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3-(*para*-Substituted phenylhydrazo)pentane-2,4-diones: Physicochemical and solvatochromic properties

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ABSTRACT

New azoderivatives of pentane-2,4-dione, 3-(4-bromophenylhydrazo)pentane-2,4-dione (HL_1) and 3-(4-acetylphenylhydrazo)pentane-2,4-dione (HL_2), have been synthesized by reaction between pentane-2,4-dione and the corresponding aryldiazonium salts, and characterized by IR, UV–vis, ^{1}H and ^{13}C NMR spectroscopies, potentiometry, X-ray diffraction analysis (for HL_2) and thermogravimetry. The collected data confirm that HL_{1-2} exist in DMSO solution and in solid phase exclusively in the hydrazo form, being stabilized by an intramolecular hydrogen bonding. The thermodynamics of proton dissociation of HL_{1-2} and of the related known 3-(4-nitrophenylhydrazo)pentane-2,4-dione (HL_3), in water–ethanol media, were studied quantitatively and the corresponding functions were calculated, showing a dependence on the inductive electron-acceptor character of the substituent in *para*-position of the aromatic part of the molecule. The thermal decompositions of HL_{1-3} were also investigated showing their high thermal stability with well-defined peaks of phase transition at 413–418 K. The wavelengths (or wavenumbers) of maxima of absorption bands in the UV–vis spectra of HL_{1-3} and the corresponding absorption coefficients are dependent on the *para* substituent, but no correlation was found with any particular property of the solvent, such as polarity, H-bond donating or accepting ability.

1. Introduction

Azo dyes constitute the largest group of colorants in terms of their number and production volume. Such an abundance is driven by the simplicity and versatility of their synthesis by diazotization and azo coupling, as well as by their generally high specific light absorption and fastness properties [1]. An important group of disperse dyes concerns the azoderivatives of β-diketones (ABD, for particular examples described in this paper see Scheme 1) which were found to have interesting semiconducting [2], antineoplastic [3,4], spectral [5], analgesic [6,7], antipyretic [6], antibacterial [8–10] and photoluminescent [11] properties, being also studied as perspective optical recording media and spin-coating films [12,13] or being applied for further organic synthesis [14,15]. ABD containing an hydroxy group in *ortho*-position of the aromatic part of the molecule were also applied for spectrophotometric determinations of copper(II) and iron(III) in various industrial and natural objects [16,17], as effective ionophores for copper-selective electrodes [18] or for the synthesis of metal complex catalysts for some oxidation reactions [19].

Relevant properties of ABD dyes, such as colour, thermal stability and solubility, can significantly vary with the substituents in the aromatic or β-diketone fragments, which also affect the hydrazo ⇌ enol-azo tautomerism within the molecule [19]. This tautomeric balance can also play an important role for the application of ABD as bistate molecular switches [20–23] or regulate the selectivity in analytical chemistry [16,17]. The equilibrium between the mentioned tautomeric forms is dependent on several factors, related to the structure of ABD or external influences (e.g. solvent or temperature) [19]. Thus, it has been observed that in ABD formed by *unsymmetric* β-diketones, a six-membered H-bonded ring is generated at the more sterically favourable side of the molecule [19,24] while the enol-azo tautomer starts to play an essential role in solution [19]. Hence, an understanding of the factors which influence the structure of ABD dyes in solution and in solid state allows to evaluate their potential applications, e.g. as induced molecular switches [20–23], optical recording media [12,13] or solvatochromic colorants [1,25–27].

The intramolecular proton transfer related to the hydrazo ⇌ enol-azo tautomerism is supported by the so-named resonance-assisted hydrogen bonding (RAHB) which describes a

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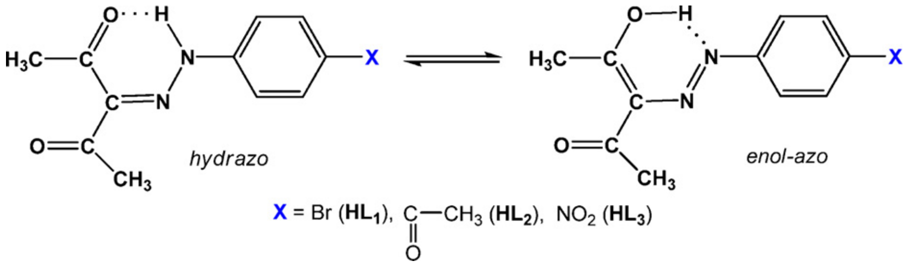


Scheme 1. 3-(*para*-Substituted phenylhydrazo)pentane-2,4-diones considered in this work (both the hydrazo and enol-azo forms are presented).

synergistic reinforcement of the hydrogen bond by delocalization of the π-conjugated chain connecting donor and acceptor atoms [20–23,28]. Consequently, the study of the influence of various factors on the RAHB is necessary for understanding how to play with this tautomery. For example, the intramolecular proton transfer is strongly influenced upon dissolution, when intermolecular hydrogen and van-der-Waals interactions with the solvent molecules change the distribution of the tautomers. Thus, the solvent induces changes in the electronic transitions of the colorant, which are dependent on the nature and extent of the solute–solvent interactions (solvatochromism) [25–27]. However, the presence of both tautomeric forms can hamper the interpretation of the spectroscopic data due to the bands overlapping [19], while theoretical calculations sometimes allow to overcome these difficulties by rationalizing the relation between the tautomeric ratio and properties [20–23,29]. Thus, the synthesis of new ABD performing solvatochromism and the search for correlations between their physicochemical and spectral properties would be an important contribution to the effective preparation of new dyes.

Taking in mind the above considerations, we focused this work on the following aims: (i) to synthesize new ABD with bromo- and acetyl- substituents in *para*-position of the aromatic ring of the molecule (Scheme 1); (ii) to trace the influence of the introduced substituents on the tautomeric balance and the physicochemical properties of ABD; (iii) to study solvatochromism of the newly synthesized ABD as well as their known analog 3-(4-nitrophenylhydrazo)pentane-2,4-dione (HL_3), bearing the stronger electron acceptor nitro substituent.

2. Experimental

2.1. Equipment and materials

The ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Avance II + 300 (UltraShield^{TM} Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts (δ) are reported in ppm using tetramethylsilane as the internal reference. The infrared spectrum (4000–400 cm^{-1}) was recorded on a Nicolet FT-IR Nexus spectrophotometer on KBr pellets. Thermal properties were analyzed with a Perkin-Elmer Instruction system (STA6000) at a heating rate of 10 K min^{-1} under a dinitrogen atmosphere. The acidity of the solutions was measured using an I-130 potentiometer with an ESL-43-07 glass electrode and an EVL-1M3.1 silver–silver chloride electrode adjusted by standard buffer solutions. The pH-metric titration was carried out in water–ethanol with consideration of the Bates correction [30] at different temperatures of 298 ± 0.5, 308 ± 0.5, and 318 ± 0.5 K. A constant temperature was maintained within ±0.5 K by using an ultrathermostat (Neslab 2 RTE 220). Solvents of spectrophotometric grade were purchased from Sigma–Aldrich and used without extra purification. The UV–vis absorption spectra in the 200–700 nm region were recorded with a scan rate of 240 nm min^{-1} by using a Lambda 35 UV–vis spectrophotometer (Perkin-Elmer) in 1.00 cm quartz cells at room temperature, with a concentration of HL_{1-3} of 3.50×10^{-5} M.

2.2. Synthesis of HL_{1-2}

The bromo- and acetyl-*para*-substituted azoderivatives of pentane-2,4-dione were synthesized via the Japp–Klingemann reaction [24,28,31] between the aromatic diazonium salts of the corresponding 4-bromoaniline or 4-acetylaniline and pentane-2,4-dione in water solution containing sodium hydroxide.

2.2.1. Diazotization

4-Bromoaniline or 4-acetylaniline (0.025 mol) was dissolved in 50 mL of water and then 1.00 g of crystalline NaOH was added. The solution was cooled in an ice bath to 273 K and then 1.725 g (0.025 mol) of $NaNO_2$ was added; 5.00 mL (33%) HCl were then added in portions for 1 h. The temperature of the mixture should not exceed 278 K. The resulting diazonium solution was used directly in the following coupling procedure.

2.2.2. Coupling

NaOH (1.00 g, 0.025 mol) was added to a mixture of 2.55 mL (0.025 mol) of pentane-2,4-dione with 50 mL of water. The solution was cooled in an ice bath to *ca.* 273 K, and a suspension of 4-substituted diazonium (see above) was added in three portions under vigorous stirring for 1 h.

The identity of HL_{1-2} was demonstrated by element analysis, IR and ^1H and ^{13}C NMR spectroscopies.

HL_1: yield 85% (based on pentane-2,4-dione), orange powder soluble in DMSO, methanol, ethanol and acetone, and insoluble in water. Elemental analysis: $C_{11}H_{11}BrN_2O_2$ (M = 283.1); C 46.58 (calc. 46.66); H 3.90 (3.92); N 9.87 (9.89)%. IR (KBr): 3448 ν(NH), 1671 ν(C=O), 1623 ν(C=O···H), 1581 ν(C=N) cm^{-1}. ^1H NMR in DMSO, internal TMS, δ (ppm): 2.09 (s, 3H, free CH_3CO), 2.41 (s, 3H, CH_3CO in H-bond), 7.15–7.29 (m, 2H, Ar–H), 7.52–7.55 (m, 2H, Ar–H), 10.22 (s, 1H, N–H). ^{13}C–{^1H} NMR in DMSO, internal TMS, δ (ppm): 28.81 (CH_3), 30.70 (CH_3), 116.85 (Ar–Br), 118.49 (Ar–H), 120.85 (Ar–H), 131.42 (Ar–H), 132.20 (Ar–H), 134.14 (C=N), 142.48 (Ar–NH–N), 194.20 (C=O), 196.23 (C=O).

HL_2: yield 79% (based on pentane-2,4-dione), orange powder soluble in DMSO, methanol, ethanol and acetone, and insoluble in water. Elemental analysis: $C_{13}H_{14}N_2O_3$ (M = 246.3); C 63.28 (calc. 63.40); H 5.69 (5.73); N 11.32 (11.38)%. IR (KBr): 3449 ν(NH), 1675 ν(C=O), 1642 ν(C=O), 1599 ν(C=O···H), 1509 ν(C=N) cm^{-1}. ^1H NMR in DMSO, internal TMS, δ (ppm): 1.79 (s, 3H, free CH_3CO), 2.05 (s, 3H, free CH_3CO), 2.39 (s, 3H, CH_3CO in H-bond), 7.57 (m, 2H, Ar–H), 7.93 (m, 2H, Ar–H), 12.87 (s, 1H, N–H). ^{13}C–{^1H} NMR in DMSO, internal TMS, δ (ppm): 26.51 (CH_3), 27.03 (CH_3), 30.69 (CH_3), 115.91 (Ar–H), 122.96 (Ar–H), 129.62 (Ar–H), 129.98 (Ar–H), 132.65 (Ar–$COCH_3$), 135.58 (C=N), 147.01 (Ar–NH–N), 173.30 (C=O), 196.40 (C=O), 196.71 (C=O).

2.3. Crystallography

The crystals of HL_2 suitable for X-ray structural analysis were grown by slow evaporation at room temperature of its ethanol solution. Intensity data were collected at room temperature on a Rigaku Mercury CCD diffractometer with a graphite monochromator using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and Fourier's difference, and refined by least squares on F^2 with anisotropic displacement parameters for non-H atoms. All hydrogen atoms were located from difference Fourier maps and refined isotropically. All calculations to solve the structures, to refine the model proposed and to obtain the data were carried out with SHELXS-97 and SHELXL-97 and SHELXTL/PC computer programs [32–35]. The crystallographic and selected structural details are listed in Tables S1 and S2, respectively. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC (764147) for compound HL_2. Copies of this information may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Potentiometric measurements

The following mixtures (i) and (ii) were prepared and titrated potentiometrically against standard 0.005 M KOH in 40/60% (v/v) water–ethanol mixture at 298 K.

$$5\,\text{mL}\;0.001\,\text{M}\,\text{HCl} + 5\,\text{mL}\;1\,\text{M}\,\text{KCl} + 30\,\text{mL ethanol}; \qquad \text{(i)}$$

$$5\,\text{mL}\;0.001\,\text{M}\,\text{HCl} + 5\,\text{mL}\;1\,\text{M}\,\text{KCl} + 25\,\text{mL ethanol} + 5\,\text{mL}\;0.001\,\text{M}\,\text{HL}_{1-3}; \qquad \text{(ii)}$$

For each mixture, the volume was made up to 50.00 mL with bidistilled water before the titration process. These titrations were also repeated at temperatures of 308 and 318 K.

2.5. Calculation of the physico-chemical parameters of thermal decomposition of HL_{1-2}

The thermodynamic parameters of decomposition of the complexes, namely the activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and free energy of decomposition (ΔG^*), as well as the pre-exponential factor (A), were evaluated graphically using the Coats–Redfern relationship [36–38]:

$$\ln\left\{\frac{-\ln(1-\alpha)}{T^2}\right\} = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right],$$

where α is the fraction of sample decomposed at temperature T, A is the pre-exponential factor, φ is the heating rate, E^* is the activation energy, R is the gas constant. A plot of $\ln\{[-\ln(1-\alpha)]/T^2\}$ against $1/T$ gives a slope from which E^* was calculated and A was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated using the following equations:

$$\Delta S^* = 2.303R\log\left(\frac{Ah}{kT_s}\right)$$

$$\Delta H^* = E^* - RT_s$$

$$\Delta G^* = \Delta H^* - T_s\,\Delta S^*$$

where k, h and T_s are the Boltzmann constant, Planck constant and the DTG peak temperature, respectively.

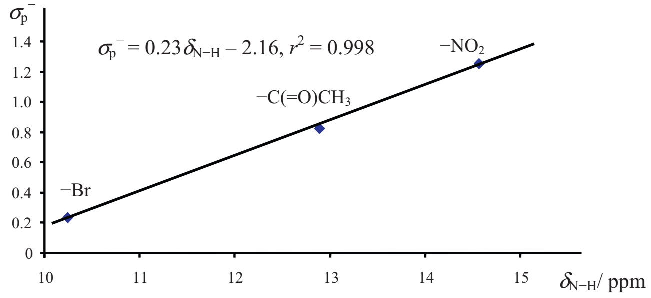


Fig. 1. Correlation between the polar conjugation substituent constant σ_p^- and δ_{N-H} for HL_{1-3}.

3. Results and discussion

3.1. Synthesis of HL_{1-2} and their spectroscopic study

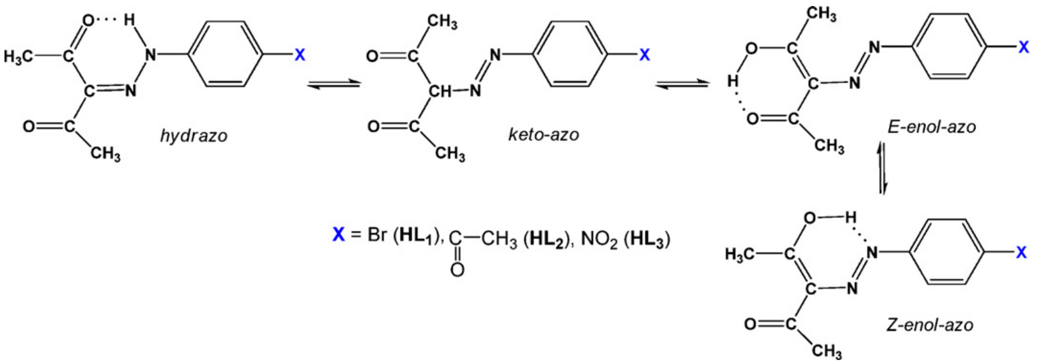
The new ABD compounds HL_{1-2} (Scheme 1) were synthesized by diazotation of the corresponding 4-substituted aniline and reaction of the thus formed diazonium salt with pentane-2,4-dione, following the Japp–Klingemann procedure [24,28,31]. Although this reaction is usually performed in the presence of sodium acetate, attempts to prepare the bromo- and acetyl-*para*-substituted ABD using this base gave low yields of highly impure products. Thus, we have modified the reported procedure and found that good yields of those ABD can be obtained when the coupling is undertaken in a sodium hydroxide solution [29]. For comparative purposes, we have also studied the known [39] analogous *para*-NO_2 substituted ADB (HL_3).

The IR spectra of the thus synthesized ABD reveal ν(NH) at *ca.* 3448–3449 cm^{-1}. The carbonyl [ν(C=O) 1642–1675, ν(C=O···H) 1623–1599 cm^{-1}] and ν(C=N) (1509–1581 cm^{-1}) vibrations indicate that in the solid state HL_{1-2} are stabilized in the H-bonded hydrazo form, what is also supported by X-ray data (see below). ^1H NMR spectra of HL_{1-3} in dimethylsulfoxide-d^6 solution at room temperature show a resonance at δ 10.22 (HL_1), 12.87 (HL_2) or 14.54 (HL_3) [39], which is assigned to the proton of the protonated nitrogen atom adjacent to the aryl unit (=N–NH– hydrazo form). In the ^{13}C–{^1H} NMR spectra, the two methyl groups of the β-diketone moiety yield two resolved singlets, indicating their non-equivalence, presumably due to formation of an intramolecular six-membered H-bonded ring involving one of the carbonyl groups and the NH of the hydrazo form (Scheme 2) similar to other reported ABDs [20–23,28,29,39–42].

The functional groups in *para* position of the aromatic ring of the molecule influence the NH chemical shift (δ_{N-H}) of HL_{1-3} and possible relations between the Hammett's [$\sigma_p = 0.23$ (–Br), 0.51 (–C(=O)CH_3), 0.78 (–NO_2)] or related [inductive $\sigma_I = 0.47$ (–Br), 0.29 (–C(=O)CH_3), 0.63 (–NO_2); Taft's $\sigma_p^o = 0.26$ (–Br), 0.46 (–C(=O)CH_3), 0.83 (–NO_2); polar conjugation $\sigma_p^- = 0.25$ (–Br), 0.84 (–C(=O)CH_3), 1.27 (–NO_2)] substituent constants [43–45] and δ_{N-H} were analyzed. The best correlation was found for the polar conjugation σ_p^- substituent constant (Fig. 1) (for comparison: $\sigma_p = 1.25\delta_{N-H} - 1.06$, $r^2 = 0.986$; $\sigma_p^o = 1.27\,\delta_{N-H} - 1.07$, $r^2 = 0.912$), but there is no reasonable relation with the inductive σ_I substituent constant ($\sigma_I = 0.027\delta_{N-H} + 0.12$, $r^2 = 0.124$).

3.2. Crystal structure of HL_2

The molecule is quasi planar with small deviations around the C(1)–C(7), C(9)–C(10) and C(9)–C(12) bonds (Fig. 2). As expected, the bond lengths of free C(12)–O(3) 1.209(2) Å and H-bonded C(10)–O(2) 1.217(2) Å carbonyl groups are not equal. The molecular structure of HL_2 involves an intramolecular six-membered



Scheme 2. Possible tautomeric equilibria in HL_{1-3}.

Table 1
Distances/Å and angles/° of hydrogen bond interactions in HL_2.

D–H•••A	Symmetry	Distances			Angles
		D–H	D···A	H···A	D–H···A
N(1)–H(1 N)··· O(2)	*x*, *y*, *z*	0.8387(14)	2.588(18)	1.983(14)	128.30(12)
N(1)–H(1 N)··· O(1)	*x*, *y*,−1 + *z*	0.8387(14)	3.432(23)	2.689(14)	148.42(12)
C(2)–H(2)··· O(3)	−*x*, 1 − *y*,−*z*	0.9300(13)	3.369(25)	2.705(13)	129.00(11)
C(5)–H(5)··· O(1)	*x* + 0.5, −*y* + 1.5, *z* − 0.5	0.9300(15)	3.248(21)	2.390(13)	153.34(12)

hydrogen-bonded ring, H(1 N)–N(1)–N(2)–C(9)–C(10)–O(2), formed by the NH-moiety and one of the carbonyl groups, similarly to the other described ABD [20–23,28,29,39–42]. This cycle is a distorted hexahedron with mutual angles N(1)–N(2)–C(9), C(9)–C(10)–O(2), O(2)–H(1 N)–N(1) and N(2)–C(9)–C(10) equal to 122.81(13)°, 118.97(14)°, 128.30° and 123.62(14)°, respectively (Table S2). The N–H···O bond with the N···O distance of 2.588(18) Å falls in the N···O distances range, 2.538–2.603 Å, observed for other ABD [20–23,28,29,39–42], and indicates a low delocalization within the heterodienic moiety. The N–H···O angle of 128.30° (Table 1) significantly differs from the average O–H···O angle (149° [46]) of β-diketone enols involved in similar intramolecular RAHB. No H-bond-induced lengthening of the N–H bond distance is observed. In contrast, the N–H distance of 0.8387 Å is even shorter than the average distance in such moieties unperturbed by H-bonding. This bond shortening can be explained by a combination of the RAHB effect and proton affinity equalization of the atoms involved, which, in its turn, is tuned by the electronic properties of the substituents at the phenyl rings bonded to the nitrogen atom [46–48].

Thus, the *para*-C(=O)CH_3 substituent (with $\sigma_p = 0.51$) causes a significant shortening of the N–H bond and a slight elongation of the N···O distance. These discrepancies can be explained by the electron-withdrawing properties of this substituent which seem to favour the equalization of O(1) and N(2) proton affinities, lengthening of N···O hydrogen bond distance, and the heterodienic delocalization. Finally, the intermolecular interactions through the O1 atom of the *para*-acetyl group stabilize the overall structure of HL_2 (Table 1). In the overall, the above mentioned factors create a multi-state switchable pattern induced by a proton transfer and an interchange of the single and double bonds within the resonant spacer. Hence, some applications of the compound in the field of functional materials can be envisaged. For that purpose, the dissociation process connected to the described H-bonds must be quantified and further discussed.

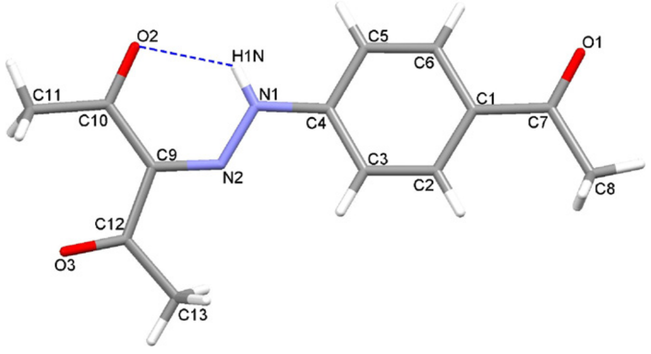


Fig. 2. Molecular structure of HL_2.

3.3. Thermodynamics of HL_{1-2} dissociation

The dissociation constants of HL_{1-2} were determined by pH-metric titration using known equations [49] (see Section 2), in water–ethanol media (Table 2). The ionic strength was maintained constant ($I = 0.1$ M) by adding a calculated amount of KCl. The ability to abstract a proton from various groups in tautomeric forms of related ligands was evaluated previously [19,50] and it was considered that pK concerns the proton abstraction from the hydrazo group (=N–NH–) (See Scheme 2, hydrazo form). The thermodynamic parameters of the dissociation process of HL_{1-2} were determined using the dependence of the dissociation constants from temperature and calculated by the following known equations [51]:

$$\Delta G^\circ = 2.303RT\mathrm{p}K; \quad \Delta H^\circ = \frac{-R(\mathrm{p}K_{(T_3)} - \mathrm{p}K_{(T_1)})}{(1/T_3) - (1/T_1)}; \quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}.$$

The data thus obtained (Table 2) testify that, with an increase of temperature and of the inductive electron-withdrawing properties of the functional groups in *para*-position of the aromatic ring [$\sigma_I = 0.29$ (–C(=O)CH_3), 0.47 (–Br), 0.63 (–NO_2)] the acidity of HL_{1-3} increases (pK values decrease) and hence the deprotonation is endothermic. On the other hand, with an increase of the inductive effect of the *para*-functional groups, ΔS° and ΔH° decrease, the dissociation processes of HL_{1-3} thus being mainly contributed by the enthalpy factor. Those data are consistent with the facts that

Table 2
Thermodynamic characteristics of dissociation of HL_{1-3} in water-ethanol solution.

HL_{1-3}	T, K	pK	ΔG°, kJ mol^{-1}	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}
HL_1	298 ± 0.5	8.43 ± 0.03	48.09 ± 0.12		−24.16 ± 2.29
	308 ± 0.5	8.21 ± 0.03		40.89 ± 2.17	
	318 ± 0.5	7.98 ± 0.06			
HL_2	298 ± 0.5	8.50 ± 0.01	48.50 ± 0.10		−13.35 ± 2.42
	308 ± 0.5	8.26 ± 0.02		44.52 ± 2.32	
	318 ± 0.5	8.01 ± 0.03			
HL_3 [29]	298 ± 0.5	8.10 ± 0.02	46.22 ± 0.11		−51.40 ± 1.81
	308 ± 0.5	7.95 ± 0.03		30.90 ± 1.70	
	318 ± 0.5	7.76 ± 0.05			

with an increase of temperature the solvent molecules can induce new conformations of HL_{1-3} (growing of entropy) but at the cost of breaking a part of the hydrogen bonds among them (dropping of enthalpy). Hence, the solvent and temperature are essential factors which potentially allow to shift the tautomeric balance and consequently the dependent properties of the compounds such as their colour, transparence, conductivity, etc. The influence of the solvents on the colour of the dyes is described in the following section.

3.4. UV–vis spectra of ABD

As mentioned above, the influences of specific interactions in solutions, mainly hydrogen bonds, on the absorption spectra is important and depend on whether the solute molecules act as donors or acceptors upon interaction with the solvent [25,52,53]. Since polarities of the ground and excited state of a chromophore are typically different, a change in the solvent polarity will lead to different stabilizations of the ground and excited states, and thus, to a change in the energy gap between them. Consequently, the position, intensity, and shape of the absorption spectra are driven by the specific interactions between the solute and solvent molecules. The investigated ABD dyes show colour dependence on the *para*-substituent and on the protic properties of the solvents (Fig. S1). Thus, HL_1 (ABD with –Br substituent) is yellow in acetone, acetonitrile, DMF, DMSO, methanol and ethanol (Fig. S1f), while HL_2 (ABD with –C(=O)CH_3 substituent) is green in acetone, acetonitrile, DMF, DMSO and yellow in methanol and ethanol (Fig. S1g). On the other hand, HL_3 (ABD with –NO_2 substituent) is pink in acetone, acetonitrile, DMF, DMSO and yellow in methanol and ethanol (Fig. S1h). Thus, in acetone, acetonitrile, DMF and DMSO the studied ABD exhibit the following colours, depending on the *para*-substituent: yellow (–Br), light green (–C(=O)CH_3) or pink (–NO_2) (Fig. S1a–e), what can be used for, e.g. qualitative determination of such aprotic solvents in protic ones, e.g. methanol.

The quantitative parameters of the solvatochromic effect are given in Table 3 and Fig. 3. All the investigated ABD show two or three (this depends on the solvent used and on the substituent within the molecule of the colorant) absorption maxima in the UV-vis spectra. The first band at 236–245 nm can be assigned [25,52–54] to the excitation of the π-electrons within the C=O bonds of the pentane-2,4-dione. The position of this band as well as the molar absorption (ε_{max}) are dependent on the electron-withdrawing properties of the *para*-substituent [$\sigma_I = 0.63$ (–NO_2), 0.47 (–Br), 0.29 (–C(=O)CH_3)] (Table 3). The λ_{max} values of ABD do not correlate with any particular property of the solvent, such as polarity, H-bond donor or acceptor ability or electric permittivity. Thus, neither the electrostatic solvation nor specific solute–solvent interactions can solely explain the observed solvatochromism.

The second UV absorption bands around 268–276 nm can be assigned [25,52–54] to the $\pi \rightarrow \pi^*$ transition of the C=N and aromatic ring of ABD. Apparently, in this case the *para*-substituents and the nature of solvents do not strongly influence λ_{max}, in contrast to the molar absorption (Table 3 and Fig. 3). The third band (363–383 nm) can be associated [25,52–54] to the $n \rightarrow \pi^*$ transition or electron transitions of the hydrazo to the enol-azo form. A bathochromic shift is also observed for the compound HL_3 in comparison with HL_1 and HL_2. Under excitation, the ADB dyes can differently shift between the hydrazo and the enol-azo tautomeric forms, depending on the substituent and on the bonding acceptor-donating ability (α or β) of the solvent. The obtained data confirm that ε_{max} depends on the solvent and on the nature of ABD, but no any clear correlation was found. One can only speculate that due to different polarizabilities of the ground and excited states, ABD with non-polarized ground state are better polarized in protic solvents. In this case the excited state is lowered while the ground

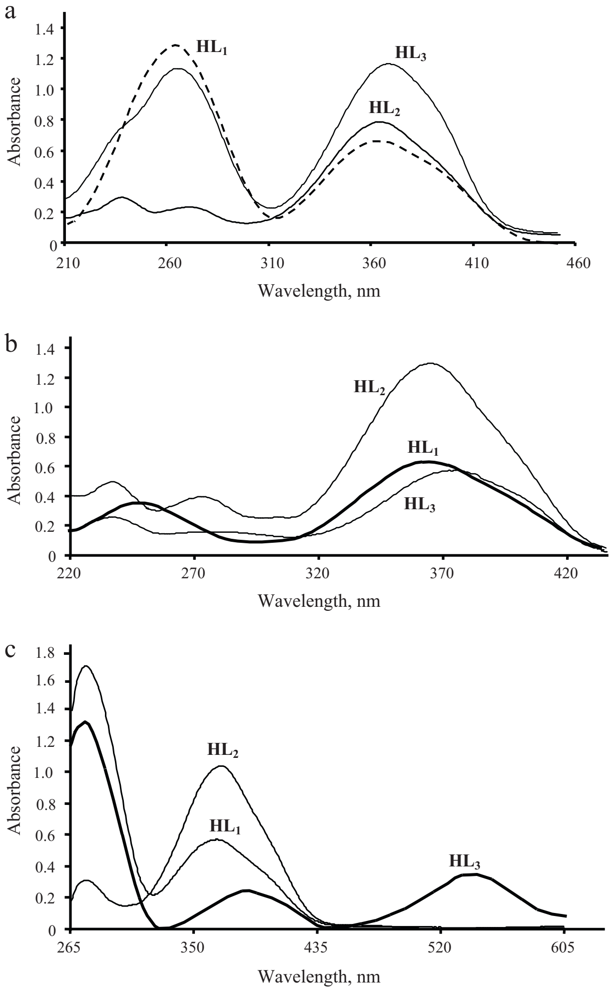


Fig. 3. Absorption spectra of HL_{1-3} in CH_3OH (a), CH_3CN (b) and DMF (c).

Table 3
Data from UV–vis spectra of HL_{1-3} in different solvents at 298 K.

HL_{1-3}	Solvent	ε[a]	α[b] [52]	β[c] [54]	Peak 1		Peak 2		Peak 3	
					λ_{max}, nm	ε_{max}[d]	λ_{max}, nm	ε_{max}[d]	λ_{max}, nm	ε_{max}[d]
HL_1	$CHCl_3$	5	0.44	0.00	–[e]	–[e]	–[e]	–[e]	371	27492
HL_2					243	9014	274	7324	372	24789
HL_3					–[e]	–[e]	–[e]	–[e]	383	24786
HL_2	THF	8	0.00	0.54	240	9014	269	4788	369	23098
HL_2	Acetone	21	0.08	0.48	–[e]	–[e]	–[e]	–[e]	367	6760
HL_2	Ethanol	30	0.83	0.77	239	9039	272	6780	369	25423
HL_1	Methanol	33	0.93	0.62	–[f]	–[f]	268	36363	365	18787
HL_2					239	7345	273	5650	368	22599
HL_3					–[f]	–[f]	270	33142	375	33714
HL_1	CH_3CN	37	0.19	0.31	245	9970	–[g]	–[g]	363	18127
HL_2					237	14370	274	11540	366	36901
HL_3					236	7122	278	4273	373	15954
HL_1	DMF	38	0.00	0.76	–[e]	–[e]	274	49576	365	16928
HL_2					–[e]	–[e]	275	9019	368	30440
HL_3[g]					–[e]	–[e]	276	37628	381	6841
HL_2	DMSO	47	0.00	0.76	–[e]	–[e]	276	25352	370	42243

[a] Electric permittivity of solvent.
[b] H-bond donating ability of solvent.
[c] H-bonding acceptor ability of solvent.
[d] $L\,mol^{-1}\,cm^{-1}$.
[e] Due to high absorbance by solvent, the peaks were overlapped.
[f] Peak not observed.
[g] A new peak is observed at 537 nm with $\varepsilon_{max} = 9122\,L\,mol^{-1}\,cm^{-1}$.

state is hardly affected, and hence the energy difference between the ground and excited states decreases. Thus, H_{1-3} exhibit specific solvent-dependent absorptions at 236–537 nm that made them efficient solvatochromophores.

3.5. Thermal behaviour of HL_{1-3}

Potentially ADB can be good candidates for optical recording media [12,13] or optical sensors [1]. For such and similar applications, the thermal behaviour of the material is an important issue [55–57]. Thus, we investigated the thermal decomposition of the dyes by simultaneous thermogravimetry–differential calorimetry, and the corresponding physicochemical parameters of this process were calculated (Table 4).

Differential thermogravimetric (DTG) curves of HL_{1-3} show phase transition peaks at 413 ($-NO_2$), 415 (–Br) and 418 K ($-C(=O)CH_3$) without significant mass loss (Fig. 4, for HL_1). As the temperature increases, TG and DTG curves exhibit a sharp mass loss in the interval 435–588 K, obviously related to decomposition of the compounds. The kinetic parameters of this process were evaluated (Table 4) and show that the activation enthalpy of decomposition (and hence the rate of decomposition) lay in the following order: $HL_3 > HL_2 > HL_1$, which is in accord with the Hammett's and related substituent constants of the functional groups. The values of E^* and ΔH^* differ by a small value of 4.24–4.39 $kJ\,mol^{-1}$ meaning that within experimental error they are equivalent. The negative entropy of activation suggests that the thermal decomposition reaction is slow [55]. The values of the pre-exponential factor in the Arrhenius equation (A) are within 10^8–10^{10} s^{-1}, not allowing to establish the reaction molecularity [55–57]. The found parameters with a sharp thermal decomposition threshold and high mass loss rate are characteristic for optical storage materials forming a small and sharp recording mark edge [58].

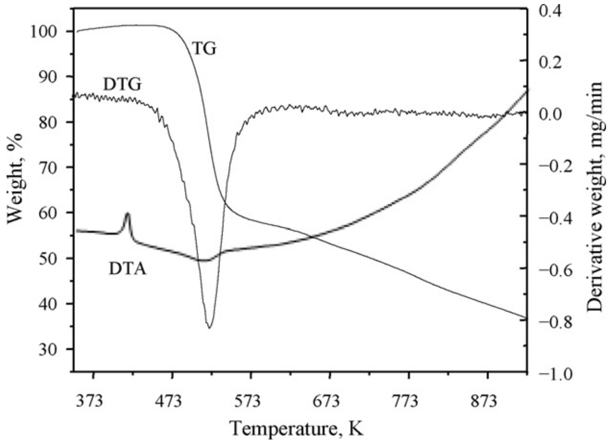


Fig. 4. Thermal decomposition of HL_1.

Table 4
Parameters of thermal decomposition of HL_{1-3}.

Dye	Temperature of phase transition (K)	Temperature of decomposition (maximum) (K)	Weight loss, %	A (s^{-1})	E^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}mol^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔG^* ($kJ\,mol^{-1}$)
HL_1	415	435–587 (528)	44.95	1.5×10^8	93.53	−93.12	89.14	138.35
HL_2	418	448–583 (514)	45.56	1.2×10^{10}	112.24	−56.50	108.00	137.05
HL_3	413	453–588 (513)	33.48	8.5×10^{10}	120.55	−40.21	116.29	95.66

4. Conclusions

New *para*-Br (HL_1) and $-C(=O)CH_3$ (HL_2) substituted phenylhydrazo derivatives of pentane-2,4-dione were synthesized and fully characterized. It was found that HL_{1-2} are stabilized in the hydrazo form in solution and in the solid state by an intramolecular six-membered, hydrogen-bonded ring. A higher inductive effect of the substituent [$-C(=O)CH_3 < -Br < -NO_2$] leads to decreases of pK and of ΔG°, ΔH° and ΔS° for the proton dissociation process of HL_{1-3}. The maxima and intensity of $\pi \to \pi^*$ and $n \to \pi^*$ absorption bands of the studied compounds (λ_{max} and ε_{max}) depend on their structure and solvent, but no correlation was found with any particular property of the solvent such as polarity, H-bond donating and H-bond accepting ability. However, the investigated dyes can be used for qualitative determinations of aprotic solvents in protic ones. On the other hand, their absorption in the blue part of the spectrum in combination with their thermal stability, high weight loss rate and sharp thermal decomposition threshold make them potential high-density optical recording materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.02.006.

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