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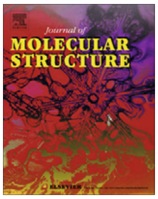

Structural and thermal properties of three cyano-substituted azoderivatives of β-diketones

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ABSTRACT

3-(2-Cyanophenylhydrazo)pentane-2,4-dione (HL^1), 3-(4-cyanophenylhydrazo)pentane-2,4-dione (HL^2) and 1-ethoxy-2-(4-cyanophenylhydrazo)butane-1,3-dione (HL^3), and the Pd(II) complex $[Pd(L^2)_2]$ were synthesized and characterized by IR, ^1H and ^{13}C NMR spectroscopies, ESI-MS, elemental and X-ray diffraction analyses (for HL^1). HL^3 derived from the unsymmetric 1-ethoxybutane-1,3-dione exists in solution as a mixture of the enol-azo and hydrazo tautomeric forms and a decrease of the solvent polarity shifts the tautomeric balance to the hydrazo form, while for HL^1 and HL^2, derived from the symmetric pentane-2,4-dione, the hydrazo form is dominating under all the studied conditions. HL^{1-3} and $[Pd(L^2)_2]$ show a high thermal stability with well-defined peaks of phase transition at 438 (HL^1), 462 (HL^2), 392 (HL^3) and 404 K ($[Pd(L^2)_2]$).

1. Introduction

It is well known that many azocompounds and β-diketones, under certain conditions, tend to perform tautomeric transformations. Thus, diazocompounds can exist as a mixture of azo- and hydrazone tautomeric forms [1], while β-diketones easily switch to the enol form [2,3]. These tautomeric equilibria are important from theoretical and practical aspects: about 92% of azo dyes published in Colour Index possess this tautomery [4] which affects their tone, photostability, etc. On the other hand, tautomeric equilibria of β-diketones also influence their spectral properties, reactivity, coordination ability, etc. [5,6]. However, there is a lack of experimental data on the tautomerism of the pigments combining both of the those functionalities, i.e. azoderivatives of β-diketones (ADB).

Moreover, this tautomeric balance can play an important role for the application of ADB as bistate molecular switches [8–10] or regulation of the ionophore selectivity in analytical chemistry [11,12]. Within this view, special attention should be paid to the nature of the strong intramolecular O···H—N hydrogen bond and its influence on the enol-azo ⇌ hydrazo transformation [7]. Additionally, the synthetic potential of ADB for coordination chemistry was underestimated, notwithstanding their potentially rich chelating ability [7,13–18].

On the other hand, the cyano group has a well-recognized chemical versatility [19]. In particular, in organic chemistry the addition of nucleophiles or electrophiles and the asymmetric dipolar cycloaddition to the C≡N triple bond offer attractive routes for the creation of C—C, C—N, C—O and C—S bonds. Therefore, cyano-substituted ADB are expected to be good candidates towards the development of a rich organic chemistry.

Thus, taking in mind all the above mentioned considerations, the main aims of the current work are as follows: (i) to synthesize new ADB with cyano substituents in the aromatic part of the molecule (Scheme 1) and prove their coordination ability by synthesizing a new Pd(II)-ADB complex; (ii) to study the influence of the introduced substituents on the tautomeric balance and thermal properties of the synthesized materials.

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^1H, $^{13}C\{^1H\}$) and 2D (^1H, ^1H-COSY, ^1H, ^{13}C-HMQC, ^1H, ^{13}C-HSQC and ^1H, ^{13}C-HMBC) NMR spectra were recorded on Bruker Avance II + 300 and 400 MHz (UltraShield™ Magnet) spectrometers at ambient temperature. Chemical shifts (δ) are relative to internal TMS. Carbon, hydrogen, and nitrogen elemental

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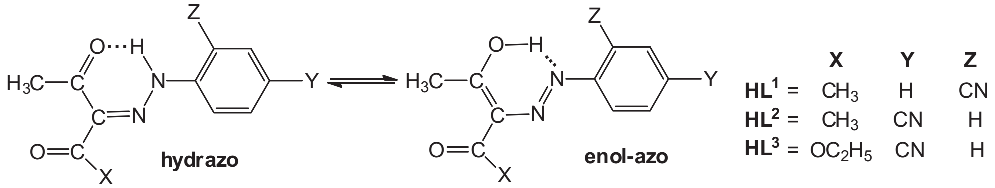

Scheme 1. ADB studied in this work.

analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Electrospray mass spectra were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m*/*z* 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V). Thermal properties were analyzed with a Perkin–Elmer Instruction system (STA6000) at a heating rate of 10 K min^{-1} under a dinitrogen atmosphere.

2.2. Synthesis of HL^{1-3}

HL^{1-3} were synthesized according to the Japp–Klingemann reaction [20–22] between the diazonium salts of 2- or 4-cyanoaniline and pentane-2,4-dione or 1-ethoxybutane-1,3-dione.

2.2.1. Diazotization

0.0250 mol of 2- or 4-cyanoaniline were dissolved in 50.00 mL of water upon addition of 1.000 g of crystalline NaOH. The solution was cooled in an ice bath to 0 °C, and 0.025 mol of $NaNO_2$ were added with subsequent addition of 5.00 mL HCl in portions of 0.20 mL for 1 h, under vigorous stirring. During the reaction the temperature of the mixture must not exceed +5 °C.

2.2.2. Azocoupling

1.000 g of NaOH was added to a mixture of 0.0250 mol of pentane-2,4-dione or 1-ethoxybutane-1,3-dione with 50.00 mL of water. The solution was cooled in an ice bath, and a suspension of 2- or 4-cyanoaniline diazonium (prepared according to the procedure of Section 2.2.1) was added in two equal portions, under vigorous stirring for 1 h. On the next day, the formed precipitate of HL^{1-3} was filtered off, washed with water, recrystallized from ethanol and dried in air. The characterization of HL^{1-3} was undertaken by elemental analysis, ESI-MS, IR, ^1H and ^{13}C NMR spectroscopies and, in the case of HL^1, also by single-crystal X-ray analysis.

HL^1: yield 81% (based on pentane-2,4-dione), yellow powder soluble in DMSO, methanol, ethanol, chloroform and acetone, and insoluble in water. Elemental analysis: $C_{12}H_{11}N_3O_2$ (*M* = 229); C 62.72 (calc. 62.87); H 4.85 (4.84); N 18.76 (18.33)%. IR (KBr): 3437 (NH), 2220 (C≡N), 1677 (C=O), 1639 (C=O···H), 1601 (C=N) cm^{-1}. ESI-MS: *m*/*z*: 230 $[M + H]^+$. ^1H NMR in DMSO-d_6, δ (ppm): 2.43 (s, 3H, free CH_3CO), 2.50 (s, 3H, CH_3CO in H-bond, overlapping with DMSO-d_6), 7.28–7.85 (4H, Ar–H), 14.35 (s, 1H, N—H). ^{13}C-{^1H} NMR in DMSO-d_6, δ (ppm): 26.60 (CH_3), 31.31 (CH_3), 99.01 (CN), 116.00 (Ar–CN), 116.13 (Ar–H), 125.08 (Ar–H), 133.48 (Ar–H), 134.98 (Ar–H), 135.19 (C=N), 143.94 (Ar–NH–N), 196.48 (C=O), 197.97 (C=O).

HL^2: yield 92% (based on pentane-2,4-dione), yellow powder soluble in DMSO, methanol, ethanol, chloroform and acetone, and insoluble in water. Elemental analysis: $C_{12}H_{11}N_3O_2$ (*M* = 229); C 62.63 (calc. 62.87); H 4.89 (4.84); N 18.65 (18.33)%. IR (KBr): 3447 (NH), 2220 (C≡N), 1672 (C=O), 1637 (C=O···H), 1607 (C=N) cm^{-1}. ESI-MS: *m*/*z*: 230 $[M + H]^+$. ^1H NMR in DMSO-d_6, δ (ppm): 2.42 (s, 3H, free CH_3CO), 2.47 (s, 3H, CH_3CO in H-bond), 7.68–7.86 (4H, Ar–H), 13.39 (s, 1H, N—H). ^{13}C-{^1H} NMR in DMSO-d_6, δ (ppm): 26.24 (CH_3), 31.23 (CH_3), 106.11 (CN), 116.42 (2Ar–H), 118.95 (Ar–CN), 133.82 (2Ar–H), 135.76 (C=N), 145.83 (Ar–NH–N), 196.44 (C=O), 197.57 (C=O). ^1H NMR in $CDCl_3$, δ (ppm): 2.50 (s, 3H, free CH_3CO), 2.61 (s, 3H, CH_3CO in H-bond), 7.50–7.70 (4H, Ar–H), 14.49 (s, 1H, N—H). ^{13}C-{^1H} NMR in $CDCl_3$, δ (ppm): 26.76 (CH_3), 31.94 (CH_3), 108.45 (CN), 116.41 (2Ar–H), 118.70 (Ar–CN), 134.00 (2Ar–H), 134.73 (C=N), 145.11 (Ar–NH–N), 196.93 (C=O), 198.76 (C=O).

HL^3: yield, 70% (based on 1-ethoxybutane-1,3-dione), yellow powder, soluble in methanol, ethanol, acetone, dichloromethane, chloroform, tetrahydrofuran and insoluble in water. Elemental analysis: $C_{13}H_{13}N_3O_3$ (*M* = 259); C 60.58 (calc. 60.22); H 5.10 (5.05); N 16.25 (16.21)%. IR (KBr): 3448 (NH), 2220 (C≡N), 1690 (C=O), 1660 (C=O···H), 1608 (C=N) cm^{-1}. ESI-MS: *m*/*z*: 260 $[M+H]^+$. ^1H NMR of a mixture of tautomeric hydrazone and enol-azo forms in DMSO-d_6, δ (ppm). Hydrazo, 1.36–1.42 (s, 3H, CH_3CH_2O), 2.59 (s, 3H, CH_3CO in H-bond), 4.33–4.45 (s, 2H, CH_2), 7.61–7.89 (4H, Ar–H), 13.82 (s, 1H, NH). Enol-azo, 1.36–1.42 (s, 3H, CH_3CH_2O), 2.60 (s, 3H, CH_3COH in H-bond), 4.33–4.45 (s, 2H, CH_2), 7.61–7.89 (4H, Ar–H), 11.67 (s, 1H, HO-enol). ^{13}C{^1H} NMR in DMSO-d_6, δ (ppm): Hydrazo, 13.83 (CH_3CH_2O), 30.53 (CH_3CO), 60.80 (CH_2), 104.72 (CN), 114.98 (2Ar–H), 116.32 (Ar–CN), 119.14 (2Ar–H), 133.78 (C=N), 145.75 (Ar–NH–N), 162.18 (C=O), 193.89 (C=O). Enol-azo, 14.10 (CH_3CH_2O), 30.66 (CH_3CO), 61.48 (CH_2), 106.25 (CN), 115.32 (2Ar–H), 118.91 (Ar–CN), 128.31 (2Ar–H), 134.18 (C=N), 146.30 (Ar–NH–N), 163.67 (C—O), 196.26 (C=O). ^1H NMR of a mixture of tautomeric hydrazone and enol-azo forms in $CDCl_3$, δ (ppm). Hydrazo, 1.34–1.40 (s, 3H, CH_3CH_2O), 2.47 (s, 3H, CH_3CO in H-bond), 4.29–4.39 (s, 2H, CH_2), 7.35–7.65 (4H, Ar–H), 14.46 (s, 1H, NH). Enol-azo, 1.34–1.40 (s, 3H, CH_3CH_2O), 2.57 (s, 3H, CH_3COH in H-bond), 4.29–4.39 (s, 2H, CH_2), 7.35–7.65 (4H, Ar–H), 12.59 (s, 1H, HO-enol). ^{13}C{^1H} NMR in $CDCl_3$, δ (ppm): Hydrazo, 14.07 (CH_3CH_2O), 26.91 (CH_3CO), 61.43 (CH_2), 107.33 (CN), 115.61 (2Ar–H), 118.78 (Ar–CN), 129.75 (2Ar–H), 133.89 (C=N), 145.06 (Ar–NH–N), 163.24 (C=O), 194.12 (C=O). Enol-azo, 14.31 (CH_3CH_2O), 30.89 (CH_3CO), 61.96 (CH_2), 108.07 (CN), 116.41 (2Ar–H), 128.07 (Ar–CN), 133.76 (2Ar–H), 133.89 (C=N), 145.22 (Ar–NH–N), 164.33 (C—O), 197.57 (C=O).

2.3. Synthesis of $[Pd(L^2)_2]$

229 mg of HL^2 were dissolved in 50.00 mL of chloroform and 112 mg of $Pd(CH_3COO)_2$ were added, with stirring. The mixture was refluxed for 5 h and left standing for slow solvent evaporation. Orange microcrystals started to form in the reaction mixture after 1 d at room temperature, whereafter they were filtered off and dried in air. Yield, 47% (based on Pd). Elemental analysis: $C_{24}H_{20}N_6O_4Pd$ (*M* = 562.87); C 51.10 (calc. 51.21); H 3.45 (3.58); N 14.86 (14.93)%. IR (KBr): 2229 (C≡N), 1670 (C=O), 1638 (C=O), 1608 (C=N) cm^{-1}. ESI-MS: *m*/*z*: 596 $[M + CH_3OH]$. ^1H NMR in $CDCl_3$, δ (ppm): 2.28 (s, 6H, CH_3CO), 2.42 (s, 6H, CH_3CO), 7.59–7.73 (8H, Ar–H). ^{13}C-{^1H} NMR in $CDCl_3$, δ (ppm): 28.66 (2CH_3), 29.85 (2CH_3), 111.31 (2CN), 118.80 (2Ar–CN), 124.92

(2Ar–H), 132.48 (2Ar–H), 135.45 (2C=N), 152.84 (2Ar–NPd–N), 176.50 (2C=O → Pd), 197.05 (2C=O).

2.4. X-ray structure determination

Crystals of HL^1 suitable for X-ray structural analysis were grown by slow evaporation at room temperature of its chloroform solution. The data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo Kα radiation. Data were collected at 150 K using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [23] on all the observed reflections. Absorption corrections were applied using SADABS [23]. Structures were solved by direct methods using the SHELXS-97 package [24] and refined with SHELXL-97 [24] with the WinGX System-Version 1.80.03. [25] The crystallographic details are listed in Table 1. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC (805136) HL^1. 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.

3. Results and discussion

3.1. Spectroscopic and crystallographic investigation of HL$^{1-3}$

The new cyano-substituted azoderivatives of β-diketones HL$^{1-3}$ were synthesized via the Japp–Klingemann reaction [20–22] between the respective cyano-substituted aromatic diazonium salts and pentane-2,4-dione or 1-ethoxybutane-1,3-dione in water solution containing sodium hydroxide. IR spectra of the isolated compounds show ν(NH) vibrations at 3437–3448 cm^{-1}, while ν(C=O), ν(C=O···H), ν(C=N) and ν(C≡N) are observed at 1672–1690, 1637–1660, 1601–1608 and 2220 cm^{-1}, correspondingly, what is related to the presence of the H-bonded hydrazone structure in the solid state (as confirmed by an X-ray diffraction analysis – see below). This conclusion is supported by ^{1}H and ^{13}C{^{1}H} NMR data, e.g. the ^{1}H NMR spectra of HL$^{1-3}$ show a signal at δ 13.4–14.5 which can be assigned to the proton of the NH moiety adjacent to the aryl unit (=N—NH— hydrazo, Scheme 1) [7–18].

Table 1
Crystallographic data and structure refinement details for HL^1.

Empirical formula	$C_{12}H_{11}N_3O_2$
fw	229.24
λ (Å)	0.71069
Cryst syst	Monoclinic
Space group	P21 (No. 4)
a (Å)	8.3358(7)
b (Å)	6.6477(6)
c (Å)	10.2664(9)
β (deg)	92.893(2)
V (Å^3)	568.18(9)
Z	2
ρ_{calc} (Mg/m^3)	1.340
μ (Mo Kα) (mm^{-1})	0.095
No. reflns. read	2866
No. reflns. unique	1356
No. reflns. obs.	1220
GOOF	1.080
R_{int}	0.0181
$R1^a$ ($I \geq 2\sigma$)	0.0325
$wR2^b$ ($I \geq 2\sigma$)	0.0950

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $$wR2 = \left[\sum\left[w\left(F_o^2 - F_c^2\right)^2\right]\Big/\sum\left[w\left(F_o^2\right)^2\right]\right]^{1/2}.$$

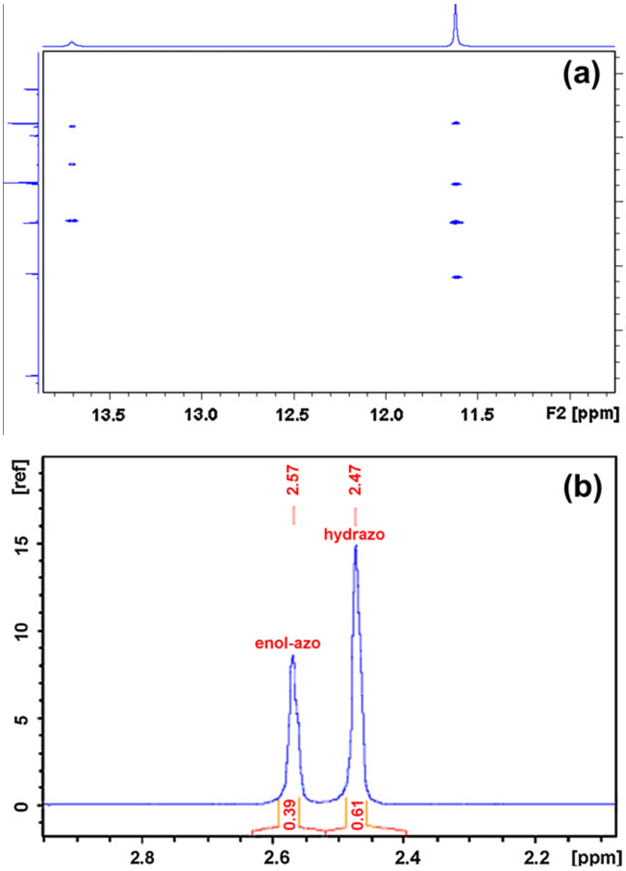

Fig. 1. ^{1}H,^{13}C-HMQC/^{1}H NMR spectra in DMSO-d_6 (20 °C) (a), and determination of tautomeric ratio of HL^3 in $CDCl_3$ by ^{1}H NMR (b).

In addition, the enol-azo form was also detected in solution for HL^3. In fact, its ^{1}H NMR spectra in DMSO-d_6, or $CDCl_3$ show the presence of a mixture of two tautomeric forms. In order to assign the spectra and determine their ratio, two-dimensional ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-HMQC/^{1}H, ^{13}C-HSQC, ^{1}H, ^{13}C-HMBC and ^{1}H NMR experiments in both DMSO-d_6 and $CDCl_3$ solvents were performed. The short-range correlations (^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HMQC/^{1}H, ^{13}C-HSQC) (Fig. 1a) were useful to assign the signals of the ester groups of HL^3, while the long-range shift correlation experiments

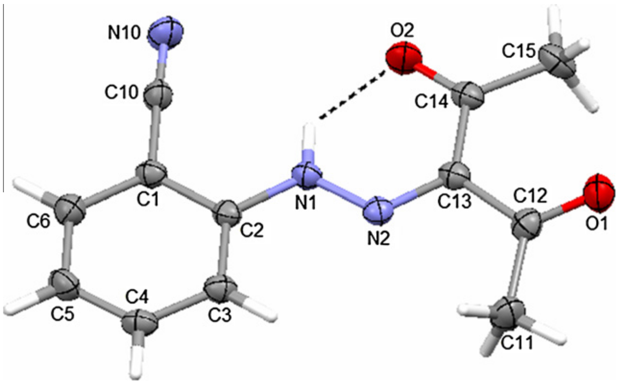

Fig. 2. Thermal ellipsoid plot, drawn at the 50% probability level, with atomic numbering scheme for HL^1. Selected bond lengths (Å) and angles (°): O1—C12 1.212(3); O2—C14 1.231(3); N1—N2 1.311(3); N1—C2 1.394(3); N2—C13 1.309(3); C1—C10—N10 178.3(3); C2—N1—N2 119.36(16); N1—N2—C13 121.37(17); O2—C14—C13 119.1(2); C13—C12—O1 121.74(19). Intramolecular hydrogen bond (dotted line), D—H···A [d(D···A) Å; ∠(DHA)°]: N1—H1···O2 [2.567(2) Å, 132.00°].

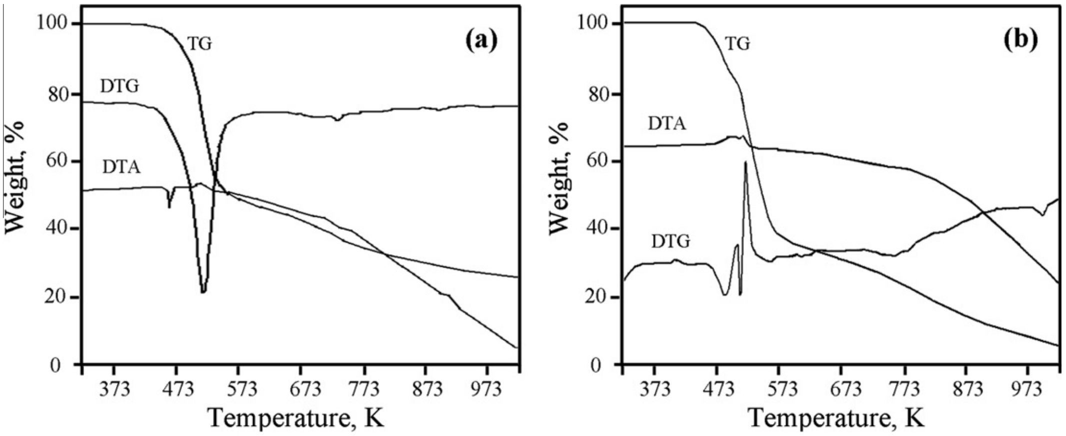

Fig. 3. Thermal decomposition of HL^2 (a) and $[Pd(L^2)_2]$ (b).

Table 2
Parameters of thermal decomposition of HL^{1-3} and $[Pd(L^2)_2]$.

Compound	Temperature of phase transition (K)	Temperature of decomposition (maximum) (K)	Weight loss, %	A (s^{-1})	E_a (kJ mol^{-1})	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})	$\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}G$ (kJ mol^{-1})
HL^1	438	438–601 (525)	39.02	28.4	47.3	−229	42.9	163
HL^2	462	462–612 (513)	50.18	8.3	40.8	−248	36.6	164
HL^3	392	418–601 (488)	64.07	49.3	48.2	−229	45.3	157
$[Pd(L^2)_2]$	404	455–493 (484)	9.72	2.4×10^5	79.2	−146	75.2	146
		498–540 (506)	18.00	3.7	36.6	−238	32.4	153

via $^2J_{H,C}$ and $^3J_{H,C}$ coupling (^1H, ^{13}C-HMBC) allowed the discrimination of the carbon signals of the carbonyl groups from the imine moieties for each tautomer. These data indicate that a decrease of the solvent polarity shifts the tautomeric balance towards the hydrazo form (Fig. 1b and Scheme 1). Thus, the equilibrium between the enol-azo and hydrazo forms depends on the polarity of the solvent used (enol-azo 89%, hydrazo 11% in DMSO-d_6; enol-azo 39%, hydrazo 61% in $CDCl_3$). It is worth mentioning that the obtained data may be useful for some analytical applications [11,12] which require the knowledge of the distribution of the tautomers in a particular solvent.

The single crystal X-ray diffraction study of HL^1 (Fig. 2) indicates that the compound crystallizes in the hydrazo form (Scheme 1). The C13—N2 distance has a typical double bond length [1.309(3) Å]. The two carbonyl bond distances are slightly different [1.231(3) and 1.212(3) Å], the longer one concerning the intramolecular hydrogen bonding involving its oxygen atom (see Fig. 2 and its footnote), where the donor(N)···acceptor(O) distance of 2.567(2) Å falls within the range (2.50–2.62 Å) observed for other studied ADBs [7,8,14,22,26].

Thus, based on IR, NMR and X-ray structural analyses, we can conclude that the studied cyano-substituted ADB derived from *symmetric* β-diketones exist in solution and in solid phase mainly in the hydrazo form, while that derived from the *unsymmetric* β-diketone is present in solution as a mixture of hydrazo and enol-azo forms.

3.2. Synthesis and characterization of $[Pd(L^2)_2]$

The palladium(II) complex $[Pd(L^2)_2]$ was prepared in 47% yield upon refluxing, for 5 h, a chloroform solution of HL^2 and palladium(II) acetate. The IR spectrum of this complex displays $\nu(C{\equiv}N)$, $\nu(C{=}O)$ at 2229, 1670 and 1638 cm^{-1}, values shifted in relation to those (2220, 1672 and 1637 cm^{-1}) of the free ligand. ν(NH) was not observed in the complex, confirming the deprotonation of the hydrazone group. Moreover, in the ^1H NMR spectrum of $[Pd(L^2)_2]$, N—H protons were also not detected, while the peaks of methyl protons are shifted to 2.28 and 2.42 ppm (compare with values for free HL^1 – 2.42 and 2.47 ppm, respectively). In the ^{13}C-{^1H} NMR spectrum, the resonances of the coordinated C=O groups (176.5 ppm) and those of the uncoordinated ones (197.0 ppm) are also shifted in comparison to those of free HL^1 (196.9 and 198.8 ppm, correspondingly). Elemental analysis and ESI-MS in methanol (peak at m/z 596 $[M + CH_3OH]^+$) support the proposed formulation as a diligand monomer, $[Pd(L^2)_2]$, as previously reported [27] for other ADB-Pd(II) complexes. Unfortunately, all the attempts to get crystals suitable for X-ray analysis have failed.

3.3. Thermal behaviour of HL^{1-3} and $[Pd(L^2)_2]$

In order to get more information about their thermal stability, HL^{1-3} and $[Pd(L^2)_2]$ were studied by thermogravimetric (DTA–TG) techniques in the 303–1073 K temperature range, under dinitrogen atmosphere. The thermodynamic parameters of decomposition, namely the activation energy (E_a), enthalpy ($\Delta^{\ddagger}H$), entropy ($\Delta^{\ddagger}S$) and free energy of decomposition ($\Delta^{\ddagger}G$), as well as the pre-exponential factor (A), were evaluated graphically using the Coats–Redfern relationship [28–30].

The thermograms of HL^{1-3} and $[Pd(L^2)_2]$ exhibit a single peak of phase transition at 438 (HL^1), 462 (HL^2), 392 (HL^3) and 404 K ($[Pd(L^2)_2]$) (Fig. 3). TG and DTG curves exhibit a sharp mass loss, obviously related to decomposition of the compounds. The kinetic parameters of this process were evaluated (Table 2) showing that activation energies of decomposition (and hence the rate of decomposition) follow the sequence: $HL^3 > HL^1 > HL^2$. The negative entropy of activation suggests that decomposition is slow [30]. The values of the pre-exponential factor in the Arrhenius equation (A) are within the 3.7–2.4×10^5 s^{-1} range, thus not allowing to establish the molecularity of the reaction [26–28]. The sharp thermal decomposition threshold and the high mass loss rate of HL^{1-3} make them good candidates for optical recording media [31,32] or optical sensors [33], although experiments with polarized light indicate that they do not possess liquid crystal properties under the studied conditions, in contrast to related compounds [34].

4. Conclusions

Three new cyano-substituted ADB, HL^{1-3}, were synthesized and characterized by IR and multi-nuclear NMR spectroscopies, ESI-MS, elemental and X-ray diffraction analysis (for HL^1). The derivative of the unsymmetric β-diketone, HL^3, exists in solution as a mixture of the enol-azo and hydrazo tautomeric forms, and a decrease of the solvent polarity shifts the tautomeric balance to the hydrazo form. The formation of the heterodienic system, HN—N=C—C=O, and the fairly weak heteronuclear resonance-assisted hydrogen bond, N—H···O, is supported by the analytical data. These structural properties are important for the design of functional materials related to smart hydrogen bonding [8–10] or the photo-triggered structural switching [35]. On the other hand, the thermal stability, high weight loss rate and sharp thermal decomposition threshold of the studied ADB make them good potential candidates for high-density optical recording media [31,32].

The coordination ability of this type of ADB was also demonstrated by the synthesis of a Pd(II) complex, and the extension of this study to the preparation of metal complexes with potential interest on biological and catalytical applications deserves to be pursued.

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