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DFT B3-LYP/3-21G geometry optimisation and effective charge values calculations for azodiazaphenanthrenes and acylaminodiazaphenanthrenes

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Abstract

For four azodiazaphenanthrenes **1**–**4** and three acylaminodiazaphenanthrenes **5**–**7** the geometry was optimised and their effective charge and dipole moment values were calculated using DFT B3-LYP/3-21G method. For **5**–**7** the results have been compared with those obtained by AM1 method. The UV experimental values of **1**–**4** are presented. With the use of DFT B3-LYP/6-31G** optimised geometry the simulation of UV spectra of **5**–**7** by AM1 and ZINDO/S methods was made and correlations with experimental UV values have been performed.

Keywords: Calculations; Effective charge; Geometry optimisation; Wavenumber

1. Introduction

In a continuation of our study concerning calculations and spectral properties of diazaphenanthrene derivatives, such as amino- [1], formyl- [2] and methyldiazaphenanthrenes [3], as well as their quaternary salts with haloalkanes [4], the present paper deals with four azodiazaphenanthrenes **1**–**4** and three acylaminodiazaphenanthrenes **5**–**7** derived from parent 1,5- and 4,6-diazaphenanthrenes (DAP) **8** and **9**.

DAPs and their derivatives are a topic of our research. DAPs are interesting for their reactivity [5,6]; due to the presence of nitrogen atoms they may be oxidized and quaternized. DAP *N*-oxides and quaternary salts undergo a variety of reactions, for example *N*-oxides form ylides [7]; quaternary salts afford tetracyclic products [8] or alkylbenzonaphthyridones [9]. Various quaternary salts of DAPs have been obtained [10–12], some of them are precursors of 1,3-dipoles in cycloaddition reactions [13]. AminoDAPs upon diazotization and coupling reactions afford azoDAPs [14], they also in the Skraup procedure yield pyridoDAPs [15], and with aldehydes the tetracyclic products [16,17]. DAPs form complexes with metal ions [18] and are interesting for their antibacterial [19] and enzyme enhancing [20] activities.

In the present work the geometry of **1**–**7** has been optimised and their effective charge values and dipole moments calculated using DFT B3-LYP/3-21G method.

For **5**–**7** the geometry, effective charge values and dipole moments calculated by DFT B3-LYP/3-21G method (next referred to as DFT) have been compared with those calculated by AM1 method [1]. The UV spectral data for **1**–**4** are presented and differences of their experimental wavenumber values as compared with those of parent daps **8** and **9** are given.

Using DFT B3-LYP/6-31G** optimised geometry the UV spectra of **5**–**7** have been calculated by semiempirical AM1 and ZINDO/S methods and correlations with experimental UV data have been made.

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Table 1
Bond lengths and angles for **1**–**7** calculated by DFT B3-LYP/3-21G method

1		**2**		**3**		**4**		**5**		**6**		**7**	
Bond length (Å)													
N1–C2	1.336	N1–C2	1.334	C1–C2	1.382	C1–C2	1.382	N1–C2	1.336	N1–C2	1.334	C1–C2	1.382
C2–C3	1.408	C2–C3	1.406	C2–C3	1.410	C2–C3	1.410	C2–C3	1.404	C2–C3	1.407	C2–C3	1.411
C3–C4	1.384	C3–C4	1.382	C3–N4	1.333	C3–N4	1.333	C3–C4	1.383	C3–C4	1.381	C3–N4	1.333
C4–C4a	1.408	C4–C4a	1.423	C4–C4a	1.364	C4–C4a	1.364	C4–C4a	1.407	C4–C4a	1.409	C4–C4a	1.363
C4a–C10b	1.420	C4a–C10b	1.423	C4a–C10b	1.419	C4a–C10b	1.418	C4a–C10b	1.423	C4a–C10b	1.423	C4a–C10b	1.418
C10b–N1	1.358	C10b–N1	1.359	C10b–C1	1.414	C10b–C1	1.419	C10b–N1	1.365	C10b–N1	1.360	C10b–C1	1.415
C4a–N5	1.392	C4a–N5	1.359	C4a–C5	1.436	C4a–C5	1.436	C4a–N5	1.389	C4a–N5	1.391	C4a–C5	1.436
N5–C6	1.309	N5–C6	1.307	C5–N6	1.306	C5–N6	1.306	N5–C6	1.307	N5–C6	1.306	C5–N6	1.308
C6–C6a	1.442	C6–C6a	1.440	N6–C6a	1.386	N6–C6a	1.386	C6–C6a	1.440	C6–C6a	1.440	N6–C6a	1.390
C6a–C10a	1.422	C6a–C10a	1.427	C6a–C10a	1.428	C6a–C10a	1.428	C6a–C10a	1.425	C6a–C10a	1.427	C6a–C10a	1.426
C10a–C10b	1.441	C10a–C10b	1.453	C10a–C10b	1.454	C10a–C10b	1.454	C10a–C10b	1.453	C10a–C10b	1.456	C10a–C10b	1.453
C6a–C7	1.409	C6a–C7	1.408	C6a–C7	1.429	C6a–C7	1.428	C6a–C7	1.407	C6a–C7	1.409	C6a–C7	1.453
C7–C8	1.385	C7–C8	1.384	C7–C8	1.392	C7–C8	1.391	C7–C8	1.381	C7–C8	1.380	C7–C8	1.389
C8–C9	1.402	C8–C9	1.396	C8–C9	1.398	C8–C9	1.399	C8–C9	1.400	C8–C9	1.402	C8–C9	1.403
C9–C10	1.397	C9–C10	1.398	C9–C10	1.385	C9–C10	1.385	C9–C10	1.402	C9–C10	1.392	C9–C10	1.382
C10–C10a	1.420	C10–C10a	1.431	C10–C10a	1.410	C10–C10a	1.410	C10–C10a	1.445	C10–C10a	1.428	C10–C10a	1.411
C10–N11	1.438	C10–N11	1.408	C7–N11	1.413	C7–N11	1.416	C10–N11	1.388	C10a–N11	1.416	C7–N11	1.415
N11–N12	1.274	N11–N12	1.315	N11–N12	1.298	N11–N12	1.297	N11–C12	1.395	N11–C12	1.391	N11–C12	1.396
N12–C13	1.432	N12–C13	1.379	N12–C13	1.413	N12–C13	1.406	C12–O13	1.240	C12–O13	1.236	C12–C13	1.517
C13–C14	1.405	C13–C14	1.421	C13–C14	1.403	C13–C14	1.406	C12–C14	1.521	C12–C14	1.497	C12–O14	1.237
C14–C15	1.384	C14–C15	1.425	C14–C15	1.383	C14–C15	1.413			C14–C15	1.400		
C15–C16	1.415	C15–C16	1.365	C15–C16	1.414	C15–C16	1.369			C15–C16	1.396		
C16–C17	1.414	C16–C16a	1.431	C16–C17	1.419	C16–C16a	1.420			C16–C17	1.397		
C17–C18	1.383	C16a–C17	1.416	C17–C18	1.380	C16a–C17	1.420			C17–C18	1.399		
C18–C13	1.404	C17–C18	1.380	C18–C13	1.407	C17–C18	1.376			C18–C19	1.392		
C16–N19	1.371	C18–C19	1.412	C16–N19	1.369	C18–C19	1.412			C19–C14	1.400		
		C19–C20	1.382			C19–C20	1.380						
		C20–C20a	1.414			C20–C20a	1.422						
		C20a–C13	1.445			C20a–C16a	1.437						
		C20a–C16a	1.426			C20a–C13	1.444						
		C14–O21	1.334			C14–O21	1.373						
Angle (°)													
N1–C2–C3	123.097	N1–C2–C3	122.838	C1–C2–C3	119.213	C1–C2–C3	119.203	N1–C2–C3	122.764	N1–C2–C3	123.309	C1–C2–C3	119.283
C2–C3–C4	118.670	C2–C3–C4	118.168	C2–C3–N4	122.957	C2–C3–N4	122.971	C2–C3–C4	118.282	C2–C3–C4	118.174	C2–C3–N4	122.921
C3–C4–C4a	119.416	C3–C4–C4a	119.882	C3–N4–C4a	117.949	C3–N4–C4a	117.949	C3–C4–C4a	119.964	C3–C4–C4a	119.679	C3–N4–C4a	117.908
C4–C4a–C10b	118.150	C4–C4a–C10b	118.669	N4–C4a–C10b	123.387	N4–C4a–C10b	123.358	C4–C4a–C10b	118.742	C4–C4a–C10b	118.716	N4–C4a–C10b	123.468
C4a–C10b–N1	121.882	C4a–C10b–N1	120.182	C4a–C10b–C1	116.879	C4a–C10b–C1	116.918	C4a–C10b–N1	120.030	C4a–C10b–N1	120.608	C4a–C10b–C1	116.888
C10b–N1–C2	118.733	C10b–N1–C2	120.261	C10b–C1–C2	119.615	C10b–C1–C2	119.601	C10b–N1–C2	120.217	C10b–N1–C2	119.507	C10b–C1–C2	119.531
C4a–N5–C6	117.868	C4a–N5–C6	117.598	C4a–C5–N6	123.963	C4a–C5–N6	123.943	C4a–N5–C6	117.494	C4a–N5–C6	117.613	C4a–C5–N6	123.991
N5–C6–C6a	124.974	N5–C6–C6a	124.928	C5–N6–C6a	119.584	C5–N6–C6a	119.513	N5–C6–C6a	125.159	N5–C6–C6a	124.873	C5–N6–C6a	119.306
C6–C6a–C10a	117.947	C6–C6a–C10a	118.960	N6–C6a–C10a	122.063	N6–C6a–C10a	122.176	C6–C6a–C10a	118.906	C6–C6a–C10a	118.951	N6–C6a–C10a	122.289
C6a–C10a–C10b	117.715	C6a–C10a–C10b	116.614	C6a–C10a–C10b	117.509	C6a–C10a–C10b	117.468	C6a–C10a–C10b	116.387	C6a–C10a–C10b	116.683	C6a–C10a–C10b	117.563
C10a–C10b–C4a	118.785	C10a–C10b–C4a	118.716	C10a–C10b–C4a	118.593	C10a–C10b–C4a	118.575	C10a–C10b–C4a	119.095	C10a–C10b–C4a	118.405	C10a–C10b–C4a	118.558
C10b–C4a–N5	122.577	C10b–C4a–N5	120.927	C10b–C4a–C5	118.115	C10b–C4a–C5	118.137	C10b–C4a–N5	122.956	C10b–C4a–N5	123.384	C10b–C4a–C5	118.281
C6a–C7–C8	119.478	C6a–C7–C8	119.952	C6a–C7–C8	119.133	C6a–C7–C8	119.380	C6a–C7–C8	119.051	C6a–C7–C8	119.948	C6a–C7–C8	118.955
C7–C8–C9	120.582	C7–C8–C9	119.919	C7–C8–C9	121.340	C7–C8–C9	121.141	C7–C8–C9	120.956	C7–C8–C9	119.554	C7–C8–C9	121.289

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