

Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc.00(0)S1-S12 (2023)



# New pyrene and fluorene-based $\pi$ -conjugated Schiff bases: Theoretical and experimental investigation of optical properties

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## EXPERIMENTAL

A. General Information: All chemicals and solvents were purchased from Sigma Aldrich. 2-Amino-4-methyl benzothiazole (97 %), pyrene-1-carbaldehyde (98 %), fluorene-2carbaldehyde (99 %), hydrochloric acid (HCl, 99.7 %) were used without further purification. The organic solvents (ethanol (EtOH, 99.8 %), dichloromethane (DCM, 99 %), petroleum ether (90 %)) were used of HPLC grade or purified by a standard procedure. Melting points of synthesized compounds were determined by the Gallenkamp melting point apparatus using capillary tubes. FT-IR and UV-Visible absorption spectroscopy were taken at Eskisehir Osmangazi University Inorganic Chemistry Research Laboratory. FT-IR spectra were recorded with Bruker FT-IR spectrometer in the range of 4000-400 cm<sup>-1</sup> wavelengths. UV-Visible absorption spectra were recorded with a SHIMADZU UV-2600 spectrometer using and the optical band gap was determined using Tauc methods and evaluated using UV Probe Software. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS internal standard) and <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, TMS internal standard) spectroscopic analyses were carried out on using Jeol ECZ500R (11.75 Tesla) NMR equipment in Eskisehir Osmangazi University Central Research Laboratory Application and Research Center (ARUM). ESI-Mass and elemental analyses were recorded by Waters Alliance HPLC, 2Q micromass spectrometer, and Leco CHNS 932 Elemental Analyzer, respectively, in Ankara University Central Research Laboratory. Thin layer chromatography (TLC) plates were purchased as ready-coated from MERCK and used to control the reactions. With the help of the hybrid functional (B3LYP) and a specific basis set of 6-31G(d,p), a Gaussian 09 program was successfully operated. For extended electrochemical analyses of synthesized moieties, the energy gaps between their HOMO and LUMO states were determined using the readily available tool Gauss View 6.0.

B. General method for 4-methyl-N-(pyren-1-yl-methylene) benzo[d]thiazol-2-amine (7a) and N-(9H-fluoren-3-yl-methylene)-4-methylbenzo[d]thiazol-2-amine (9a)



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A solution of 4-methyl-2-amino benzothiazole (1 eq.) in ethyl alcohol was added to appropriate aldehyde (0.8 eq) . 2-3 drops of 5 % HCl solution were added to the reaction medium and refluxed in a nitrogen atmosphere at 75 °C for 4 hours. The reaction was terminated with TLC control (1:10 Petroleum ether / DCM). After cooling the solution at room temperature overnight, the precipitates were filtered and extracted with DCM and then recrystallized from ethyl alcohol. It was obtained **7a** as orange crystals and **9a** as yellow crystals. (The protocol followed for the synthesis of the **7a** and **9a** Schiff bases and the numbering of the protons in the molecule is summarized in Scheme S1).



*i*: EtOH, 75 °C, reflux, %5 HCl, N<sub>2</sub>(g)

Scheme S1. Synthesis method and numbers of protons

### SPECTROSCOPIC DATA OF MAIN COMPOUNDS

*N-(pyren-1-ylmethylene)-4-methylbenzo[d]thiazol-2-amine (7a)* Yield: 50 %, mp. 212-216 °C. FT-IR (KBr, cm<sup>-1</sup>): 3038 (Aromatic C-H), 2965-2918 (Aliphatic C-H), 1593 (CH=N), 1576, 1537 and 1478 (C=C) (Fig.S1). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$  ppm): 9.98 (s, 1H, CH=N), 9.28 (d, 1H, J=9 Hz, H17), 8.84 (d, 1H, J= 7 Hz, H10), 8.44 (m, 5H, H9, H11, H14, H15, H16), 8.28 (d, 1H, J= 8.9 Hz, H13), 8.15 (t, 1H, J= 8.6 Hz, H12), 7.88 (dd, 1H, H6), 7.31 (d, 2H, H5 ve H7), 2.45 (s, 3H) (Fig.S2). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$  ppm): 135.0 (CH=N), 134.36, 132.80, 131.74, 131.21, 130.86, 130.61, 130.53, 129.08, 127.09, 127.67, 127.59, 127.50, 127.41, 125.83, 124.51, 123.93, 123.28, 120.25. ESI-MS (m/z): 377.68 (M<sup>+</sup>), 378.71 (M<sup>+</sup>+1), 379.77 (M<sup>+</sup>+2), 245.48 (M<sup>+</sup>-C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>S), 165.15 (M<sup>+</sup>-C<sub>17</sub>H<sub>19</sub>). Anal. Calcd. for C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>S: C, 79.76; H, 4.28; N, 7.44; S, 8.52. Found: C, 79.52; H, 4.44; N, 7.37; S, 8.40.

*N*-(9*H*-fluoren-3-ylmethylene)-4-methylbenzo[d]thiazol-2-amine (9a) Yield: 60 %, mp. 180-183 °C. FT-IR (KBr, cm<sup>-1</sup>): 3046 (Aromatic C-H), 2957, 2910 (Aliphatic C-H), 1620 (CH=N), 1586, 1549 and 1518 (C=C) (Fig.S3). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$  ppm): 9.14 ( s, 1H, -CH=N-), 8.26 ( s, 1H, H9 ), 8.07 ( d, 2H, J=1.5 Hz H14 and H15 ), 7.99 ( d, 1H, J= 7.0 Hz, H7 ), 7.80 ( dd, 1H, J=2.5 Hz, J=8 Hz, H10 ), 7.62 ( d, 1H, J=8.0 Hz, H5 ), 7.39 ( t, 1H, J=7.5 Hz, H6 and dt, 1H, J=8 Hz, H12 ), 7. 28 ( d, 1H, J=8.0 Hz, H13 and t, 1H J=7 Hz, H11 ),

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#### SUPPLEMENTARY MATERIAL

S3









![](_page_3_Figure_1.jpeg)

![](_page_4_Figure_0.jpeg)

![](_page_5_Figure_0.jpeg)

![](_page_6_Picture_0.jpeg)

Fig S7. Front (left) and side (right) view of the optimized structure of compound 7a

![](_page_7_Picture_1.jpeg)

| Thermal correction | to Gibbs Free Energy | (Hartree) = 0.2 | 287006  |
|--------------------|----------------------|-----------------|---------|
| С                  | -5.7557              | -4.0026         | 0.0403  |
| С                  | -4.8025              | -4.9499         | 0.0676  |
| С                  | -3.5033              | -4.6125         | 0.1156  |
| С                  | -3.1932              | -3.3093         | 0.1353  |
| С                  | -4.1457              | -2.3685         | 0.108   |
| С                  | -5.4488              | -2.6917         | 0.0598  |
| S                  | -1.8702              | -2.6883         | 0.1863  |
| C                  | -2.3634              | -1.2992         | 0.1789  |
| N                  | -3 6308              | -1 2171         | 0 1341  |
| N                  | -1 7306              | -0 1971         | 0 2101  |
| C                  | -0 4709              | -0.0485         | 0 2569  |
| C                  | -0 5637              | 2 2588          | 0 2734  |
| Č                  | -0.0138              | 3 4781          | 0.2791  |
| C                  | 1 319                | 3 6125          | 0.3545  |
| C                  | 2 0969               | 2 5118          | 0.3343  |
| C                  | 1 53/1               | 1 2785          | 0.3/08  |
| C                  | 0 1027               | 1 1260          | 0.3400  |
| C                  | 2 1270               | 2 6906          | 0.2900  |
| C                  | 1 2569               | 2.0000          | 0.4232  |
| C                  | 4.2300               | 0 2961          | 0.4431  |
| C                  | 2 2051               | 0.3001          | 0.4110  |
| C                  | 2.3031               | 0.232           | 0.3017  |
| C                  | 5.9001<br>E 2010     | 3.9133          | 0.4547  |
| C                  | 5.5219               | 4.0057          | 0.5040  |
|                    | 0.1272<br>5.5016     | 2.995           | 0.0209  |
| C                  | 1 9605               | 1 0/10          | 0.4951  |
| C                  | 1.00UJ<br>2 1005     | 4.0410          | 0.3037  |
| C                  | 5.1095               | 4.994           | 0.4337  |
| U U                | -6.9147              | -1.2026         | 0.0200  |
| п                  | -0.0147              | -6.0151         | 0.001   |
| п                  | -3.009               | -0.01J1         | 0.0300  |
|                    | -2.7207              | -3.3977         | 0.1370  |
| п                  | 0.1072               | -0.9000         | 0.2704  |
| п                  | -1.000               | Z.Z343<br>1 261 | 0.2333  |
| п                  | -0.0762              | 4.301<br>0.5126 | 0.2005  |
| П                  | 4.5565               | -0.5126         | 0.4207  |
| П                  | Z.USS/<br>E.7010     | -0.8168         | 0.3395  |
| П                  | J./810<br>7.0010     | 5.0685          | 0.5307  |
| Н                  | 7.2219               | 3.123           | 0.5648  |
| • H                | 6.2682               | U.8959          | 0.3096  |
| Н                  | 1.2281               | 5./462          | U.3/1   |
| H                  | 3.60/                | 6.UI51          | 0.4605  |
| H                  | -6.15/               | -0.6105         | 0.060/  |
| Н                  | -/.1454              | -1./565         | -0.9027 |
| Н                  | -7.2219              | -1./825         | 0.9027  |

Sum of electronic and thermal Free Energies (Hartree)= -1469.786060

![](_page_8_Figure_0.jpeg)

Fig S7. Front (left) and side (right) view of the optimized structure of compound 9a.

![](_page_9_Picture_1.jpeg)

С 7.0316 0.69762 0.24052 С 7.26734 -0.65893 -0.0043 С 6.22069 -1.54738 -0.19256 С 4.91385 -1.06566 -0.13392 С 4.67582 0.30957 0.11157 1.20826 С 5.73912 0.30349 3.41762 -1.94978 -0.32722 S С 2.5349 -0.41676 -0.07801 3.29832 0.64939 0.13484 Ν -0.05995 1.12015 -0.39232 Ν С 0.42027 0.68441 -0.25694 С -1.04407 0.63639 -0.20738 С -1.74033 -0.55218 0.06513 С -3.12127 -0.51314 0.09489 С -3.81911 -0.14285 0.69399 -3.13384 С 1.86797 -0.41156 -1.74169 С 1.82843 -0.44165 С -4.09047 0.35997 -1.63175 0.25127 С -5.42491 -0.94853 С -5.25135 0.42454 -0.04592 С -6.69227 -1.48005 0.39949 -7.79082 С -0.62966 0.24879 С -7.61911 0.71905 -0.04313 С -6.34252 1.26387 -0.19443 С 5.49993 2.649 0.56448 Η 7.88589 1.36978 0.38561 Η 8.29958 -1.02318 -0.04675 Η 6.41233 -2.60878 -0.38288 Η 0.87647 1.6678 -0.4669 -1.2047 Η -1.49079 0.25044 -0.59496 Η -3.67581 2.80149 Η -1.18593 2.75032 -0.65236 Η -3.98584 -2.44856 -0.3778 -3.93785 -2.07827 Η 1.35986 -6.83293 -2.54066 Η 0.62927 -8.80209 0.36289 Η -1.03412 Η -8.49628 1.3647 -0.1563 Η -6.20451 2.3253 -0.42418 Η 4.94652 3.11196 -0.26377 Η 4.90548 2.78929 1.4775 6.43807 3.20643 0.68978 Η

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![](_page_10_Figure_0.jpeg)

Fig. S9. HOMOs and LUMOs of **7a** (left) and **9a** (right) estimated at the B3LYP/6-31 G (d, p) level in the gas phase.

A dispersion component was added to the B3LYP 6-31 G (d,p) level of theory used in DFT calculations, and re-optimization and frequency calculations of the investigated 7a and 9a molecules were completed. The command line for frequency calculations with added dispersion component is given below:

freq=noraman b3lyp/6-31g(d,p) scrf=(cpcm,solvent=dmso) guess=save geom=connectivity EmpiricalDispersion=GD3BJ

First, there is no difference in the dihedral angles and therefore the geometry of the optimized structures by using the dispersion component.

Then, excited energy calculations were rerun with the freshly optimized geometries, and results were compared with previously obtained theoretical results.

When the HOMO-LUMO band gap energies of 7a and 9a were examined, narrower band gap energies were detected compared to the calculations done without using this dispersion component. The band gap energy values obtained both without and using the dispersion component tend to decrease or increase in the same way as the experimental study. However, it is seen that the band gap value obtained by adding the dispersion component deviates further from the experimental data.

![](_page_10_Picture_7.jpeg)

![](_page_11_Picture_0.jpeg)

|          |       | Calculation with dispersion |          | Calculation without dispersion |          |
|----------|-------|-----------------------------|----------|--------------------------------|----------|
|          |       | component                   |          | component                      | t 🔰 🖉    |
| Compound |       | The sum of thermal          | Band gap | The sum of thermal             | Band gap |
|          | Phase | and free energy             | energy   | and free energy                | energy   |
|          |       | (Hartree)                   | (eV)     | (Hartree)                      | (eV)     |
| 7a -     | Gas   | -1469.9010                  | 2.85     | -1469.7861                     | 2.85     |
|          | DMSO  | -1469.9125                  | 2.66     | -1469.7974                     | 2.87     |
| 9a       | Gas   | -1355.5595                  | 3.22     | -1355.4612                     | 3.20     |
|          | DMSO  | -1355.5644                  | 3.04     | -1355.4801                     | 3.19     |

Table S1. The results of the calculations with and without the dispersion component

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