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An AM1 study on a certain cyclophane fused spirooxazine system and some of its isomers

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Abstract

A certain spirooxazine system containing azaindoline moiety as well as a cyclophane system has been considered. Also its isomeric forms, acyclic isomers, of the spirocompound have been the present concern for the AM1 (RHF) type semiempirical quantum-chemical treatment. Some geometrical and physicochemical data, thermodynamic as well as molecular orbital energetics and UV–Vis spectral characteristics have been presented.

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Keywords: Spirocompounds; Spirooxazines; Azaindoline; Cyclophanes; AM1 calculations; UV–Vis spectra

1. Introduction

Photochromism is the phenomenon whereby the absorption spectrum of a molecule or crystal changes reversibly on exposure to light of certain wavelength [1]. A large number of organic and inorganic materials which exhibit photochromism have been known for many years and have found application in many areas, such as optical recording media and molecular electronic devices [2–5].

Photochromism is based on reversible light-induced molecular rearrangements (photochromic rearrangements). Generally they are reversible transformations of a chemical species between two states with different absorption spectra induced by electromagnetic radiation [2]. Photochromism was first described at the end of the 19th century. However, more than 50 years had to elapse for

the commencement of extensive studies of organic photochromes. Spirocyclic compounds composed of two heterocyclic fragments, which are linked through the sp^3 -carbon atom, immediately have come to the forefront [2–11] (see Fig. 1).

Spiropyranes which were the best studied organic photochromes [3–7] curtailed the work concentrated on spirooxazines (SPO) [11]. The starting impetus for the studies of the chemistry of SPO was the work of Chi [12]. SPO compounds have attracted the attention of researches as photochromes showing promise for the practical application in materials with varying optical density [13]. However, many problems remain with respect to the practical application of photochromic materials such as improvement of thermal stability, self life sensitivity and retrieval of recorded data. Based on more sophisticated molecular requirements, novel photochromic compounds targeting to those requirements are expected to be developed.

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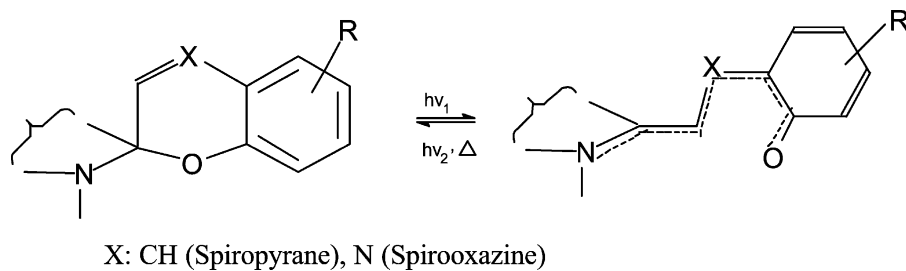


Fig. 1. The cyclic and acyclic forms of a photochromic spirocompound.

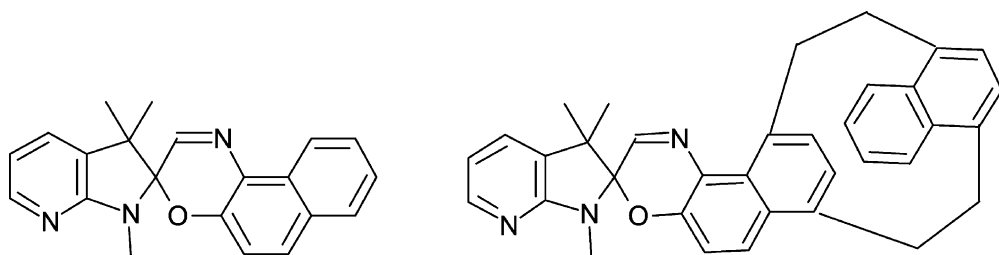


Fig. 2. The spirooxazine structure presently considered as the base compound (on the left) and the derived cyclophane system (on the right).

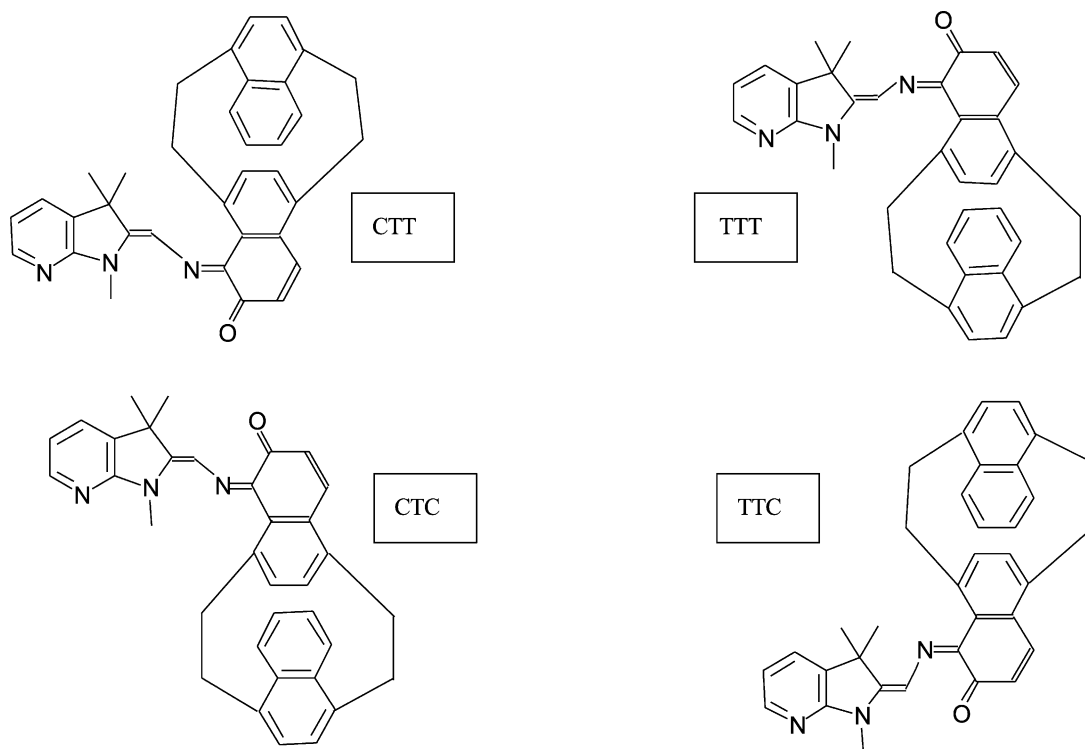


Fig. 3. The acyclic structures of present concern.

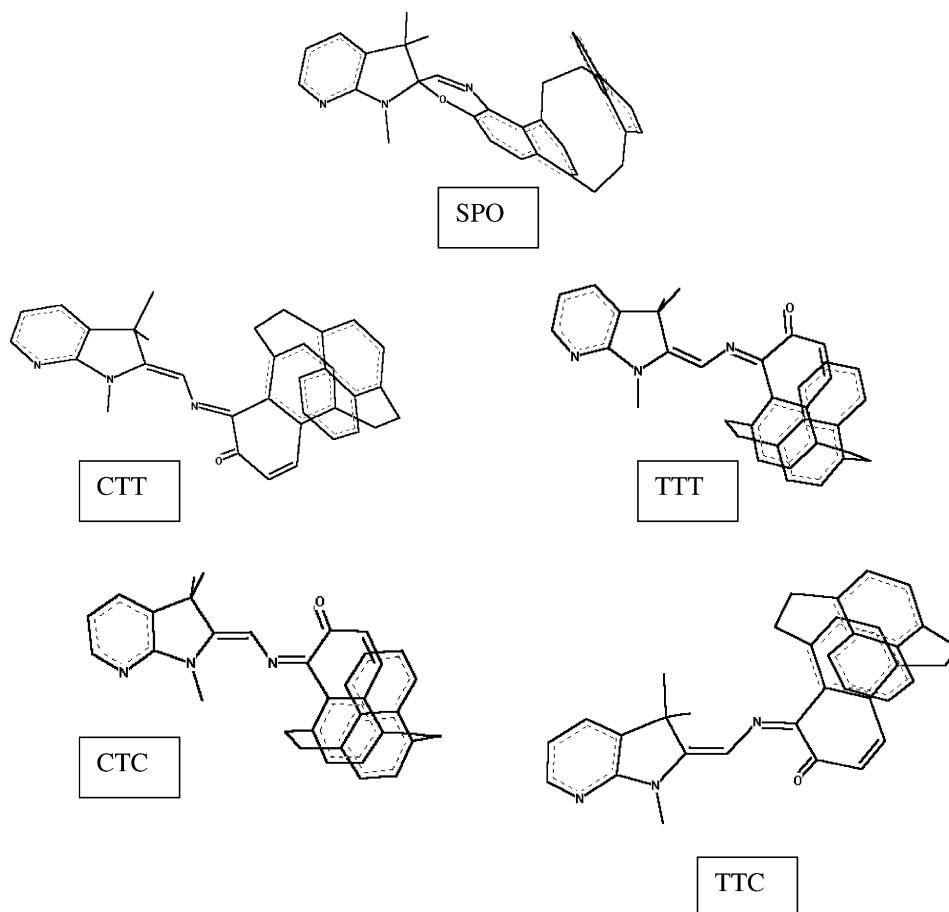


Fig. 4. The geometry optimized structures for the presently considered systems.

In the present study, the SPO structure shown in the left hand side of Fig. 2 was taken as the starting compound and a [2₂]-type cyclophane structure on the naphthalene moiety was constructed. Then, various isomers of acyclic forms supposedly obtained by photoinduced destruction of the spiro linkage were considered (see Fig. 3 where C and T stand for *cis* and *trans* forms, respectively). Note that all the presently considered structures having phane bridges are nonexistent molecules yet.

2. Method

In the present study, the considered structures were subjected to strict geometry optimization by using

Table 1
Some calculated geometrical and physicochemical properties of the structures presently considered

	SPO	CTT	TTT	CTC	TTC
Area	684.15	698.13	696.43	709.55	706.94
Volume	1321.85	1339.73	1340.68	1344.24	1341.30
log <i>P</i>	9.46	7.85	7.85	7.85	7.85
Refractivity	157.72	160.67	160.67	160.67	160.67
Polarizability	62.54	61.67	61.67	61.67	61.67
Dipole moment	5.82	17.56	9.41	4.16	10.44

Area, volume, refractivity, polarizability and dipole moments are in the order of 10^{−20} m², 10^{−30} m³, 10^{−30} m³, 10^{−30} m³ and 10^{−30} C m, respectively.

Table 2

Some calculated energies of the presently considered structures

Energy	SPO	CTT	TTT	CTC	TTC
Total	− 563,961	− 563,941	− 563,931	− 563,946	− 563,936
Binding	− 32,783	− 32,763	− 32,753	− 32,768	− 32,758
Isolated atomic	− 531,178	− 531,178	− 531,178	− 531,178	− 531,178
Electronic	− 5,984,476	− 5,887,953	− 5,889,536	− 5,847,098	− 5,862,528
Core–core interaction	5,420,515	5,324,012	5,325,605	5,283,152	5,298,592
Heat of formation	667.54	687.44	697.12	682.49	692.56
Energy of hydration	− 12.88	− 10.54	− 10.37	− 9.66	− 10.16

Energies in kJ/mol.

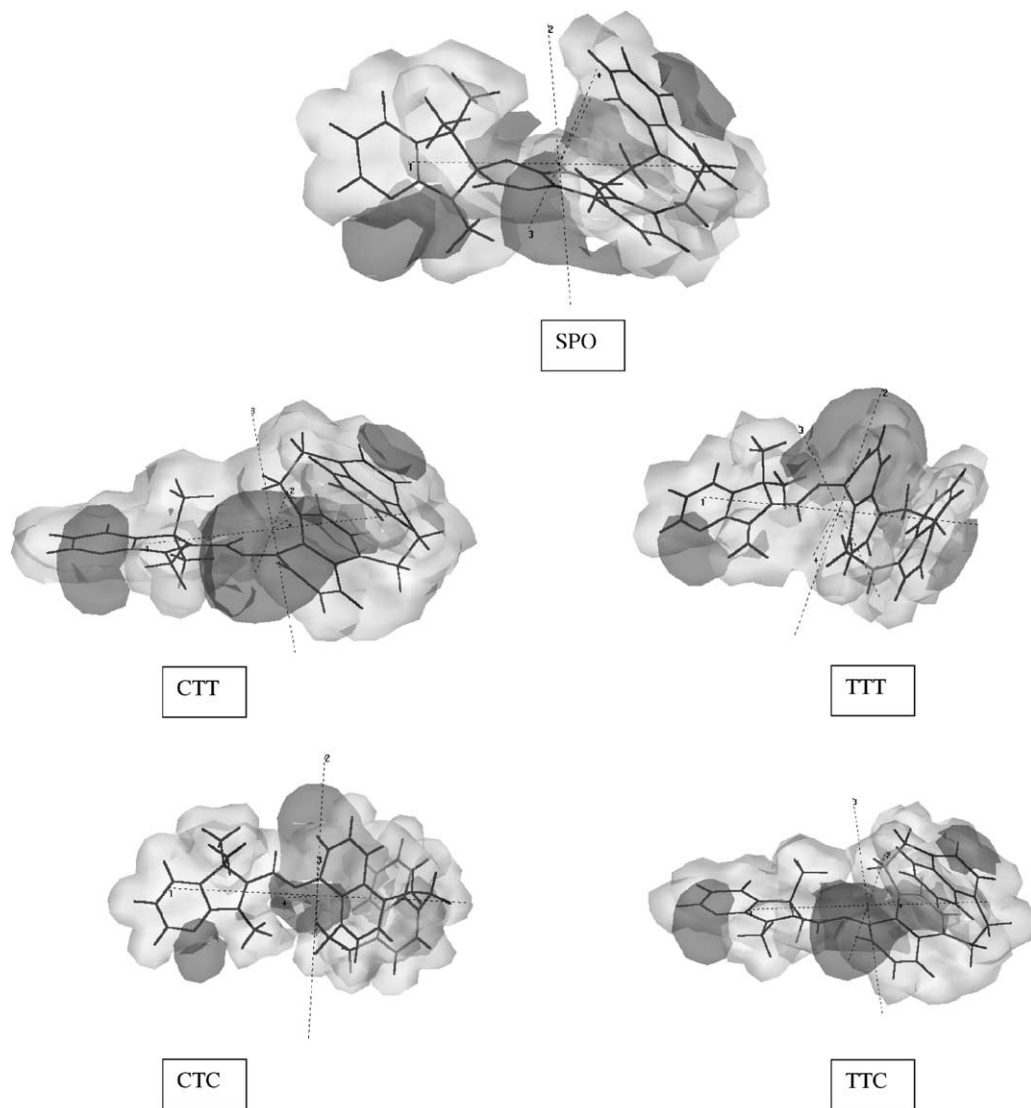


Fig. 5. 3D-electrostatic potential maps of the structures presently considered.

Table 3

The HOMO, LUMO energies and the interfrontier energy gaps of the structures

Energy	SPO	CTT	TTT	CTC	TTC
LUMO	− 1.6063	− 1.4538	− 1.4811	− 1.5941	− 1.6036
HOMO	− 12.7942	− 12.7391	− 12.9521	− 12.6755	− 12.7770
ΔE	11.1879	11.2853	11.4710	11.0814	11.1734

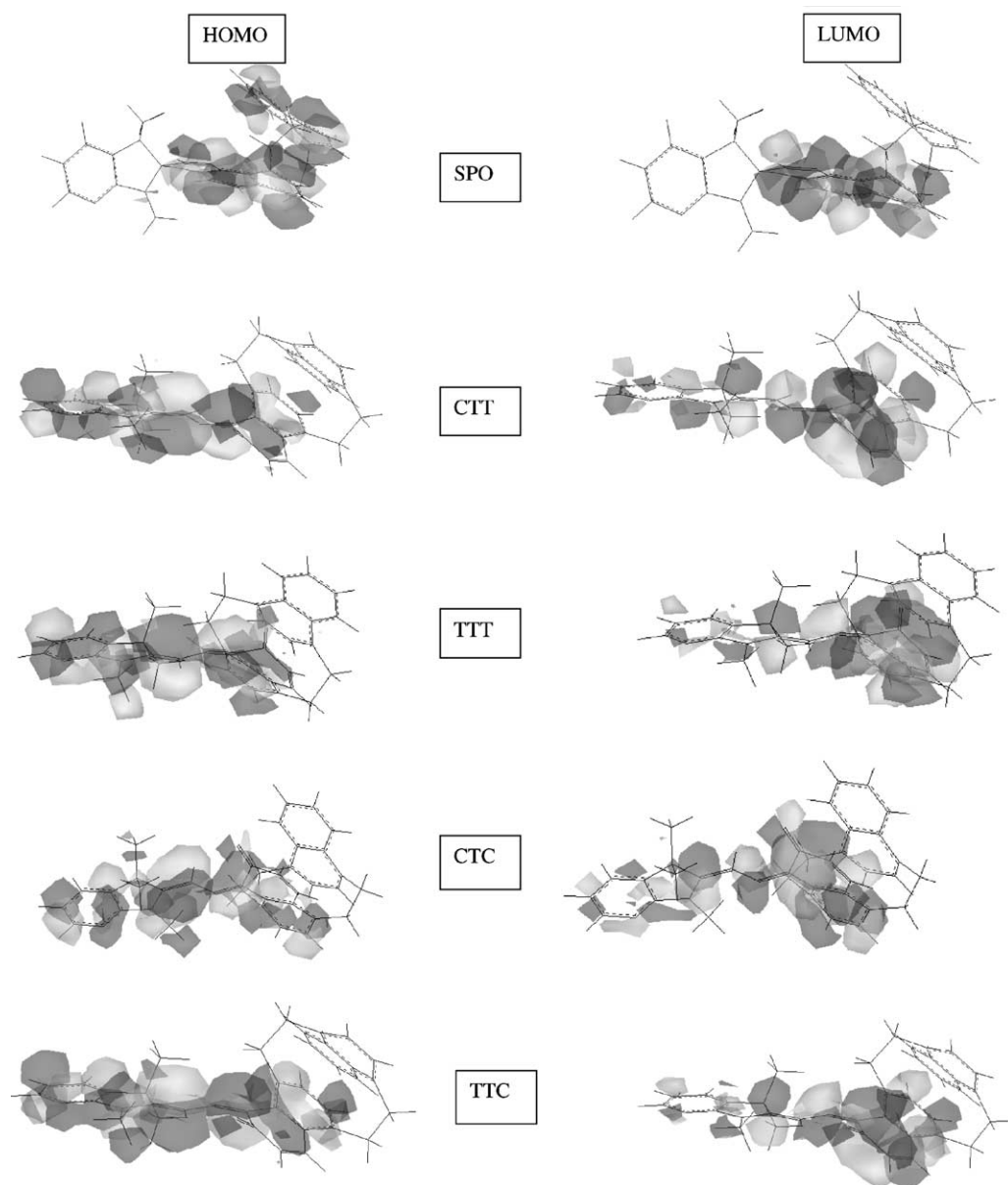
Energies in the order of 10^{-19} J. Symmetries are all of A-type.

Fig. 6. The HOMO and LUMO of the presently considered structures.

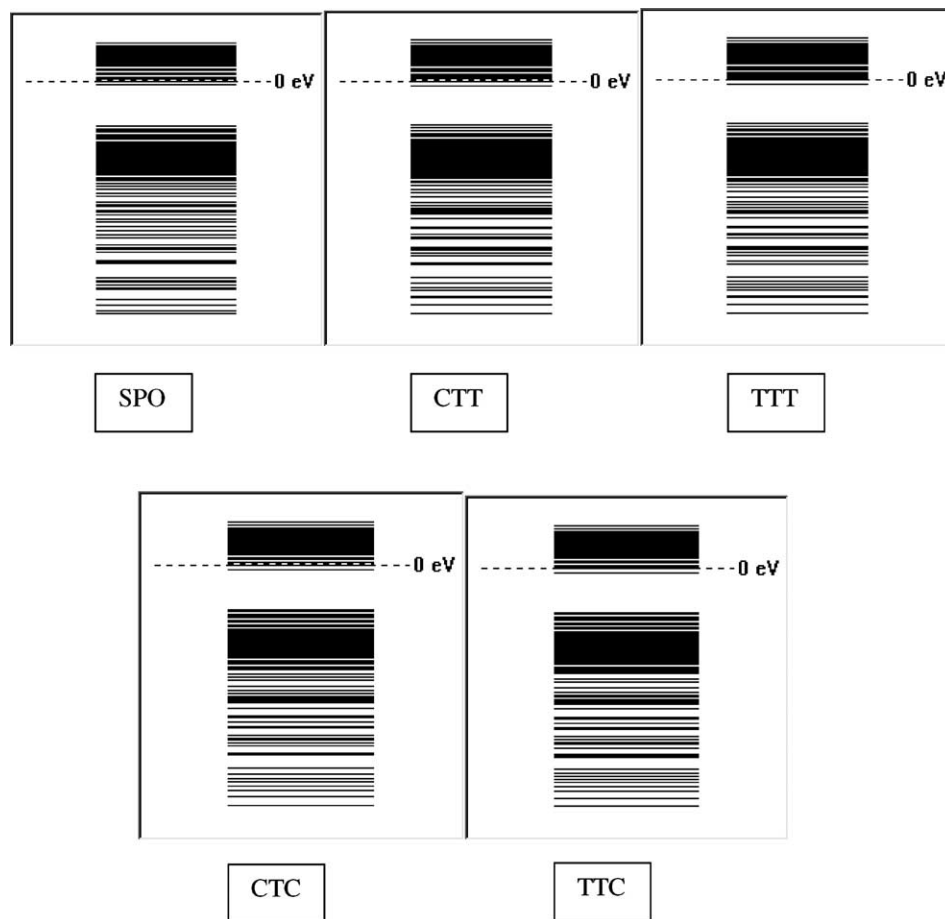


Fig. 7. The molecular orbital energy spectra for the species considered.

AM1 type semiempirical quantum-chemical method [14] at the level of restricted Hartree–Fock (RHF) approach [15]. Throughout the calculations, the convergence limit and the gradient (RMS) values were maintained below 4.18×10^{-3} kJ/mol (0.001 kcal/mol) and 4.18×10^7 kJ/m mol (0.001 kcal/A mol), respectively. The geometry optimizations were achieved by using the steepest descent technique followed by conjugate gradient methods, Fletcher–Reeves and Polak–Ribiere [17]. UV–Vis spectra of all the structures have been estimated by using ZINDO/S method [16,17] with singly excited configuration interaction (CI) calculations. For that purpose, ZINDO/S single point calculations were carried out, involving 20 of each of the uppermost occupied and the lowermost

unoccupied molecular orbitals (totally 801 configurations) with the overlap weighting factors [18] 1.267 and 0.585 for σ – σ and π – π types, respectively. All these computations were carried out by using the hyperchem (5.1) package program [19].

3. Results and discussion

Fig. 4 shows the geometry optimized structures of all the molecules presently considered. Table 1 contains some calculated geometrical and physico-chemical properties of them. Note that all these structures are isomeric systems. Table 2 shows some calculated energies of the structures. The total and binding energy values indicate that the spiro structure

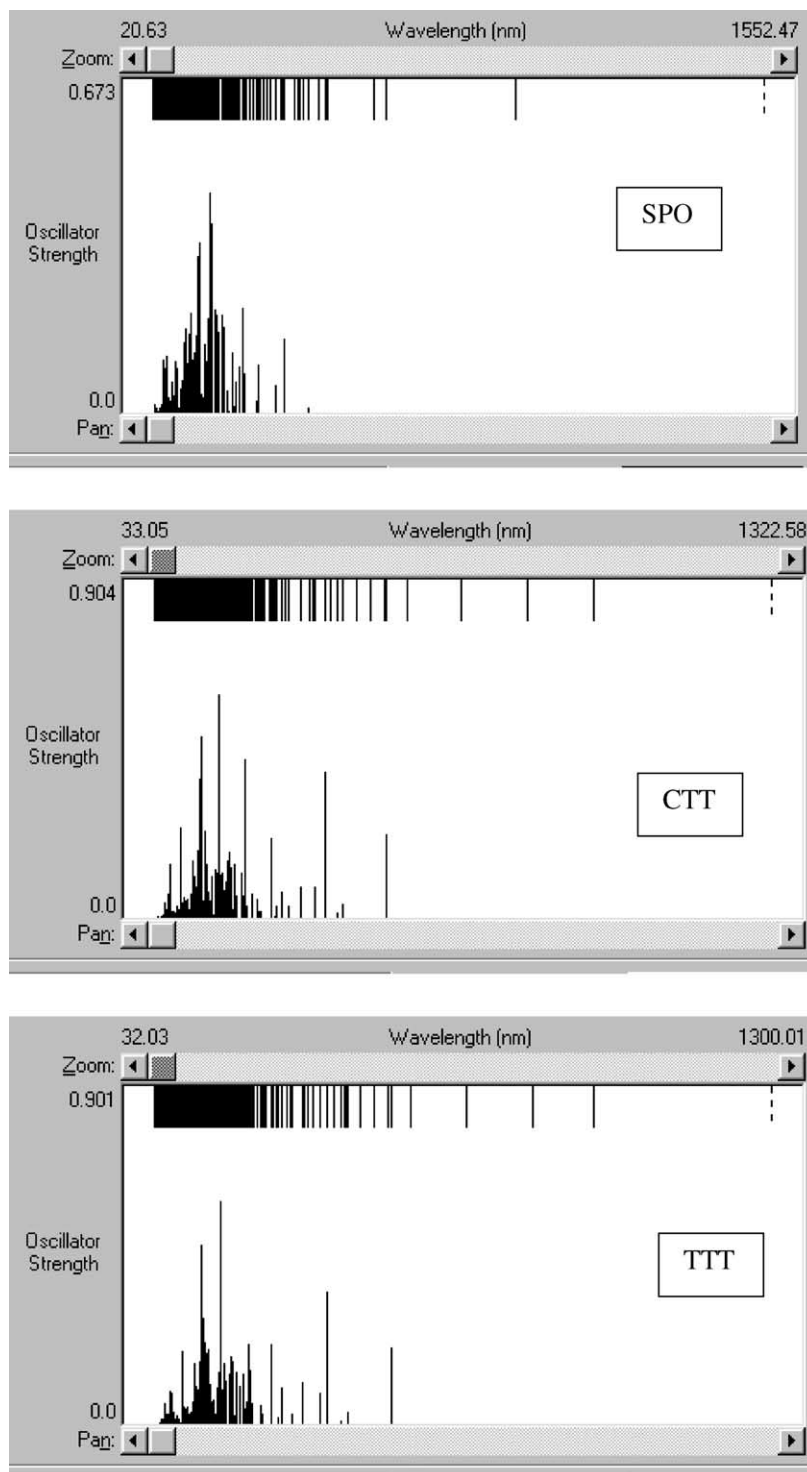


Fig. 8. The calculated UV-Vis spectra for the species considered.

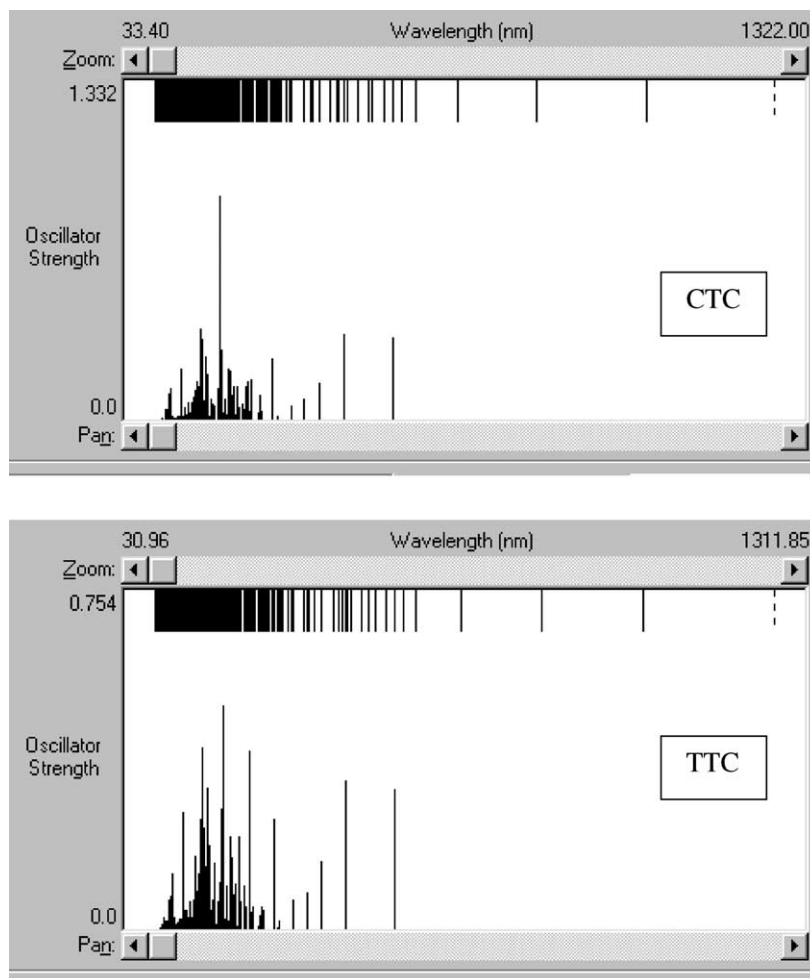


Fig. 8 (continued)

(SPO) is the most stable and the least endothermic of all. However, nonspiro structures follow the order of CTC > CTT > TTC > TTT for the stability (the total and binding energies are considered). A reverse order of trends exists for the endothermic nature of the structures, namely TTT > TTC > CTT > CTC. However, core–core interaction energy which is repulsive in character is the greatest for the SPO structure and the following order exists that is SPO > TTT > CTT > TTC > CTC. Seemingly, opening of SPO ring causes some relief thus a decrease occurs in core–core repulsion energy. Indeed, area and volume calculations indicate that SPO structure possesses more compact arrangement

of atoms (see Table 1). Fig. 5 shows the 3D-electrostatic potential maps of the structures of present concern.

The HOMO, LUMO energies and the interfrontier molecular orbital energy gaps of the structures are shown in Table 3. Among them TTT is characterized with the lowest lying HOMO energy. The lowest lying LUMO energy coincides with SPO structure. On the other hand, the highest HOMO and LUMO energies stand for CTC and CTT structures, respectively. As a consequence of the HOMO–LUMO energy separation, the interfrontier energy gaps ($\Delta E = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) follow the order of TTT > CTT > SPO > TTC > CTC.

Fig. 6 shows the HOMO and LUMO of these species and Fig. 7 contains molecular orbital energy spectra of them. As seen in Fig. 6, the upper plane deck with exception of SPO-HOMO contributes neither to the HOMO nor the LUMO of the species considered. Fig. 7 shows the presence of band-like gathering of molecular orbital energy levels.

The calculated UV–Vis spectra of these species are shown in Fig. 8 and some spectral characteristics

are displayed in Tables 4 and 5. The UV–Vis data indicate that the main absorption bands of the spirocompound should be in the UV region whereas acyclic isomers have some appreciably strong bands above 400 nm. The NHOMO, HOMO, LUMO and NLUMO of all of these structures possess the same orbital numbers, 95, 96, 97 and 98, respectively. Thus, most of the transitions shown in Tables 4 and 5 are among these orbitals.

Table 4
Some calculated spectral characteristics of the compounds

No.	λ_{\max} (nm)	Oscillator strength	State dipole components (Debye)			Transition dipole components (Debye)		
<i>SPO</i>								
9	443.9	0.0155	−0.2953	0.1034	−2.5299	0.8014	0.4446	−0.7879
14	387.1	0.1550	4.8120	4.9434	−3.2699	3.3479	1.0266	−0.7029
17	369.4	0.0590	−0.2734	0.8355	−0.8996	0.2956	−1.9099	−0.9501
22	329.9	0.1036	0.2084	0.6651	−2.9841	0.5625	−2.0759	1.6257
23	327.1	0.0291	2.7788	2.9345	−2.1064	0.4047	−1.2498	0.5442
27	300.0	0.0857	0.4668	−0.1142	−2.6862	−2.2912	−0.1113	0.4520
31	294.3	0.2184	0.9626	−0.1508	−2.7410	−1.7670	−3.2447	−0.1359
32	293.4	0.1314	−0.5031	−0.3860	−3.2598	0.3033	2.7305	−0.8042
72	225.3	0.3623	−1.0750	−3.1291	−3.1781	−0.3037	−4.1280	−0.4747
122	196.4	0.3492	−1.3275	−3.5112	−0.7227	−3.3106	1.7849	0.6610
131	191.7	0.3215	0.5257	2.4306	−3.7381	−0.3124	3.1492	−1.7579
<i>CTT</i>								
6	531.3	0.2294	7.5351	−14.1193	−0.9401	−4.1280	1.8091	2.3674
11	450.4	0.0439	4.4167	−7.7829	1.0922	−1.7123	−0.9897	0.5413
17	416.3	0.3967	−0.4081	−10.0892	4.1477	5.5227	0.7432	−2.0152
18	397.2	0.0909	6.6496	−12.4738	2.2672	−0.7199	2.6370	0.4507
22	368.2	0.0923	3.7529	−13.1387	2.3479	2.3023	0.9525	−1.0099
78	230.6	0.1616	2.1778	−9.3310	3.6992	−1.5293	−2.1848	−0.9002
<i>TTT</i>								
6	531.8	0.2092	4.9535	10.7601	−1.9479	−3.1668	−3.5009	−1.1705
17	411.4	0.3613	−1.1436	3.8980	−4.9261	−5.1087	−1.3883	−1.8940
18	397.4	0.0898	4.4550	7.4338	−4.1929	0.1350	2.6596	−0.7087
22	366.5	0.1165	0.6167	7.2315	−4.9172	2.6748	0.0706	1.3855
26	327.6	0.1060	0.4098	2.5635	−3.9208	−2.7059	0.0252	0.2502
33	309.0	0.2199	6.4037	5.6705	−2.2401	3.4800	1.4174	0.5740
<i>CTC</i>								
7	541.4	0.3312	8.1768	1.7483	2.8398	6.1526	−0.3968	0.3502
13	450.7	0.3449	1.2666	2.5137	1.2268	4.4224	−1.9126	−3.1365
18	402.4	0.1541	4.2839	2.8646	−0.7027	−3.3709	−1.0192	−0.8852
21	374.2	0.0960	4.4204	3.0269	1.9597	2.2043	−0.7247	−1.5013
32	312.6	0.2523	6.5976	−0.3304	−3.2430	3.6609	−0.3528	−1.8021
<i>TTC</i>								
7	538.5	0.3162	5.0033	−10.3117	6.8300	−4.7102	3.5419	−1.2189
14	448.7	0.3351	−0.8310	−4.8178	5.6939	5.6498	0.1914	0.1092
18	401.8	0.1577	2.9172	−5.3924	7.6379	2.0031	−2.5827	1.6696
32	312.5	0.2510	6.5122	−4.4500	5.7902	3.9812	−0.3616	0.8355

Table 5
 λ_{\max} values and the corresponding transitions

No.	λ_{\max} (nm)	Spin up: Occ. MO \rightarrow Unocc. MO	Coefficients
<i>SPO</i>			
9	443.9	96 \rightarrow 100	–0.532035
14	387.1	96 \rightarrow 98	–0.549830
17	369.4	96 \rightarrow 103	–0.429144
22	329.9	96 \rightarrow 100	0.330163
		95 \rightarrow 97	0.529085
23	327.1	96 \rightarrow 102	–0.559705
27	300.0	94 \rightarrow 97	0.324240
31	294.3	95 \rightarrow 98	0.402327
32	293.4	93 \rightarrow 99	0.554551
72	225.3	91 \rightarrow 97	0.382713
		90 \rightarrow 97	–0.365749
122	196.4	91 \rightarrow 100	–0.419738
131	191.7	88 \rightarrow 101	0.344867
<i>CTT</i>			
6	531.3	96 \rightarrow 97	0.641504
11	450.4	90 \rightarrow 97	–0.334094
17	416.3	95 \rightarrow 97	–0.507014
18	397.2	94 \rightarrow 98	0.322201
22	368.2	94 \rightarrow 97	–0.517593
78	230.6	94 \rightarrow 104	–0.417536
<i>TTT</i>			
6	531.8	96 \rightarrow 97	0.642353
17	411.4	95 \rightarrow 97	–0.500912
18	397.4	94 \rightarrow 98	–0.316754
26	327.6	85 \rightarrow 97	0.446782
33	309.0	95 \rightarrow 100	0.334466
<i>CTC</i>			
13	450.7	95 \rightarrow 97	0.638354
21	374.2	94 \rightarrow 97	–0.542336
32	312.6	95 \rightarrow 100	–0.362231
<i>TTC</i>			
7	538.5	96 \rightarrow 97	0.654428
14	448.7	95 \rightarrow 97	–0.629778
18	401.8	96 \rightarrow 99	–0.323954
		94 \rightarrow 98	0.344919
32	312.5	95 \rightarrow 100	0.362771

4. Conclusion

Generally, SPO compounds are important photochromic dye systems. In the present study, a special

type SPO system and some of its acyclic isomers having both azaindoline and a cyclophane moieties have been considered for AM1 (RHF) type semi-empirical calculations. The results indicated that they are all stable and endothermic. However, the spirocompound appears to be more stable and less endothermic than the acyclic isomer. Moreover, it is hydrated better.

UV–Vis spectra of the spirocompound is mainly in the UV region whereas in the case of acyclic isomers, some absorption peaks in the visible region emerge.

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