LOW-LYING EXCITED STATES AND THEIR RELAXATION PATHWAYS OF PHENOTHIAZINE

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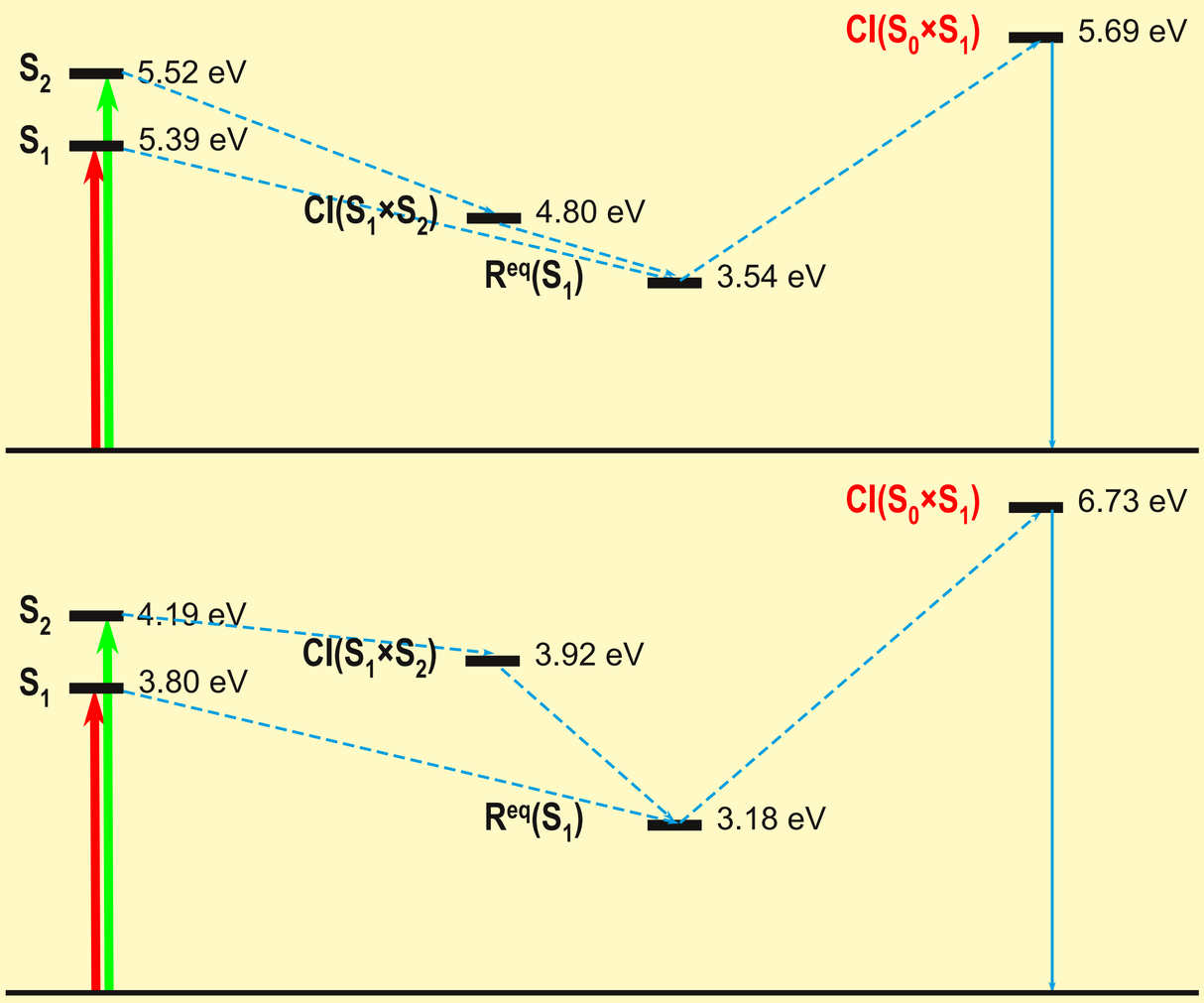
Abstract: The first two, low-lying electronic excited states and the their relaxation pathways for the phenothiazine has been investigated using multi-configuration self-consistent field, equation-of-motion coupled cluster and density functional theory (DFT) methods considering the def2-TZVP triple-ξ quality basis set as well as the MN12-SX exchange correlation functional in the case of DFT. The electronic configurations of the first three vertical excited states as well as the geometries of conical intersections between different excited states were discussed in details. Different relaxation pathways over the potential energy surfaces are identified and discussed.

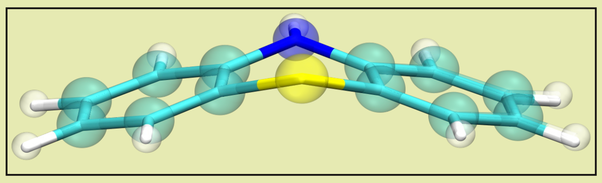
Method:

- The equilibrium geometries of the first excited (S_1) and ground states (S_0) as well as the conical intersection (CI) points between $S_0 \times S_1$ and $S_1 \times S_2$ potential energy surfaces have been obtained using the multireference self-consistent field (MCSCF) and DFT (MN12-SX [2,3] exchange-correlation functional) methods.
- The MCSCF [4] active space includes 16 electrons and 12 active orbitals (*16,12*).
- The control methods for vertical excitation energies are: EOM-CCSD and LT-DF-LCC2 [4] methods.
- The CI points were localized with the "Penalty Function" Algorithm [5].

	S_1 $n\pi^*$	S_2 $n\pi^*$	S_3 $n\pi^*$
MCSCF	5.39 eV 230 nm (0.0027)	5.52 eV 224.7 nm (0.0344)	5.71 eV 217.2 nm (0.0607)
EOM-CCSD	4.34 eV 285.9 nm (0.0006)	4.50 eV 275.5 nm (0.0274)	4.64 eV 267.3 nm (0.0497)
LT-DF-LCC2	3.66 eV 338.9 nm (0.0006)	3.94 eV 314.7 nm (0.0271)	4.10 eV 302.3 nm (0.0778)
MN12-SX	3.80 eV 326.3 nm (0.0004)	4.19 eV 296.1 nm (0.0301)	4.33 eV 286.3 nm (0.1090)

Table 1. Vertical excitation energies (and their oscillator strength in parenthesis) for the first three lowest excited states of phenothiazine obtained at different levels of theories.





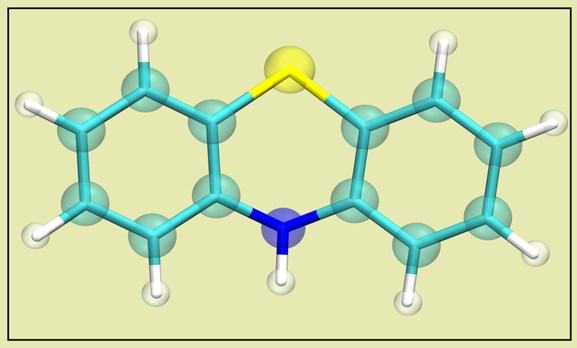


Figure 1. The ground state (S_0) equilibrium geometry obtained with MCSCF (stick) and MN12-SX (transparent ball&stick) methods.

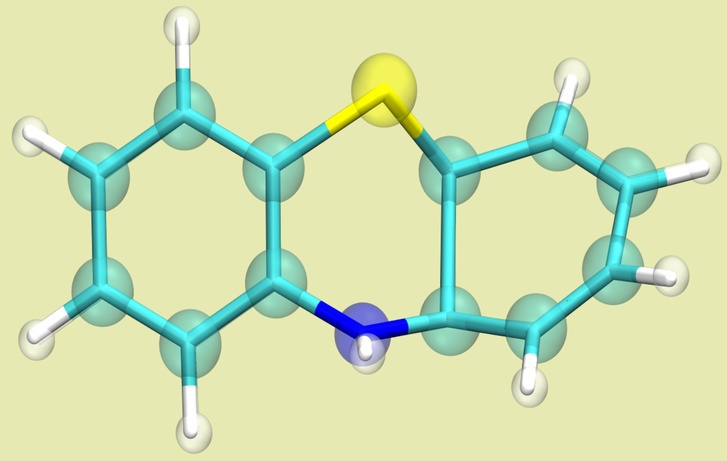


Figure 3. The S_0xS_1 conical intersection point geometry obtained with MCSCF (stick) and MN12-SX (transparent ball&stick) methods.

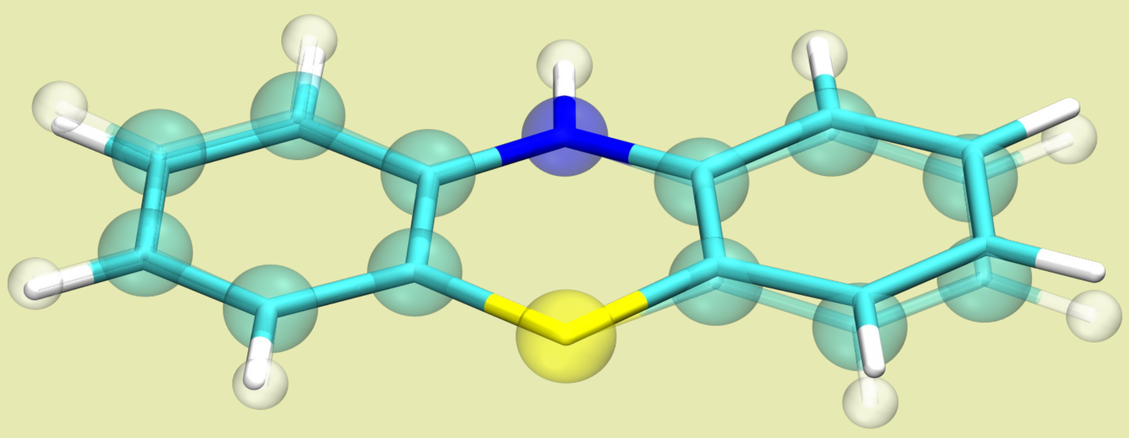


Figure 2. The first excited state (S_1) equilibrium geometry obtained with MCSCF (stick) and MN12-SX (transparent ball&stick) methods.

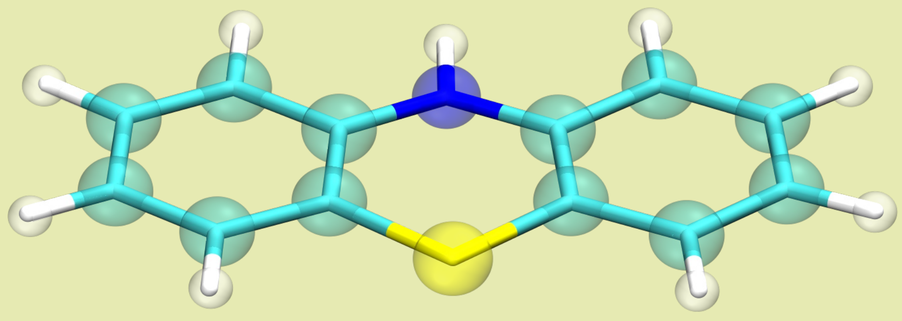


Figure 4. The S_1xS_2 conical intersection point geometry obtained with MCSCF (stick) and MN12-SX (transparent ball&stick) methods.

Conclusions

- The best estimation of the vertical excitation energy is given by the MN12-SX and DF-LT-LCC2 methods (S_2(exp) = 312.6 nm) [1].
- The relaxation pathway of the S_2 vertical state does not include any equilibrium geometry, it directly crosses the S_1xS_2 conical intersection point and reaches the S_1 equilibrium geometry.
- The radiationless decay through the S_0xS_1 conical intersection point is energetically unfeasible.
- The MN12-SX exchange-correlation DFT functional works well close to the electronically degenerated potential energy sufraces (conical intersection points), the overlap with the MCSCF geometries is almost perfect.
- There is a major difference between the energy values obtained with MN12-SX exchange-correlation functional and the MCSCF multiconfigurational Hartree-Fock method.
- This difference is given by the presence of electron correlation effects included in the MN12-SX functional.

Acknowledgement

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REFERENCES

[1] J. A. VanAllan, G. A. Reynolds, R. E. Adel, J. Org. Chem., 27, 1659 (**1962**).
[2] R. Peverati, D. G. Truhlar, Phys. Chem. Chem. Phys. 14, 16187 (**2012**).
[3] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, et. al . Gaussian, Inc.: Wallingford CT, **2009**.
[4] MOLPRO, version 2012.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others , see http://www.molpro.net.
[5] C. Ciminelli, G. Granucci, M. Persico, Chem. Eur. J. 10, 2327 (**2004**).