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What do the azobenzene oligomer helixes have to do with the Golden Ratio?

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ABSTRACT

Azobenzene (di-phenyl-diazene) is a widely-studied prototype for its photoisomerisation capability. Whereas the *trans*-azobenzene is perfectly planar, the *cis* conformer assumes an inherent helicity, caused by the steric hindrance of each of the two benzene rings. In this study we explore by first principle DFT calculations the structural, mechanical, and chiroptical properties (Electronic Circular Dichroism spectra, ECD) of *n*-(phenylazo)-azobenzenes ($n = 1$–10) from a computational point of view. The idea is that these polymers may photo-switch from a “strip”-like conformation (when each monomer is *trans*) to a “spring”-like conformation (when each monomer is *cis*). By studying the mechanical properties of these photo-induced nano-springs, we surprisingly obtain a nexus between the geometrical and elastic parameters and the Golden Ratio.

1. Introduction

Since the most ancient times, mankind has been fascinated and attracted by a special and mysterious number, that expresses the perfect harmony and beauty. This number, the so-called Golden Ratio or Golden Section (in Latin, *Sectio Aurea*) surprisingly turns out in nature, especially in the world of the plants and that of the *Gastropoda*, but also in the human body dimensions [1]. Over the centuries, architects, painters, musicians, and writers have wildly used the Golden Ratio in their works. We may find references of the Golden Ratio also in Bible (Genesis 6:15, Exodus 25:10, and Exodus 27:1–2), and in everyday life objects, like credit cards or mobile phone cards. A sensational discovery has been recently made by Coldea et al., who for the first time has found the Golden Ration also in a nanoscale quantum system, like the magnetic material cobalt niobate [2].

Apparently far from this world, during the last two decades, the research activities have been remarkably addressed to the design and the production of molecular and super-molecular reversible switchable devices [3–9]. Thanks to their reversible *trans*–*cis* photoisomerisation capability and the large geometrical and optical changes after excitation, azobenzene (diphenyldiazene) and its derivatives represent one of the most attractive class of organic compounds for these aims [10–17]. Moreover, whereas the *trans*-azobenzene is perfectly planar, the *cis* conformer may assume two different inherent helicities (*P*- or *M*-kind) because of the steric hindrance of the two benzene rings. Therefore, azobenzene and its derivatives have been investigated [18–36] as possible reversible light-induced chirality switchers. Recently [37] we have computationally predicted the chiroptical activity of the di-(mono)-, di-bis-, di-tris-, and di-tetraphenly-diazene (Ph_n–N = N–Ph_n, $n = 1$–4), for which we observed that, enlarging the system size by adding phenyls, the molecular geometry deviates from the planarity because of the torsions of the external phenyls with respect to the central moiety. This torsion is regular and causes the molecules with $n = 2$, 3, and 4 in both *trans* and *cis* forms to assume a spiral shape. (For *cis* conformers that is true locally for the two external moieties.) Both for *trans* and *cis* conformers the dihedral angles between two neighbour phenyls is about 37°. This behaviour can be straightforwardly explained as the result of two opposing “forces”: on one hand, the systems tries to keep the largest possible conjugation, on the other hand, the sterical interaction between the Hydrogen atoms of two neighbour phenyls must be minimised. In this study, significant differences emerged between *trans* and *cis* conformers concerning the optical activity. Nevertheless both conformers show two optically active electronic states, *trans* conformers are less optically active than the respective *cis* conformers. The intrinsic helicity induced by the *trans*–*cis* photoisomerization plays the main role for the chiroptical activity, whereas the effect of the rotation of the phenyls is secondary for *cis*. (For *trans* it is actually the only element for the chiroptical activity.)

In this study, we continue our investigation on the properties of azobenzene derivatives. More precisely, we have examined from a theoretical and computational point of view the mechanical and the optical properties of the first 10 poly(*para*-phenyl-diazenes) Scheme 1. Poly-azobenzenes and derivatives have a long history

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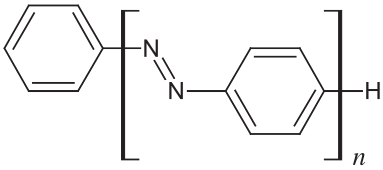

Scheme 1. The azobenzene oligomers investigated in this study, *n*-(phenylazo)-azobenzenes (with $n = 1–10$).

[38]. Principally these compounds have found interesting application in the field of liquid crystals, electrophotographic photoreceptor and inks. In these studies the properties of the all-*trans* conformers were investigated. Many of them were object of patents [39]. Only in recent times [40,41], a series of oligomers composed of repeating azobenzene chromophores have been described to exhibit conformational properties ideally suited to permit the induction of a helical handedness.

We can have helixes of two kinds, i.e. clockwise, from *P*, and anti-clockwise, from *M*. In this study we are interested into investigating the structural, mechanical, and chiroptical properties of *n*-(phenylazo)-azobenzenes from a computational point of view.

2. Computational technical details

The molecular geometries of the first 10 azobenzene oligomers (see Scheme 1), in the possible *trans* and *cis* conformations, were obtained, *in vacuo* phase, after optimisation at Hartree Fock (HF) and Density Functional Theory (DFT) [42–45] levels of theory using the following basis sets: 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d), 6-311+G(d), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ, and cc-pVTZ. For DFT calculations, the Becke three-parameter Lee–Yang–Parr (B3-LYP) exchange–correlation functional [46] was employed. The azobenzene oligomers with $n = 1$, 2, and 3 were also optimised at second-order Møller–Plesset perturbation (MP2) theory [47]. The geometries were then submitted to vibrational analysis in order to investigate whether the convergence points were "genuine" energy minima and calculate the thermochemical quantities. The environment conditions were set $T = 298.15$ K, $p = 1.00$ atm. Since for our systems the correlation energy could have a relevant incidence on the geometries, especially when in *cis* conformation, in order to demonstrate whether the B3-LYP functional provides good results, the azobenzene oligomers with $n = 1$, 2, and 3 were also optimised at DFT level by using more elaborated functionals, discussed in recent literature [48], *viz.* Grimme's functionals including dispersion B97D [49] and B2PLYP-D3 [50,51], and the latest functional from Head-Gordon and coworkers ωB97XD [52]. The cc-pVTZ basis set was employed in these optimisations. The approach which best matches with the X-ray data was therefore selected for the subsequent calculations. The properties of the first five singlet excited electronic states, the wave functions and the electronic spectra were then investigated at Time Dependent DFT (TD-DFT) level of theory. Gaussian 09 computational package [53] was used for all of these calculations.

3. Results and discussion

3.1. On the structure and the energy

In our previous work [54], the role played by the basis extention and the theory levels (HF, DFT, and MP2) was widely presented. In this work, for all the optimised geometries, we confirm the same trends and discrepancies, that in any case are not particularly remarkable. Good results are also those obtained at DFT B3-LYP/6-31+G(d,p) level, especially for bonds distances and angles. According to the experimental characterisations, the bond lengths for the benzene rings are not equal as results from our calculations. For *trans* conformers, we obtain shorter and longer bonds alternating each other. This emerges at HF and DFT level, especially when large basis sets are employed, whereas MP2 does not show such behaviour. In the *cis* conformer, the differences in bond lengths of the same ring are described at all the different levels of theory applied so far.

The case $n = 1$ was discussed in two recent works of ours [37,54]. Here we want to evaluate the effect of the dispersions introduced at DFT level by employing the B97D [49], B2PLYP-D3 [50,51], and ωB97XD [52] functionals with respect to the best description obtained with the B3-LYP functional. In Table 1a we show the main geometrical parameters. We can evaluate the goodness of the functional by calculating the discrepancies with respect to the experimental data. For *trans* azobenzene, the best description of the chromophore is providen with the functionals B3-LYP and B2PLYP-D3, whereas the most accurate prediction of *b*(NC) is obtained when ωB97XD is employed. For the two bond angles α(CCN) and α(CNN), B2PLYP-D3 gives the values closest to the experiment. For the dihedral angles all the considered functionals provide the correct prediction. Overall, the best description is obtained with B2PLYP-D3 followed by B3-LYP and ωB97XD, whereas the worst geometry is that obtained with B97D. Conversely, for *cis* azobenzene, the use of both B97D and B2PLYP-D3 guarantees the most accurate geometries with respect to the experiment; the bond lengths obtained with the functional B97D are better than those obtained with the B2PLYP-D3, which instead gives better angles. Also B3-LYP enables to describe well the geometry of the *cis* azobenzene, whereas ωB97XD does not offer a sufficiently good picture. Thence, from what emerged above about the azobenzene geometry, we may consider the following rank of functionals for the appropriate geometrical description for azobenzene: B2PLYP-D3 > B3-LYP > ωB97XD ~ B97D. When the functionals B2PLYP-D3 and B3-LYP are employed, both *trans* and *cis* conformers are well described in comparison with experimental data [55–57] and other computational approaches [58–63]. Whereas *trans* conformer is perfectly flat, for *cis* the CNNC dihedral angle is not zero. Another important aspect which must be accurately reproduced is the energy difference between the two conformers. The *trans* isomer is more stable with respect to the *cis* isomer by approximately 50 kJ/mol, and the barrier to photoisomerisation is approximately 200 kJ/mol [64]. From a computational point of view, the chosen functionals provide different energy gaps, *viz.* 63.7 (B3-LYP), 44.4

Table 1a

Selected geometrical parameters of azobenzene ($n = 1$). Bond lengths (*b*) in Å, bond (α) and dihedral (δ) angles in degrees.

	trans					*cis*				
	comp.*	comp.#	comp.†	comp.§	exp. [54]	comp.*	comp.#	comp.†	comp.§	exp. [56]
b(NN)	1.248	1.261	1.246	1.237	1.247	1.239	1.248	1.247	1.232	1.253
b(NC)	1.417	1.418	1.418	1.422	1.428	1.433	1.435	1.434	1.433	1.449
α(CCN)	115.5	115.1	115.3	115.4	115.3	117.8	116.8	116.8	116.7	117.3
α(CNN)	115.5	115.3	114.9	115.1	114.1	124.2	123.8	122.7	122.9	121.9
δ(CCNN)	0.0	0.0	0.0	0.0	0.0	52.2	40.2	44.2	49.1	53.3
δ(CNNC)	180.0	180.0	180.0	180.0	180.0	9.3	10.8	8.2	5.7	8.0

Functionals: B3-LYP (*), B97D (#), B2PLYP-D3 (†), ωB87XD (§).