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Theoretical study of UV spectra of diazaphenanthrenesulfonamides calculated by AM1 and DFT B3-LYP methods

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Abstract. Two diazaphenanthrenesulfonamides have been synthesized. For calculation of experimental and 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.

1. 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 (dап) 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-alkylbenzonaphthyridones [14]. Nitration of daps followed by reduction affords aminodaps which after diazotization and coupling yield azo dyes [15]. Methyldaps may be nitrated to give nitro methyldaps [16] or oxidised with SeO$_2$ yielding formyldaps [17]. Crystallographic structure determination of a few dap derivatives [20,21] has been made.

Daps are interesting for their potential use as pharmaceutics, 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.

2. 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 HyperChem 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 cm³) was treated with benzenesulfonyl chloride (0,172 g, 1 mmol) and refluxed for 2 hours. To a cooled reaction mixture conc. HCl (4 cm³) was added, the formed solid was filtered off and recrystallised from 95% ethanol. 5, m.p. 176° C, yield 51%; 6, m.p. 170° C, yield 42 %.

3. 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 |
|------|--------------|------------|
|      | $\bar{\nu}$ x $10^3$ (cm$^{-1}$) | log $\varepsilon$ | $\bar{\nu}$ x $10^3$ (cm$^{-1}$) | $f$ |
| 5    |              |            |                          |   |
| $\alpha$ | 28.4         | 3.530      | 27.428                   | 0.078 |
| $\beta$  | 40.1         | 4.041      | 40.766                   | 0.476 |
| 6    |              |            |                          |   |
| $\alpha$ | 31.6         | 3.580      | 32.806                   | 0.066 |
| $\beta$  | 41.7         | 3.710      | 40.073                   | 0.534 |

Table 2
Differences in the experimental wavenumber values of $\alpha$, $p$ 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$^{-1}$) | 5/1 | 6/2 | 5/3 | 6/4 |
|------|---------------------------------------------------|-----|-----|-----|-----|
| $\alpha$ | +0.17 | -3.80 | -2.30 | -7.50 |
| $p$    | -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 $p$ 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:

For 5:

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

For 6:

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

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:

For 5/1: $a = 0.907$  $b = 2.302$  $r = 0.971$

For 5/3: $a = 0.905$  $b = 3.068$  $r = 0.992$

For 6/2: $a = 1.064$  $b = -1.714$  $r = 0.958$

For 6/4: $a = 1.069$  $b = -2.086$  $r = 0.972$

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.
Table 3
Total energy, binding energy, heat of formation and dipole moments values for 5,6 calculated by AM1 and DFT methods

|                 | AM1       | DFT       |
|-----------------|-----------|-----------|
|                 | 5         | 6         | 5          | 6          |
| 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      |
| Dipole moments (D) |           |           |           |            |
| $M_x$            | -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.

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 bonds as the shortest ones for 5 and 6, similar result is for N5-C6 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.
Table 4

Bond lengths and angles for 5,6 calculated by AM1 and DFT methods

| Bond length (Å) | AM1 | DFT |
|-----------------|-----|-----|
| N1-C2           | 1.329 | C1-C2 | 1.309 |
| C2-C3           | 1.417 | C2-C3 | 1.420 |
| C3-C4           | 1.387 | C3-C4 | 1.386 |
| C4-C4a          | 1.425 | C4-C4a | 1.405 |
| C4a-C10b        | 1.397 | C4a-C10b | 1.400 |
| C10b-N1         | 1.368 | C10b-N1 | 1.387 |
| C4a-N5          | 1.393 | C4a-N5 | 1.382 |
| N5-C6           | 1.303 | N5-C6 | 1.312 |
| C6-C6a          | 1.451 | C6-C6a | 1.450 |
| C6a-C10a        | 1.416 | C6a-C10a | 1.407 |
| C10a-C10b       | 1.463 | C10a-C10b | 1.472 |
| C6a-C7          | 1.405 | C6a-C7 | 1.408 |
| C7-C8           | 1.381 | C7-C8 | 1.378 |
| C8-C9           | 1.396 | C8-C9 | 1.399 |
| C9-C10          | 1.408 | C9-C10 | 1.407 |
| C10-C10a        | 1.435 | C10-C10a | 1.424 |
| C10-N11         | 1.401 | C10-N11 | 1.411 |
| C11-N12         | 1.637 | C11-N12 | 1.635 |
| C12-O13         | 1.402 | C12-O13 | 1.411 |
| C12-O14         | 1.408 | C12-O14 | 1.410 |
| C12-C15         | 1.687 | C12-C15 | 1.685 |
| C15-C16         | 1.401 | C15-C16 | 1.399 |
| C16-C17         | 1.392 | C16-C17 | 1.398 |
| C17-C18         | 1.396 | C17-C18 | 1.395 |
| C18-C19         | 1.395 | C18-C19 | 1.385 |
| C19-C20         | 1.393 | C19-C20 | 1.395 |
| C20-C15         | 1.401 | C20-C15 | 1.400 |

| Angle (°) | AM1 | DFT |
|-----------|-----|-----|
| N1-C2-C3  | 124.029 | C1-C2-C3 | 118.775 |
| C2-C3-N4  | 118.258 | C2-C3-N4 | 123.725 |
| C3-C4-N4  | 119.414 | C3-C4-N4 | 117.429 |
| C4-C4a-C10b | 118.542 | C4a-C10b-C1 | 117.258 |
| C10b-N1-C2 | 119.265 | C10b-N1-C2 | 119.503 |
| C4a-N5-C6  | 117.772 | C4a-N5-C6 | 124.063 |
| N5-C6-C6a  | 124.937 | N5-C6-C6a | 119.753 |
| C6-C6a-C10a | 119.224 | C6a-C10a-C10b | 112.706 |
| C6a-C10b-C10a | 116.824 | C6a-C10b-C10a | 118.313 |
| C10b-C10b-C4a | 116.226 | C10b-C10b-C4a | 119.119 |
| C4a-C4b-N5  | 123.007 | C4a-C4b-N5 | 119.233 |
| C6a-C7-C8   | 117.918 | C6a-C7-C8 | 118.643 |
| C7-C8-C9    | 120.141 | C7-C8-C9 | 120.909 |
| C8-C9-C10   | 121.519 | C8-C9-C10 | 121.078 |
| C9-C10-C10a | 119.047 | C9-C10-C10a | 119.233 |
| C10-C10a-C6a | 117.783 | C10-C10a-C6a | 119.828 |
| C10a-C6a-C7  | 121.788 | C10a-C6a-C7 | 119.194 |
| C10-N11-S12 | 125.348 | C10-N11-S12 | 126.483 |
| C11-S12-O13 | 112.245 | C11-S12-O13 | 110.814 |
| C12-O14-N12 | 110.644 | C12-O14-N12 | 110.883 |
| C13-O15-N12 | 120.554 | C13-O15-N12 | 120.638 |
| C14-C15-N12 | 120.799 | C14-C15-N12 | 120.786 |
| C15-C16-N12 | 119.842 | C15-C16-N12 | 119.857 |
| C16-C17-N12 | 119.997 | C16-C17-N12 | 120.005 |
| C17-C18-N12 | 119.879 | C17-C18-N12 | 119.897 |
| C18-C19-N12 | 120.758 | C18-C19-N12 | 120.785 |
| C19-C20-N12 | 118.725 | C19-C20-N12 | 118.707 |
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