

Trans-1-(2-anthryl)-2-phenylethene conformer equilibrium. Spectroscopic and thermodynamic Q-M study

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Affiliations

The research should be considered as a part of the Master's Degree Thesis.

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Rotational equilibrium in 1,2-trans-diarylethenes

The chemical compounds classified as **1,2-diarylethenes** exhibit a possibility of the aromatic rings rotation around the single-bonded part of the junction. As a result, several conformational forms of the same molecule – **the rotamers** – are simultaneously present in a solution. The mole fractions **x** of both forms in the mixture are unambiguously defined by the equilibrium constant **K**.



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Experimental data – changes in UV-Vis spectra



$$\Delta G = \Delta G^{\circ} + RT \ln K$$
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{S^{\circ}}{R}$$

Each of the rotamers is characterised by slightly different photochemical properties. Yet, their separation for selective measurements is **practically impossible** due to a low conversion energy barrier – two forms can easily transform into each other. A contribution of conformers to the overall mixture spectra can be however modified by a change of temperature (van't Hoff equation) or – in the case of fluorescence – excitation wavelength.

What is already known about the system?



Aim of the research



Schematic algorithm of calculations



<u>1.</u> Search for the most stable conformers (relaxed PES scan = optimisation of geometry with "freezed" parameters)

<u>2.</u> Thermochemistry + normal modes (geometry optimisation + frequency calculation of the molecule in the gorund state)

<u>**3.</u>** Order of the excited states (calculations of the vertical transitions)</u>

<u>4.</u> Normal modes of the excited states (geometry optimisation + frequency calculation of the molecule in the excited state)

 $I \simeq \langle \Psi | \hat{\mu} | \Psi' \rangle \approx \langle \Psi_{v} | \hat{\mu}_{e} | \Psi_{v}' \rangle$ $\hat{\mu}_{e}(Q') \approx \hat{\mu}_{e}(Q_{0}') + \sum_{n}^{N} \frac{\partial \hat{\mu}_{e}}{\partial Q_{n}'} Q_{n}' + \dots$ $FC \qquad HT$

allowed - transitions - forbidden

<u>5.</u> Fine-structured spectrum simulation (Franck-Condon-Herzberg-Teller vibronic spectra approximation)

V. Barone, J. Bloino, M. Biczysko, F. Santoro, *J. Chem Theory Comput.*, **5** (2009), 540-554

Computational methods and details

DFT Theory levels:



- <u>Calculation methodology:</u>
- \rightarrow Density Functional Theory (DFT)
- Excited States Time Dependent DFT approach:
- \rightarrow Random Phase Approx. (RPA = TD)
- \rightarrow Tamm-Dancoff Approx. (TDA)
- <u>Computational details:</u>
- \rightarrow Basis set: 6-311G**
- \rightarrow Solvent: SCRF (toluene, cyclohexane)
- \rightarrow Emp. Dispersion correction: D3 Grimme
- \rightarrow FCHT Duschinski Transform
- <u>Software</u>
- \rightarrow Gaussian09

PES scan results



B3LYP PES scan with 'freezed' dihedral angles between arene rings and ethene bridge; without D3 correction.

Rotational barriers energy values



PES scan revealed two stable conformers, one of them planar (s-*trans*), and the other in a shape of a letter X (s-*cis*).



Rotations energy profiles obtained as lines form 3D Scan.



B3LYP anthracene ring rotation scan with only one 'fixed' parameter.

In therms of the thermodynamic parameters:

 $\Delta E_{rot.} = 20.0 \text{ kJ/mol}$ $\Delta H_{rot.} = 14.4 \text{ kJ/mol}$ $\Delta G_{rot.} = 18.2 \text{ kJ/mol} \approx 1500 \text{ cm}^{-1}$ $\Delta E_{rot. [B]} = 20.8 \text{ kJ/mol}$

> [B] = G. Bartocci, F. Masetti U. Mazzucato, J. Mol. Struct., **193** (1989), 173-183

Thermodynamic parameters of the system

Results obtained from the vibrational analysis of molecules in the ground state; reaction direction: s-*cis* \rightarrow s-*trans*.

Method	ΔΕ	ΔH	ΔS	ΔG	K	x s-cis		∆x s-cis	
	[kJ/mol]	[kJ/mol]	[J/mol·K]	[kJ/mol]	T 25°C	T 25ºC	T 5°C	T 85°C	T 5°C \rightarrow 85°C
BP86	-4.697	-4.503	-2.256	-3.830	4.689	0.176	0.158	0.224	+0.067
B3LYP	-4.553	-4.387	-2.528	-3.633	4.331	0.188	0.169	0.237	+0.068
CAM- B3LYP	-3.702	-3.413	6.412	-5.325	8.569	0.105	0.096	0.128	+0.033
M06-2X	-3.634	-3.295	1.632	-3.782	4.598	0.179	0.165	0.214	+0.049
MP2	-2.001	-1.875	4.089	-3.094	3.484	0.223	0.214	0.246	+0.032

 $\Delta H_{[F]} = 4.5 \text{ kJ/mol}$ $\Delta H_{[S, B]} = 1.3 - 6.5 \text{ kJ/mol}$

 $\Delta G_{[F]} = 3.7 \text{ kJ/mol}$ $\Delta G_{[S, B]} = 1.2 - 4.5 \text{ kJ/mol}$

$$\ln \frac{x_{cis}}{1 - x_{cis}} = \ln K = \frac{-\Delta G^{\circ}}{RT} = -\frac{\Delta H^{\circ}}{RT} + \frac{S^{\circ}}{R}$$

The most 'optimistic' results are provided by usage of BP86 and B3LYP functionals – the bigger the change in contribution of s-*cis* rotamer is, the more probable chemometrical resolution becomes.

[B] = G. Bartocci, F. Masetti U. Mazzucato, *J. Mol. Struct.*, **193** (1989), 173-183 [F] = K. P. Ghiggino, P. F. Skilton, E. Fischer, *J. Am. Chem. Soc.*, **108** (1986), 1146-1149 [S] = J. Saltiel, Y. Zhang, D.F. Sears, J.-O. Choi, *Res. Chem. Intermed.*, **21** (1995), 899-921 11/19

Order of transitions and their oscillator strengths

Method		s- <i>trans</i> (L)						s-cis (A)					
		S ₁	S ₂	S ₁ - S ₂	f ₂ : f ₁	S ₃	S₃	S ₁	S ₂	S ₁ - S ₂	f 2 : f 1	S₃	S₃
		E _{vert.} [nm]	E _{vert.} [nm]	E _{relaxed} [nm]	-	E _{vert.} [nm]	E₀₋₀ [nm]	E _{vert.} [nm]	E _{vert.} [nm]	E _{relaxed} [nm]	-	E _{vert.} [nm]	E₀₋₀ [nm]
BP86	TD	486.7	461.0	-	0.003	383.0	-	512.9	461.8	-	0.156	384.6	-
	TDA	460.7	457.1	1089	23.1	365.5	390.0	482.2	459.7	1033	0.311	367.2	385.4
B3LYP	TD	418.0	376.6	2958	0.007	341.9	366.5	435.3	374.9	4022	0.262	341.9	368.5
	TDA	394.5	375.6	1347	0.005	326.9	347.7	410.2	373.5	2440	0.143	327.4	349.8
CAM- B3LYP	TD	358.8	320.7	4526	0.041	302.7	324.7	367.1	318.2	5504	0.403	301.1	325.1
	TDA	338.5	316.6	3057	0.016	290.4	310.4	345.8	313.8	4176	0.125	289.2	312.0
M06- 2X	TD	358.3	321.2	-	0.069	303.2	-	366.7	318.3	-	0.337	250.5	-
	TDA	338.1	317.4	2880	0.023	290.1	310.5	345.6	314.1	4050	0.101	289.1	311.7

Oscillator strength of transition $S_0 \rightarrow S_2$ was expected to be significantly larger than $S_0 \rightarrow S_1$. However, that was obtained only for TDA-BP86.

In most cases, the difference between two relaxed states S_1 and S_2 is apparently smaller for s-*trans* rotamer, which may be connected with the observed dual fluorescence.

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Finally, $S_0 \rightarrow S_3$ 0-0 transition energy is slightly higher for s-*trans* rotamer [S].

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Simulation of the spectral fine structure – verification



'Crude' (above) and corrected (below) simulated spectral profiles of anthracene.





In order to verify the whole proposed algorithm, simulations of vibrationally resolved spectra were performed for **naphthalene** and **anthracene**.

Although the simulated fine structure is comparable with experimental data, some mathematical corrections can be applied to the 'crude' results:

 \rightarrow x-axis translation **T** (with E₀₋₀ transitions)

- \rightarrow x-axis scaling **S** (x' = s·x)
- \rightarrow peak broadening B

Inversion of states?

Simulated absorption (at the top) and fluorescence (at the bottom) spectra of s-*trans-t*-APE S₁ and S₂ transitions are presented below. An inversion of states between TDA-BP86 and TD-B3LYP can be clearly seen. The same phenomenon was observed for naphthalene.



The final simulated spectra - TDA-BP86



The final simulated spectra - TD-B3LYP



Conclusions

- Two conformerical forms of *t*-APE are energetically favoured, s-*trans* rotamer is practically planar while s-*cis* is X-shaped; that may be one of the reasons why absorption spectra of the latter one is less 'sharp' and 'structured'.
- The rotational barrier is low enough to make physical separation impossible.
- The equilibrium between both rotamers changes with temperature, which theoretically should allow to obtain 'pure' spectra by a chemometrical way; however, this change may not be significant enough as brought in by termochromic effects.
- FCHT approach for simulation the vibronic structure of the electron spectra gave quite good results for all considered compounds. In case of s-*cis-t*-APE conformer, where the ground state geometry significantly differs form those in the excited states, the approximation is not sufficiently adequate. However, a fine structure of the $S_0 \rightarrow S_2$ transition can be observed (BP86, B3LYP).
- Energy difference between S₁ and S₂ states of s-*trans-t*-APE is lower than for s-*cis* rotamer – that may explain the dual fluorescence phenomena observed only for the former one.

 \triangleright S₀ \rightarrow S₃ transition energy most likely is lower for s-*cis-t*-APE than for its analogue.

Further perspectives

 \blacktriangleright Investigation of the excited states stability.

 \triangleright Assessment of the rotational barrier in the excited states.

Experimental and Chemometrical research – an attempt to decompose the overall spectra into the contributions form the 'pure' rotamers.





Thank you for your attention!

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Basis set



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SCRF solvent model – vert. transitions (TDA-B3LYP-D3)



SCRF solvent model – thermochemistry (B3LYP-D3)

3	1,00	1,88	2,37	24,85	35,69	78,36
E <i>-line</i> [a.u.]	-848,220187	-848,222861	-848,223759	-848,228466	-848,228682	-848,228960
E -angle [a.u.]	-848,218504	-848,221141	-848,222025	-848,226652	-848,226863	-848,227135
ΔE (l-a) [kJ/mol]	-4,4182	-4,5158	-4,5524	-4,7633	-4,7756	-4,7921
F - <i>line</i> [a.u.]	-847,960457	-847,961868	-847,962661	-847,967467	-847,967767	-847,968225
F -angle [a.u.]	-847,957491	-847,960376	-847,961277	-847,965944	-847,966111	-847,966335
ΔF (1-a) [kJ/mol]	-7,7872	-3,9172	-3,6337	-3,9986	-4,3478	-4,9622
N -angle / N -line	0,0432	0,2059	0,2309	0,1993	0,1731	0,1351

Scaling parameters values



		Т	D		TDA				
Method	E0-0	RE	S	R ²	E0-0	RE	S	R ²	
	[nm]	[%]	-	-	[nm]	[%]	-	-	
BP86	474.5	98.93	0.641	0.9996	433.0	15.29	0.742	0.9997	
B3LYP	429.1	53.49	0.768	0.9998	393.0	4.62	0.887	0.9999	
CAM- B3LYP	386.9	11.35	0.929	0.9999	354.6	-5.60	1.082	1.0000	
M06-2X	385.7	10.14	0.930	1.0000	353.4	-5.90	1.082	1.0000	

Calculated spectra of naphthalene

