Conjugated Schiff's Bases. Part 8.[1] Structures and Spectral Properties of *p*-*NN*-Dimethylaminoanils of Some Vicinal Diketo-compounds. Positive Solvatochromic Effect

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Solvent effects on the long wavelength u.v. absorption of some conjugated Schiff's bases containing strong electron-releasing substituents in the anil fragment have been investigated. As found from theoretical calculations the absorption in question is due to the $n \longrightarrow \pi^*$ transitions of the unshared electrons of the azomethine nitrogen atom. This absorption exhibits a bathochromic shift when the polarity of the solvent increases. Such abnormal behaviour can be explained by assuming a superdonating character for the azomethine nitrogen atom. The solute forms a molecular arrangement with the solvent which is stabilized in high degree by charge transfer. This seems to be the cause of the bathochromic shift of the $n \longrightarrow \pi^*$ absorption. The charge transfer model considered for the interactions between the solute and aromatic solvents corresponds well to the experimental data. On the other hand the experimental data found for non-aromatic solvents correlate with the Dimroth parameter E_T. Considering the complementary influences of Lewis acidity and basicity of the solvent the acidic interactions were estimated by the parameter Z^+ defined similarly to the Kossower parameter Z. The estimates of the percentage contribution from solvent acidity and bascity were 96.5 and 3.5%, respectively.

IN contrast to extensive studies on the negative solvatochromic effect, the reverse phenomenon responsible for the hypsochromic shift of an $n \longrightarrow \pi^*$ absorption upon an increase of solvent polarity,[2-6] a positive solvatochromic effect, has been little investigated. We have observed a positive solvatochromic effect in the case of some conjugated Schiff's base derivatives of vicinal diketo-anilides [7,8] containing an *NN*-dimethylamino-group in the *para*-position of the aniline ring relative to the azomethine nitrogen. These Schiff's bases are easily obtainable by condensation of the appropriate aceto-acetanilide with *p*-nitroso-*NN*-dimethylaniline.[9] Their spectral and chemical properties differ distinctly from those of the other aniline derivatives of vicinal poly-carbonyl compounds.[10-12] Derivatives (I) are intensively orange or red coloured and exhibit medium absorption in the long wave region at *ca.* 402 nm

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(ε 10 000), in n-hexane. The use of a more polar solvent causes a bathochromic shift of up to 45 nm.

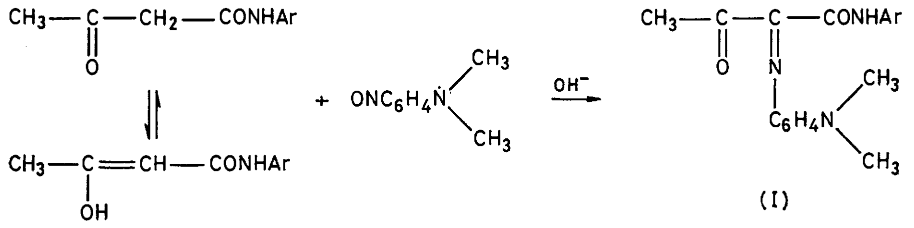
RESULTS

Compound (I; Ar = Ph) was chosen as the model for investigating the positive solvatochromic effect. In order to assign the u.v. absorption bands of the model, theoretical calculations were carried out. It was assumed that the model molecule is either planar [13] (planar conformation) or that the aniline ring is twisted round the ring carbon and azomethine nitrogen linkage [14] (perpendicular conformation). The calculations of the MO energy and LCAO coefficients for the model in the ground state were performed by the Pariser–Parr–Pople method using Kuprevich [15] parametrization. The values of the coulomb integrals were estimated with the help of the Mataga–Nishimoto formula.[16] The resonance integrals were evaluated according to the exponential equation (1) where $R_{i,j}$ designates the bond

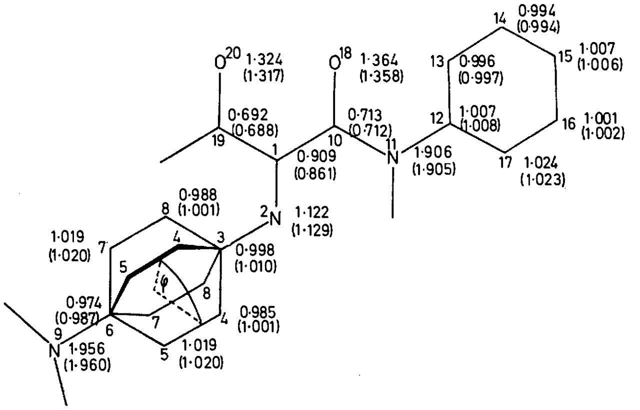
$$\beta_{i,j} = \beta_{X,Y}(-5.007R_{i,j}) \qquad (1)$$

length between the X_i and Y_j atoms. The values of the molecular core ω_X, coulomb integral $g_{X,X}$, and $\beta_{X,Y}$ coefficient for the azomethine nitrogen atom were assumed to be analogous to that of pyridine nitrogen (−14.12, 12.34, and −2 335 eV, respectively). The other nitrogen atoms were considered to be equivalent to that of an ordinary amino-group (−28.71, 16.75, and −1 927 eV). The same parameters were attributed to all the carbon atoms (−11.16, 11.13, and −2 518 eV). The parameters for the oxygen atoms were −17.70, 15.23, and −1 349 eV. Taking into consideration the dihedral angle connected with the rotation of the aniline ring the parameter for the =N–C$_{\text{ring}}$ linkage was formulated by equation (2) where ϕ designated the dihedral angle.

$$\beta_{X,Y} = \beta^{\circ}_{X,Y}\cos\phi \qquad (2)$$



(I)



Numbering of the atoms of compound (I) and the π electron densities calculated by the PPP method. Values in parentheses are for the perpendicular conformation

The calculations of the MO energy and the oscillator strength of the singlet–singlet transitions were performed by the PPP–CI–1 method. The Hamiltonian matrix elements of the excited states were taken from the Ciẑek equation.[17] Two different procedures of the configuration interaction were considered: (a) The classical variant of the procedure included only the $\pi \longrightarrow \pi^*$ transitions. The first seven occupied and four unoccupied orbitals were considered. (b) In the modified variant three π orbitals possessing the lowest energy were replaced by the n orbitals corresponding to the unshared pairs of electrons. These pairs were assumed to be entirely localized on the $2p_y$ orbitals (Table 1). Thus three n, four occupied, and four unoccupied π orbitals were taken into account.

On the basis of the Shortley–Condon parameters (0.715 and 0.870 eV for the nitrogen and oxygen atoms, respectively [18]) the exchange one-centre integrals $\langle p_z p_y | p_y p_z \rangle$ were estimated. The values of the coulomb one-centre integrals were identified with the $g_{X,X}$ parameters of the nitrogen (X = N) and oxygen (X = O) atoms. The values of energy, ε_N and ε_O, of the unshared orbitals were evaluated by the iterative procedure in such a way as to reproduce properly the position of the absorption bands at 320 and 402 nm. The characterization of the MO considered in the configuration interaction of the PPP-CI-1 method, based on the analysis of the LCAO coefficients, is given in Table 1.

The absorption occurring because of the $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions of the carbonyl group conjugated with the π-electron system is correctly reproduced by both variants of the interaction procedure. The band corresponding to the $\pi \longrightarrow \pi^*$ transition appears at 211 nm in the spectrum and the calculated position is a little over 212 nm (Table 2). This absorption depends weakly on changes in the dihedral angle ϕ. However, a better value is obtained by assuming it is equal to 90°. The absorption at 320 nm is caused by the $n \longrightarrow \pi^*$ transition. When the dihedral angle was assumed to be 90° a distinct decrease of energy ε_0 was found (from −13.5 to −15.3 eV) for the isolated π-electron system CO–aniline.

The absorption at 257 nm is due to the $\pi \longrightarrow \pi^*$ transition of the aniline fragment (of the anilide) and occurs in the N-methylaniline spectrum.[19] It is rather weakly

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affected by the changes of dihedral angle ϕ. The changes of angle ϕ affect to the highest degree the absorption at 252 nm corresponding to the $\pi \longrightarrow \pi^*$ transition of the aniline ring. If the dihedral angle is 0° (planar conformation) the calculated position of the absorption band is 281.1 nm. When it is 90° (perpendicular conformation) the absorption band is displaced to 228.5 nm. The absorption band appearing in the spectrum conforms to the dihedral angle ϕ 55°. This is consistent with the reported data.[20-24] The longwave absorption band at 402 nm is caused by an $n \longrightarrow \pi^*$ transition within the azomethine group. It is moderately influenced by the changes of dihedral angle ϕ, but better reproduction is obtained for the perpendicular conformation.

TABLE 1

Characteristics of the molecular orbitals of compound (I) considered in the configuration interaction procedure of the PPP-CI-1 method

	Planar conformation		Perpendicular conformation	
MO [a]	Energy (eV)	Localization of the electron pair (after LCAO coefficients)	Energy (eV)	Localization of the electron pair (after LCAO coefficients)
π_4^*	−0.933	Ph, CO	−0.974	PhNH
π_3^*	−1.100	Ph, CO	−1.112	Aniline ring
π_2^*	−1.246	Aniline ring	−1.228	Ph, CO
π_1^*	−2.585	Aniline ring, C=N, CO	−1.935	C=N, CO
π_1	−9.671	Aniline ring, C=N	−9.917	Anilide fragment
π_2	−9.865	Anilide fragment	−9.980	Aniline ring, C=N
π_3	−10.043	Anilide fragment	−10.090	Anilide fragment
π_4	−10.400	Aniline ring	−10.235	Aniline ring
π_5	−12.046	Aniline ring, C=N, CO	−12.337	Ph, CO
π_6	−12.292	Aniline ring, NH	−12.390	Aniline ring
π_7	−13.143	Aniline ring, NH	−13.142	Ph, CO, C=N
n_1	−10.900	N-2	−10.900	N-2
n_2	−13.500	O-20	−15.300	O-20
n_3	−13.500	O-18	−15.300	O-18

[a] Orbitals π_5—π_7 were replaced by orbitals n_1—n_3 in the modified variant of the configuration interaction procedure.

TABLE 2

Interpretation of the absorption bands of compound (I) with the help of the PPP-CI-1 method

λ/nm	Calculated			
Measured	*a*	*b*	Characteristics [b]	Oscillator strength *f* [b]
			Planar conformation	
211.1	216.8	216.1	$\pi_1^* \longleftarrow \pi_4$ 41.1%, $\pi_2^* \longleftarrow \pi_1$ 56.7%	0.615
234.0	235.2	235.0	$\pi_1^* \longleftarrow \pi_3$ 29.8%, $\pi_3^* \longleftarrow \pi_3$ 18.7%, $\pi_4^* \longleftarrow \pi_2$ 32.9%	0.129
252.1	281.1	280.2	$\pi_1^* \longleftarrow \pi_1$ 94.9%	0.988
330.1		329.4	$\pi_3^* \longleftarrow n_3$ 24.0%, $\pi_3^* \longleftarrow n_2$ 20.8%, $\pi_1^* \longleftarrow n_2$ 18.6%, $\pi_1^* \longleftarrow n_3$ 16.8%, $\pi_4^* \longleftarrow n_2$ 5.2%, $\pi_4^* \longleftarrow n_3$ 1.8%, $\pi_1^* \longleftarrow n_1$ 12.7%	0.403
401.9		422.8	$\pi_1^* \longleftarrow n_1$ 78.7%, $\pi_3^* \longleftarrow n_2$ 10.2%, $\pi_1^* \longleftarrow n_2$ 8.6%, $\pi_4^* \longleftarrow n_2$ 2.6%	0.369
			Perpendicular conformation	
211.1	212.6	212.4	$\pi_1^* \longleftarrow \pi_3$ 60.0%, $\pi_4^* \longleftarrow \pi_1$ 21.7%	0.242
234.0	237.1	237.1	$\pi_4^* \longleftarrow \pi_1$ 65.0%, $\pi_2^* \longleftarrow \pi_3$ 23.7%	0.216
251.1	228.6	228.5	$\pi_3^* \longleftarrow \pi_2$ 100%	0.441
330.1		331.6	$\pi_2^* \longleftarrow n_3$ 27.0%, $\pi_1^* \longleftarrow n_2$ 26.5%, $\pi_1^* \longleftarrow n_3$ 21.4%, $\pi_2^* \longleftarrow n_2$ 14.5%, $\pi_1^* \longleftarrow n_1$ 7.6%	0.579
401.9		409.6	$\pi_1^* \longleftarrow n_1$ 79.6%, $\pi_1^* \longleftarrow n_2$ 12.4%, $\pi_2^* \longleftarrow n_2$ 7.0%	0.565

[a] The classical variant of the configuration interaction procedure. [b] The modified variant of the configuration interaction procedure including *n* orbitals.

As mentioned longwave absorption is shifted bathochromically when solvent polarity increases. It was measured using over 30 pure solvents. The data are listed in Table 3. Among those investigated aromatic solvents proved to be the most convenient for the study of the positive solvatochromic effect. The model compound was capable of forming relatively stable adducts with benzene which could even be isolated and analysed,[9] but the tendency to form such adducts decreased rapidly when the donating activity of the solvent increased. This was also supported by the position of the longwave absorption band measured in various aromatic solvents. Thus the largest bathochromic shift, compared with the absorption found in n-hexane, occurred when nitrobenzene was used as solvent.

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As was expected the smallest shift was observed in the case of mesitylene. These facts seemed to be related to charge transfer (CT) interactions because ionic interactions are beyond consideration owing to the structure of the solvent. The bathochromic shift suggested that the conjugated aniline molecules played the role of super-donors which forced an accepting function upon the aromatic solvent molecules. Such an assumption is well correlated with observations.

TABLE 3

Absorption frequency [a] of compound (I) measured in various solvents at 22 ± 0.2 °C and polarity parameters

Solvent	Frequency (cm^{-1})	Z^+/kcal mol^{-1}	E_T/kcal mol^{-1}	DN/kcal mol^{-1}
n-Hexane	24 880	71.15	30.9	
Cyclohexane	24 840	71.04	31.2	
Carbon tetrachloride	24 500	70.06	32.5	
Diethyl ether	24 440	69.89	34.6	20.0
Dioxan	24 080	68.86	36.0	
Tetrahydrofuran	23 960	68.52	37.4	20.0
Ethyl acetate	24 040	68.75	38.1	17.1
Ethylene glycol monomethyl ether	24 020	68.69	38.2	
Chloroform	23 720	69.83	39.1	
Hexamethylphosphoramide	23 640	67.60	40.9	38.8
Methylene chloride	23 570	67.40	41.1	
Ethylene chloride	23 600	67.49	41.9	0.0
Acetone	23 680	67.72	42.2	17.0
NN-Dimethylformamide	23 400	66.92	43.3	26.6
t-Butyl alcohol	23 600	67.49	43.9	
Acetonitrile	23 380	66.86	46.0	14.1
Nitromethane	23 320	66.69	46.3	2.7
Ethyl alcohol	23 300	66.63	51.9	31.5
Methyl alcohol	23 160	66.23	55.5	25.7
Ethylene glycol	22 400	64.06	56.3	
Formamide	22 360	63.94	56.6	24.7
Triethylamine	24 780	70.92		
Di-n-hexylamine	24 380	69.76		

The values measured in aromatic solvents are listed in Table 4.

Consider that the weak CT complex is formed due to the solvation of the model compound molecules [equation (3)

$$M + S \rightleftharpoons (M - S) \qquad (3)$$

where M is the model molecule and S the solvent molecule]. The wave function of the ground state formulated in terms of the resonance structure theory of CT complexes is given by equation (4) with $a \gg b$. Then negative charge ΔQ

$$\psi_N = a\psi_0(\text{M–S}) + b\psi_1(\text{M}^+\text{S}^-) \qquad (4)$$

transferred from molecule M to molecule S due to donor–acceptor coupling is described by the Sakurai formula (5).[25]

$$\Delta Q = b/(a + b) \cong b/a \qquad (5)$$

Hence, the value of (5) predicted in accordance with the Mullikan theory [26] is expressed by formula (6) where

$$\frac{b}{a} = \frac{W_{01} - S_{01}W_0}{W_1 - W_0} = \frac{kS_{m,s}}{\varepsilon_s - \varepsilon_m - (ss|mm)} \qquad (6)$$

$W_0 = \langle\psi_0|\hat{\text{H}}|\psi_0\rangle$, $W_1 = \langle\psi_1|\hat{\text{H}}|\psi_1\rangle$, $W_{01} = \langle_0|\hat{\text{H}}|\psi_1\rangle$, $S_{01} = \langle\psi_0|\psi_1\rangle$, $S_{m,s} = \langle\psi_m|\psi_s\rangle$, m designates the occupied orbital of the donor, s designated the orbital of the acceptor S receiving the electron of the donor, ε_s and ε_m designate the energies of the s and m orbitals, respectively, $(ss|mm)$ is the coulomb integral of the electronic interactions between the s and m orbitals, and k is constant.

In the donor–acceptor coupling model the change of the $n_1 \longrightarrow \pi_1{}^*$ transition energy $\Delta E_{n1} \longrightarrow \pi_1{}^*$ is assumed to depend upon changes of the electron density of the azomethine nitrogen atom. These changes of electron density are induced by charge transfer ΔQ. To find the quantitative dependence between ΔQ and $\Delta E_{n_1 \rightarrow \pi_1{}^*}$ the latter value was conditioned to the shielding changes in the radial element of the Slater orbital.[27] The changes in the Slater index of the nitrogen, oxygen, and carbon atoms are equal to $\Delta\mu = 0.175\Delta Q$. Considering the specific character of the $n_1 \longrightarrow \pi_1{}^*$ transitions and the large value of the LCAO coefficient of the unoccupied π orbital of the azomethine group, the dependence may be formulated as in equation (7). The $g_{\text{N,N}}$ integral expressed as a function of

$$\Delta E_{n_1 \rightarrow \pi_1{}^*} = -\Delta(p_yp_y|p_zp_z)_{\text{N}} = -\Delta g_{\text{N,N}} \qquad (7)$$

μ_{N} is given by the Roothaan equation.[28] The changes of the one-centre integral $g_{\text{N,N}}$ are described by the simple linear function (8). To compare the accepting strength of

$$g_{\text{N,N}} = 93\Delta\mu_{\text{N}}/256 \qquad (8)$$

solvents belonging to the same class of simple benzene derivatives, the unoccupied, degenerated orbital possessing symmetry E_{2u} was chosen. This orbital contains a constant LCAO coefficient within the aromatic ring for all the solvents examined. On the other hand the donor function is fulfilled by these compounds in all cases. These facts distinctly simplify equation (6) because the integrals $S_{m,s}$, $(ss|mm)$, and the energy ε_m have constant values. Taking into consideration equations (5)—(8) formula (9) may be deduced where A and B are constants and ε_s is the energy

$$\Delta E_{n_1 \rightarrow \pi_1{}^*} = -\text{A}/(\varepsilon_s - B) \qquad (9)$$

of the accepting orbital. The theoretical values of the $E_{n_1 \rightarrow \pi_1{}^*}$ transitions were calculated with regard to the

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value measured in n-hexane for which no donor–acceptor coupling was assumed [equation (10)] where 24 880 cm^{-1}

$$E_{n_1 \rightarrow \pi_1^*} = 24\,880 - A/(\varepsilon_s - B) \text{ cm}^{-1} \qquad (10)$$

corresponds to the absorption in n-hexane. The values of the energy ε_s were calculated by the SC$_\alpha$ Hückel method [29] and are listed in Table 4. The constants A and B were evaluated with the help of the experimental data found for pyridine and benzene. Hence equation (9) is finally modified to (11). This formula is obeyed by the other aromatic solvents.

TABLE 4

Ionization potentials of aromatic solvents and comparison between measured and calculated $n_1 \longrightarrow \pi_1^*$ transition energy of the model (I)

Solvent	Ionization potential (β units)	$n_1 \longrightarrow \pi_1^*$ Transition energy (cm^{-1})	
		Calculated	Measured
n-Hexane			24 880
Pyridine	0.979 45	22 880	22 880
Nitrobenzene	0.980 04	22 945	22 960
Benzonitrile	0.991 13	23 571	23 000
Acetophenone	0.981 36	23 040	23 080
Methyl benzoate	0.985 05	23 290	23 440
Chlorobenzene	1.003 23	23 914	23 600
Benzene	1.000 00	23 840	23 840
Toluene	1.009 61	24 024	23 920
p-Xylene	1.018 90	24 150	24 040
Mesitylene	1.095 98	24 550	24 150

$$E_{n_1 \rightarrow \pi_1^*} = 24\,880 - \frac{44.52}{\varepsilon_s - 0.959\,17} \text{ cm}^{-1} \qquad (11)$$

The values $E_{n_1 \rightarrow \pi_1^*}$, calculated according to relationship (11), reproduce correctly the experimental values (correlation coefficient r −0.914).[30]

In the case of non-aromatic solvents the same model for the positive solvatochromic effect may be considered. An increase in Lewis acidity of the solvent should then involve a greater bathochromic shift, and conversely an increase in Lewis basicity should cause the reverse effect. In fact the lowest bathochromic shift is observed in the case of triethylamine and di-n-hexylamine (Table 3). Taking into account this nature of the positive solvatochromic effect a relationship analogous to that formulated by Kosower [31] may be developed: $Nh.c.\bar{v} = Z^+$ kcal mol^{-1} where parameter Z^+ corresponds to polarity parameter Z, N is the Avogadro number, h is the Planck constant, c the light velocity, and $\bar{v}$ the absorption frequency in cm^{-1}. Since parameter Z^+ represents the tendency of the solvent molecules to accept electrons from the model molecules a correlation with the Dimroth parameter E_T which expresses the Lewis acidity of the solvent [32] should be found. On the basis of the experimental data, including the measurements made for 21 solvents (Table 3), relationship (12) was formulated.

$$Z^+ = -0.231 \mp 0.002 E_T + 77.49 \mp 0.07 \qquad (12)$$

This relationship is properly obeyed (r −0.994).

Considering the Lewis acid–base description of the solvent effects reported recently by Krygowski and Fawcett,[33] the relative importance of the solvent acidity and basicity could be estimated. The Lewis acidity is described by the Dimroth parameter E_T, the basicity by the Gutmann donor number DN.[34,35] The relationship including parameters Z^+, E_T, and DN is expressed by formula (13).[30] The multiple linear regression is less well obeyed by the experimental data than the linear regression $Z^+ = f(E_T)$ with r −0.905. The relative importance of the acidity and basicity can be expressed as percentage contributions. Thus the estimates of the percentage contributions from the solvent acidity and basicity were found to be 96.5 and 3.5%, respectively. This is in accord with the proposed model for the positive solvatochromic effect.

$$Z^+ = 75.804 \mp 0.029 - 0.196 \mp 0.001 E_T + 0.007 \mp 0.001 \text{ DN} \qquad (13)$$

DISCUSSION

As mentioned the model compound was assumed to be either planar or twisted but only in the aniline fragment. In fact α-anilino-derivatives of α,β-diketobutyric acid anilides exist in the 'pseudo-gauche' conformation [36] in which aniline, anilide, and acetyl fragments are arranged in three different planes. The twist of these planes is smaller for the derivatives in question than for other compounds of this kind [36] and may be neglected owing to the fact that the solvatochromic effects are mainly connected with the aniline fragment itself. As shown by the PPP calculations the reproduction of the experimental data is quite satisfactory even in the case of such a rough approximation.

The positive solvatochromic effect can be properly explained with the help of charge transfer interactions between the solute and solvent molecules, assuming strong donating activity by the former. Thus the solute molecules play the role of donor component forcing an accepting function upon the solvent molecules. This donor function is induced by the presence of a highly electron-releasing substituent, *i.e.* an *NN*-dimethylamino-group in the *para*-position of the aniline ring and is mainly attributed to the n_1 orbital of the azomethine nitrogen atom. Participation of the π_1 orbital in acceptor–donor coupling is also possible but only to a very limited extent (its LCAO coefficient varies from 0 to 0.1 according to changes in the dihedral angle ϕ).

The assumption that there are no charge transfer interactions when n-hexane is used as a solvent is limited only to the aromatic solvents for which the $n_1 \longrightarrow \pi_1^*$ transition is considered. On the other hand, the absorption appears at the lowest wavelength in n-hexane, which suggests the weakest influence of the n-hexane molecules on the $n_1 \longrightarrow \pi_1^*$ absorption.

As for the relationship of parameter Z^+ and the other solvent parameters E_T and DN it can be noticed that the points of maximum deviation correspond to the protic

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solvents, *i.e.* methyl and ethyl alcohol. It seems to be related to the partial blocking of the donor function of the azomethine nitrogen atom due to protonation or addition processes.[37]

EXPERIMENTAL

U.v. spectra were determined on a VSU-2P Vis Zeiss spectrophotometer using 1 cm silica transmission cells. Samples of compound (I) were prepared in *ca.* 5×10^{-5}M concentrations in pure solvents (Tables 3 and 4). The samples had been placed in a thermostat at 22 ± 0.2 °C for 1 h before the u.v. spectra were recorded.

The model (I) was synthesized using as before,[9] by catalytic condensation of acetoacetanilide with *p*-nitroso-*NN*-dimethylaniline in ethanol as solvent. Small amounts of a concentrated ethanol solution of sodium hydroxide were used as a catalyst. The crude product was purified by repeated crystallization from cyclohexane, m.p. 123—124 °C.

Theoretical calculations were performed on an ODRA-1204 computer using our own programs. The calculations of the MO energies ε_s were carried out with the help of the SC$_\alpha$ Hückel method. The following parametrization was used: ω 0.75; h_{C} 0, $h_{\mathrm{CH_3}}$ 2.0, h_{Cl} 2.0, $h_{\mathrm{N^{\cdot}}}$ 0.5, $h_{\mathrm{N(NO_2)}}$ 2.0, $h_{\mathrm{0^{\cdot}}}$ 1.0—1.2, $h_{\mathrm{0^{:}}}$ 2.0; $k_{\mathrm{C=C}}$ 1.0, $k_{\mathrm{C-O}}$ 0.8, $k_{\mathrm{C=N}}$ 1.0, $k_{\mathrm{C-Cl}}$ 0.4, $k_{\mathrm{C-CH_3}}$ 0.7, $k_{\mathrm{NO(NO_2)}}$ 0.7, $k_{\mathrm{N=O(NO_2)}}$ 1.0 $k_{\mathrm{C=O}}$ 1.0.

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