Dyes and Pigments 85 (2010) 1–6

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Quantum-chemical calculations, tautomeric, thermodynamic, spectroscopic and X-ray studies of 3-(4-fluorophenylhydrazone)pentane-2,4-dione

Abel M. Maharramov, Rafiga A. Aliyeva, Ismayil A. Aliyev, Faig H. Pashaev, Arzuman G. Gasanov, Saida I. Azimova, Rizvan K. Askerov, Atash V. Kurbanov, Kamran T. Mahmudov*

Department of Chemistry, Baku State University, Az 1148, Baku street, Z.Khalilov 23, Azerbaijan

ARTICLE INFO

Article history:
Received 22 June 2009
Received in revised form
30 August 2009
Accepted 6 September 2009
Available online 11 September 2009

Keywords:
3-(4-Fluorophenylhydrazone)
pentane-2,4-dione
Hydrogen bonding
Hydrazone dyes
Tautomeric studies
X-ray characterization
Thermodynamic parameters
Quantum-chemical calculations

ABSTRACT

The structural and tautomeric characteristics of 3-(4-fluorophenylhydrazone)pentane-2,4-dione were studied using IR, ^1H and ^{13}C NMR spectroscopy, X-ray diffraction analysis and quantum-chemical calculations. Crystallographic data shows that the compound has a hydrazone structure that contains intramolecular H-bonds assisted by resonance, with a N–O distance of 2.5872 Å. The effective atomic charges in the tautomeric forms of the colorant (enol-azo, keto-azo and hydrazone), was calculated using an MO LCAO quantum-chemical method employing the Hückel approximation; the compound was stabilized in the hydrazone form and displayed high reactivity. The thermodynamic functions of the proton dissociation constant of the colorant were determined by potentiometry; the dissociation process was unspontaneous, endothermic and entropically unfavorable. The findings reveal that the colorant has the same structure in both DMSO solution and the solid state.

1. Introduction

The coupling of aryldiazonium salts with β-dicarbonyl compounds results in the formation of a series of azoderivatives of β-diketones (**ADB**) that have been shown to exist as intramoleculary H-bonded arylhydrazone tautomers (Scheme 1) [1–5]:

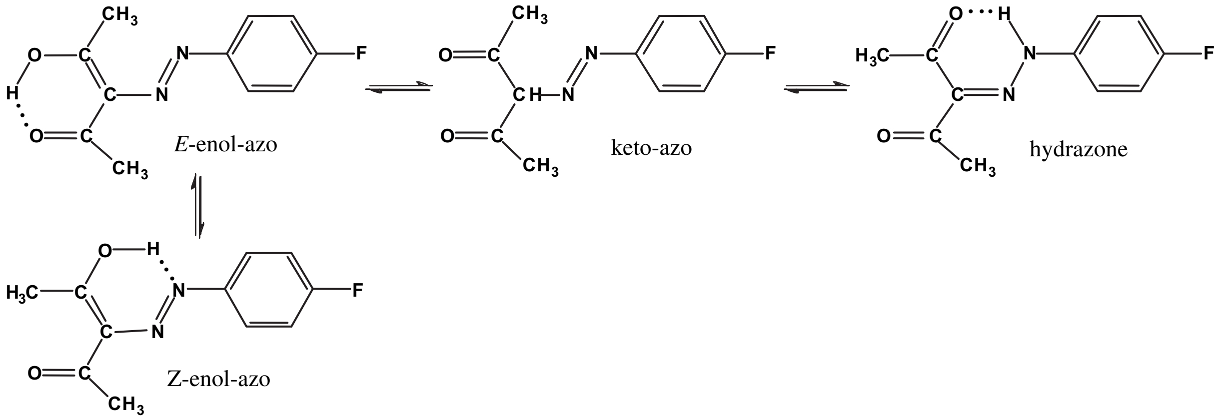
In recent years, much attention has been devoted to structural studies of heterodienic systems that form strong intramolecular hydrogen bonds, N–H···O, which are assisted by resonance (RAHB) and which, *inter alia*, may offer potential technological applications as bistate molecular switches [6–11]. ADB's enjoy manifold applications, that include its use as a semiconductor [12], an analytical reagent for spectrophotometric determination of metal ions [13–15], high-density recordable optical storage [16], spin-coating films [17] liquid crystals [18], self-assembled layers [19] and organic synthesis [20]. The RAHB model [21] was employed to interpret both the intra- and inter-molecular hydrogen bonds within compounds that contain a β-diketo-enol fragment. The current authors [8] have reported the crystal structures and spectroscopic data of five, ADB's derived from dibenzoylmethane and showed that the interplay between the N–O H-bond strength and π-delocalization was a general phenomenon. In a furthet study using six, ADB's derived from benzoylacetone or acetylacetone of the nature of the intramolecular hydrogen bond formed by the HN–N═C–C═O moiety in these compounds [9], the same authors showed that the magnitude of this strong H-bond was determined by the degree of π-delocalization within the ketohydrazone hetero conjugated system and was modulated by all other factors which can influence the degree of conjugation, including inductive effects and non-bonded inter-molecular interactions.

This paper concerns the precise nature of the products formed by this coupling reaction. $F\text{-}4\text{-}C_6H_4NHN{=}C(COCH_3)_2$ (**HL**) was prepared using the method described [22] and both structural and tautomeric studies were undertaken using IR, ^1H and ^{13}C NMR spectroscopy, as well as thermodynamic and quantum-chemical calculations. The crystalline and molecular structures of HL obtained using X-ray diffraction analysis were also determined.

---

* Corresponding author.
E-mail address: kamran_chem@mail.ru (K.T. Mahmudov).

0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.09.003



Scheme 1. Possible tautomeric equilibria in HL.

2. Experimental

2.1. Materials and methods

The synthetic work was performed in air and at room temperature. All chemicals were obtained from commercial sources and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruccer 300 spectrometer 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. 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 aqueous-ethanol with consideration of the Bates correction [23] at different temperatures 298 ± 0.5, 308 ± 0.5, and 318 ± 0.5 K. A constant temperature was maintained to within 0.5 K by using an ultrathermostat (Neslab 2 RTE 220).

2.2. Synthesis of the 3-(4-fluorophenylhydrazone) pentane-2,4-dione

The free arylhydrazone ligand of HL was synthesized via the Japp–Klingemann reaction [22] of the aromatic diazonium salt of 4-fluoroaniline and pentane-2,4-dione, in an ethanolic solution containing sodium acetate.

2.2.1. Diazotization

A 2.40 mL (0.025 mol) portion of 4-fluoroaniline (caution: highly toxic; combustible liquid and vapour; incompatible with acids, acid chlorides, strong oxidizing agents, acid anhydrides, chloroformates) was dissolved in 50 mL of water and 1 g of crystalline KOH was added. The ensuing solution was cooled in an ice bath to 273 K and 1.725 g (0.025 mol) of $NaNO_2$ added; 5 mL HCl was then added in portions over 40 min. The temperature of the mixture should not exceed 278 K.

2.2.2. Azocoupling

8 g CH_3COONa were added to a mixture of 2.43 mL (0.025 mol) pentane-2,4-dione and 50 mL of ethanol. The resulting solution was cooled in an ice bath and a suspension of 4-fluoroaniline diazonium was added in three portions. In the diazocoupling, the pH should be maintained in the range of 8–10; crystalline CH_3COONa may be added if needed.

Yield 81% (based on pentane-2,4-dione), yellow powder is soluble in DMSO, methanol, ethanol and acetone but insoluble in water.

The identification of the HL was demonstrated by element analysis, IR and ^{1}H and ^{13}C NMR spectrometry.

Elemental analysis: $C_{11}H_{11}F_1N_2O_2$ ($M = 222.03$); C 59.38 (calc. 59.45); H 4.90 (4.99); N 12.57 (12.61) %. IR (KBr): 3436 ν(NH), 1670 ν(C=O), 1626 ν(C=O–H), 1587 ν(C=N) cm^{-1}. ^{1}H NMR in DMSO, internal TMS, δ (ppm): 2.51 (s, 3 H, free CH_3CO), 2.62 (s, 3 H, CH_3CO in H-bond), 7.45–7.56 (m, 2 H, Ar–H), 7.24–7.28 (m, 2 H, Ar–H), 14.56 (s, 1 H, N–H). ^{13}C NMR in DMSO, internal TMS, δ (ppm): 26.14 (CH_3), 30.05 (CH_3), 111.34 (Ar–H), 113.11 (Ar–H), 115.20 (Ar–H), 117.18 (Ar–H), 133.44 (C=N), 144.22 (Ar–NH–N), 157.23 (Ar–F), 195.45 (C=O), 196.12 (C=O).

2.3. Data collection

Highly redundant single crystal X-ray diffraction data sets were collected at 150 K up to a max 2θ of ca. 58.84° on a Bruccer AXS SMART APEX CCD diffractometer using monochromatic MoKα radiation, λ 0.71073 Å, and a 0.5° separation between frames. Data integration was performed using SAINT program in the diffractometer package [24]. The structures were 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 results were carried out with the computer programs SHELXS-97 and SHELXL-97 and SHELXTL/PC [24–27]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC 716531 Registered in England No. 2155347, Registered Charity No. 800579 for compound HL. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033. E-mail: data_request@ccdc.cam.ac.uk. Web page: http://www.ccdc.cam.ac.uk.

2.4. Potentiometric measurements

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

(i) 5 mL 0.001 M HCl + 5 mL 1 M KCl + 30 mL ethanol;
(ii) 5 mL 0.001 M HCl + 5 mL 1 M KCl + 25 mL ethanol + 5 mL 0.00l M ligand;

For each mixture, the volume was made up to 50 mL with bidistilled water before the titration process. These titrations were also repeated at temperatures of 308 and 318 K.

3. Results and discussion

3.1. Synthesis of HL and spectroscopic study

HL was synthesized via the Japp–Klingemann reaction [22] between 4-fluoroaniline and acetylacetone in an ethanolic solution containing sodium acetate. The ^{1}H NMR spectrum of HL in dimethylsulfoxide-d^6 solution at room temperature shows a signal at δ 14.56 which is assigned to the proton of the protonated nitrogen atom adjacent to the aryl unit (=N–NH– hydrazone form). The two methyl groups of the pentane-2,4-dione moiety yield separate singlets in the proton spectrum. These data support the predominance of the hydrazone form (Scheme 1) with a six-membered H-bonded ring involving one of the carbonyl groups and the protonated nitrogen moiety of the hydrazone structure. The IR spectrum of the isolated compound shows ν(NH) vibration at 3436 cm^{-1}, while ν(C=O), ν(C=O–H) and ν(C=N) are observed at 1670, 1626 and 1587 cm^{-1}, correspondingly, also supporting the existence of the H-bonded hydrazone structure in the solid state.

3.2. X-Ray study

Fig. 1 presents the molecular diagram of HL, while Table 1 provides a survey of crystallographic and refinement data; Table 2 shows bond distances and Table 3 the intra and inter-molecular H-bonding interactions stabilizing the structure (hydrazone form). The structure has been well refined with final indices, [$I > 2\sigma(I)$], of $R1 = 0.0459$ and $wR2 = 0.1435$, Table 1. The relevant characteristics, Fig. 1 are (*i*) the presence of the β-diketohydrazone core, confirming the route followed by the coupling reaction and the tautomerization process [1–5]; (*ii*) the presence of one HN–N=C–C=O heterodienic system with the ideal geometry to form the heteronuclear N(2)–H(2N)···O(2) RAHB, Fig. 1 that may be considered fairly weak, Table 3 (vide infra); and (*iii*) the molecule is basically planar, (Table 2), the main deviations being due to slight rotations around the C(4)–F(1), C(9)–C(10) and C(8)–C(9) bonds (Table 2).

Here, it is possible to see that N–H···O, H-bond found in HL, with N···O distance, 2.5872(12) Å, falls in the middle of the N···O distances range, 2.538–2.597 Å, as observed in previous studies on β-diketo-arylhydrazones [28]. Comparatively, this suggests that the 4-F group, $\sigma_p = 0.06$, located far from the N–H···O center, may be causing an efficient shortening of the N–H distance. The two remaining inter-molecular H-contacts, Table 3, is of C–H···O type. The one involving H(3) defines chains parallel to the *b*-axis, while the other involving H(2), links chains together into a weakly connected 3D network. As it can be expected, the lengths of free C(8)–O(1) 1.2245(15) Å and H-bonded C(10)–O(2) 1.2375(15) Å carbonyl groups are not equal. The six-membered cycle H(2N)–N(2)–N(1)–C(9)–C(10)–O(2) is hexahedra with mutual angles N(2)–N(1)–C(9) and C(9)–C(10)–O(2) equal to 122.01(11)° and 119.87(11)° respectively, but the angles O(2)–H(2N)–N(2) 129.16(12)° and N(1)–C(9)–C(10) 123.50(11)° are not equal with connected H-bond.

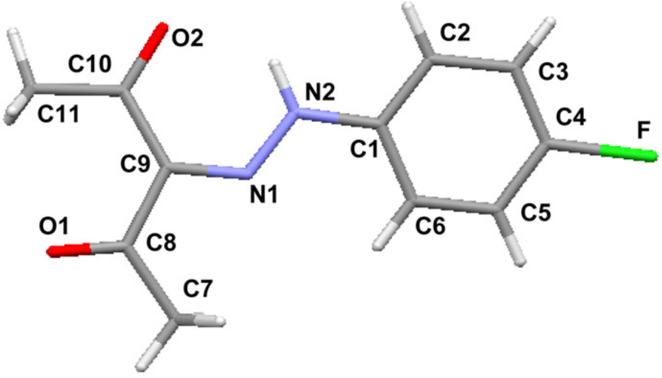


Fig. 1. Molecular structure of HL.

Table 1
Crystal data, experimental parameters and selected details of the refinement calculations of compounds HL.

Empirical formula	$C_{11}H_{11}F_1N_2O_2$
Formula weight	222.03
Crystal system	Monoclinic
Space group	*C*2/*c*
a, Å	18.827(3)
b, Å	12.839(2)
c, Å	26.425(5)
α, deg	90
β, deg	104.834(2)
γ, deg	90
Z	16
Volume, Å^3	6186.1(18)
F(000)	2808
D_c, g cm^{-3}	1.438
μ, mm^{-1}	0.112
Index ranges	$-24 \leq h \leq 25$, $-17 \leq k \leq 17$, $-34 \leq l \leq 27$
Theta range for data collection	1.99–29.42°
Reflections collected	19 416
Independent reflections	7748 [R(int) = 0.0253]
Completeness to theta = 29.42°	90.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9779 and 0.9671
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7748/0/433
Goodness-of-fit on F^2	0.931
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0459$, w$R2 = 0.1435$
R indices (all data)	$R1 = 0.0559$, w$R2 = 0.1548$
Largest diff. peak and hole	0.375 and −0.833 e.Å−3

3.3. Quantum-chemical calculations of the tautomeric forms of HL

It is known that the development of procedures for direct analysis depends on the sensitivity of the method, which is determined by the sensitivity of both the selected procedure and the organic reagent to the analyte. The synthesis of these reagents and the revelation of correlations between their structure, selectivity, and other properties are important problems in using of organic reagents. The selectivity of organic reagents is improved by doubling the number of functional analytical groups, introducing a substituent into the reagent molecule, and modifying with surface-active substances, nonaqueous, aqueous-organic, and organized media [29–32]. We modified organic reagents (using the example of ADB) based on the theory of shifting the tautomeric equilibrium, to improve the sensitivity and selectivity of the reagents. The study of the effect of the structure of the reagents on their analytical characteristics and the properties of the complexes and the use of the effect of the functional groups for developing direct photometric procedures without element preseparation are important analytical problems [5,15]. To determine the reactivity of tautomers of HL and the specific character of deprotonation of their functional groups, we performed quantum-chemical calculations using the Hückel method (MOLCAO)

Table 2
Structural parameters (distances Å, angles°, torsion angles°) of compound HL.

Bond	Length (Å)	Torsion angle	Length (°)
F(1)–C(4)	1.3606(14)	C(9)–N(1)–N(2)–C(1)	179.24(11)
O(1)–C(8)	1.2245(15)	N(1)–N(2)–C(1)–C(6)	8.36(18)
O(2)–C(10)	1.2375(15)	N(1)–N(2)–C(1)–C(2)	−172.24(11)
N(1)–N(2)	1.3040(14)	C(6)–C(1)–C(2)–C(3)	−0.52(19)
N(1)–C(9)	1.3207(15)	N(2)–C(1)–C(2)–C(3)	−179.93(11)
N(2)–C(1)	1.4130(16)	C(1)–C(2)–C(3)–C(4)	−0.31(18)
C(1)–C(6)	1.3878(18)	C(2)–C(3)–C(4)–F(1)	−178.14(11)
C(1)–C(2)	1.3913(17)	C(2)–C(3)–C(4)–C(5)	0.9(2)
C(2)–C(3)	1.3930(17)	F(1)–C(4)–C(5)–C(6)	178.42(11)
C(3)–C(4)	1.3756(19)	C(3)–C(4)–C(5)–C(6)	−0.6(2)
C(4)–C(5)	1.3798(19)	C(2)–C(1)–C(6)–C(5)	0.80(19)
C(5)–C(6)	1.3891(18)	N(2)–C(1)–C(6)–C(5)	−179.81(11)
C(7)–C(8)	1.5020(18)	C(4)–C(5)–C(6)–C(1)	−0.3(2)
C(8)–C(9)	1.4930(16)	N(2)–N(1)–C(9)–C(10)	−1.59(18)
C(9)–C(10)	1.4709(18)	N(2)–N(1)–C(9)–C(8)	−179.29(10)
C(10)–C(11)	1.5001(17)	O(1)–C(8)–C(9)–N(1)	−171.21(11)
Angle	Length (°)	C(7)–C(8)–C(9)–N(1)	8.75(16)
N(2)–N(1)–C(9)	122.01(11)	O(1)–C(8)–C(9)–C(10)	11.10(18)
N(1)–N(2)–C(1)	118.95(10)	C(7)–C(8)–C(9)–C(10)	−168.95(11)
C(6)–C(1)–C(2)	120.93(12)	N(1)–C(9)–C(10)–O(2)	3.46(19)
C(6)–C(1)–N(2)	121.18(11)	C(8)–C(9)–C(10)–O(2)	−179.09(11)
C(2)–C(1)–N(2)	117.89(11)	N(1)–C(9)–C(10)–C(11)	−175.48(11)
C(1)–C(2)–C(3)	119.74(12)	C(8)–C(9)–C(10)–C(11)	1.97(18)
C(4)–C(3)–C(2)	118.18(12)		
F(1)–C(4)–C(3)	118.72(12)		
F(1)–C(4)–C(5)	118.24(12)		
O(1)–C(8)–C(9)	121.14(12)		
O(1)–C(8)–C(7)	120.39(11)		
N(1)–C(9)–C(10)	123.50(11)		
N(1)–C(9)–C(8)	112.65(11)		
O(2)–C(10)–C(9)	119.87(11)		
O(2)–C(10)–C(11)	119.75(12)		

[33–37]. The Hückel method involves a π-electron approximation: the molecular orbitals are written as a linear combination of the atomic orbitals of π-electrons ($2p_z$orbitals of the C, O, and N atoms, etc.):

$$\varphi_i = \sum_{q=1}^{m} C_{q_i}\chi_q(2p_z) \tag{1}$$

where C_{qi} are unknown coefficients determined by solving a system of equations in the simple version of MO LCAO:

$$\sum_q (H_{pq} - ES_{pq})C_{q_i} = 0, \quad p = \overline{1,m} \tag{2}$$

where the following definitions are introduced:

$$H_{pq} = \int \chi_p^* \widehat{H} \chi_q \mathrm{dV}, \tag{3}$$

$$S_{pq} = \int \chi_p^* \chi_q \mathrm{dV}, \tag{4}$$

The H_{pq} values are the matrix elements of the effective Hamiltonian for a π-electron moving in an effective field with no regard to other π-electrons; S_{pq} are the overlap integrals for the atomic orbitals χ_p and χ_q. The system of equations (2) has nontrivial solutions if the determinant of the coefficients C_{qi} is zero:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \cdots H_{1m} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \cdots H_{2m} - ES_{2m} \\ - - - - - - - - & - - - - - - - - - - - - \\ H_{m1} - ES_{m1} & H_{m2} - ES_{m2} \cdots H_{mm} - ES_{mm} \end{vmatrix} = 0 \tag{5}$$

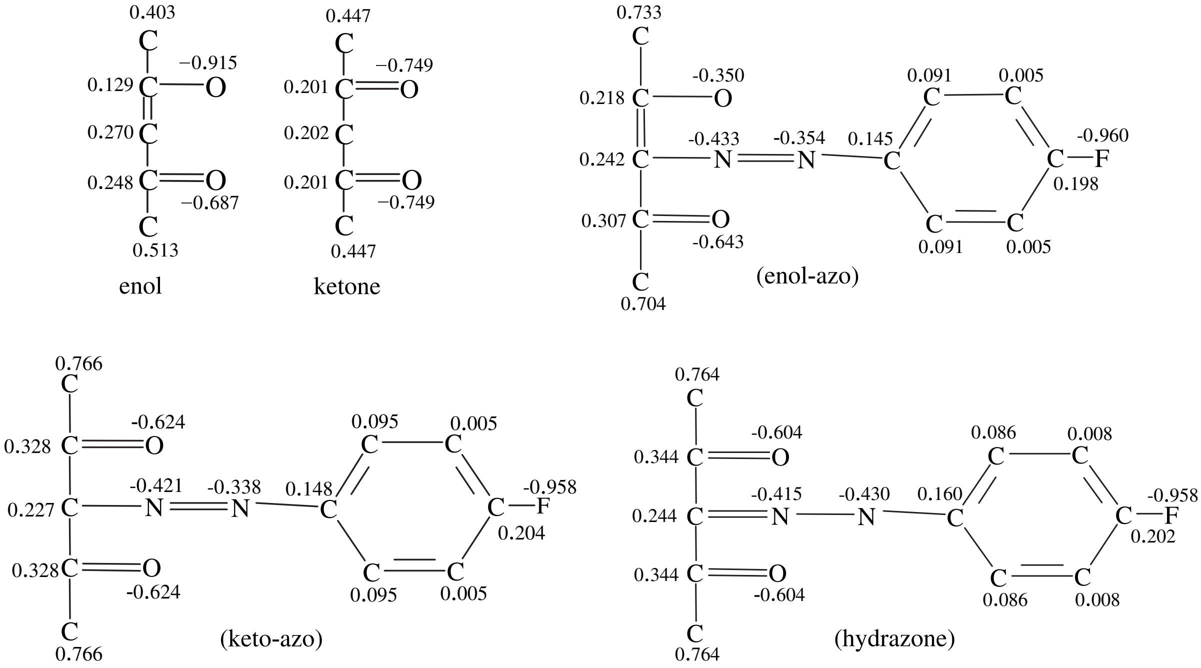
Opening of this determinant leads to an m-order equation with respect to E. Solution of this equation gives m real roots $E_1, E_2, \ldots. E_m$ called the orbital energies of the molecule in the π-electron approximation. Each of these roots E_i is substituted into Eq. (2) to determine the ratios of the coefficients C_{qi} and the numerical values of these coefficients are found from the normalization condition for the molecular orbitals φ_i:

$$\int U_i^* U_i \mathrm{dV} = \int |U_i|^2 \mathrm{dV} = \sum_{q,q^\iota} C_{q_i}^* C_{q_i^\iota} S_{qq^\iota} = 1 \tag{6}$$

Thus, for solution of the system of equations (2) (*i.e.*, for determination of the orbital energies E_i and the corresponding sets of coefficients C_{qi}), one must know numerical H_{pq} and S_{pq} values. However, H_{pq} values cannot be calculated exactly because the explicit expression for the operator $\widehat{H}$ is unknown. In the Hückel method, H_{pq} and S_{pq} are estimated from the Hückel approximations [35].

Table 3
Distances/Å and angles/° of hydrogen bond interactions.

D–H···A	Symmetry	Distances			Angles
		D–H	D···A	H···A	D–H···A
N(2)–H(N2)···O(2)	x, y, z	0.9070(13)	2.5872(12)	1.9160(13)	129.16(12)
C(2)–H(2)···O(2)	$-x, 1-y, -z$	0.9492(14)	3.4474(17)	2.5380(14)	160.10(12)
C(3)–H(3)···O(1)	$x + 0.5, -y + 1.5, z - 0.5$	0.9510(13)	3.3632(15)	2.4464(13)	162.05(11)



Scheme 2. Effective π-electron charges in the tautomeric forms of pentane-2,4-dione and HL.

The numerical values of coefficients C_{qi} allow one to determine the effective charge q_A (au) of an atom A in the molecule according to the MO method by the formula [37]:

$$q_A = n_A^0 - \sum_i n_i \sum_{q\in A} |c_{q_i}|^2 \tag{7}$$

where n_A^0 is the positive charge of the nuclear core of the atom A (in the Hückel method, $n_A^0 = 1$ for all atoms), n_i is the number of electrons in the ith molecular orbital; summation for i is performed over the occupied molecular orbitals. We designed a program for Hückel computations and determined the numerical values of coefficients C_{qi} in Eq. (1). Using formula (7), we calculated the effective atomic charges for molecule HL under study and constructed its molecular diagrams (Scheme 2).

The molecular diagrams show that the introduction of functional groups (=N–NH–Ar) into a molecule of pentane-2,4-dione changes the reaction centers. Because absolute values of the atoms $\overset{-0.430}{\mathrm{N}}$ and $\overset{-0.604}{\mathrm{O}}$ are greater (hydrazone) than $\overset{-0.350}{\mathrm{O}}$ and $\overset{-0.643}{\mathrm{O}}$ (enol-azo). Also we can report that hydrogen migrated from enol-azo ($\overset{-0.350}{\mathrm{O}}$) to hydrazone ($\overset{-0.430}{\mathrm{N}}$).

3.4. Determination of thermodynamic functions of the dissociation processes of reagent

To determine the dissociation constants of the reagents, we used pH-metric titration in aqueous-ethanol media. The ionic strength was maintained constant ($I = 0.1$ M) by adding a calculated amount of KCl. The dissociation constants of HL at different temperatures were calculated by the equation [30]:

$$-\log K_{dis} = \mathrm{pH} + \log[\mathrm{HL}] - \log[\mathrm{L}^-]; \quad -\log K_{dis} = \mathrm{p}K.$$

The dissociation constants of the reagent was p$K = 8.12 \pm 0.01$. As follows from the molecular diagrams of the reagent tautomeric forms, upon potentiometric titration in groups, where a proton is detached (from −OH (enol-azo) and from =N–NH (hydrazone), the absolute effective charges at the atoms are greater $\overset{-0.430}{\mathrm{N}}$ than at the atoms of $\overset{-0.350}{\mathrm{O}}$. Therefore, we believe that the proton is detached from a hydrazone form.

The dissociation constant has been evaluated at 298, 308 and 318 K and it is given in Table 4. The slope of the plot (pK *versus* $1/T$) was utilized to evaluate the enthalpy change (ΔH°) for the dissociation process. From the Gibbs energy change (ΔG°) and (ΔH°) values one can deduce the entropy change (ΔS°) using the well known relationships [33]:

$$\Delta G^\circ = 2.303RT\mathrm{p}K; \quad \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$$

All thermodynamic parameters of the dissociation process of HL are recorded in Table 4.

Inspection of these values reveals that [38–42]: *i* The pK values decrease with increasing temperature revealing that its acidity increases with increasing temperature; *ii* A positive value of ΔH^o indicates that its dissociation is accompanied by adsorption of heat and the process is endothermic; *iii* A large positive value of ΔG^o indicates that the dissociation process is not spontaneous; *iv* A negative value of ΔS^o is obtained due to increased order as a result of solvation processes.

Table 4
Thermodynamic characteristics process dissociation HL in aqueous-ethanol solution.

T, K	pK	ΔG°, kJ mol^{-1}	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}
298 ± 0.5	8.12 ± 0.01	46.33 ± 0.09		−48.72 ± 1.76
308 ± 0.5	7.95 ± 0.03		31.81 ± 1.67	
318 ± 0.5	7.77 ± 0.05			

4. Conclusions

The novel compound, 3-(4-fluorophenylhydrazone)pentane-2,4-dione (HL) dye was synthesized via the Japp–Klingemann reaction between the aromatic diazonium salt 4-fluoroaniline and pentane-2,4-dione in an ethanolic solution containing sodium acetate. The results of MO LCAO quantum-chemical calculations was showed that HL stabilized in hydrazone form (hydrogen migrated from enol-azo to hydrazone) and this form has high reactivity. In addition, the proton is detached from a hydrazone form (dissociation process). The dissociation process is unspontaneous, endothermic and entropically unfavorable, which showed by potentiometric titration. The X-ray diffraction, IR and NMR show that the studied compound presents in the same hydrazone structure in solid phases and in DMSO solution. The presence of one heterodienic system, HN–N=C–C=O, forming a fairly weak heteronuclear RAHB, N–H···O, has been supported by crystallographic data, and length of this distance N···O 2.5872(12) Å falls in the middle of the N···O distances range, 2.538–2.597 Å, as observed in previous studies on β-diketo-arylhydrazones [28]. This might be useful in the design of functional materials attributed to smart hydrogen bonding [6–11], photo-triggered structural switching [43], and targeted metal ion complexes [1–5,13–15].

References

[1] Gadjieva SR, Mahmudov KT. Russian Journal of Inorganic Chemistry 2004;49:1291–4.
[2] Aliyeva RA, Chyragov FM, Mahmudov KT. Russian Journal of Inorganic Chemistry 2004;49:1458–60.
[3] Aliyeva RA, Chyragov FM, Babanly IM, Mahmudov KT, Babanly MB. Russian Journal of Inorganic Chemistry 2004;49:1461–4.
[4] Aliyeva RA, Chyragov FM, Mahmudov KT, Babanly MB. Russian Journal of Inorganic Chemistry 2005;50:131–4.
[5] K.T. Mahmudov. Cand. Sci. (Chem.) Dissertation, Baku, 2006.
[6] Olivieri AC, Wilson RB, Paul IC, Curtin DY. Journal of the American Chemical Society 1989;111:5525–32.
[7] Inabe T. New Journal of Chemistry 1991;15:129–36.
[8] Bertolasi V, Ferretti V, Gilli P, Gilli G, Issa YM, Sherif OE. Journal of the Chemical Society, Perkin Transactions 2 1993;11:2223–8.
[9] Bertolasi V, Nanni L, Gilli G, Ferretti V, Gilli P, Issa YM, et al. New Journal of Chemistry 1994;18:251–61.
[10] Bertolasi V, Gilli P, Ferretti V, Gilli G. Acta Crystallographica Section B 1994;50:617–25.
[11] Krygowski TM, Wozniak K, Anulewics R, Pawlak D, Kolodziejski W, Grech E, et al. Journal of Physical Chemistry A 1997;101:9399–404.
[12] Hassib HB, Issa YM, Mohamed WS. Journal of Thermal Analysis and Calorimetry 2008;92:775–82.
[13] Aliyeva RA, Chyragov FM, Mahmudov KT. Journal of Analytical Chemistry 2005;50:137–40.
[14] Gadjieva SR, Mursalov TM, Mahmudov KT, Pashaev FH, Chyragov FM. Journal of Analytical Chemistry 2006;61:550–5.
[15] Mahmudov KT, Aliyeva RA, Gadjieva SR, Chyragov FM. Journal of Analytical Chemistry 2008;63:435–8.
[16] Chen ZM, Huang FX, Wu YQ, Gu DH, Gan FX. Inorganic Chemistry Communications 2006;9:21–4.
[17] Chen ZM, Wu YQ, Gu DH, Gan FX. Spectrochimica Acta Part A 2007; 68:918–26.
[18] Jeong MJ, Park JH, Lee C, Chang JY. Organic Letters 2006;8:2221–4.
[19] Marten J, Erbe A, Critchley K, Bramble JP, Weber E, Evans SD. Langmuir 2008;24:2479–86.
[20] Shchegolkov EV, Burgart YaV, Khudina OG, Saloutin VI, Chupakhin ON. Russian Chemical Bulletin, International Edition 2004;53:2584–90.
[21] Bertolassi V, Gilli P, Ferretti V, Gilli G. Journal of the American Chemical Society 1991;113:4917–25.
[22] Japp FR, Klingemann F. Liebigs Annalen der Chemie 1888;247:190–225.
[23] Bates RG. Determination of pH: theory and practice. New York: Wiley; 1973.
[24] Brucer. APEX2 & SAINT. Madison, Wisconsin, USA: Brucer, AXS Inc.; 2004.
[25] Sheldrick GM. Acta Crystallographica Section A 1990;46:467–73.
[26] Sheldrick GM. Acta Crystallographica Section A 2008;64:112–22.
[27] Farrugia LJ. Journal of Applied Crystallography 1999;32:837–8.
[28] Marten J, Seichter W, Weber E, Bohme U. Journal of Physical Organic Chemistry 2007;20:716–31.
[29] Christian GD. Analytical chemistry. New York: Phoenix Color Corp; 1994.
[30] Harvey D. Modern analytical chemistry. New York: Wiley; 2000.
[31] Vogel AI. Textbook of macro and semimicro qualitative inorganic analysis. New York: Bungay; 1979.
[32] Chow Chan Chung, editor. Analytical method validation and instrument performance verification. New York: Wiley; 2004.
[33] Atkins P, Paula De J. Physical chemistry, Oxford: Oxford Univ., p. 1150.
[34] Levin Ira N. Physical chemistry. New Delhi: Pashupati Printers Pvt. Ltd.; 2002.
[35] Streitwieser A. Molecular orbital theory for organic chemists. New York: Wiley; 1961.
[36] Khigasi K, Baba H, Rembaum A. Quantum organic chemistry. New York: Wiley; 1965.
[37] Dmitriev IS. Elektron glazami khimika (electron as chemists see it). Leningrad: Khimiya; 1986.
[38] Gadjieva SR, Mursalov TM, Mahmudov KT, Chyragov FM. Russian Journal of Coordination Chemistry 2006;32:304–8.
[39] Gadjieva SR, Pashaev FH, Chyragov FM, Gasanov AG, Mahmudov KT. Russian Journal of Inorganic Chemistry 2007;52:640–4.
[40] Gadjieva SR, Mahmudov KT, Pashaev FH, Gasanov AG, Chyragov FM. Russian Journal of Coordination Chemistry 2008;34:534–8.
[41] Aliyeva RA, Pashaev FH, Gasanov AG, Mahmudov KT. Russian Journal of Coordination Chemistry 2009;35:241–6.
[42] Aliyeva RA, Pashaev FH, Gasanov AG, Mahmudov KT. Russian Journal of Inorganic Chemistry 2009;54:1407–11.
[43] McVie J, Alastair D, Sinclair RS, Truscott RG. Journal of the Chemical Society, Perkin Transactions 2 1980;2:286–90.