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Density functional theory calculations on azobenzene derivatives: a comparative study of functional group effect

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Abstract Density functional theory (DFT) calculations have been used to investigate the structural properties, dipole moments, polarizabilities, Gibbs energies, hardness, electronegativity, HOMO/LUMO energies, and chemical potentials of *trans* and *cis* configurations of eight *para*-substituted azobenzene derivatives. All properties have been obtained using the B3LYP functional and 6-31++G(d,p) basis set. The planar structures have been obtained for all optimized *trans* configurations. The energy difference between *trans* and *cis* configurations for considered derivatives was found to be between 64.2–73.1 kJ/mole. It has been obtained that the *p*-aminodiazo-benzene (ADAB) has the difference in the dipole moments between *trans* and *cis* forms higher than for *trans* and *cis* azobenzene.

Keywords Azobenzene derivatives · *cis-trans* · Density functional theory · Dipole moment · Polarizability · Homo-Lumo

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Introduction

Since the year 1937, when Harley published his work [1] about *cis* isomerization of azobenzene, this photochemical phenomena became widely studied. The idea behind it is photoisomerization of azobenzene under irradiation when non-polar *trans* azobenzene can be photoisomerized into the polar *cis*-azobenzene. Due to relatively simple molecular structure and unique characteristics, azobenzene and its derivatives were investigated in different studies as photoswitchable substances [2–4]. Moreover, azobenzene derivatives have vivid colors, which caused them to be used as dyes. Due to the formation of polar *cis*-isomer, the contact angle can be significantly decreased. This feature can be used to control wettability of surface by photoisomerization [5]. Furthermore, changes in dipole moment cause changes in the surface potential, which can be used to create a surface with the controlled motion and net mass transport [2]. Thus, it would be highly profitable to have an ability to design a specific molecule for certain applications.

Therefore, the correct characterization of both *trans* and *cis* forms of azobenzene derivatives is required. From the experimental point of view, synthesis and determination of the properties of interest can be expensive and difficult. In this case, molecular modeling could help to find structures with desirable properties in a relatively short time. In the present study, the effect of structural diversity on electronic properties will be analyzed. A set of molecules has been chosen:

1. Azobenzene as a parent compound;
2. Azobenzene's derivatives of the type of aminoazobenzene, i.e., azobenzene substituted with an electron-donating groups NH_2, SO_2-NH_2, N-$(CH_3)_2$;

Table 1 Functional groups (R_1 and R_2) of studied molecules and theirs IUPAC names (see the figure below)

	R_1	R_2	IUPAC name
AB	H	H	(E)-diphenyldiazene
HOAB	OH	H	4-[(E)-phenylazo]phenol
CH_2CH_2HOAB	CH_2-CH_2-OH	H	2-[4-[(E)-phenylazo]phenyl]ethanol
DO$_3$	NO_2	NH_2	N-[4-[(E)-[4-(hydroxyamino)phenyl]azo]-phenyl]hydroxylamine
AAB	H	NH_2	4-[(E)-cyclohexa-1,5-dien-1-ylazo]aniline
SO_2NH_2AB	SO_2-NH_2	NH_2	4-(E)-[4-(Dimethylamino)phenyl]diazenylbenzenesulfonamide
ADAB	N-$(CH_3)_2$	NH_2	4-[(E)-(4-dimethylaminophenyl)azo]aniline

3. Azobenzene's derivatives substituted with an electron acceptor group OH, NO_2, CH_2-CH_2-OH;
4. Azobenzene's derivatives of the pseudostilbene type, i.e., substituted with an electron acceptor at the *para*-position of a phenyl ring and an electron-donating group at the other *para*-position of another phenyl ring. This type is also known as push-pull azobenzene due to charge transfer within the molecule.

All considered molecules are listed and are presented in the Table 1, the Fig. 1.

The aim of this research is to investigate the effect of substituents of a group of eight azobenzene derivatives in *trans* and *cis* forms on structural and electronic properties by DFT method, which was widely and successfully used in studies concerning structural and electronic properties of azobenzene derivatives [6–8].

Methods

Calculations were carried out using the Gaussian03 [9] program with the DFT method and the B3LYP [10–12] functional. The energies of the structures were calculated with a self-consistent field (SCF) convergence of 10^{-8} a.u. for the density matrix. All structures were optimized using the Berny algorithm [13] with the criteria for convergence being a maximum force less than 45×10^{-5} and an rms force of less than 3×10^{-4}. We used 6-31++G(d,p) basis set, which is the most appropriate in terms of time, accuracy, and cost of computing resources for the

determination of electronic properties [8]. Geometry parameters for each structure were free of constraints and allowed to relax during the optimization process.

The chemical potential μ, absolute hardness η, and electronegativity χ were evaluated by the finite-difference approximation from the ionization potential (I) and electron affinity (A). The last occupied Kohn-Sham orbital energy can be equated with the energy of the highest occupied molecular orbital (HOMO) associated to $-I$. Moreover, the first unoccupied Kohn–Sham orbital energy is often [13, 14] used as the value for the energy of the lowest unoccupied molecular orbital (LUMO) and so can be equated with $-A$ even through it is crude approximation since the DFT is a ground state theory.

For each considered molecule we have examined *trans* and *cis* forms and all possible configurations concerning positions of functional groups in the molecule. The stationary configurations were confirmed by vibrational frequencies analysis: only configurations with real frequencies were used for calculations. In the case of more than one possible configuration, we used Boltzmann statistics to find the probability for each configuration and then to evaluate the average value for desirable property.

Results and discussion

In the present chapter, results of DFT calculations on considered azobenzenes will be analyzed.

Optimized structures

The characteristic geometric parameters of optimized *trans* and *cis* configurations are given in the Table 2. It should be noted that planar structures were obtained for all optimized *trans* configurations.

From Table 2 it was found that upon substitution of the parent *trans*-AB by an electron donor (NH_2 and N-$(CH_3)_2$ groups in AAB, SO_2NH_2AB, MY, ADAB), electron acceptor (HO, CH_2CH_2HO groups in HOAB and CH_2CH_2HOAB), and electron donor-acceptor (NH_2 and
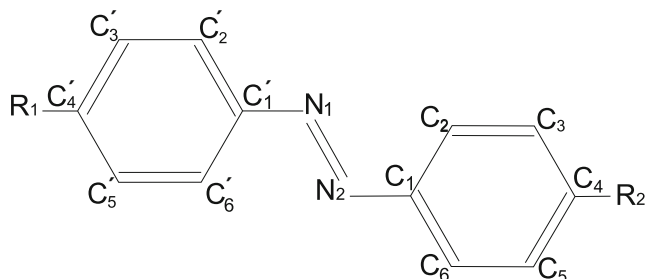

Fig. 1 Structure of *trans* configuration of molecules studied

Table 2 Optimized geometrical parameters (angles in degrees, bond length in Å) for the most stable *trans* and *cis* configurations for each molecule obtained from B3LYP 6-31++G(d,p) calculations

	N_1C_1'	N_1N_2	N_2C_1	C_4C_4'	$N_2N_1C_1'$	$N_1N_2C_1$	$C_1'N_1N_2C_1$	$N_1N_2C_1C_6$	$N_2N_1C_1'C_2'$
Trans									
AB	1.419	1.258	1.420	1.251	115.3	115.3	180	180	180
HOAB	1.419	1.260	1.413	1.260	115.5	115.2	180	180	180
CH$_2$CH$_2$HOAB	1.418	1.258	1.420	1.251	115.3	115.2	180	180	180
DO$_3$	1.415	1.265	1.399	1.265	114.5	116.0	180	180	180
AAB	1.419	1.262	1.408	1.262	115.1	115.7	180	180	180
SO$_2$NH$_2$AB	1.418	1.263	1.403	1.263	114.7	115.9	180	180	179
ADAB	1.408	1.265	1.410	1.265	115.6	115.5	180	179	179
MY	1.419	1.263	1.405	1.263	115.0	115.8	180	180	179
Cis									
AB	1.437	1.249	1.436	1.241	124.1	124.2	9.94	48.5	51.7
HOAB	1.435	1.251	1.432	1.244	124.3	124.6	9.97	40.9	55.0
CH$_2$CH$_2$HOAB	1.437	1.250	1.435	1.242	124.0	124.1	9.78	48.4	52.5
DO$_3$	1.419	1.253	1.423	1.253	125.1	125.5	11.31	61.4	29.7
AAB	1.435	1.253	1.427	1.253	124.3	125.0	10.16	36.0	57.6
SO$_2$NH$_2$AB	1.429	1.253	1.422	1.263	125.0	125.3	10.29	30.8	61.3
ADAB	1.428	1.256	1.431	1.256	124.9	124.6	11.83	45.2	41.7
MY	1.432	1.247	1.423	1.247	124.6	125.3	10.06	34.9	58.6

NO$_2$ groups in DO$_3$), the N_1N_2 bond distance increases in the following order: AB = CH$_2$CH$_2$HOAB < HOAB < AAB < MY = SO$_2$NH$_2$AB < ADAB = DO$_3$ i.e., for the parent azobenzene, electron acceptor, electron-donating and electron donating-acceptor azobenzenes, respectively. Thus, the electronic effect of substitution causes the change of N_1N_2 distance: electron-donating groups elongate the N_1N_2 distance, the electron acceptor groups have no or little effect on this bond and the electron donating-acceptor groups elongate this bond.

As for the *cis* forms, the following order was found: MY < AB < CH$_2$CH$_2$HOAB < HOAB < DO$_3$ = AAB = SO$_2$NH$_2$AB < ADAB. The biggest distance was found for ADAB molecule.

It was obtained that the $C_1'N_1N_2C_1$ torsion angles for *cis* configuration are in the following order: CH$_2$CH$_2$HOAB < AB < HOAB < MY < AAB < SO$_2$NH$_2$AB < DO$_3$ < ADAB. The DO$_3$ and ADAB molecules present the biggest dihedral angles. The first of them is a push-pull molecule and the second one is an electron-donor-type molecule with bulky substitutes on both sides, whereas molecules with electron-acceptor groups show small angles.

The shortest C$_5$C$_6$ distance in *trans*-form was obtained for DO$_3$ being the push-pull molecule, the distance equal to 9.09 Å was obtained for AB, HOAB, and SO$_2$NH$_2$AB molecules. The C$_5$C$_6$ distance equal to 9.12 Å was found for CH$_2$CH$_2$HOAB and AAB, and the biggest distance was found for MY and ADAB. As for the *cis*-forms, the distance increases in the same order as the dihedral angle.

Electronic properties

Energies *E* and equilibrium constants *K* of both the most stable *trans* and *cis* configurations are given in Table 3. The equilibrium constants were obtained using formula:

$$K = exp\left(-\triangle G/RT\right),$$

where the $\triangle E$ is difference in the Gibbs energies of *cis* and *trans* configurations, *T* is temperature, *R* is gas constant.

As expected, *trans* configurations for each molecule were found to be more stable than *cis*. From our calculations, the difference between *trans* and *cis* configuration energies is 64.2–73.1 kJ/mole, where the smallest difference was found for AB, and the biggest one for ADAB.

It is not so important to consider all configurations in case of energy because we have not obtained a big discrepancy between the average value and energy of the most stable configuration.

Components of polarizability matrix can be determined spectroscopically, but this data is poor because of a hard experimental procedure, especially for molecules with low or no symmetry. This is why molecular modeling calculations can help in this purpose. In Table 4 dipole moments, mean and anisotropic polarizabilities are presented for eight considered azobenzene derivatives.

For most of the molecules, dipole moment of *cis*-form was found to be greater than that of *trans*-form. However,

Table 3 Calculated energies, energy differences E (kJ/mole) and equilibrium constants K of the most stable *trans* and *cis* configurations obtained from B3LYP 6-31++G(d,p) calculations

	E_{trans}	E_{cis}	$\triangle E(trans\text{-}cis)$	K
AB	−1504390.5	−1504327.4	−64.2	1.79×10^{11}
HOAB	−1701178.2	−1701108.6	−69.5	1.57×10^{12}
CH_2CH_2HOAB	−1907501.0	−1907434.9	−66.2	4.00×10^{11}
DO_3	−2186537.6	−2186470.9	−66.7	5.05×10^{11}
AAB	−1648994.5	−1648924.4	−70.1	1.98×10^{12}
SO_2NH_2AB	−3234761.7	−3234692.1	−69.8	1.71×10^{12}
ADAB	−2000618.1	−2001007.7	−73.1	6.71×10^{12}
MY	−1855705.3	−1855636.1	−69.3	1.40×10^{12}

for CH_2CH_2HOAB and DO_3 the situation is opposite. This could be due to more unequal distribution in the *trans*-isomer. In the [7] negative *cis-trans* dipole moment was found for molecules with the NO_2 group at the *para*-position.

The biggest dipole moment in the *trans*-form was found for push-pull DO_3 molecule. Comparatively big values were obtained also for CH_2CH_2HOAB and SO_2-NH_2AB molecules with bulky functional groups at the *para*-positions. In the *cis*-form: SO_2NH_2AB, DO_3 and ADAB have big dipole moments. Since the ADAB molecule has small dipole moment in *trans*-form and big in the *cis*-form, the difference in dipole moments is the biggest among considered molecules. This difference is equal to 4.7 and is greater than that for AB by 1.5 Debye.

The dipole moment of molecule

$$p = p_0 + \alpha E + \frac{1}{2}\beta EE + ...,$$

where p_0 is a dipole moment without an electric field, α is a polarizability second-order tensor, β is the first in an infinite series of hyperpolarizabilities. The polarizability tensor was firstly diagonalized and mean and anisotropic polarizabilities have been obtained using following formulas:

$$a_{mean} = \frac{1}{3}\left(a_{xx} + a_{yy} + a_{zz}\right),$$

$$a_{anis} = \sqrt{\frac{(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{xx} - a_{zz})^2}{2}},$$

where a_{xx}, a_{yy}, a_{zz} are diagonal elements of polarizability matrix. The biggest mean and anisotropic polarizabilities have been obtained for the ADAB molecule.

Molecular properties

The frontier orbitals of the chemical compounds are very important parameters in identifying their reactivity [15, 16]. A molecule with a high value of HOMO can give electrons to appropriate acceptor molecules with low energy and empty molecular orbitals. Calculated HOMO and LUMO energies for eight azobenzene derivatives are presented in the Table 5. Both *trans* and *cis* configurations of ADAB molecule have the highest HOMO value.

Table 4 Calculated dipole moments μ (Debye), mean, and anisotropic polarizabilities α (au) of the most stable *trans* and *cis* configurations obtained from B3LYP 6-31++G(d,p) calculations

	μ_{trans}	μ_{cis}	$\Delta\mu$	Mean α_{trans}	Anis α_{trans}	Mean α_{cis}	Anis α_{cis}	$\Delta\alpha$ mean	$\Delta\alpha$ anis
AB	0.0	3.2	3.2	185	201	160	81	24	120
HOAB	1.4	3.3	1.8	195	230	169	102	26	129
CH_2CH_2HOAB	5.2	3.9	−1.3	221	245	192	98	29	147
DO_3	9.9	7.5	−2.4	251	352	211	145	41	207
AAB	3.1	5.2	2.0	210	262	180	114	30	148
SO_2NH_2AB	8.0	8.2	0.2	259	328	220	135	39	193
ADAB	1.4	6.1	4.7	272	367	229	158	43	208
MY	4.2	6.0	1.8	250	312	214	142	36	170

Table 5 Hardnesses (η), electronegativities (χ), chemical potentials (μ), and HOMO/LUMO energies in eV of the most stable *trans* and *cis* configurations obtained from B3LYP 6-31++G(d,p) calculations

	η_{trans}	η_{cis}	χ_{trans}	χ_{cis}	μ_{trans}	μ_{cis}	HOMO$_{trans}$	HOMO$_{cis}$	LUMO$_{trans}$	LUMO$_{cis}$
AB	1.96	1.86	4.50	4.17	−4.50	−4.17	−6.46	−6.03	−2.54	−2.31
HOAB	1.86	1.83	4.26	4.02	−4.26	−4.02	−6.11	−5.84	−2.40	−2.19
CH$_2$CH$_2$HOAB	1.94	1.86	4.45	4.15	−4.45	−4.15	−6.38	−6.00	−2.51	−2.29
DO$_3$	1.51	1.57	4.63	4.50	−4.63	−4.50	−6.13	−6.07	−3.12	−2.93
AAB	1.75	1.77	3.94	3.79	−3.94	−3.79	−5.68	−5.56	−2.19	−2.01
SO$_2$NH$_2$AB	1.67	1.76	4.30	4.16	−4.30	−4.16	−5.97	−5.92	−2.63	−2.4
ADAB	1.61	1.63	3.41	3.35	−3.41	−3.35	−5.02	−4.98	−1.80	−1.72
MY	1.65	1.74	3.73	3.64	−3.73	−3.64	−5.38	−5.38	−2.08	−1.90

In order to investigate the correlation between chemical quantities and molecular properties, calculated hardness (η), electronegativity (χ), and chemical potential (μ) are presented in Table 5 for both configurations of considered molecules. These parameters were obtained using HOMO and LUMO energies according to [17].

The hardness is $\eta = (E_{LUMO} - E_{HOMO})/2$ [18]. This parameter shows the reactivity of the system: a system with a larger η should be less reactive than a system having smaller η [18]. The electronegativity defined by Mulliken [19] as $\chi = -(E_{HOMO} + E_{LUMO})/2$ as hardness is used to predict chemical behavior. The chemical potential is opposite to electronegativity [20] $\mu = (E_{HOMO} + E_{LUMO})/2$.

From our calculations it follows that the hardness of presented systems increases in the following order: DO$_3$ < ADAB < MY < SO$_2$NH$_2$AB < AAB < HOAB < CH$_2$CH$_2$HOAB < AB. So, it means that AB is the least reactive, DO$_3$ and ADAB are the most reactive molecules among considered. As was expected, *trans* configurations have smaller chemical potentials than *cis*, and this means that molecules tend to move from *cis* to *trans* configurations.

Conclusions

In the present study, results of DFT calculations on eight azobenzene derivatives have been presented. Concerning the structural properties of considered azobenzene derivatives, the planar *trans* structure has been obtained for all considered molecules. On both configurations, an asymmetry in structural parameters was obtained for all molecules. The *trans* configurations were found to be more stable than *cis*. The relative difference in the dipole moment between the *trans* and *cis* configurations was found to be lower than for azobenzene for all considered molecules except for ADAB, for which the difference was obtained equal to 4.7

Debye. For this molecule, the largest mean and anisotropic polarizabilities have been obtained. Concerning molecular properties, the highest reactivities were found for DO$_3$ and ADAB molecules.

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