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An ab initio molecular orbital study of structural isomers of diketopyrrolopyrrole

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Abstract

Ab initio molecular orbital calculations at HF/6-31G**, HF/6-311+G**, and B3LYP/6-311+G** levels of theory for geometry optimization and RMP2-FC/6-311+G**, for a single point total energy calculation are reported for 1,4-diketo-pyrrolo[3,4-*c*]pyrrole (DPP, **1**) and 12 structural isomers of DPP (**2**–**13**). Compounds **1**–**3** include 2 C=CH and 2 HN–CO units. Structural isomers **4**–**7** include 2 C=CH units, together with 2 NH and 2 C=O groups. Isomers **8**–**13** possess 2 CH, 2 C, 2 NH, and 2 C=O fragments. These calculations show that isomers **2**, **4**, and **8** are more stable than **1**. The λ_{max} values for **1**–**13** are calculated from the HOMO–LUMO energies.

Keywords: Ab initio calculation; Diketopyrrolopyrrole; Molecular modeling; Structural isomers

1. Introduction

The building blocks in organic pigments are molecules that determine, directly or indirectly, important performance properties of pigments [1]. Such organic pigment molecules are generally characterized by planar conjugated chromophoric systems featuring functional groups such as C=O and NH groups. In comparison with classical organic pigments, high performance organic pigments tend to be of more recent origin and feature excellent fastness properties [1–3]. They are more costly to manufacture and find use in specialized and more demanding applications, such as in automotive paints and construction plastics, where exceptional light, weather, and heat fastness are required. The most recent addition to the class of high performance pigments are the 1,4-diketo-3,6-diarylpyrrolo[3,4-*c*]pyrroles. Diketopyrrolopyrroles (abbreviated to DPPs; shown in Fig. 1) are chromophoric systems which combine in a rigid planar structural frame, essentially representing the lactam analogue of the 8π-electron fused ring hydrocarbon pentalene [1–3].

Diketopyrrolopyrrole **1** may be considered to be constructed from 2 C=CH and 2 HN–CO structural units. Two other structures, namely, **2** and **3** are also possible, which include these structural features (see Fig. 1). It would be interesting, of course, to compare the structural and electronic properties of compounds **1**–**3**. Moreover, DPP can be divided into 2 C=CH units, together with 2 C=O and 2 NH groups. Thus,

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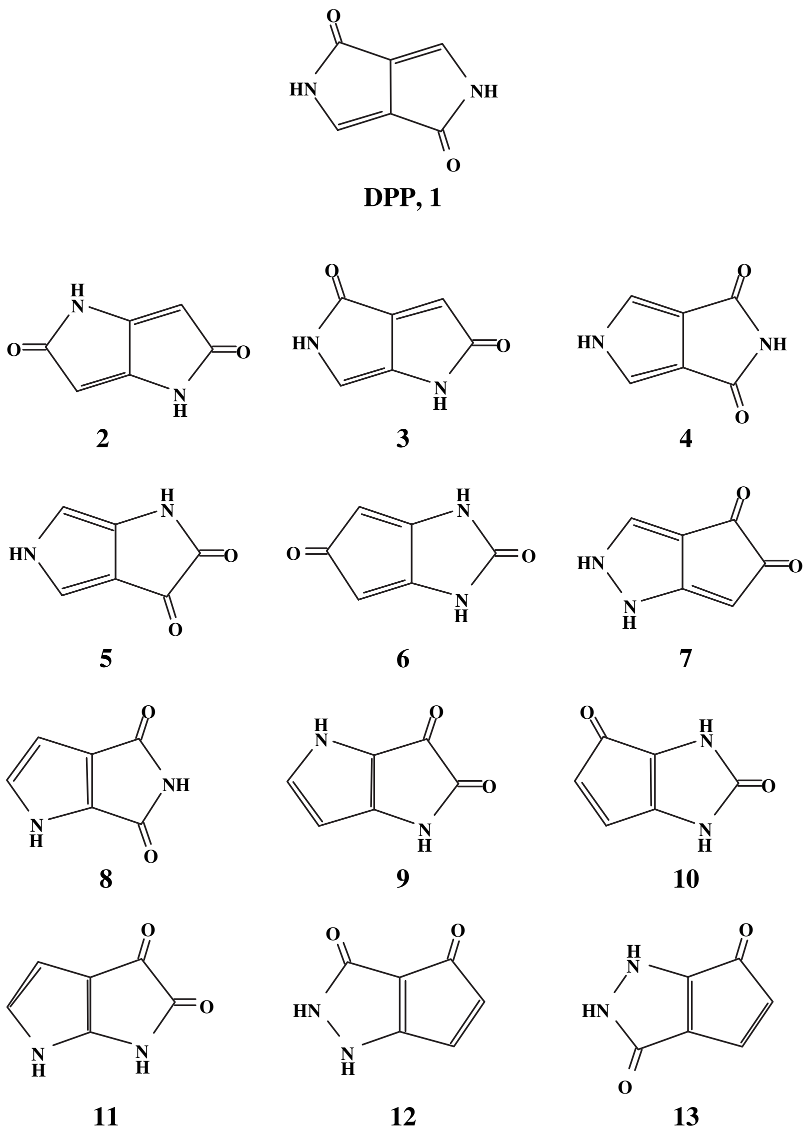


Fig. 1. Diketopyrrolopyrrole (DPP, **1**) and 12 structural isomers of DPP (**2**–**13**).

4 additional structures **4**–**7** are possible. Finally, DPP may be considered as 2 CH, 2 C, 2 C=O, and 2 NH fragments. Structures **8**–**13** in Fig. 1 are the result of such fragmentation of DPP.

Even though the structural isomers of DPP (**2**–**13**) are not presently available for more studies, it is possible to carry out ab initio calculations at the Hartree–Fock level, from which many properties and structural features can be obtained with an accuracy that is competitive with experiment. Since the theoretical results are free from intermolecular interactions, they are valuable tool for systematic study of structural effects in simple organic molecules. This study was undertaken to investigate the structural optimization of DPP and its structural isomers shown in Fig. 1. The results from B3LP/6-311+G**//B3LP/6-311+G** calculations are used in the energies discussion later.

2. Calculations

The ab initio molecular orbital calculations were carried out using the GUSSIAN 98 [4] program. Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints [5,6]. Initial geometry optimizations were carried out at the HF/6-31G* levels, and zero-point energies, obtained at this level, were scaled by a factor of 0.895. In light of the fact that correction for electron correlation is often important in

Table 1
Calculated total and zero-point vibrational energies (Hartree; zero-point vibrational energy is scaled by a factor of 0.893 to eliminate known systematic errors in calculations), relative energy including zero-point energy (kcal mol^{-1}), and HOMO–LUMO energies (Hartree) for DPP and 2 structural isomers of DPP (**2**, **3**) with 2 NH–CO and 2 C=CH structural units

Structure	**1**, C_{2h}	**2**, C_{2h}	**3**, C_s
HF/6-31G**//HF/6-31G**	−488.14694	−488.16885	−488.14081
ZPE	66.6123	66.1276	65.8645
E_{rel}[a]	0	−14.18	3.17
HF/6-311+G**//HF/6-311+G**	−488.27412	−488.29671	−488.26847
ZPE	65.9946	65.5396	65.2045
E_{rel}[b]	0	−14.74	2.84
RMP2-FC/6-311+G**//RMP2-FC/6-311+G**	−488.14683	−488.16874	−488.14071
ZPE	65.99	65.5396	65.2045
E_{rel}[c]	0	−14.32	3.13
B3LYP/6-311+G**//B3LYP/6-311+G**	−491.12556	−491.13804	−491.11539
ZPE	65.99463	65.3596	66.2045
E_{rel}[d]	0	−8.40	6.57
E_{HOMO}	−0.227	−0.263	−0.228
E_{LUMO}	−0.102	−0.106	−0.116
$\Delta E_{\mathrm{HOMO-LUMO}}$	0.125	0.157	0.112
λ (nm)	364	290	407

[a] Relative energy with respect to **1** from HF/6-31G**//HF/6-31G**.
[b] Relative energy with respect to **1** from HF/6-311+G**//HF/6-311+G**.
[c] Relative energy with respect to **1** from RMP2-FC/6-311+G**//RMP2-FC/6-311+G**.
[d] Relative energy with respect to **1** from B3LYP/6-311+G**//B3LYP/6-311+G**.

conformational studies, we have made use of several methods for calculating this correction. One approach involved the density functional theory at B3LYP/6-311+G** level [7]. This makes use of a 3-parameter functional that is a hybrid of exact (Hartree–Fock) exchange terms, similar to those first suggested by Becke in Koch and Holthausen [8]. Geometry optimizations were also carried out using HF/6-31G*, HF/6-31G**, HF/6-311+G**, RMP2-FC/6-311+G**, and B3LYP/6-311+G**.

Table 2
Calculated total and zero-point vibrational energies (Hartree; zero-point vibrational energy is scaled by a factor of 0.893 to eliminate known systematic errors in calculations), relative energy including zero-point energy (kcal mol^{-1}) and HOMO–LUMO energies (Hartree) for 4 structural isomers of DPP, **4**–**7**, with 2 NH, 2 C=O and 2 C=CH structural units

Structure	**4**, C_{2v}	**5**, C_s	**6**, C_s	**7**, C_1
HF/6-31G**//HF/6-31G**	−488.30432	−488.13710	−488.16516	−488.08436
ZPE	67.3810	66.2225	66.5754	66.6092
E_{rel}[a]	−18.36	5.83	−4.47	39.27
HF/6-311+G**//HF/6-311+G**	−488.30432	−488.26489	−488.28060	−488.20162
ZPE	66.7615	65.5130	66.0023	66.0236
E_{rel}[b]	−18.27	5.36	−4.06	45.52
RMP2-FC/6-311+G**//RMP2-FC/6-311+G**	−488.17717	−488.13710	−488.27376	−488.19271
ZPE	66.7615	65.5130	66.0023	66.0236
E_{rel}[c]	−18.36	5.67	−2.64	28.76
B3LYP/6-311+G**//B3LYP/6-311+G**	−491.14919	−491.11520	−491.12059	−491.05295
ZPE	66.7615	66.0023	65.5130	66.0236
E_{rel}[d]	−14.14	6.51	2.69	45.59
E_{HOMO}	−0.263	−0.239	−0.237	−0.228
E_{LUMO}	−0.072	−0.090	−0.102	−0.095
$\Delta E_{\mathrm{HOMO-LUMO}}$	0.191	0.149	0.135	0.133
λ (nm)	239	306	338	343

[a–d] See footnotes to Table 1.

Table 3
Calculated total and zero-point vibrational energies (Hartree; zero-point vibrational energy is scaled by a factor of 0.893 to eliminate known systematic errors in calculations), relative energy including zero-point energy (kcal mol^{-1}) and HOMO–LUMO energies (Hartree) for 6 structural isomers of DPP, **8**–**13**, with 2 NH, 2 C=O, 2 C, and 2 CH structural units

Structure	**8**, C_s	**9**, C_s	**10**, C_s	**11**, C_1	**12**, C_1	**13**, C_1
HF/6-31G**//HF/6-31G**	−488.17366	−488.13592	−488.14199	−488.13619	−488.09069	−488.09363
ZPE	67.0024	66.0962	65.9883	65.9050	66.6141	66.5868
E_{rel}[a]	−16.43	6.45	8.55	6.11	35.2998	33.43
HF/6-311+G**//HF/6-311+G**	−488.29112	−488.263860	−488.257940	−488.26444	−488.21680	−488.21071
ZPE	66.6267	65.51309	65.31236	65.3269	66.0330	66.0046
E_{rel}[b]	−10.11	6.01	9.54	5.48	36.01	39.80
RMP2-FC/6-311+G**//RMP2-FC/6-311+G**	−488.17353	−488.13577	−488.24941	−488.65851	−488.20956	−488.20252
ZPE	66.6267	65.5131	65.3124	65.3269	66.0330	66.0046
E_{rel}[c]	−16.19	6.51	9.98	6.68	32.26	34.94
B3LYP/6-311+G**//B3LYP/6-311+G**	−491.14609	−491.11569	−491.10363	−491.11123	−491.06288	−491.05851
ZPE	66.6267	65.5131	65.3124	65.3269	66.0330	66.0046
E_{rel}[d]	−12.32	5.77	13.15	8.40	39.37	42.09
E_{HOMO}	−0.259	−0.237	−0.218	−0.239	−0.250	−0.229
E_{LUMO}	−0.088	−0.096	−0.116	−0.129	−0.119	−0.088
$\Delta E_{\mathrm{HOMO-LUMO}}$	0.171	0.141	0.102	0.110	0.131	0.141
λ (nm)	267	324	447	415	348	323

[a–d] See footnotes to Table 1.

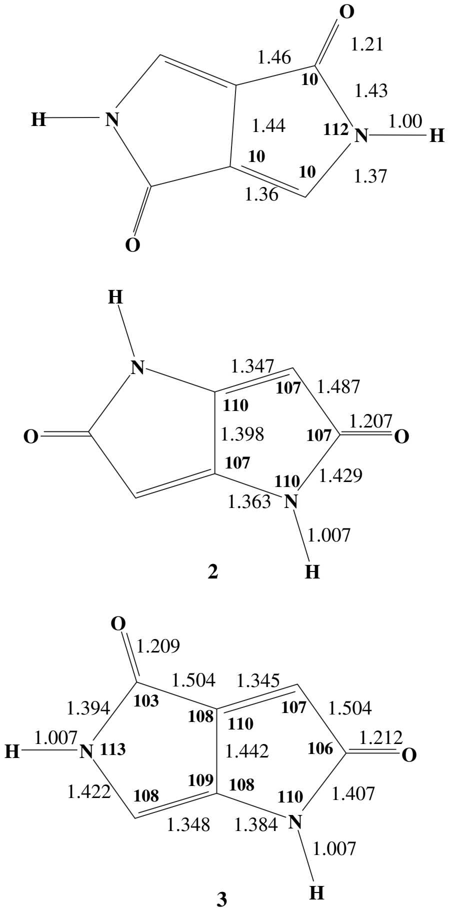


Fig. 2. B3LYP/6-311+G**//B3LYP/6-311+G** calculated bond lengths (in Å) and bond angles (in °) for DPP and 2 structural isomers of DPP (**2**, **3**) with 2 HN–CO and 2 C=CH structural units.

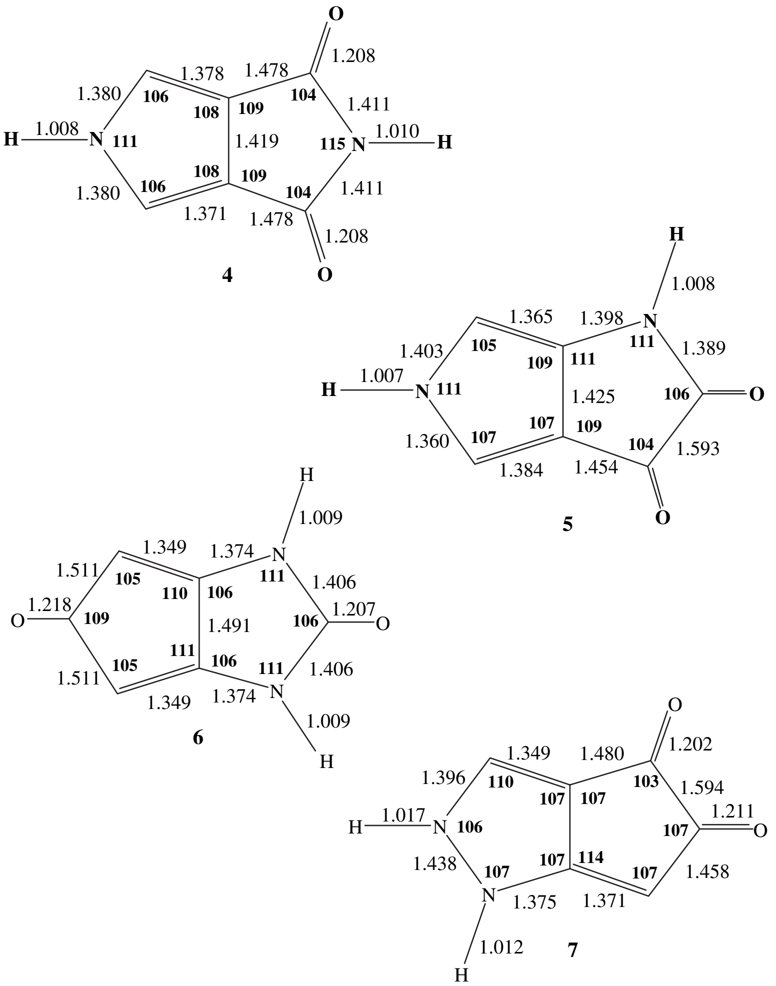


Fig. 3. B3LYP/6-311+G**//B3LYP/6-311+G** calculated bond lengths (in Å) and bond angles (in °) for 4 structural isomers of DPP (**4**–**7**) with 2 NH, 2 C=O, and 2 C=CH structural units.

HOMO–LUMO energies are obtained for fully optimized geometries, therefore, $\lambda_{\max}$ values are obtained by equation: $\lambda = hc/\Delta E = 6.63 \times 10^{-34}$ (J s) $\times 3 \times 10^{8}$ (m/s)/$\Delta E \times 4.36 \times 10^{-18}$ (J) then, λ (nm) $= 45.62/\Delta E$.

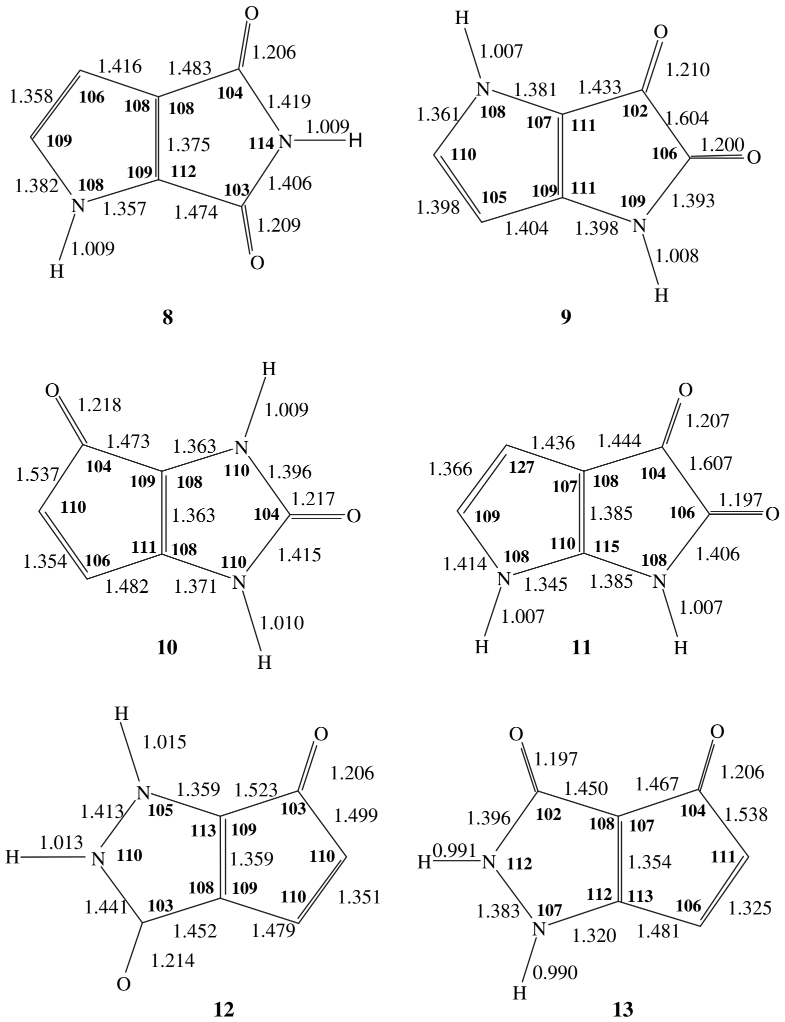
3. Results and discussion

The results of ab initio calculations for diketopyrrolopyrrole (DPP, **1**) and its structural isomers **2**–**13** are shown in Tables 1–3 and Figs. 2–4. According to these calculations, DPP is not the most stable structural isomer. Isomers **2**, **4**, and **8** are more stable than DPP by 8.4, 14.1, and 12.3 kcal mol^{-1}, respectively. Structure **7** is the least stable isomer and it is calculated to be 45.6 kcal mol^{-1} less stable than DPP. The energy difference between **7**, **13** and **12** with DPP are substantially higher than those calculated for the other isomers. Selected geometrical data for DPP and 2 isomers containing 2 CH=C and 2 HN–CO moieties are given in Fig. 2. The structural parameters for isomers **4**–**7** with 2 C=O, 2 NH and 2 C=CH groups are shown in Fig. 3. The 6 isomers with 2 C=O, 2 NH, 2 C and 2 CH fragments are given in Fig. 4.

Using B3LYP/6-311+G** method, structure **4** is calculated to be the most stable isomer of DPPs, and **7** is 45.59 kcal mol^{-1} less stable than **1** (see Table 2). Isomers **7**, **12**, and **13**, containing HN–NH moieties are least stable isomers.

The HOMO–LUMO energies calculated from B3LYP/6-311+G** method were employed to obtain the $\lambda_{\max}$ values for isomers **1**–**13** (see Tables 1–3). All calculated $\lambda_{\max}$ values are in the UV–Vis region of the electromagnetic spectrum.

Although isomers **2**, **4**, and **8** are calculated to be more stable than **1**, their $\lambda_{\max}$ values are much less than that calculated for **1**. However, isomers **3**, **10**, and **11**, which are predicted to be less stable than **1**, have more effective conjugation and exhibit longer $\lambda_{\max}$ values. Isomer **3**, which is very similar to **1**, may be a good choice for synthesis and comparison with DPP, since it possesses the longest $\lambda_{\max}$ value.



8 **9**

10 **11**

12 **13**

Fig. 4. B3LYP/6-311+G**//B3LYP/6-311+G** calculated bond lengths (in Å) and bond angles (in °) for 6 structural isomers of DPP (**8**–**13**) with 2 NH, 2 C=O and 2 C=CH structural unit.

In summary, ab initio calculations provide a picture of diketopyrrolopyrrole and its isomers from both structural and energetic points of view.

References

[1] Hao Z, Iqbal A. Chem Soc Rev 1997;26:203 and references therein.

[2] Iqubal A, Jost M, Kirchmayer R, Pfenninger J, Rochat A, Wallquist O. Bull Soc Chim Belg 1988;97:615.

[3] Morton CJH, Gilmour R, Smith DM, Lightfoot P, Slawin AMZ, Maclean EJ. Tetrahedron 2002;58:5547.

[4] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 98, Revision A.6. Pittsburgh, PA: Gaussian Inc.; 1998.

[5] Jensen F. Introduction to computational chemistry. New York: Wiley; 1999.

[6] Hehre WJ, Radom L, Schleyer PvR, Pople JA. Ab initio molecular orbital theory. New York: Wiley; 1986.

[7] Hariharan PC, Pople JA. Theor Chim Acta 1973;28:213.

[8] Koch W, Holthausen MC. A chemist's guide to density functional theory. Weinheim: Wiley-VCH; 2000.