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EXCITED STATE DIPOLE MOMENT OF 4-(P-TOLYL-DIAZENYL)-PHENYL ACRYLATE (AZD) ESTIMATED BY VARIATIONAL METHOD

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Abstract: The azobenzene derivative 4-(p-tolyl-diazenyl)-phenyl acrylate (AZD) is studied here from the solvatochromic point of view in order to characterize the interactions from its binary and ternary solutions and to estimate the excited state dipole moment. The molecular descriptors of the AZD molecule were computed using quantum chemical software. The hypothesis of McRae was applied to determine the value of the excited state dipole moment based on both correlation coefficients deduced from the solvatochromic study and computed molecular descriptors of the solute molecule. The new variational method for computing the excited state dipole moment based on McRae hypothesis is applicable to the molecules which show only absorption bands but are not fluorescent. The higher value of the excited state dipole moment of AZD (3.73D) comparative to that in its ground state (1.98D) agrees with the bathochromic shift of its $\pi - \pi^*$ absorption band both in binary and ternary solutions.

Keywords: Azobenzene derivative; Solvatochromic study; Excited state dipole moment.

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Introduction

Azobenzene compounds are organic-nitrogen derivatives with a characteristic double bridge between two benzene cycles, assuring a large π-conjugation along the molecular skeleton. The molecular structure of the type R-C_6H_4-N=N-C_6H_4-R', with -R and -R' different atomic groups in positions 4 and 4', exhibits intense electronic absorption bands of the type $\pi - \pi^*$ in UV range and also a low intense band $n - \pi^*$ in the visible range,[1,2] due to the large conjugation between the aromatic rings through the azo-bond. The 4,4'-disubstituted azoderivatives are colored substances with a large area of important applications[3-5] such as in the dye stuff industry, cosmetics or alimentary industry, while they have some side effects.[5] Azoderivatives are used as acid-base, redox and acid metallochromic indicators, photo-aligning substrates for liquid crystals, photo-reactive media, optical actuators or optical storage media.

AZD is one 4,4'-azoderivative with such applications, studied here in order to obtain information about the excited state dipole moment because its use in situ asks for understanding the solvent effects on the absorption process and also the molecular changes in interaction with the sunlight.

AZD was synthetized by the conventional diazotization-coupling reaction,[6] starting from 4-methylaniline and 4-nitroaniline. The preparation procedure supposes diazotization of 4-methylaniline, coupling reaction of phenol with diazonium salt and esterification reaction with hydrochloric acid.

In order to characterize the intermolecular interactions in AZD solutions, a solvatochromic study was realized with 36 solvents of various chemical and physical properties. The results corroborated with quantum mechanical computations are used for estimating the excited state dipole moment of AZD.

Theoretical notions

As a dipolar molecule, AZD can participate in solutions to universal interactions (orientation, polarization, dispersion) as well as to specific interactions of the hydrogen bond type. In order to estimate the strength of these interactions, spectral shifts of the wavenumber in the maximum of $\pi - \pi^*$ absorption band were expressed by multilinear dependence on the solvent parameters[7-10], usually described by:

$$\nu_{calc} = \nu_0 + C_1 f(\varepsilon) + C_2 f(n) + C_3 \beta + C_4 \alpha \,. \qquad (1)$$

The following notations were made in Eq. (1): ν is the wavenumber in the maximum of the absorption band, calculated (indexed by *calc*) and approximating the value for isolated molecule (indexed by 0); $f(\varepsilon) = \dfrac{\varepsilon - 1}{\varepsilon + 2}$ and $f(n) = \dfrac{n^2 - 1}{n^2 + 2}$ are functions theoretically established[11-13] (depending on the solvent permittivity, ε, and refractive index, n) to describe the influence of the universal interactions on the wavenumber in maximum of absorption band; the empirically introduced parameters[14] β and α give the ability of the solvent for participating in hydrogen bonds by accepting, respectively by donating protons, and C_i, i = 1, 2, 3, 4 are regression coefficients, giving by their value the strength of interaction and by their sign the direction of the spectral shift in the scale of the wavenumbers.

The importance of the first two regression coefficients from relation (1) is given by their theoretical dependences (2) and (3) on the microscopic parameters of the solute[8,9] which permits us to estimate the solute excited state dipole moment:

$$C_1 = \frac{2\mu_g\left(\mu_g - \mu_e \cos\varphi\right)}{r^3} + 3kT\frac{\alpha_g - \alpha_e}{r^3}, \tag{2}$$

$$C_2 = \frac{\mu_g^2 - \mu_e^2}{r^3} - C_1 + \frac{3}{2}\frac{I_u I_v}{I_u + I_v}\frac{\alpha_g - \alpha_e}{r^3}. \tag{3}$$

Equations (2) and (3) contain the solute dipole moments in the electronic state participating to the transition responsible for the $\pi - \pi^*$ band appearance, the angle φ between them and the electric polarizabilities of molecule in the ground and excited electronic states participating to the same transition. The solute's radius, r, was calculated using the volume and area of the solute molecule computed by Spartan software, and I is the ionization potential of solvent (indexed by v) and of solute (indexed by u).

There are a great number of articles in which the solute dipole moments are estimated when the substance is active both in absorption and fluorescence spectra.[15-19] In these references, the ground state parameters of solute were estimated by using quantum mechanical calculations. The values of the coefficients C_1 and C_2, determined by solvatochromic method both in absorption and fluorescence, were used to compute the excited state descriptors of the solutes.

For the molecules showing only absorption spectrum, the regression coefficients C_1 and C_2 contain two unknown parameters in the excited state, dipole moment and polarizability, as well as the angle φ between the dipole moments in the electronic states of the transition. One approaches the variational method[8,9,19] in which the relations (2) and (3) are used to obtain an equation in $\mu_e \cos\varphi$ and the angle φ is varied until the excited state polarizability of solute becomes equal to the electric polarizability from the ground state.[11] This condition corresponds to McRae hypothesis that the electric polarizability of molecule does not change its value in the light absorption process.

To obtain the optimized structure of the molecule, the density functional (DFT) EDF2 method[20] was approached, together with the basis set 6-311G**,[21] by using Spartan'14 software.[22,23]

Experimental

The azobenzene derivative 4-(p-tolyl-diazenyl)-phenyl acrylate (AZD) (with structural formula shown in Figure 1) is the studied compound from solvatochromic point of view in order to analyze the interactions solute-solvent and to estimate the excited state dipole moment based on the $\pi - \pi^*$ absorption band.

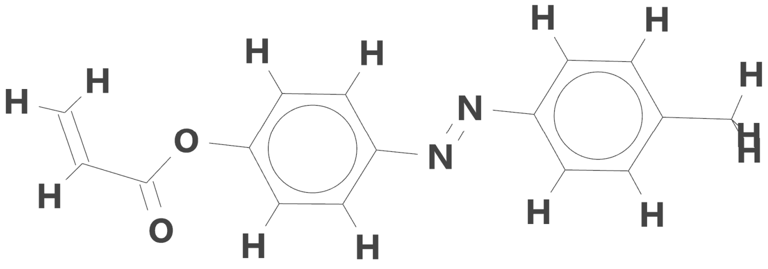

Figure 1. Schematic structure of AZD molecule.

The electronic absorption spectra of AZD were recorded in 36 solvents with different physical and chemical properties. Multilinear correlation between the wavenumber in the maximum of the absorption band and the solvent parameters electric permittivity, ε, refractive index, n, (both of them describing the band shift due to the universal interactions[11-13]) and Kamlet-Abboud-Taft[14] parameters α and β (taking into consideration the specific interactions by hydrogen bonds) were established.

The substances used for AZD preparation and the spectral grade solvents were purchased from Fluke and Aldrich Chemical Co. The solvent parameters listed in Table 1 were taken from previous articles.[8,9]

The solute substance was prepared as it was described[6] by diazotization 4-methyl aniline, coupling reaction of phenol with diazonium salt and esterification reaction with hydrochloric acid.

The electronic absorption spectra were recorded with a spectrophotometer Specord UV Vis Carl Zeiss Jena with data acquisition system.

The statistical analysis was achieved by multilinear regression technique.

The molecular descriptors of the studied molecule were computed using the program Spartan'14.

Results and Discussion

According to the results obtained by Spartan'14, the optimized structure of AZD is illustrated in Figure 2, where the charges near the atoms are listed and the electric dipole moment in the ground state is drawn.

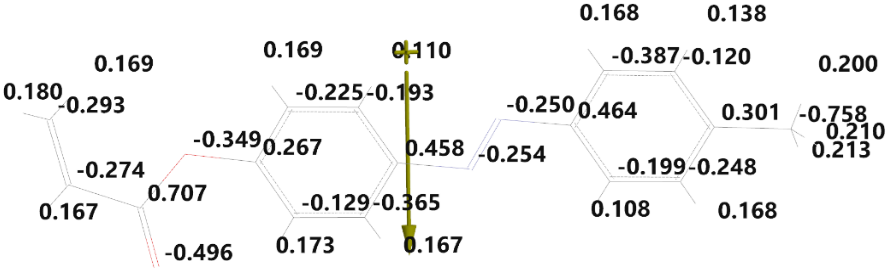

Figure 2. Optimized structure of AZD. The numbers represent the electrostatic charges near the atoms of the molecule, expressed in elementary charge *e*. The arrow indicates the direction of the molecule’s dipole moment.

The charge distribution in ground and excited molecular orbitals is given in Figure 3, in which the arrow suggests the orientation of the molecular dipole moment, as it resulted from computation.

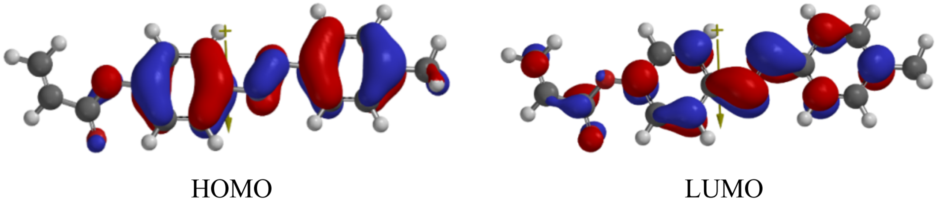

Figure 3. Ground state molecular orbitals (MOs) involved in the formation of the intense $\pi - \pi^*$ transition of AZD. These orbitals correspond to the ground state of HOMO and LUMO.

The studied absorption band of AZD is due to a $\pi - \pi^*$ transition. The solvatochromic study was realized on 36 solutions (18 protic and 18 a-protic solvents). The solvent parameters and the wavenumber in the maximum of the visible absorption band of the azoderivative are listed in Table 1.

Table 1. Solvent parameters and the wavenumber in the maximum of visible absorption band of AZD.

No.	Solvent	$f(\varepsilon)$	$f(n)$	β	α	ν (cm^{-1})
1	n-Heptane	0.227	0.240	0	0	30410
2	n-Hexane	0.229	0.229	0	0	30490
3	Cyclohexane	0.254	0.257	0	0	30300
4	1,4-Dioxane	0.286	0.254	0.37	0	29990
5	CCl_4	0.292	0.274	0	0	30170
6	p-Xylene	0.299	0.291	0.12	0	30390
7	Benzene	0.299	0.295	0.1	0	30350
8	Toluene	0.302	0.297	0.11	0	29810
9	Diethyl ether	0.522	0.261	0.47	0	30350
10	Anisole	0.524	0.302	0.32	0	29850
11	Chloroform	0.552	0.267	0	0.44	29900

12	Butyl acetate	0.577	0.240	0.45	0	29980
13	Iso-Amyl acetate	0.589	0.221	0.43	0	30010
14	Chlorobenzene	0.605	0.307	0.07	0	29950
15	Ethyl acetate	0.625	0.228	0.45	0	30120
16	Methyl acetate	0.655	0.241	0.42	0	29920
17	Dichloromethane	0.727	0.256	0	0.30	30080
18	1,2-Dicloroethane	0.729	0.266	0	0	29900
19	1-Octanol	0.745	0.258	0.81	0.77	30040
20	1-Pentanol	0.825	0.230	0.92	0.70	30080
21	1-Butanol	0.833	0.242	0.88	0.79	30080
22	Iso-Butanol	0.833	0.242	0.88	0.79	30080
23	Acetophenone	0.833	0.312	0.49	0.04	29810
24	Butanone	0.854	0.231	0.48	0.06	29850
25	2-Propanol	0.865	0.230	0.95	0.76	29810
26	1-Propanol	0.868	0.235	0.85	0.78	30120
27	Acetone	0.868	0.222	0.48	0.08	29720
28	Ethanol	0.890	0.221	0.77	0.83	29940
29	Methanol	0.914	0.203	0.62	0.93	30120
30	Acetonitrile	0.924	0.212	0.50	0.90	30350
31	DMF	0.924	0.258	0.69	0	29730
32	Dimethylacetamide	0.925	0.263	0.76	0	29720
33	Ethylene glycol	0.931	0.259	0.52	0.90	29630
34	DMSO	0.939	0.282	0.76	0.00	29590
35	Water	0.964	0.206	0.51	1.21	30210
36	Formamide	0.973	0.271	0.48	0.51	29630

The LSER[14,24] (Linear Solvation Energy Relationships) achieved with the data from Table 1 gives the dependence of the type (1) with the regression coefficients from Table 2.

In order to obtain Figure 4, the solvents 4, 8, 9, 11, 23, 25, 30, 33 and 36 from Table 1 were eliminated in the statistical analysis as being outliers. The characteristics of the line from Figure 4 are the following: slope = 0.886 ± 0.064; cut at origin = 3420.095 ± 1908.537 and R = 0.88. The regression coefficients of the Eq. 1 obtained based on the data of Table 1 are written in Table 2.

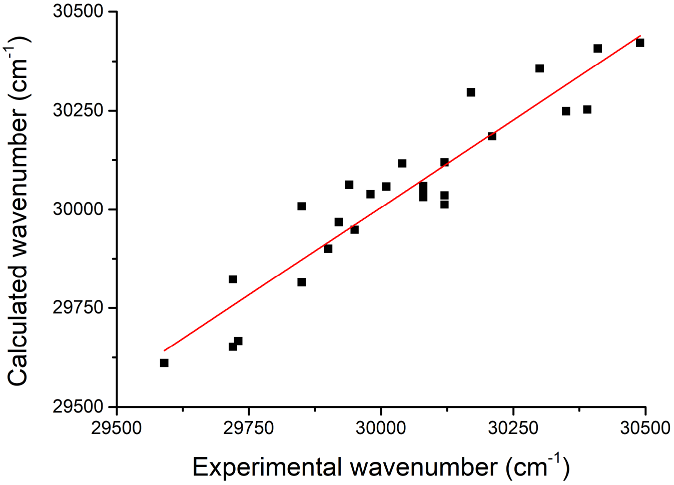

Figure 4. Computed values vs. experimental values of wavenumber in the maximum of $\pi - \pi^*$ band of AZD.

Table 2. Regression coefficients (expressed in cm^{-1}) of LSER obtained based on Eq. (1) for AZD.

$\nu_0 \pm \Delta\nu_0$	$C_1 \pm \Delta C_1$	$C_2 \pm \Delta C_2$	$C_3 \pm \Delta C_3$	$C_4 \pm \Delta C_4$	R	SD	N
30977 ± 189	-933 ± 106	-1491 ± 679	-92 ± 83	382 ± 56	0.87	102	27

As results from Table 2, the universal interactions are predominant in AZD solutions achieved with the solvents listed in Table 1.

The values of the regression coefficients C_1 and C_2 from Table 2 were used to estimate the excited dipole moment of AZD. Molecular descriptors of AZD computed by Spartan'14 for vacuum and used in estimating the excited state dipole moment are: μ_g = 1.98 D, α_g = 63.45 Å^3, A = 308.28 Å^2, V = 282.52 Å^3, E_{HOMO} = - 5.81 eV, r = 2.74932 Å, r^3 = 20.7814 Å^3.

The regression coefficients used in the variational model are C_1 = -933 cm^{-1} and C_2 = -1491 cm^{-1}. The ionization potential of cyclohexane, used as solvent ionization potential, is I_v = 9.8 eV.

With this data one obtains, from Eqs. (2) and (3), the following equations:

$$\alpha_e = 65.0383 - 0.1141\mu_e^2 , \tag{4}$$

$$0.0138\mu_e^2 - 3.96\mu_e \cos\varphi + 11.4980 = 0 . \tag{5}$$

The discriminator of Eq. (5) must be higher than zero. It results: $\varphi \le 78.54°$. The solutions of Eq. (5) are:

$$\mu_{e1,2} = \frac{3.96\cos\varphi \pm \sqrt{(3.96\cos\varphi)^2 - 0.6347}}{0.0276} . \tag{6}$$

In order to obtain the solution of Eq. (5), one uses the supposition of McRae[11] that the electrical polarizability of the solute does not change its value in the absorption process. This hypothesis is necessary when estimates the excited dipole moment in the case of solute molecules which do not show fluorescence spectra. In this purpose, one varies the angle φ between zero and the limit value 78.54º. One considers that the transition $\pi - \pi^*$ takes place when the computed (with Eq. (4)) value for the excited state polarizability equalizes that of ground state polarizability: $\alpha_e = \alpha_g$. The results obtained when the angle φ is varied are written in Table 3.

Table 3 contains the values of the excited state dipole moment of solute for transition $\pi - \pi^*$ computed using Eq. 5 for different angles between the dipole moments. The electronic transition takes place when the computed excited state of polarizability equalizes that in the ground state.

Table 3. Computed excited dipole moment for various angles φ.

No.	φ (°)	μ_e (D)	α_e (Å^3)
1	0	2.93	64.06
2	10	2.98	64.03
3	20	3.13	63.92
4	30	3.40	63.72
5	35	3.60	63.56
6	37	3.69	63.48
7	37.5	3.72	63.46
8	**37.6**	**3.73**	**63.45**
9	40	3.86	63.34
10	50	4.63	62.59
11	60	6.06	60.84
12	70	9.39	54.98

The McRae hypothesis is satisfied for: $\varphi = 37.6^\circ$. The corresponding values are for the excited state dipole moment 3.73 D and for $\alpha_e = \alpha_g = 63.45$ Å^3. It results an increase in the dipole moment of AZD in the light absorption process responsible for $\pi - \pi^*$ transition.

The triangle of the dipole moments can be now solved. One obtains Figure 5.

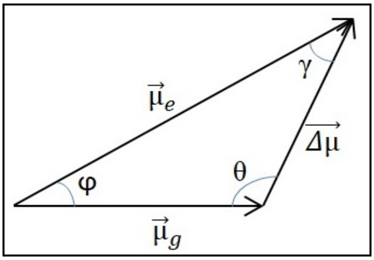

Figure 5. Triangle of the dipole moments for the $\pi - \pi^*$ absorption band of AZD.

Based on sinus theorem, the angles of dipole moments triangle and the variation of the dipole moments in the $\pi - \pi^*$ transition were estimated as being: $\theta = 113.20^\circ$, $\gamma = 29.20^\circ$, $\Delta\mu = 2.48$ D.

Universal interactions act in all binary solutions of AZD due to its dipolar character.

The compound AZD was also studied in some binary mixtures of solvents such as: Water (1) + Methanol (2); Water (1) + Ethanol (2); DCE (1) + Acetone (2); DMF (1) + Ethylene glycol (2).

The spectral data were analyzed based on statistical cell model of the solutions with three components[25,26] and the relation of the type:

$$\ln\frac{p_1}{1-p_1} = \ln\frac{x_1}{1-x_1} + \frac{w_2 - w_1}{kT} \tag{7}$$

has been verified in order to compute the difference $w_2 - w_1$ between the energies of interaction in molecular pairs AZD-solvent (1) and AZD-solvent (2), respectively. In relation (7), x_1 is the molecular fraction of active solvent (1) in ternary solution and p_1 is the average statistic weight of the same solvent in the first solvation shell of AZD. The dependences are illustrated in Figure 6.

The characteristics of the lines from Figure 6 are given in Table 4. The data from Table 4 demonstrates that the statistical cell model of the solutions with three components is applicable, and the difference $w_2 - w_1$ is estimable using the cut at origin of the computed line for the ternary solutions. The values of this difference are written in the last column of Table 4.

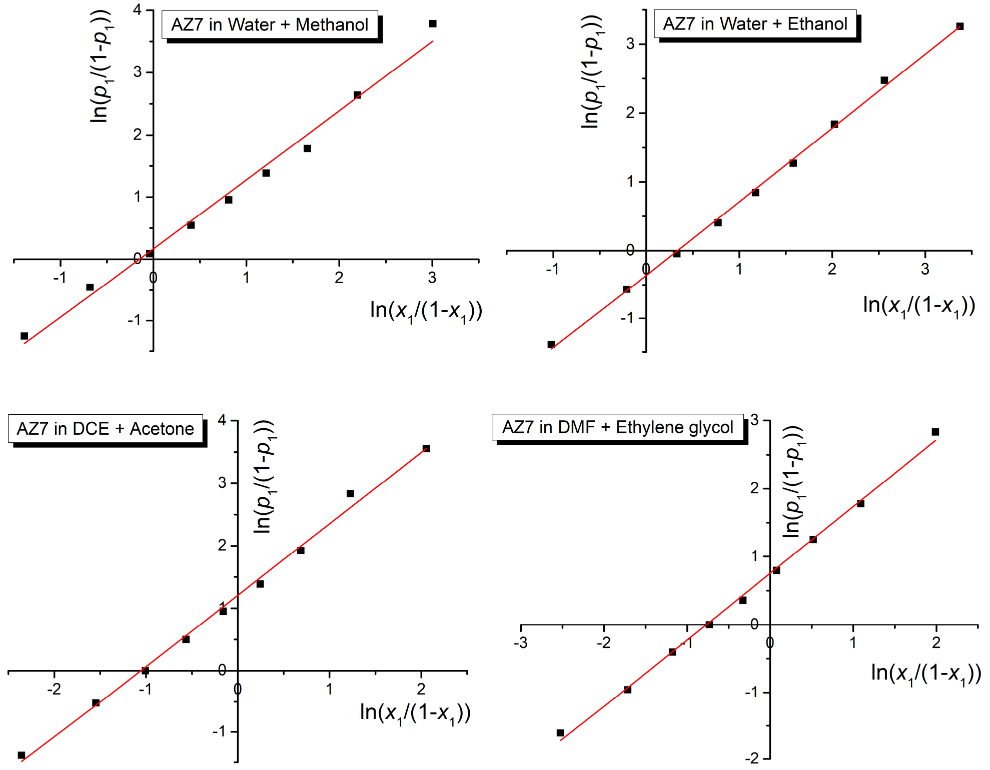

Figure 6. Dependence (7) for ternary solutions of AZD containing mixtures of protic and a-protic solvents.

Table 4. Regression coefficients in equation $\ln\frac{p_1}{1-p_1} = m\ln\frac{x_1}{1-x_1} + n$ for AZD and difference between the interaction energies in considered molecular pairs.

Solvent	$m \pm \Delta m$	$n \pm \Delta n$	R	$w_2 - w_1$ (10^{-21}J)
Water (1) + Methanol (2)	1.110 ± 0.043	0.167 ± 0.066	0.988	0.675
Water (1) + Ethanol (2)	1.072 ± 0.015	-0.361 ± 0.027	0.998	- 1.460
DCE (2) + Acetone (1)	1.143 ± 0.029	1.207 ± 0.038	0.994	4.882
DMF (2) + Ethylene glycol (1)	0.982 ± 0.189	0.756 ± 0.026	0.997	3.058

From Table 4 it results that the specific interactions by hydrogen bond in pair water-AZD are stronger than in methanol-AZD, while in binary solvent water + ethanol the hydrogen bonds are stronger in the case of molecular pair ethanol-AZD. In the first two pairs of molecules, the difference $w_2 - w_1$ is smaller because both solvents are protic and participate to hydrogen bonds, while in the last two ternary solutions these differences are higher, due to the great difference between the strengths of specific interactions, acting in them.

Conclusions

In AZD solutions both universal and specific interactions act, shifting the electronic $\pi - \pi^*$ absorption band towards small wavenumbers. The direction of the spectral shift is in accordance with the increase of the electric dipole moment in the absorption light process.

The variational method for estimating the excited state dipole moment was successfully applied to AZD based on solvatochromic study and McRae hypothesis. The computed value 3.73 D for the excited state dipole moment of the electronic transition $\pi - \pi^*$ is higher than that for the ground electronic state of AZD.

The statistical cell model applied to the ternary solutions of AZD certifies the small values of hydrogen bonds energy between the AZD and the hydroxyl solvents.

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