

Barbara Dondela

Lidia Chrząstek

Jan Długosz University, Institute of Chemistry and Environmental Protection,  
42-201 Częstochowa, Armii Krajowej Ave 13/15, e-mail: b.dondela@ajd.czyst.pl

## AM1 CI and DFT B-3 LYP study of diazaphenanthrenesulfonamides

**Abstract:** Two diazaphenanthrenesulfonamides have been synthesized. For calculation of theoretical UV values of these compounds the AM1 CI method has been used; their geometry optimisation was made with AM1 CI and DFT B-3 LYP methods.

**Keywords:** calculation, diazaphenanthrenesulfonamides, geometry optimisation, UV spectra, wavenumber

### Introduction

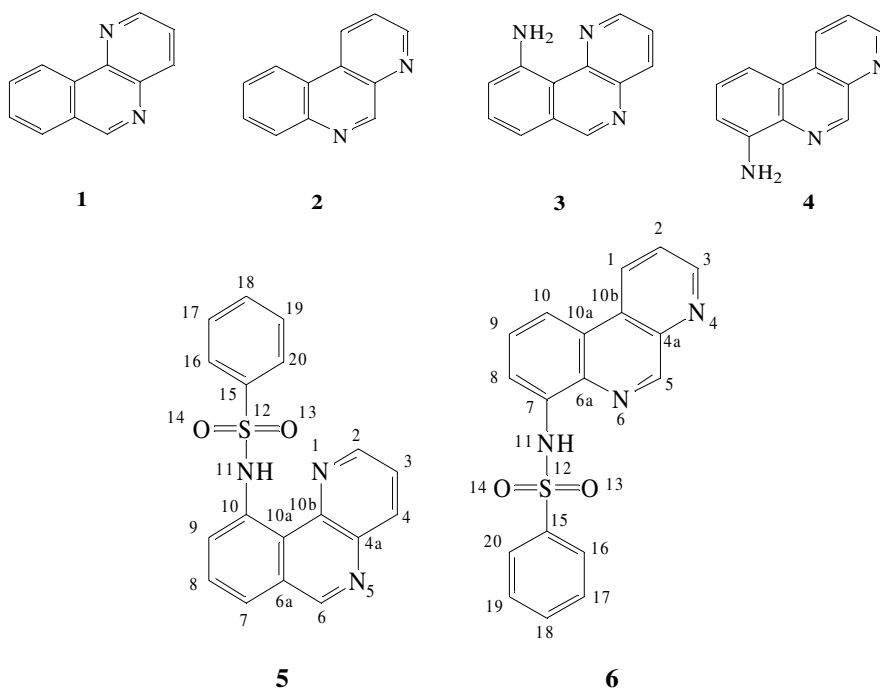
The present work is a continuation of our study concerning correlations of experimental and calculated UV spectral values for isomeric 1,5- and 4,6-diazaphenanthrenes (dap) **1**, **2** and their derivatives [1, 2]; similar investigations were made for daps substituted with formyl [3], methyl [4] and amino groups [2, 5] and with Br atom [6, 7] as well as of their quaternary salts [1, 8] and N-oxides [9].

Daps **1**, **2** and related compounds are interesting for their reactivity and biological properties; the presence of two nitrogen atoms in the molecule enables their complexation with metal ions [10], quaternization [11] and N-oxidation [12].

Dap quaternary salts [11] and N-oxides [12] undergo a variety of reactions; some quaternary salts are precursors of ylides serving as 1,3-dipoles in cycloaddition reactions [13]; N-alkyl salts of daps may be converted into corresponding N-alkylbenzophenanthridones [14]. Nitration of daps followed by reduction affords aminodaps which after diazotization and coupling yield azo dyes [15]. Methyl daps may be nitrated to give nitro methyl daps [16] or oxidized with SeO<sub>2</sub> yielding formyl daps [17]. Crystallographic structure determination of a few dap derivatives [20, 21] has been made.

Daps are interesting for their potential use as pharmaceuticals, some compounds of this class show antibacterial, fungicidal and antineoplastic activities [16–18] and influence the enzymic activity in plants [19].

In the present paper we describe reaction of aminodaps **3**, **4** with benzenesulfonyl chloride yielding dap sulfonamides **5**, **6** as well as correlations of experimental and calculated UV spectral values of these compounds, along with their geometry optimisation.



For calculation of UV spectral values of **5** and **6** and for correlation of their experimental and theoretical wavenumber values we chose AM1 CI method, (next referred to as AM1) and for geometry optimisation the AM1 and ab initio DFT B-3 LYP (next referred to as DFT) methods.

AM1 method is parametrised for heteroaromatic compounds and is used in calculations of optimised geometries, electronic properties, total energy and heat of formation values [22–26].

DFT, *i.e.* density functional theory is useful for determination of the structure and energetics of molecules. From primary results of DFT calculations, such as electron density, the spin density, the total energy and one-particle energies, the electronic and magnetic properties of molecules may be derived [27–29].

The UV spectra of **5**, **6** have been compared with those of parent daps **1**, **2** and of aminodaps **3**, **4**.

### Experimental

The UV spectra have been recorded in 1,2- dichloroethane solution ( $c = 10^{-4}$  M) on UV-vis Specord spectrophotometer. Calculations were made by AM1 CI 15 and by DFT B-3 LYP/ 3–21 G methods. The results have been obtained on a Pentium III 733 MHz computer with the use of Hyper Chem 4.5 program,.

Compounds **5**, **6** have been synthesised by reacting aminodaps [2] with benzenesulfonyl chloride as follows: Aminodiazaphenanthrene (**3** or **4**) (0,195 g; 1 mmol) dissolved in ethanol ( $2 \text{ cm}^3$ ) was treated with benzenesulfonyl chloride (0,172 g, 1mmol) and refluxed for 2 hours. To a cooled reaction mixture conc. HCl ( $4 \text{ cm}^3$ ) was added, the formed solid was filtered off and recrystallised from 95% ethanol. **5**, m.p.  $176^\circ \text{C}$ , yield 51%; **6**, m.p.  $170^\circ \text{C}$ , yield 42%.

### Results and discussion

The experimental and calculated UV spectral data of **5** and **6** are given in Table 1. The comparison of experimental wavenumber values of **5**, **6** with those of corresponding parent daps **1**, **2** [5] and with aminodaps **3**, **4** [2] is shown in Table 2.

Table 1. Experimental UV data along with calculated by AM1 method wavenumber and oscillator strength values in the dipole length approximation for **5** and **6**.

	Experimental		Calculated	
	$\bar{\nu} \times 10^3 (\text{cm}^{-1})$	$\log \epsilon$	$\bar{\nu} \times 10^3 (\text{cm}^{-1})$	$f$
<b>5</b>				
$\alpha$	28.4	3.530	27.428	0.078
$\pi$	27.5	3.820	38.460	0.854
$\beta$	40.1	4.041	40.766	0.476
<b>6</b>				
$\alpha$	31.6	3.580	32.806	0.066
$\pi$	38.7	3.780	36.904	0.808
$\beta$	41.7	3.710	40.073	0.534

$\epsilon$  = molar absorptivity index ;  $f$  = oscillator strength

Table 2. Differences in the experimental wavenumber values of  $\alpha$ ,  $\pi$  and  $\beta$  bands for **5**, **6** as compared with corresponding parent daps **1**, **2** and aminodaps **3**, **4**.

Band	$\bar{\nu}$ Differences $\times 10^3$ (cm <sup>-1</sup> )			
	5/1	6/2	5/3	6/4
$\alpha$	+0.17	-3.80	-2.30	-7.50
$\pi$	-0.36	+1.20	-0.30	-1.90
$\beta$	+1.40	+3.23	+1.00	+1.83

Positive values denote red, negative blue shifts.

Comparison of experimental wavenumber values for **5**, **6** with those of parent daps **1**, **2** indicates the red shift of  $\beta$  bands. Similar comparison with wavenumber values of aminodaps **3**, **4** shows the blue shift of  $\alpha$  and  $\pi$  bands, and the red shift for  $\beta$  bands. The strongest red shift was observed for  $\beta$  band of **6/2**, and the strongest blue shift for  $\alpha$  band of **6/4**.

The correlations of observed and calculated with AM1 method wavenumbers of **5,6** are:

**For 5/6**

$$a = 0.801 \quad b = -8.023 \quad r = 0.986$$

**for 5:**

$$a = 0.860 \quad b = 4.732 \quad r = 0.997$$

**for 6:**

$$a = 1.406 \quad b = -14.126 \quad r = 0.975$$

The correlations of observed and calculated by AM1 method wavenumber values for **5**, **6** with corresponding parent daps **1**, **2** and aminodaps **3**, **4** are:

$$\text{For } \mathbf{5/1}: a = 0.907 \quad b = 2.302 \quad r = 0.971 \quad \text{for } \mathbf{5/3}: a = 0.905 \quad b = 3.068 \quad r = 0.992$$

$$\text{For } \mathbf{6/2}: a = 1.064 \quad b = -1.714 \quad r = 0.958 \quad \text{for } \mathbf{6/4}: a = 1.069 \quad b = -2.086 \quad r = 0.972$$

The above correlations show higher  $r$  coefficients for comparison of wavenumber values of **5**, **6** with corresponding aminoderivatives **3** and **4** than those for comparison with parent daps **1**, **2** respectively; among them the highest  $r$  is for **5/3** ( $r = 0.992$ ).

The total and binding energy values as well as dipole moments for **5**, **6** calculated by AM1 and DFT methods are presented in Table 3.

Table3. Total energy, binding energy, heat of formation and dipole moments values for **5**, **6** calculated by AM1 and DFT methods

	AM1		DFT	
	<b>5</b>	<b>6</b>	<b>5</b>	<b>6</b>
Total energy (eV)	-3947.847	-3947.936	-3597.588	-3598.109
Binding energy (eV)	-183.901	-183.987	-179.829	-179.905
Heat of formation (eV)	2.094	2.006	2.051	2.004
<i>Dipole moments (D)</i>				
$M_x$	-1.986	1.490	-1.824	1.427
$M_y$	-1.542	1.457	-1.327	1.322
$M_z$	2.062	-1.776	2.109	-1.661
$M (M)$	3.251	2.738	3.151	2.348

The results show that the total energy values of **5** and **6** calculated so by AM1 as well as by DFT methods are comparable and stability of these compounds is nearly the same. In the case of DFT calculations, the total energy values for **5** and **6** show slightly higher stability than those obtained by AM1 method. Dipole moment values of **5** and **6** calculated by DFT are lower than those obtained by AM1 method, respectively.

The AM1 and DFT methods have been used for optimisation of geometry of **5**, **6**; bond length and angle values are given in Table 4.

Table 4. Bond lengths and angles for **5**, **6** calculated by AM1 and DFT methods

AM1				DFT			
<b>5</b>		<b>6</b>		<b>5</b>		<b>6</b>	
<i>Bond length (Å)</i>				<i>Bond length (Å)</i>			
N1-C2	1.329	C1-C2	1.381	N1-C2	1.309	C1-C2	1.379
C2-C3	1.417	C2-C3	1.421	C2-C3	1.420	C2-C3	1.425
C3-C4	1.387	C3-N4	1.331	C3-C4	1.386	C3-N4	1.330
C4-C4a	1.425	N4-C4a	1.368	C4-C4a	1.405	N4-C4a	1.359
C4a-C10b	1.397	C4a-C10b	1.424	C4a-C10b	1.400	C4a-C10b	1.428
C10b-N1	1.368	C10b-C1	1.416	C10b-N1	1.387	C10b-C1	1.415
C4a-N5	1.393	C4a-C5	1.462	C4a-N5	1.382	C4a-C5	1.457
N5-C6	1.303	C5-N6	1.301	N5-C6	1.312	C5-N6	1.311
C6-C6a	1.451	N6-C6a	1.396	C6-C6a	1.450	N6-C6a	1.396
C6a-C10a	1.416	C6a-C10a	1.425	C6a-C10a	1.407	C6a-C10a	1.424
C10a-C10b	1.463	C10a-C10b	1.445	C10a-C10b	1.472	C10a-C10b	1.500
C6a-C7	1.405	C6a-C7	1.446	C6a-C7	1.408	C6a-C7	1.445

Table 4. cont.

AM1				DFT			
5		6		5		6	
<i>Bond length (Å)</i>				<i>Bond length (Å)</i>			
C7-C8	1.381	C7-C8	1.401	C7-C8	1.378	C7-C8	1.400
C8-C9	1.396	C8-C9	1.398	C8-C9	1.399	C8-C9	1.389
C9-C10	1.408	C9-C10	1.389	C9-C10	1.407	C9-C10	1.392
C10-C10a	1.435	C10-C10a	1.407	C10-C10a	1.424	C10-C10a	1.405
C10-N11	1.401	C7-N11	1.400	C10-N11	1.411	C7-N11	1.399
N11-S12	1.637	N11-S12	1.641	N11-S12	1.635	N11-S12	1.649
S12-O13	1.402	S12-O13	1.402	S12-O13	1.411	S12-O13	1.400
S12-O14	1.408	S12-O14	1.406	S12-O14	1.410	S12-O14	1.410
S12-C15	1.687	S12-C15	1.685	S12-C15	1.685	S12-C15	1.681
C15-C16	1.401	C15-C16	1.401	C15-C16	1.399	C15-C16	1.401
C16-C17	1.392	C16-C17	1.392	C16-C17	1.398	C16-C17	1.399
C17-C18	1.396	C17-C18	1.396	C17-C18	1.395	C17-C18	1.393
C18-C19	1.395	C18-C19	1.396	C18-C19	1.385	C18-C19	1.395
C19-C20	1.393	C19-C20	1.392	C19-C20	1.395	C19-C20	1.390
C20-C15	1.401	C20-C15	1.401	C20-C15	1.400	C20-C15	1.402

<i>Angle (°)</i>				<i>Angle (°)</i>			
N1-C2-C3	124.029	C1-C2-C3	118.775	N1-C2-C3	123.127	C1-C2-C3	117.955
C2-C3-C4	118.258	C2-C3-N4	123.725	C2-C3-C4	117.256	C2-C3-N4	122.231
C3-C4-C4a	119.414	C3-N4-C4a	117.429	C3-C4-C4a	120.014	C3-N4-C4a	117.332
C4-C4a-C10b	118.542	N4-C4a-C10b	123.281	C4-C4a-C10b	117.425	N4-C4a-C10b	122.355
C4a-C10b-N1	120.488	C4a-C10b-C1	117.287	C4a-C10b-N1	121.472	C4a-C10b-C1	118.034
C10b-N1-C2	119.265	C10b-C1-C2	119.503	C10b-N1-C2	119.111	C10b-C1-C2	119.322
C4a-N5-C6	117.772	C4a-C5-N6	124.063	C4a-N5-C6	116.925	C4a-C5-N6	123.921
N5-C6-C6a	124.937	C5-N6-C6a	119.753	N5-C6-C6a	124.737	C5-N6-C6a	120.100
C6-C6a-C10a	119.224	N6-C6a-C10a	121.706	C6-C6a-C10a	119.233	N6-C6a-C10a	121.459
C6a-C10a-C10b	116.824	C6a-C10a-C10b	118.313	C6a-C10a-C10b	115.028	C6a-C10a-C10b	117.121
C10a-C10b-C4a	118.226	C10a-C10b-C4a	119.119	C10a-C10b-C4a	117.345	C10a-C10b-C4a	120.001
C10b-C4a-N5	123.007	C10b-C4a-C5	117.044	C10b-C4a-N5	123.112	C10b-C4a-C5	117.133
C6a-C7-C8	119.718	C6a-C7-C8	118.643	C6a-C7-C8	118.926	C6a-C7-C8	117.643
C7-C8-C9	120.141	C7-C8-C9	120.909	C7-C8-C9	121.042	C7-C8-C9	121.215
C8-C9-C10	121.519	C8-C9-C10	121.078	C8-C9-C10	123.201	C8-C9-C10	121.434
C9-C10-C10a	119.047	C9-C10-C10a	120.339	C9-C10-C10a	119.233	C9-C10-C10a	119.875
C10-C10a-C6a	117.783	C10-C10a-C6a	119.828	C10-C10a-C6a	117.021	C10-C10a-C6a	119.933
C10a-C6a-C7	121.788	C10a-C6a-C7	119.194	C10a-C6a-C7	122.346	C10a-C6a-C7	119.034
C10-N11-S12	125.348	C7-N11-S12	126.483	C10-N11-S12	125.350	C7-N11-S12	125.356
N11-S12-O13	111.245	N11-S12-O13	110.814	N11-S12-O13	110.832	N11-S12-O13	111.321
N11-S12-O14	110.644	N11-S12-O14	110.883	N11-S12-O14	110.333	N11-S12-O14	111.992
S12-C15-C16	120.554	S12-C15-C16	120.638	S12-C15-C16	119.995	S12-C15-C16	119.632
C15-C16-C17	120.799	C15-C16-C17	120.786	C15-C16-C17	121.002	C15-C16-C17	119.734
C16-C17-C18\	119.842	C16-C17-C18	119.857	C16-C17-C18\	119.742	C16-C17-C18	118.943

Table 4. cont.

C17-C18-C19	119.997	C17-C18-C19	120.005	C17-C18-C19	119.897	C17-C18-C19	120.125
C18-C19-C20	119.879	C18-C19-C20	119.859	C18-C19-C20	119.882	C18-C19-C20	119.859
C19-C20-C15	120.758	C19-C20-C15	120.785	C19-C20-C15	121.322	C19-C20-C15	120.728
C20-C15-C16	118.725	C20-C15-C16	118.707	C20-C15-C16	117.723	C20-C15-C16	118.626

The geometry optimisation for positions of the dap structure obtained by both methods shows for compounds **5** and **6** the C10a-C10b bonds as the longest ones, (except for C6a-C7 bond value of **6** calculated by AM1, which is slightly higher).

The calculations with AM1 method indicate the N5-C6 and C5-N6 bonds as the shortest ones for **5** and **6**, respectively; similar result is for C5-N6 bond of **6** calculated by DFT. In the case of **5** however, after DFT method the N1-C2 bond is the shortest. The results of both methods show bonds S12-C15 as the longest ones in whole molecules of **5** and **6**.

Analysing angle values, both methods show angles at *ortho* positions to nitrogen atoms, *i.e.* angle N5-C6-C6a for **5**, and angle C4a-C5-N6 for **6** as the largest ones. Both methods show for **5** as the smallest the angles C6a-C10a-C10b; the smallest angles for **6** calculated by AM1 and by DFT methods are C10b-C4a-C5 and C6a-C10a-C10b, respectively.

Comparing angle values in whole molecules of **5** and **6**, the largest angles are those at NH group, *i.e.* C10-N11-S12 and C7-N11-S12, respectively.

## Conclusion

The procedure of synthesis of two isomeric diazaphenanthrenesulfonamides **5** and **6** is given. Due to similar structures of **5** and **6**, their melting point values are comparable. The theoretical UV spectral data of **5** and **6** have been calculated by AM1 method, and correlations of experimental and theoretical wavenumber values have been made.

The calculation of total energy values of **5** and **6**, as well as their geometry optimisation were made by AM1 and DFT methods. The total energy values of **5** and **6** and their stabilities calculated by AM1 method are similar to each other as well as those calculated by DFT method. In geometry optimisation of **5** and **6** so AM1 as DFT calculations indicate the S12-C15 bond as the longest one in both **5** and **6** molecules.

**References**

1. B. Dondela, J. Peszke, W. Śliwa, J. Mol. Struct. Theochem. 753 (2005) 154.
2. J. Peszke, L. Chrzęstek, W. Śliwa, Chem. Papers 58 (2004) 176.
3. Peszke, B. Mianowska, W. Śliwa, Spectrochim. Acta 53A (1997) 2565.
4. B. Mianowska, W. Śliwa, Spectrochim. Acta 52A (1996) 397.
5. B. Mianowska, W. Śliwa, Acta Chim. Hung. 128 (1991) 93.
6. B. Mianowska, W. Śliwa, Acta Chim. Hung. Models Chem. 131 (1994) 761.
7. W. Śliwa, B. Mianowska, Prace Naukowe Wyższej Szkoły Pedagogicznej, Pedagogical University Issues, Chemia I, Częstochowa 1997, p. 155.
8. J. Peszke, W. Śliwa, Spectrochim. Acta 58A (2002) 2127.
9. J. Peszke, Prace Naukowe Wyższej Szkoły Pedagogicznej, Pedagogical University Issues, Chemia IV, Częstochowa 1999, p. 129.
10. A. Gaudyn, W. Śliwa, Chem. Papers 48 (1994) 306.
11. B. Bachowska, T. Zujewska, Aust. J. Chem. 54 (2001) 105.
12. B. Bachowska, T. Zujewska, Monatsh. Chem. 132 (2001) 849.
13. G. Matusiak, Aust. J. Chem. 52 (1999) 149.
14. B. Dondela, W. Śliwa, Khim. Get. Soedin. (2000) 944.
15. L. Chrzęstek, W. Śliwa, Chem. Papers 55 (2001) 42.
16. L. Chrzęstek, M. Mielniczak, Z. Staroniewicz, W. Śliwa, Khim. Get. Soedin. (1999) 139 1396.
17. L. Chrzęstek, B. Mianowska, W. Śliwa, Aust. J. Chem. 47 (1994) 2129.
18. R. Kovacič, M.A. Kassel, J.R. Ames, B.A. Feinberg, W. Śliwa, J. Biopharm. Sci. 1 (1990) 331.
19. E. Gurgul, B. Herman, R. Biczak, W. Śliwa, Sci. Agric. Bohem. 28 (1997) 245.
20. V. Davydov, V. Pavlyuk, B. Marciniak, B. Dondela, Acta Cryst. E58 (2002) 484.
21. B. Marciniak, V. Pavlyuk, M. Deska, Acta Cryst. E58 (2002) 489.
22. O. Elias, L. Karolyhazy, G. Stajer, F. Fulop, K. Czako, V. Harmath, O. Barabas, K. Keseru, P. Matyus, J. Mol. Struct. Theochem. 545 (2001) 75.
23. A.B.J. Parusel, R. Schamschule, G. Kohler, J. Mol. Struct. Theochem. 544 (2001) 253.
24. S. Bakalova, J. Kaneti, Spectrochim. Acta 56A (2000) 1443.
25. A. Optiz, E. Roemer, W. Haas, H. Gorls, W. Werner, U. Grafe, Tetrahedron 56 (2000) 5147.
26. V.I. Danilov, J.J.P. Stewart, A. Les, J.L. Alderfer, Chem. Phys. Lett. 328 (2000) 75.
27. J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, Gaussian, Pittsburgh, PA, USA (2000)
28. E.K.U. Gross, R.H. Dreizeler, Eds., Density Functional Theory, Plenum, New York (1994).
29. J. Andzelm, E. Wimmer, J. Chem. Phys. 96 (1992) 1280.



Barbara Dondela  
Lidia Chrzęstek

## **Obliczenia struktury diazafenantrenosulfonamidów metodami AM1 CI i DFT B-3 LYP**

**Streszczenie:** Przeprowadzono syntezę dwóch diazafenantrenosulfonamidów. W celu obliczenia teoretycznych wartości widm UV tych związków użyto metodę AM1 CI; optymalizację ich geometrii wykonano metodami AM1 CI i DFT B-3 LYP.

**Słowa kluczowe:** diazafenantrenosulfonamidy, liczba falowa, obliczenia, optymalizacja geometrii, widma UV