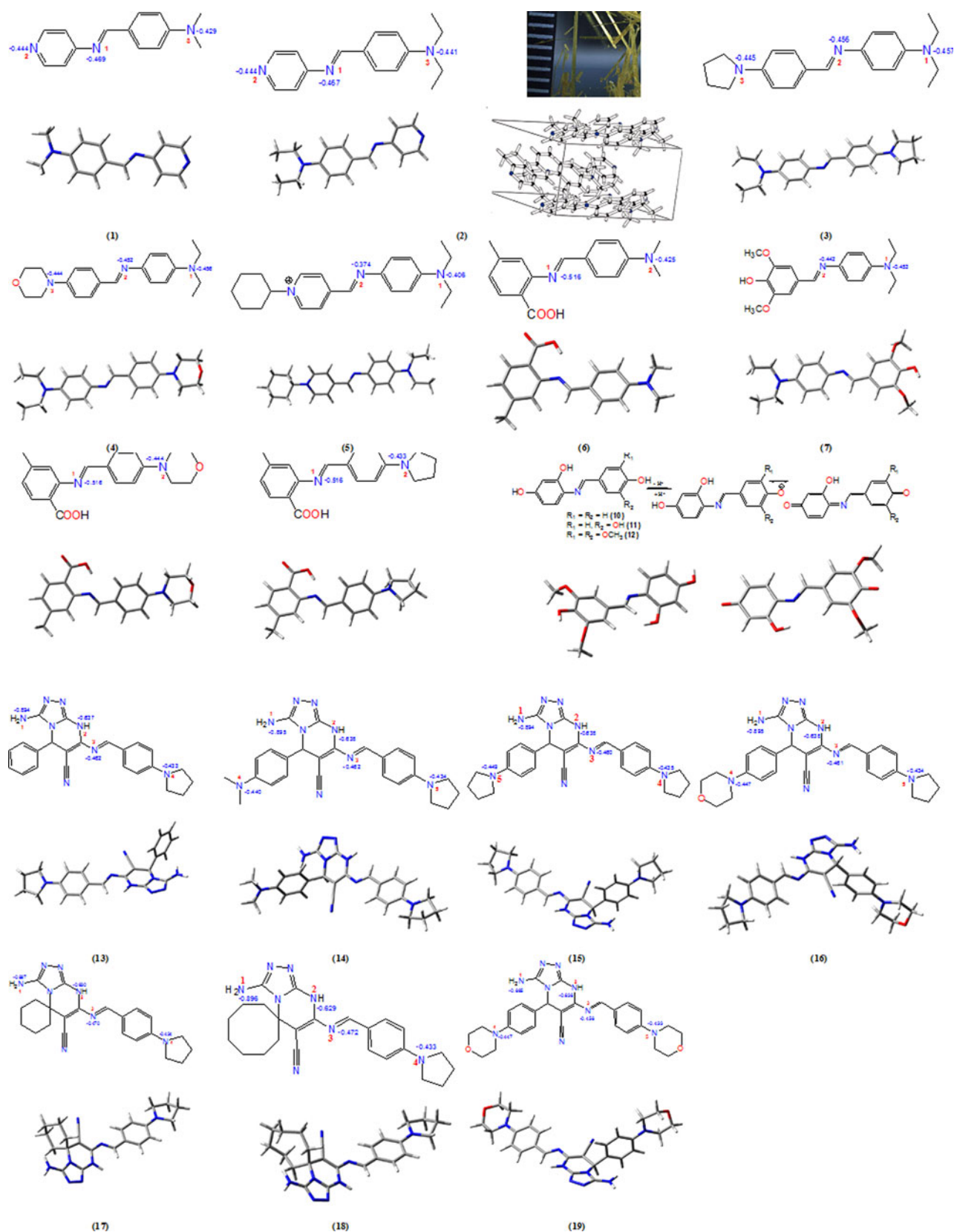
Theoretical dipole moments ( $\mu_{\text{tot}}$ ), static polarizabilities ( $\alpha_{ij}$ ) and first hyperpolarizability ( $\beta_{\text{tot}}$ ) were shown in Fig. 1. The protonated forms were elucidated, using theoretical data for NBO analysis. According the  $q_{\text{N(NBO)}}$  values obtained, conclusions about the protonation ability were presented. The corresponding forms were labeled on Scheme 2. Theoretical data were obtained using two considered the most successful theoretical approaches, i.e. CAM-B3PW91 and M06-2X functionals, showing good correlation between predicted and experimental observed physical properties [71–81]. The performed regression analysis resulted to 99.4–97.9 % level of confidence between the data of  $\alpha_{ij}$ , obtained at both methods. As seen from the data, the correlation, refers to Dirac  $\delta(X)$  and Sinc(X) the  $\alpha_{ij}$  data in various forms. The theoretical data predicted the greatest sensitivity of  $\beta_{\text{tot}}$ ,  $\alpha_{xx}$  and  $A_{V1}$  in the process of protonation. Interestingly were the obtained for the preferred protonated centers in various derivatives in accordance to the NBO analysis. In compounds (**1**), (**2**), (**6**), (**8**) and (**9**) preferred protonation position was found imine N(=C) nitrogen. Moreover, the spectral data for compounds (**6**), (**8**) and (**9**) showed zwitterion structure [99–101]. The protonation resulted to recovery of the COOH group. Such a structure was generally valid for

most derivatives. It provided, excellent opportunities of (**6**), (**8**) and (**9**) for application in the coordination chemistry as ligands for the design of metal–organic NLO materials. In many cases it was preferred to become a classical scheme for 5- or 6-member chelating between the –OH and N(=C) centres. In (**3**), (**4**), (**5**) and (**7**), was preferred –N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> nitrogen as a proton accepting center. In the series (**13**)–(**19**) as preferred protonated centre appeared NH<sub>2</sub>, followed by NH group in the heterocyclic fragment. The protonated forms of compounds (**5**) and (**6**) are characterized by significant  $\beta$ -values, 2.5–3 times higher, exceeding this of DAST core (Figs. 1, 2), which makes them particularly attractive as new materials. The dyes of similar type have been shown excellent experimental NLO properties and applicability in THz-technologies [32–43]. Protonated N(=C) imine nitrogen in the Schiff's bases affected to some extent  $\beta$ -values. Much more significant effect, has the protonation at N<sub>py</sub>- or nitrogen atoms in the aliphatic bulk substituents. The inclusion of competitive substituents with the stronger basic properties, such as morpholin, pyrrolidine or diethylamine ones, changed the basic properties in the first degree of protonation, which was preferable according the obtained  $\beta$ -values. This was a key stage in the design of these derivatives to the desired application areas. The fact that the already established in practice derivatives such as DAST, DAT2, or PyT1 have substituents of types –N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> or pyrrolidine as confirms in addition the correctness of these conclusions about the search of new materials, among derivatives of this class [20, 23, 43, 105, 106]. The neutral forms of (**1**) and (**2**) showed the comparable  $\beta$ -values with this of DAST core, moreover the (**2**) crystalized in the noncentrosymmetric *Pca*2<sub>1</sub> space group [105]. The obtained  $\beta_{\text{tot}}$  values for the isolated molecule as well as the crystals of (**2**) show 4 times higher values in the crystal (Fig. 3). These data announced to be taken into account considering the values obtained for isolated molecules. The data for (**10a**)–(**12a**), obtained by electronic absorption spectroscopy suggested the stabilization of the quinoide forms, significantly shifted bathochromically the  $\lambda_{\text{max}}$  more than 270 nm (Figs. 1, 3). A hyperchromic effect was found. For (**13**)–(**19**), the obtained  $\beta$ -values of the protonated forms were comparable with the DAST ones. Comparing theoretical and experimental data for the  $\lambda_{\text{max}}$ , difference 3–9 nm was observed. The new dyes showed intense absorption CT bands in the visible region, within 380–440 nm. The calculated properties in excited state (ES) show that the HOMO–LUMO gaps were mostly located on the electron-rich functionals, with a limited contributions to rest molecular fragments. Regarding the obtained diffuse reflectance (Ds) and fluorescence spectra (Fs) in solid-state, announced to note that CT bands was shifted and splitted, similar to the ES (Fig. 3) [107, 108]. The performed vibrational analysis

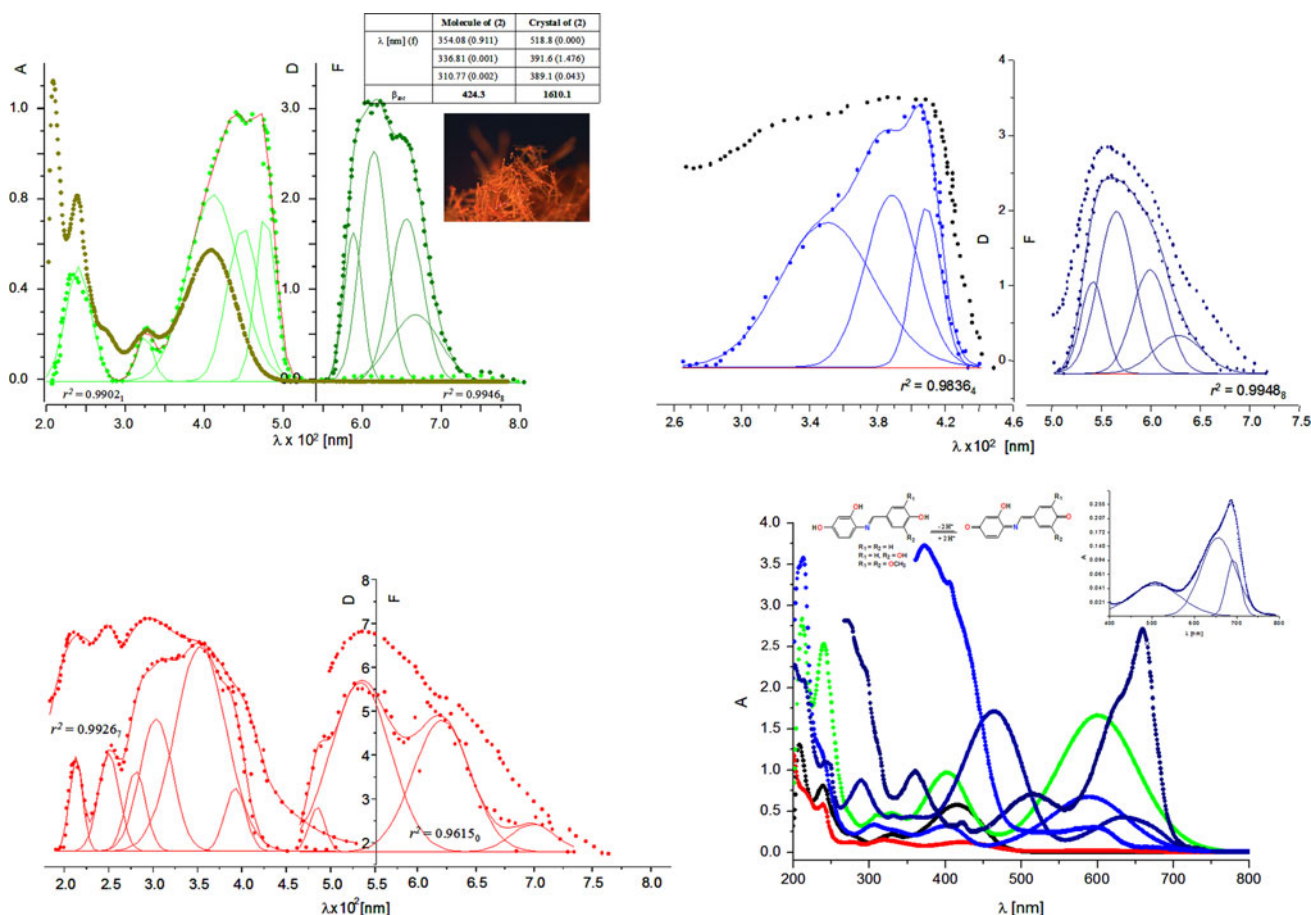




**Fig. 1** Regression and correlation dependences of the theoretically obtained optical and NLO properties of the studied compounds



**Scheme 2** Chemical diagrams of the studied bases; theoretical  $q_N(\text{NBO})$  charges, protonation positions  $i$  ( $i = 1-5$ ) optimized molecular geometries, crystal structure of (2) as well as photograph of corresponding crystals



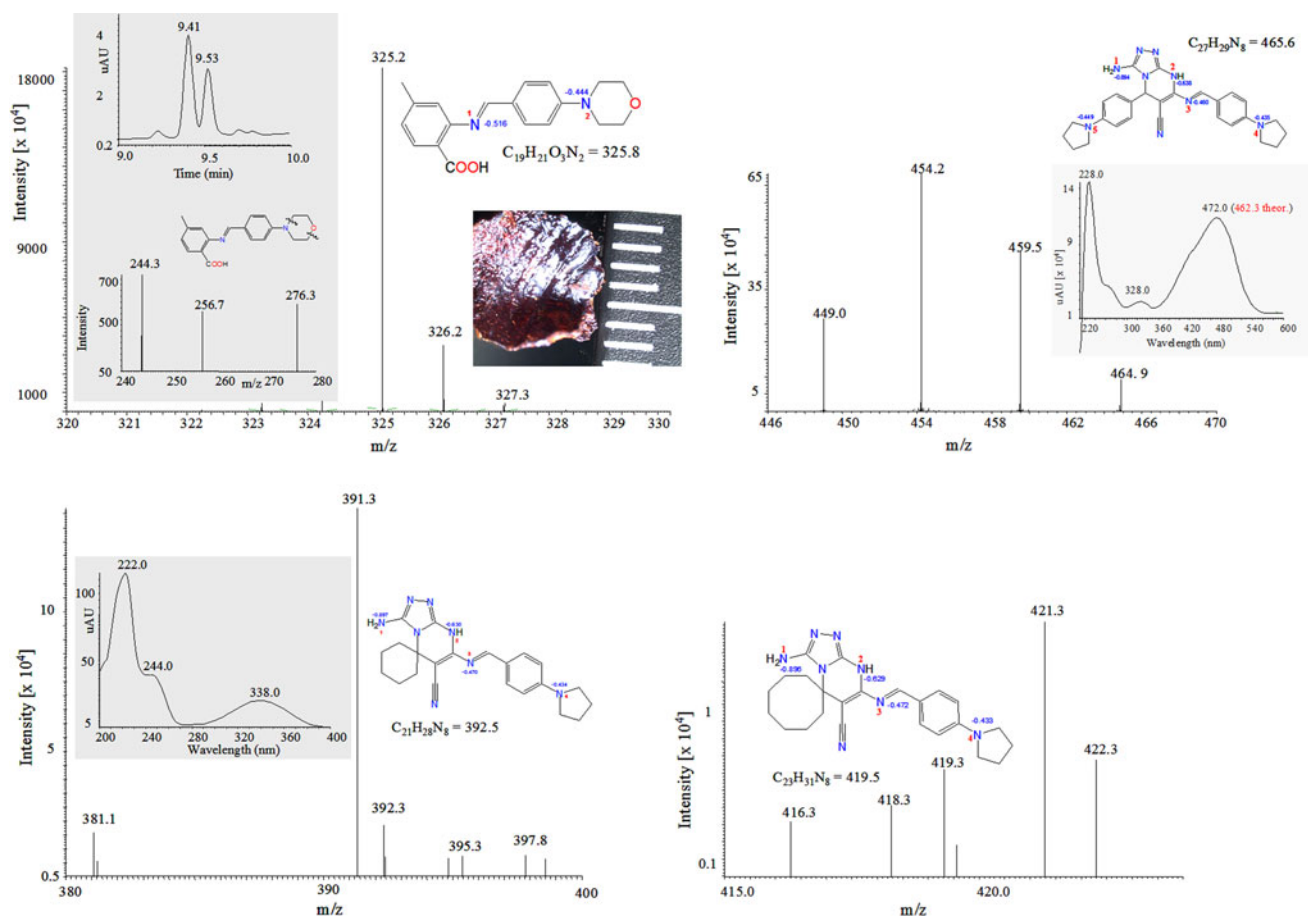
**Fig. 2** Mathematically non- and procedure (*baseline corrected*) absorption (*A*), diffuse reflectance (*D*) and fluorescence (*F*) spectra in condensed phases. Photographs of the crystals. Theoretical electronic absorption spectra and *b* values of isolated molecule and the crystal of (2), respectively

showed that common to all Schiff's bases was the disappearance in the IR- and Raman spectra of the  $\nu_{\text{C}=\text{O}}$  stretching vibration of the starting aldehyde group and the observation of the series of vibrational bands at  $1,664\text{ cm}^{-1}$ . The corresponding  $\nu_{\text{N}=\text{C}}$  vibration was observed about  $1,625\text{ cm}^{-1}$ . Significant changes were observed in vibrations associated with different types of substitution in benzene nuclei. The observed results were connected with the fact that the overall geometry of the molecules remains at a significant degree. For all compounds, the observed planar geometry of the aromatic skeleton with a deviation in the range within  $2\text{--}7^\circ$ , respectively. In the protonated forms, significantly has influenced the molecular geometry in the bulky substituents to benzene nuclei areas, because of conjugation of the electron-pair of nitrogen with the aromatic system was impaired. This significantly effected the regions of stretching and bending vibrations related to the  $\text{N}^+\text{H}$ -group about within  $3,100\text{--}2,800$  and  $1,645\text{ cm}^{-1}$ , respectively [13–17]. The nuclear magnetic resonance characteristics, also vary within narrow limits in these compounds, such significant differences are observed only at derivatives

associated with the bulk substituents in the aromatic systems. The effect of the  $-\text{OH}$  and  $-\text{N}$  substituents is evaluated in a range of  $0.5\text{--}2.1$  ppm, respectively. The shifting of the values up to  $2.0$  ppm are mainly related to the proton signals of the generated  $\text{N}^+\text{H}$  groups in salts. Interest are also data obtained from the high resolution mass spectra for the structures of the studied dyes (Fig. 3). As for waiting for all the compounds are characterized by peaks of the cations of the bases. For compounds with morpholine fragment however the chromatographic data show number of peaks corresponding to the derivatives with the cleavage morpholine cycle. It is interesting that the derivatives with pyrrol-fragment or compounds of type (17) and (18) are not observed similar processes related to cyclic fragments. Therefore, the data would be connected with the influence of  $\text{O}^-$  in the morpholine during the ionization processes.

## Conclusions

Unlike the general accepted view of applicability of the Schiff's bases as ligands in the design of new metal-



**Fig. 3** Chromatographic, electronic absorption and high resolution mass spectrometric data. Photograph of the thin 2D film

organic NLO materials, in this work has been provided new derivatives, characterising with marked optical and nonlinear optical properties, thus assuming their potential usage as novel organic materials, themselves. Certainly, the molecular architecture of some of the compounds displayed suggesting chelating-effect, made them also suitable as ligands in coordination chemistry. Much more significant, have been received properties for the derivatives with more than one proton accepting center, practically giving greater opportunities for further modeling design of organic salts, depending on the ratio of Schiff's base: acid, functionality of the acids [102–104] as well as its properties, i.e. tuning the hydrogen bonding and Coulomb interactions in the crystals. It could be noted that: (a) the classic conception for the protonation ability of the Schiff's bases, i.e. imine  $N(=C)$  nitrogen was confirmed only in the case of derivatives with a substituents  $-NH_2$ ,  $-OH$ , and/or  $-OCH_3$ ; (b) for derivatives containing heterocyclic fragments with  $-NH_2$  or cyclic  $NH$  groups or substituents such as  $-N(CH_2CH_3)_2$ , morpholine or pyrrolidine types, has been found as most preferred for

protonation. These data highlighted the novelty of the presented study towards the further molecular design of organic salts and corresponding metal–organic complexes with tunable NLO properties, and underlined the impact of the theoretical analysis of the protonation ability; (c) the optical properties both in ground and excited state show the CT band within 380–400 nm, shifted about 5–10 nm in solid-state and spitted in the diffuse reflectance and fluorescence spectra; (d) the obtained  $\beta_{tot}$  values of the protonated forms were 2.5–7.0 times higher than those of neutral ones. All novel derivative were characterized with  $\beta_{tot}$  4.0–5.5 times higher than the of DAST value, using as standard; (e) for compound (4-diethylamine-benzylidene)-pyridin-4-yl-amine, crystallizing in the non centrosymmetric space group  $Pca2_1$ , the obtained  $\beta_{tot}$  values of the crystal are 4 times higher than the corresponding one of isolated molecule.

**Acknowledgments** The authors thank the DAAD (Deutscher Akademischer Austausch Dienst), and DFG (Deutsche Forschungsgemeinschaft).



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