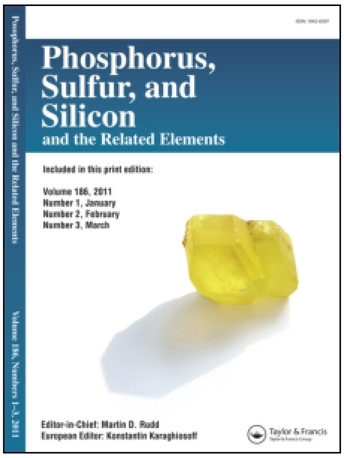

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Ab initio Molecular Orbital Study of Dithiopyrrolopyrrole and Its Structural Isomers

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Ab initio *molecular orbital calculations at HF/6-31G*, HF/6-311+G**, and B3LYP/6-311+G** levels of theory for geometry optimization are reported for 1,4-dithiopyrrolo[3,4-c]pyrrole (DtPP,* ***1****) and its twelve structural isomers (****2–13****). Compounds* ***1–3*** *include 2 C=CH and 2 NH–CS structural units. Structural isomers* ***4–7*** *include 2 C=CH units, together with 2 NH and 2 C=S groups. Isomers* ***8–13*** *possess 2 CH, 2 C, 2 NH, and 2 C=S fragments. According to these calculations, isomers* ***2, 4,*** *and* ***8****, are more stable than* ***1****.*

Keywords *Ab initio* calculation; dithiopyrrolopyrrole; pigments; structural isomers

INTRODUCTION

The thiocarbonyl, C=S, group occurs in a wide range of compounds, although the simpler thioketone and thioaldehyde systems appear to be unstable. The thioketones contrast markedly with ketones in being brightly colored, ranging from red in the case of the alkyl and cycloalkyl compounds, to deep blue in the case of the aromatic derivatives.[1] Dithiopyrrolopyrroles are important pigments and dithio-3,6-diphenylpyrrolopyrrole[2] is applied in a process for optical recording and storage of information in the form of bits.[3]

Dithiopyrrolopyrrole (DtPP, **1**) is considered to be constructed from two C=CH and two NH–CS structural units. Two other structures,

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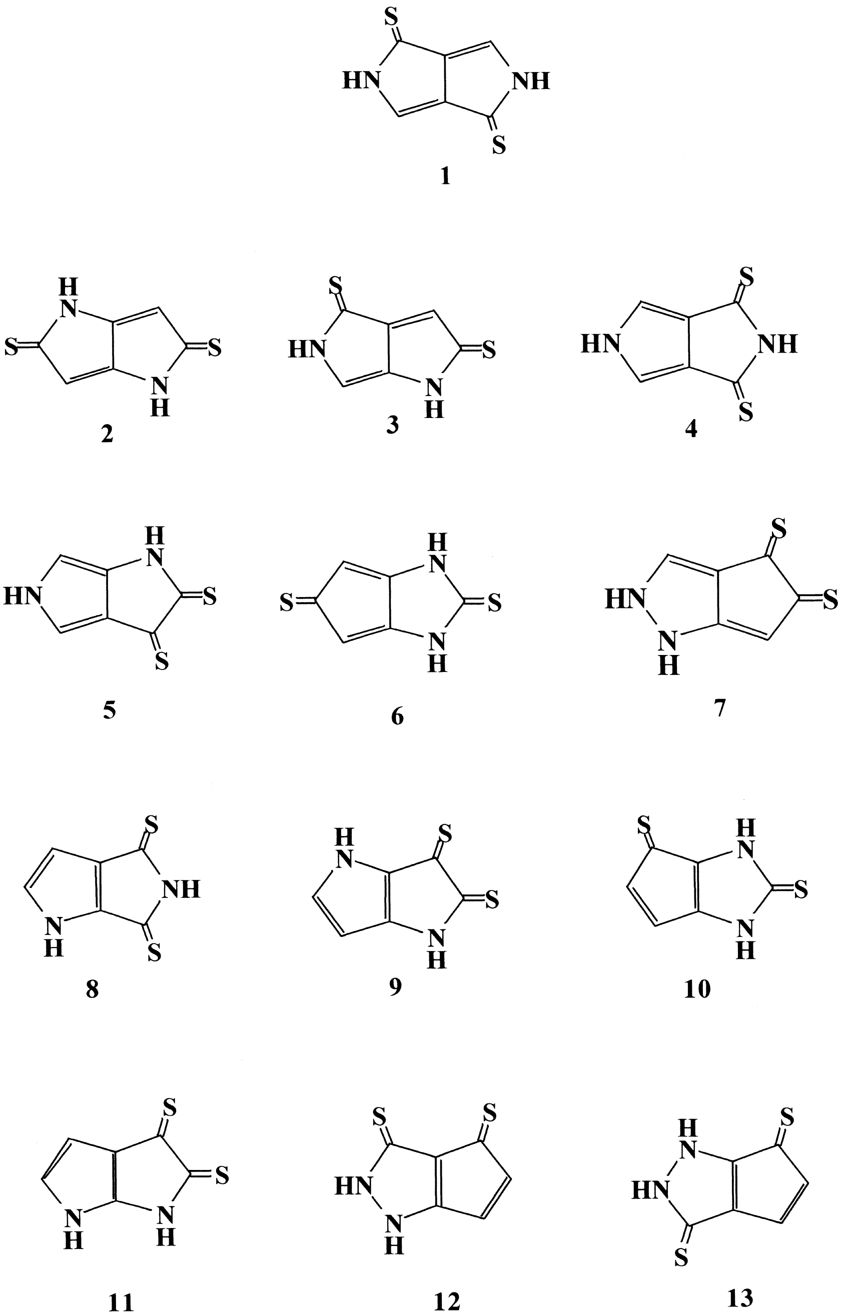

1 2 3 4 5 6 7 8 9 10 11 12 13

FIGURE 1 Dithiopyrrolopyrrole (DtPP, **1**) and it's structural isomers.

namely **2** and **3**, are also possible, which include these structural features (see Figure 1). It would be interesting, of course, to compare the structural and electronic properties of compounds **1–3**. Moreover, DtPP can be divided into two C=CH units, together with 2 C=S and 2 NH groups. Thus, the four additional structures **4–7** are possible. Finally, DtPP may be considered as 2 CH, 2 C, 2 C=S, and 2 NH fragments. Structures **8–13** are the result of such fragmentation of DtPP. Even though structural isomers **2–13** are not presently available for experimental studies, it is possible to learn something about them by using the theoretical methods that have proved to be reliable in other applications. This study was undertaken to investigate the structural optimization of molecules shown in Figure 1. The results from B3LYP/6-311+G**//B3LYP/6-311+G** calculations are used in the energies discussion later.

CALCULATIONS

The *ab initio* molecular orbital calculations were carried out using the GUSSIAN 2003[4] program. Geometries for all structures were fully

TABLE I 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 DtPP and Its Structural Isomers 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**	−1133.42375	−1133.43529	−1133.41435
ZPE	63.6307	63.1550	63.3026
Dipole moment	0.0	0.0	6.12
$E_{rel}{}^{a}$	0.0	−7.67	5.60
HF/6-311+G**//HF/6-311+G**	−1133.54930	−1133.56191	−1133.54069
ZPE	62.9339	62.2351	62.5240
Dipole moment	0.0	0.0	5.96
E^{b}_{rel}	0.0	−8.53	5.04
B3LYP/6-311+G**//B3LYP/6-311+G**	−1137.04927	−1137.05452	−1137.03840
ZPE	58.6064	58.0999	58.2102
Dipole moment	0.0	0.0	5.54
$E_{rel}{}^{c}$	0.0	−3.74	6.47
E_{HOMO}	−0.215	−0.220	−0.220
E_{LUMO}	−0.128	−0.139	−0.139
$\Delta E_{HOMO\text{-}LUMO}$	0.087	0.081	0.081
λ_{max} (nm)	524	563	563

[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 B3LYP/6-311+G**//B3LYP/6-311+G**.

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* level, and zero-point energies obtained at this level were scaled by 0.895. In light of the fact that correction for electron correlation is often important in conformation studies, we have made use of several methods for calculating this correction. One approach involved the density functional theory at B3LYP/6-31G* level.[7] This makes use of a three-parameter functional that is a hybrid of exact (Hartree–Fock) exchange terms, similar to those first suggested by Becke.[8] Geometry optimizations were also carried out using HF/6-31G*, HF/6-31G**, HF/6-311+G**, and B3LYP/6-311+G**.

RESULTS AND DISCUSSION

The results of *ab initio* calculations for DtPP and its structural isomers **2–13** are shown in Tables I–III and Figures 2–4. The important

TABLE II 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 DtPP and Structural Isomers 4–7 with 2 NH—CO and 2 C═CH Structural Units

Structure	**4**, C_{2V}	**5**, C_s	**6**, C_{2v}	**7**, C_1
HF/6-31G**// HF/6-31G**	−1133.45491	−1133.40936	−1133.42032	−1133.350482
ZPE	64.0576	63.4466	63.1094	63.2588
Dipole moment	6.26	8.69	0.38	8.72
$E_{rel}{}^{a}$	−19.17	8.86	1.68	45.64
HF/6-311+G**// HF/6-311+G**	−1133.57131	−1133.53613	−1133.54719	−1133.47817
ZPE	63.3098	62.8268	62.2226	62.7086
Dipole moment	6.11	8.36	0.44	8.59
$E_{rel}{}^{b}$	−13.47	8.17	0.69	44.43
B3LYP/6-311+G**// B3LYP/6-311+G**	−1137.06562	−1137.03537	−1137.03725	−1136.97793
ZPE	58.9157	58.3512	57.9209	58.0031
Dipole moment	5.54	8.03	1.45	8.95
$E_{rel}{}^{c}$	−9.98	8.50	6.93	44.23
E_{HOMO}	−0.232	−0.225	−0.234	−0.210
E_{LUMO}	−0.114	−0.124	−0.133	−0.126
$\Delta E_{HOMO\text{-}LUMO}$	0.118	0.104	0.101	0.104
λ_{max} (nm)	387	439	452	439

[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 B3LYP/6-311+G**//B3LYP/6-311+G**.

TABLE III 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 Structural Isomers 8–13 with 2 NH, 2 C═O, 2 C, and 2 CH Structural Units

Structure	**8**, Cs	**9**, Cs	**10**, Cs	**11**, Cs	**12**, C_1	**13**, C_1
HF/6-31G**//HF/6-31G**	−1133.44263	−1133.41120	−1133.40958	−1133.40722	−1133.36442	−1133.36136
ZPE	63.6872	63.1437	63.3773	62.8322	63.1236	63.1272
Dipole moment	4.36	7.57	5.84	8.43	9.04	4.12
$E_{\mathrm{rel}}{}^{a}$	−11.80	7.44	8.66	9.65	36.78	38.69
HF/6-311+G**//HF/6-311+G**	−1133.56912	−1133.53803	−1133.53594	−1133.53467	−1133.49212	−1133.48885
ZPE	62.7983	62.4454	62.6062	62.1066	62.5626	62.5856
Dipole moment	4.18	7.24	5.68	8.11	8.80	4.11
$E_{\mathrm{rel}}{}^{b}$	−12.55	6.64	8.09	8.45	35.55	37.63
B3LYP/6-311+G**//B3LYP/6−11+G**	−1137.06449	−1137.03901	−1137.02775	−1137.02083	−1136.97746	−1136.98344
ZPE	58.6067	58.2904	58.1289	57.9158	58.0072	57.5876
Dipole moment	3.99	6.70	4.31	7.81	8.26	3.97
$E_{\mathrm{rel}}{}^{c}$	−9.55	6.16	13.08	17.23	44.53	40.40
E_{HOMO}	−0.239	−0.223	−0.210	−0.218	−0.211	−0.216
E_{LUMO}	−0.126	−0.128	−0.143	−0.125	−0.138	−0.156
$\Delta E_{\mathrm{HOMO\text{-}LUMO}}$	0.113	0.095	0.067	0.093	0.073	0.060
λ_{max} (nm)	404	480	680	491	625	760

[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 B3LYP/6-311+G**//B3LYP/6-311+G**.

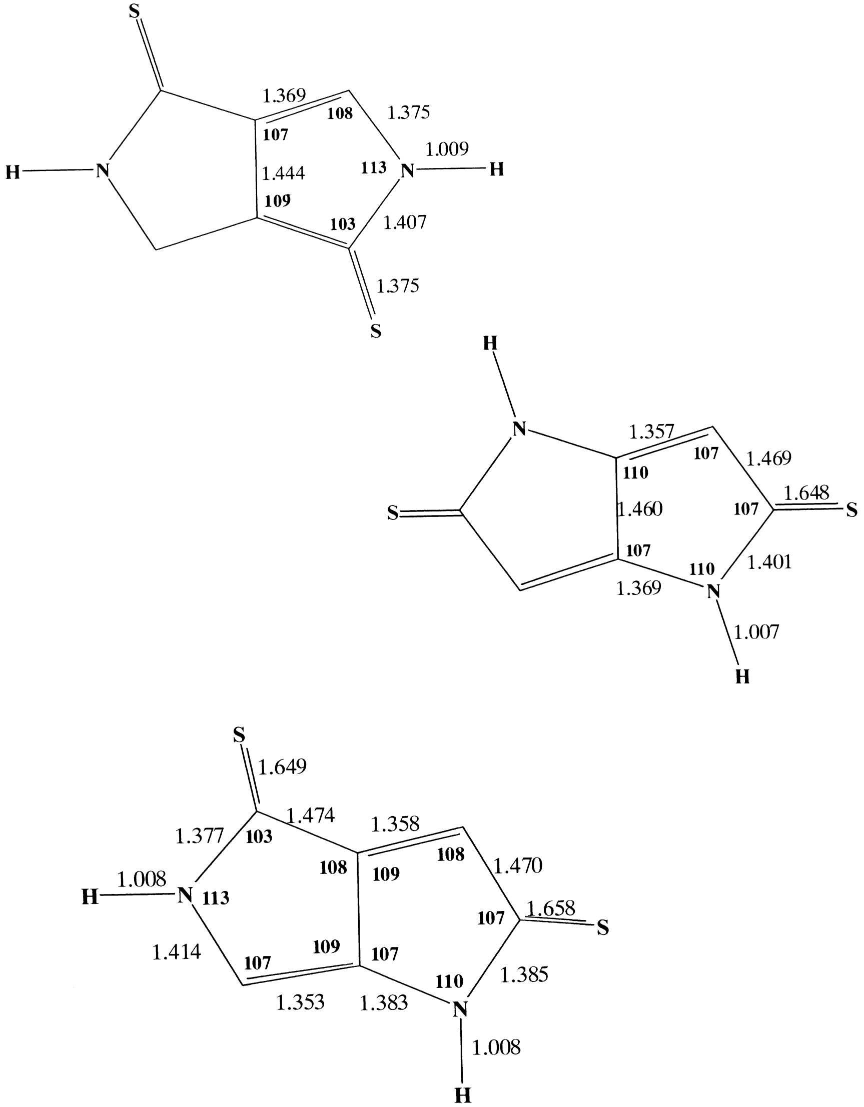

FIGURE 2 B3LYP/6-311+G**//B3LYP/6-311+G** calculated bond lengths (in Å) and bond angles (in °) for DtPP and two structural isomers with 2 NH—CS and 2 C=CH units.

conclusion from these calculations is that three isomers **4**, **8**, and **2** are more stable than DtPP itself by 9.98, 9.55, and 3.75 kcal mol^{-1}, respectively. Isomer **12** is the least stable isomer and it is 44.52 kcal mol^{-1} less stable than DtPP. Selected geometrical data for DtPP and isomers

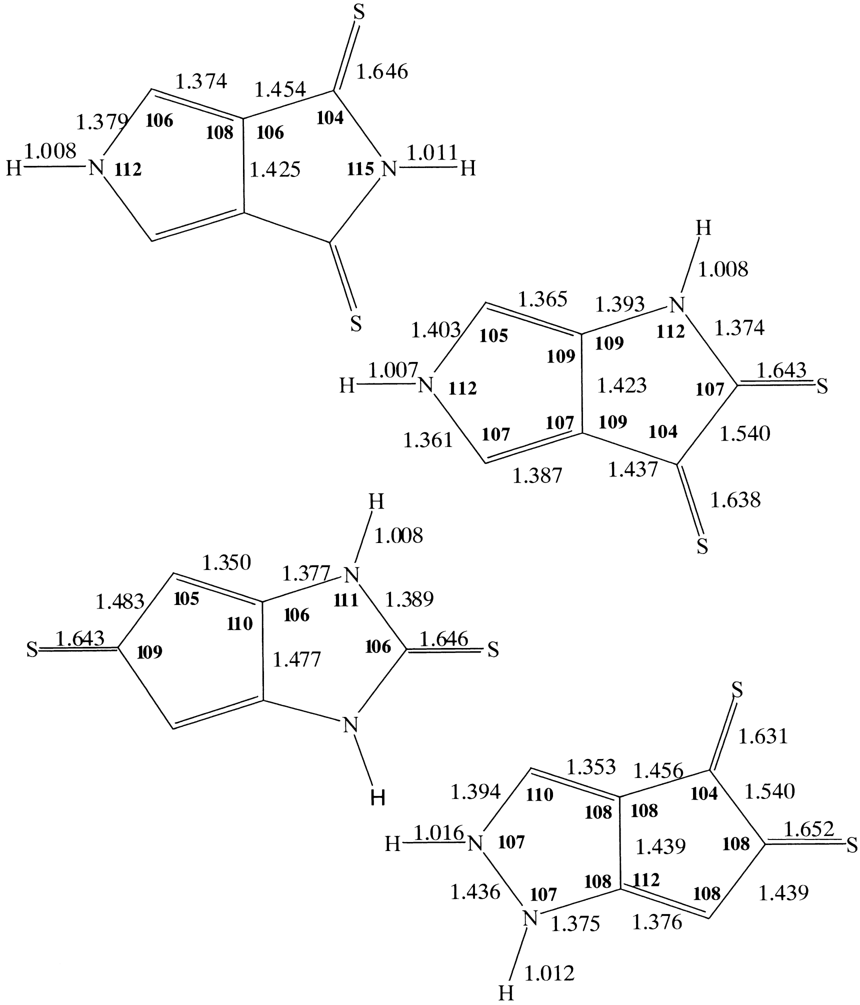

FIGURE 3 B3LYP/6-311+G**//B3LYP/6-311+G** calculated bond lengths (in Å) and bond angles (in °) for four structural isomers with 2 NH, 2 CS, and 2 C=CH units.

2 and **3** are given in Figure 2; for the isomers constructed with 2 C=S, 2 N—H, and 2 HC=S are given in Figure 3; and the six isomer constructed with 2 C=S, 2 N—H, 2C, and 2CH units are given in Figure 4.

Structure **4** is the most stable isomer and isomer **7** is calculated to be 44.22 kcal mol^{-1} less stable than DtPP (Table II). Isomers **7**, **12,** and **13,** which include N—N and S=C—C=S moieties, are the least stable isomers. Isomer **2** is more stable than DtPP and its properties such as

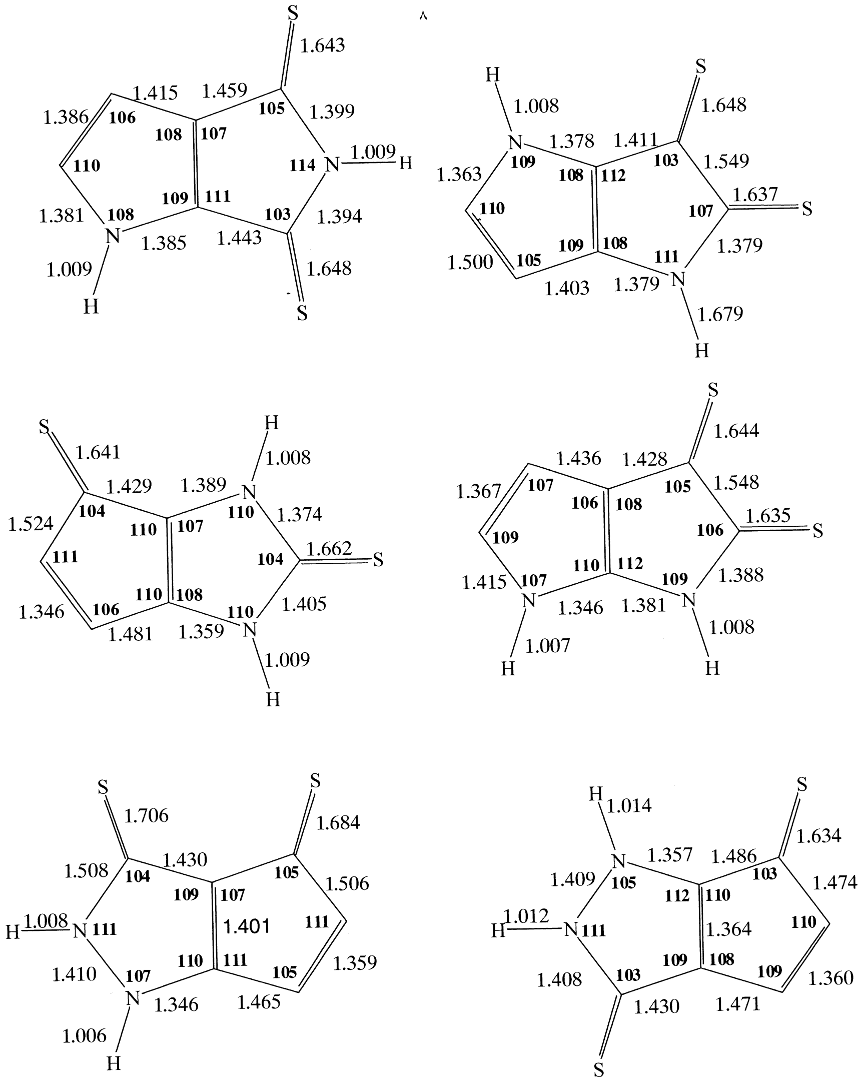

FIGURE 4 B3LYP/6-311+G**//B3LYP/6-311+G** calculated bond lengths (in Å) and bond angles (in °) for DtPP and six structural isomers with 2 NH , 2 CS, 2 C, and 2 CH fragments.

$\Delta E_{\text{HOMO-LUMO}}$ and dipole moment are similar to those calculated for DtPP, thus, it is expected to be an interesting pigment.

Using B3LYP/6-311+G** method, all structural isomers are plannar except isomers **7**, **11**, and **12**, which contain a HN—NH moiety. The torsional angles of the H—N—N—H moieties are shown in Figure 4.

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 I–III). All calculated $\lambda_{\max}$ values are in the UV-VIS region of the electromagnetic spectrum. 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) $= 45.62/\Delta E$.

Although isomers **2**, **4**, and **8** are calculated to be more stable than **1**, their λ_{max}values are much less than that calculated for **1**. However, isomers **10**, **12**, and **13**, which are predicted to be less stable than **1**, have more effective conjugation and exhibit longer $\lambda_{\max}$ values. Isomers **2** and **3**, with longer $\lambda_{\max}$ values, can be good choices for synthesis in comparison with DtPP, since they possesses the longer $\lambda_{\max}$ value. Also, isomer **10** is about 13 kcal mol^{-1} less stable than **1** and possesses longer $\lambda_{\max}$ value (680 nm compared to 524 nm).

In summary, *ab initio* calculations provide a picture of dithiopyrrolopyrrole and its isomers from structural, energetics, and electronic points of view.

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