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Ground- and excited-state stability of the conformers of 3,5-dinitrocatechol and its complexes with W(VI) and V(V): combined theoretical and experimental study

V. B. Delchev · K. B. Gavazov · I. G. Shterev

Abstract We performed a theoretical and experimental study of the (photo)stability of 3,5-dinitrocatechol (DNC) and its complexes with W(VI) and V(V). The investigation showed that irradiation of DNC is accompanied by a parallel proton migration from the hydroxy group to the neighboring NO_2 group, which results in a large Stokes shift of the absorption and emission bands. It was found that W(VI) forms a more stable 1:2 complex than V(V). The complex is stable even under UV irradiation. The most stable $W^{VI}(DNC)_2$ conformer is comprised of two mutually perpendicular DNC molecules as ligands.

Keywords BLYP calculations · CC2 calculations · Complexes · 3,5-Dinitrocatechol · Photostability

Introduction

Nitrocatechols (NCs) are important compounds that have found applications in various fields [1]. NCs form complexes with a great number of metal ions, and some of the more significant complexes have been isolated in solid state and characterized by different techniques. Some NCs [e.g., 3,5-dinitrobenzene-1,2-diol (3,5-dinitrocatechol; DNC)] exhibit biological activity [2–6]. Other representatives of the group of NCs have been detected in natural [7, 8] or industrial environments, or are products of biological [9–12] or non-biological [13–15] degradation processes.

Since many complexes involving nitrocatecholic ligands display intensive coloration under defined reaction conditions, they can be applied to the development of methodologies for spectrophotometric determination of the metal ions under consideration [16–24]. From this point of view, the most popular NCs are 4-nitrobenzene-1,2-diol (4-NC) and DNC, both of which have been included in the IUPAC list of the most important organic analytical reagents [25].

Recently, 4-NC [26] and its Al(III) complexes [27] have been investigated by time-dependent density functional theory (TD-DFT). However, to the best of our knowledge, there are no similar theoretical investigations concerning DNC, despite the experimental information that is available.

The purpose of the current research was to shed light on the photostability of DNC and some of its metal complexes. Tungsten (VI) and vanadium (V) were selected to form complexes with DNC since there is much speculation (predominantly experimental) about the structure and stability of these complexes [16–18]. The research involved a combined theoretical and experimental investigation aimed at filling the existing gap concerning the electronic structure of the aforementioned complexes and ligand. The influence of the solvent (aqueous media) was taken into account by a study of the electronic structure of several H-bonded complexes of DNC with one molecule of water.

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Computational methods

The OH conformers of interest were generated through C–O rotation of the hydroxyl groups of the DNC. The most stable structures, lying in minima on the potential energy surface (PES), were chosen for further study of their electron and geometry structure, and possibility of forming complexes with

V(V) and W(VI). The idea of possible stable conformers of DNC was also taken from the work of Cornard et al. [26], who have studied the ground states of the conformers of 4-nitrocatechol at a lower theoretical level.

The ground-state equilibrium geometries of three conformers of DNC and their H-bonded complexes with one H-bonded water molecule were calculated at the CC2 level of theory. Further, with the optimized geometries, we computed the lowest ten vertical excitation energies of each system. These were compared with experimental UV-absorption maxima. The excited states were assigned by careful analysis of all molecular orbitals involved in the electron transitions. The accuracy of the coupled-cluster methods is discussed in detail in the review of Hobza et al. [28]. As demonstrated, the coupled-cluster methods including double excitations are a good compromise to study molecules of "moderate size" like DNC.

The investigation is limited to three conformers of DNC. These are the planar OH-conformers that form intramolecular H-bonds. Interest in these isomers is provoked by the possibility of them to form octahedral complexes with V(V) and W(VI), in which the planarity of the molecules is maintained.

The $^1\pi\pi^*$ excited-state equilibrium geometries of the conformers (which form intramolecular H-bonds) were optimized at the same level as the ground states. These structures were used to calculate the emission energies of the systems in order to estimate the Stokes shifts in the fluorescence spectra as compared to the UV–vis.

Thermal conformation reactions between conformers were investigated at the MP2 level of theory. Transition states were found as first order saddle points on the S_0-PESs. Each transition state has one imaginary vibration frequency, whose form shows exactly the motion of the proton along the reaction coordinate. As is known [28], the MP2 method takes into account the same energy corrections as the CC2 method (the energies of the two methods can be compared directly) but it saves considerable time. The MP2 method is applied to the study of mechanisms of thermal reactions only, which was not the main purpose of this research.

Excited-state reaction paths were obtained through linear interpolation in internal coordinates between the ground-state and $^1\pi\pi^*$ excited-state equilibrium geometries of conformers B and C. We looked for possible internal conversion channels leading to stabilization of the conformer molecules. The excited-state reaction paths were obtained at the CC2 level.

The structures of four conformers of V(V) and W(VI) complexes with DNC as a ligand were optimized at the BLYP/CEP-31G level in order to analyze their geometries and electron structures by means of the GAUSSIAN 03 package [29]. The BLYP functional and the CEP-31G basis set were used for the complexes because of the limitations arising from the metal atoms. As discussed [28], DFT methods are computationally very efficient, and a study of these complexes

(separately from the DNC conformers) is the second stage of this research. The GAUSSIAN program was used for the MP2 calculations of the transition states of the thermal conformations. All CC2-calculations of DNC ligands were performed with the TURBOMOLE [30] program package. The augmented aug-cc-pVDZ basis functions for all atoms were applied.

Experimental methods

DNC was obtained from Sigma-Aldrich Chemie (Schnelldorf, Germany) and used without additional purification. The other reagents were NH_4VO_3 (Laborchemie Apolda, Apolda, Germany, puriss. p.a.) and $Na_2WO_4 \cdot 2H_2O$ (Lachema, Brno, Czech Republic, p.a.). The aqueous solutions of these reagents (2×10^{-4} mol dm^{-3}) were prepared with bidistilled water.

The DNC-V(V) and DNC-W(VI) complexes were prepared by mixing solutions of DNC and the metal ion in a molar ratio 1:1. A few drops of hydrochloric acid solution were added to adjust pH to 2.2±0.2 (Hanna HI 83140 pH-meter, Hanna Instruments, Padova, Italy). UV–vis absorption spectra of DNC in different solvents were registered on a Perkin Elmer Lambda 9 UV–vis-NIR spectrophotometer (Perkin Elmer, Waltham, MA), while the fluorescence spectra were registered on a LS55 Perkin Elmer spectrophotometer, λ_{exc}=380 nm (open filter) with maximal slits.

The irradiation of the samples (DNC, DNC-V(V) and DNC-W(V) aqueous solutions) were performed with a medium pressure mercury UV lamp, 125 W (Photochemical reactor RQ125), producing radiation predominantly in the interval 365–366 nm. At different irradiation times (10, 20, 30, 40, 50 and 60 min), samples of the solutions were taken (~ 3 ml) to record the UV–vis spectra in order to follow the kinetics of the processes and the photostability of the compounds under consideration.

Results and discussion

Ground- and excited-state equilibrium geometries

The ground-state equilibrium geometries of the three DNC conformers found at the CC2/aug-cc-pVDZ level are illustrated in Fig. 1. With respect to the hydroxyl groups and the aromatic ring, the conformers are planar. It is interesting to mention that H-bonding between the OH group at the *ortho*-position with the NO_2 group at the *meta*-position (in conformers B and C) leads to the conjugation of the latter group with the rest of the aromatic system. The lack of such H-bonding in conformer A provokes a deviation of the NO_2 group out of the molecular plane. This distortion leads to a slight elongation of the C(4)–N(9) bond of the conformers.
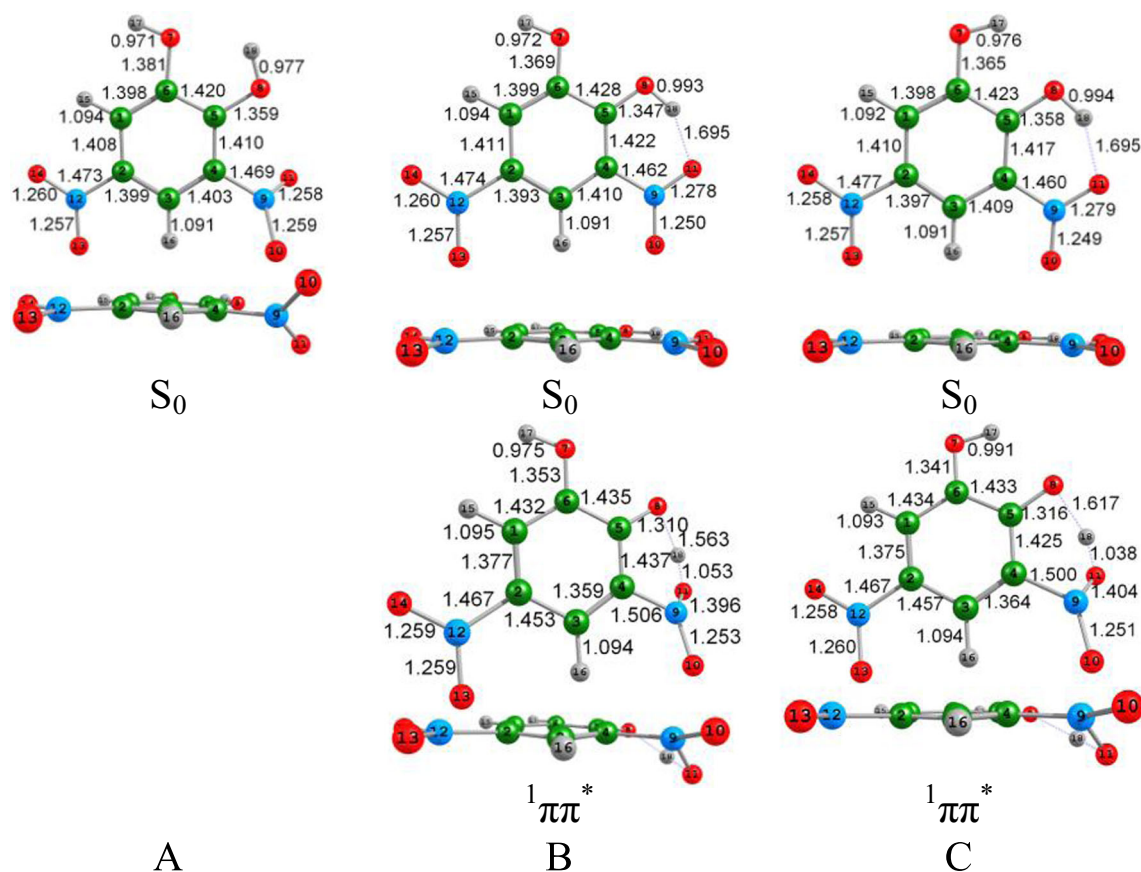
Fig. 1 CC2-optimized equilibrium geometries of S_0 and $^1\pi\pi^*$ electronic states

The intramolecular H-bonds in conformers B and C are rather short - strong. They cause an elongation of 0.02 Å (in B) and 0.03 Å (in C) of the N=O bond of the NO_2 group, which is directly involved in H-bonding, as compared to conformer A. The same feature is also exhibited by the O(8)–H bond: 0.02 Å (in B and C).

Regarding the $^1\pi\pi^*$ excited-state equilibrium geometries, the structures in Fig. 1 show that the *meta*-NO_2 group in conformers B and C is protonated, while the O(7) atom is negatively charged. The intramolecular protonation of the *meta*-NO_2 group leads preferably to the structure –N^+(OH)= O rather than to the structure H^+O=N=O. This can also be seen from the N–O distances of the *meta*-NO_2 group. Obviously, excitation of planar DNC conformers to the $^1\pi\pi^*$ excited state is attended by a parallel intramolecular proton migration. Our attempts to optimize the structure of the $^1\pi\pi^*$

excited state of conformer A failed because of strong mixing of the first several singlet excited states.

The calculated energies and the relative energies of the conformers examined here are listed in Table 1. The values show that conformer C has the lowest energy, probably because it forms two intramolecular H-bonds: between the two hydroxyl groups, and between the OH and the NO_2 group. As expected, the conformer with no H-bond between these groups (i.e., conformer A) should have much higher energy. It can be seen that the H-bonding with water does not change the relative energies of these conformers dramatically. Conversely, the H-bonding with one water molecule increases the relative energy of conformer B significantly.

The optimized geometries of the H-bonded complexes of the DNC conformers with one water molecule are illustrated in Fig. 2. As seen, the meta-NO_2 groups of systems A_{Wat} and

Table 1 Energies and relative energies of 3,5-dinitrocatechol (DNC) conformers and their water complexes

	E (a.u.)	E_{rel} (kJ mol^{-1})		E (a.u.)	E_{rel}, (kJ mol^{-1})
A	−789.887082	38	A_{Wat}	−866.164300	38
B	−789.895280	16	B_{Wat}	−866.168035	28
C	−789.901529	0	C_{Wat}	−866.178749	0
			D_{Wat}	−866.164000	39

Fig. 2 CC2-ground state equilibrium geometries of the hydrogen-bonded complexes of 3,5-dinitrocatechol (DNC) conformers and one water molecule

D_{Wat} are twisted with respect to the aromatic ring. One can see also that the water molecule in complex B_{Wat} is situated out of the molecular plane, probably because of the strong repulsion between the lone pairs of water oxygen and the oxygens from the hydroxy groups. It should be mentioned that the supersystem D_{Wat} can be optimized only as an H-bonded complex. If the water molecule is removed then the DNC molecule relaxes to conformer A, and does not form a new conformer (e.g., D), which is an analogue of the D_{Wat} complex.

The thermal conformations, investigated at the MP2/aug-cc-pVDZ level in the gas phase, are illustrated in Fig. 3. Conformer C can be obtained from conformer A via two low energy barriers of 20 and 15 kJ mol^{-1}. Obviously, the formation of intramolecular H-bonds has a stabilizing effect on DNC. As mentioned, each transition state was found as a first order saddle point with one imaginary frequency with a low absolute value. For example, the A↔B conversion has an imaginary frequency of −396 cm^{-1}, the B↔C conversion has an imaginary frequency of −379 cm^{-1}. The negative values of ΔH indicate that—according to the Leffler-Hammond postulate [31, 32]—the two transition states are recognized as reactant-like or "early" transition states.

Vertical excitation and emission energies of conformers

The recorded UV–vis spectra of DNC in chloroform (aprotic, low-polarity solvent) and water (protic, high-polarity solvent) are given in Fig. 4a, while the CC2 calculated vertical excitation energies are listed in Table 2. As seen, the vertical excitation energies of the lowest $^1\pi\pi^*$ excited state are calculated at about 335–336 nm. The experimental spectrum in chloroform shows a pronounced shoulder in the interval 330–350 nm, which can be assigned to the first $^1\pi\rightarrow\pi^*$ transition. The large peak at 275 nm might be a result of excitation to the second $^1\pi\pi^*$ excited state. Conformer A has several closely located $^1\pi\pi^*$ excited states in a broad wavelength interval, which is indicative of a broad experimental band. For conformer C, this interval is shorter. In other words, comparing the calculated vertical excitation energies and the experimental spectrum in chloroform cannot help to distinguish the three conformers A, B, and C.

The lowest bright $^1\pi\pi^*$ excited state of the H-bonded supersystems was calculated for the C_{Wat} aggregate (Table 2). The experimental spectrum of DNC in water shows three maxima: 383, 284, and 224 nm (Fig. 4), which, to a great extent, coincide with the calculated vertical excitation energies of the supersystem C_{Wat}, and correlate also with the lowest energy calculated for this aggregate. The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the most stable conformer (C) and its water complex are presented in the Electronic supplementary material. Both compounds are of π-type, which is expected because of the strong conjugation in the molecules.

With the optimized structures of the first $^1\pi\pi^*$ excited states of conformers B and C, we calculated the emission energies, which are rather low, at 0.84 and 0.90 eV, respectively. The emission energy from the second $^1\pi\pi^*$ excited states of the conformers in the gas phase were calculated at 2.61 (476 nm) and 2.60 eV (478 nm). The measured emission maximum in chloroform is at 441 nm (Fig. 4b). This large Stokes shift is due to proton migration between one of the hydroxy groups and the closest NO_2 group.

The protonation of DNC leads to a blue-shift of the absorption maxima of the compound registered in aqueous medium (see Electronic supplementary material). Further, this process causes the signal for the $^1n\pi^*$ excited state (the shoulder of the band at 379 nm) to disappear. Because of the strong interaction

Fig. 3 Energy-level diagram of the thermal conformational transformations of DNC, estimated at the MP2/aug-cc-pVDZ level

Fig. 4 a Absorption and **b** fluorescence spectra of DNC in water (*blue*) and chloroform (*red*). The fluorescence spectra are registered with excitation light of 380 nm and maximum slits

a)

b)
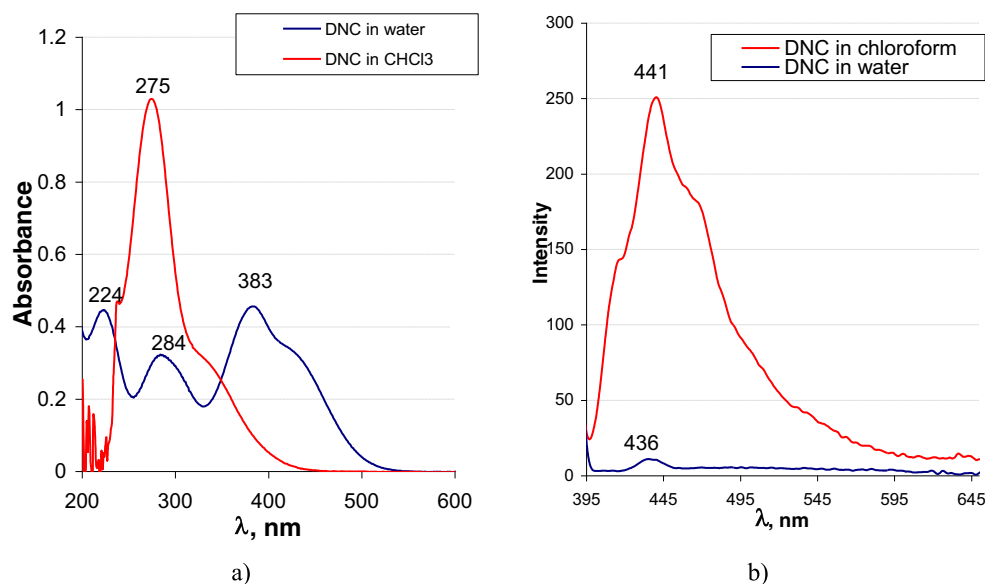
between the $^1n\pi^*$ and $^1\pi\pi^*$ excited states (they have very close energies), the band at 379 nm ($^1\pi\pi^*$) also disappears.

Internal conversions S_1 ($^1\pi\pi^*$) → S_0 through conical intersections

The deactivation of the $^1\pi\pi^*$ excited states of conformers B and C can occur through conical intersections S_0/S_1. To investigate this process, we performed linear interpolation in internal coordinates between the ground-state equilibrium geometries of the conformers and the equilibrium geometries of their $^1\pi\pi^*$ excited states. The results are depicted in Fig. 5. In both cases, the $^1\pi\pi^*$ excited-state reaction paths show shallow minima, after which they cross the ground-state reaction paths in conical intersections S_0/S_1. The mechanisms indicate that the $^1\pi\pi^*$ excited states of these conformers can

Table 2 Vertical excitation energies of the conformers of DNC and their H-bonded water complexes

A	eV	nm	B	eV	nm	C	eV	nm			
$^1n\pi^*$	3.67	338	$^1n\pi^*$	3.67	338	$^1n\pi^*$	3.66	339			
$^1\pi\pi^*$	3.69	336	$^1\pi\pi^*$	3.70	335	$^1\pi\pi^*$	3.69	336			
$^1\pi\pi^*$	4.23	293	$^1n\pi^*$	3.77	329	$^1n\pi^*$	3.79	327			
$^1n\pi^*$	4.26	291	$^1n\pi^*$	4.27	291	$^1n\pi^*$	4.26	291			
$^1\pi\pi^*$	4.28	290	$^1n\pi^*$	4.31	288	$^1n\pi^*$	4.33	287			
$^1\pi\pi^*$	4.61	269	$^1\pi\pi^*$	4.34	286	$^1\pi\pi^*$	4.42	281			
$^1\pi\pi^*$	5.18	240	$^1\pi\pi^*$	4.84	256	$^1\pi\pi^*$	4.77	260			
$^1\pi\pi^*$	5.64	220	$^1\pi\pi^*$	5.20	238	$^1\pi\pi^*$	5.26	236			
$^1\pi\pi^*$	5.72	217	$^1\pi\sigma^*$	5.77	215	$^1n\pi^*$	5.39	230			
$^1\pi\pi^*$	5.92	210	$^1\pi\pi^*$	5.89	211	$^1\pi\sigma^*$	5.87	211			
A_{Wat}			B_{Wat}			C_{Wat}			D_{Wat}		
$^1n\pi^*$	3.67	338	$^1n\pi^*$	3.67	338	$^1\pi\pi^*$	3.51	354	$^1n\pi^*$	3.66	339
$^1n\pi^*$	3.70	335	$^1\pi\pi^*$	3.68	337	$^1n\pi^*$	3.66	339	$^1\pi\pi^*$	3.69	336
$^1\pi\pi^*$	4.23	293	$^1n\pi^*$	3.78	328	$^1n\pi^*$	3.79	327	$^1\pi\pi^*$	4.20	295
$^1n\pi^*$	4.27	291	$^1n\pi^*$	4.27	291	$^1\pi\pi^*$	4.24	293	$^1n\pi^*$	4.27	291
$^1n\pi^*$	4.28	290	$^1n\pi^*$	4.32	287	$^1n\pi^*$	4.26	291	$^1n\pi^*$	4.29	289
$^1\pi\pi^*$	4.47	277	$^1\pi\pi^*$	4.34	286	$^1n\pi^*$	4.36	284	$^1\pi\pi^*$	4.60	270
$^1\pi\pi^*$	5.08	244	$^1\pi\pi^*$	4.79	259	$^1\pi\pi^*$	4.62	268	$^1\pi\pi^*$	5.06	245
$^1\pi\sigma^*$	5.46	227	$^1\pi\pi^*$	5.19	239	$^1\pi\pi^*$	5.20	238	$^1\pi\sigma^*$	5.41	229
$^1\pi\pi^*$	5.75	216	$^1\pi\pi^*$	5.47	227	$^1n\pi^*$	5.35	232	$^1\pi\pi^*$	5.65	219
$^1\pi\pi^*$	5.85	212	$^1\pi\sigma^*$	5.82	213	$^1\pi\sigma^*$	5.72	217	$^1\pi\pi^*$	5.82	213

Fig. 5 Linearly interpolated excited-state reaction paths between the ground-state equilibrium geometry (*black circles*) and the $^1\pi\pi^*$ excited-state equilibrium geometry (*red circles*) of **a** conformer B and **b** conformer C. The ground state energies of the conformers (−789.895278 a.u. and −789.901529 a.u.) are taken as reference values for the calculation of E_{rel}. *Dashed green lines* Conical intersections S_0/S_1, *blue circles* $^1n\pi^*$


a)

b)
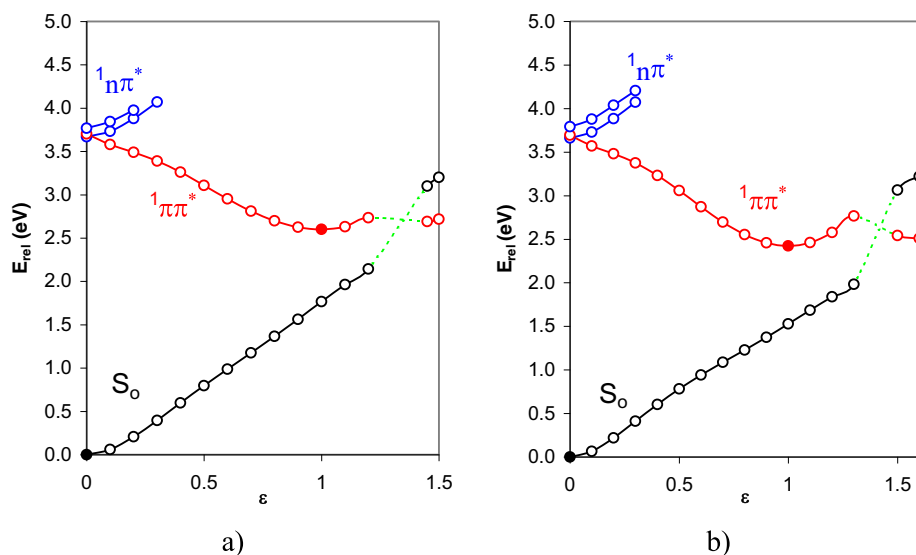
relax non-radiatively to the ground state. Parallel with this, a proton migration between NO_2 and OH groups occurs.

We performed irradiation of the aqueous solution of DNC; the absorption spectra at different irradiation times are plotted in the Electronic supplementary material. The experimental bands registered at 10 min of irradiation indicate protonation of the NO_2 group. After the next 10 min of irradiation, the OH tautomer again dominates. In other words, irradiation

provokes dynamic H exchange between the OH and NO_2 groups of conformer C of DNC.

Complexes of W(VI) and V(V) with DNC

It is known that the aqueous W(VI)-DNC system (0.01–0.5 mol dm^{-3} HCl) can produce only one complex with a composition of 1:2 (W(VI):DNC) [16]. The complex is stable
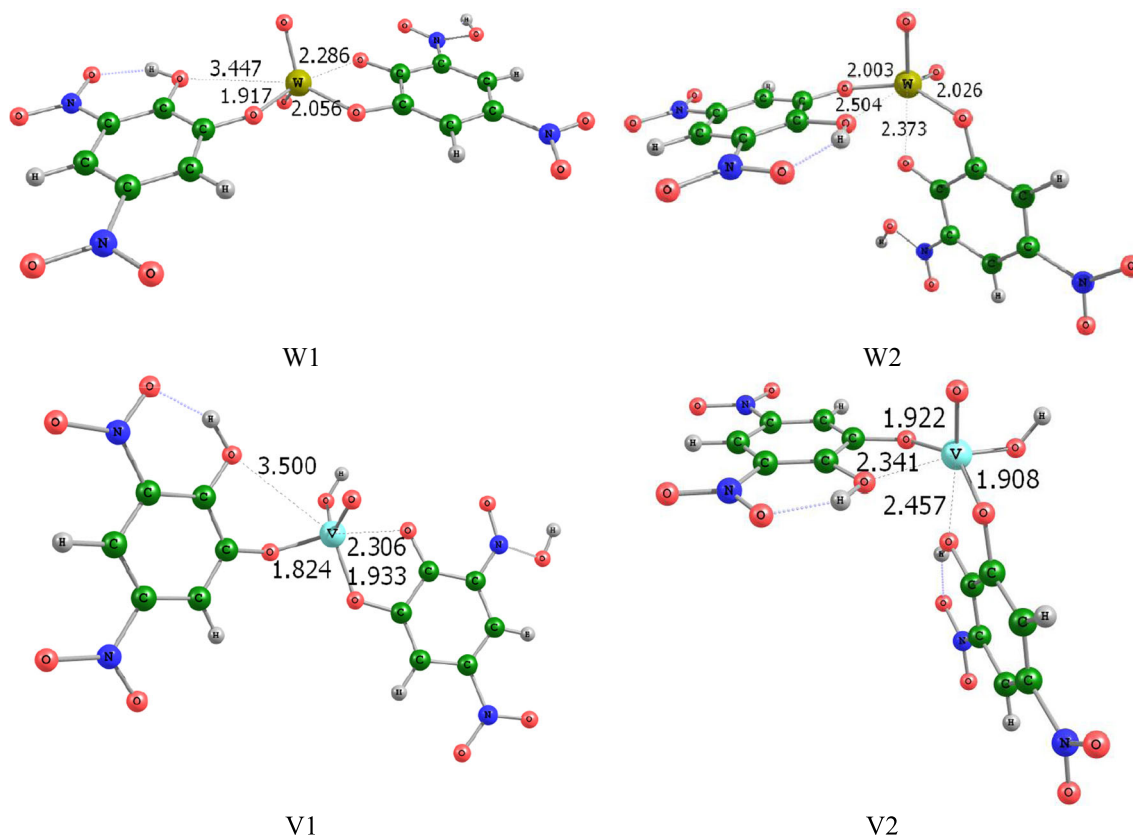
Fig. 6 Optimized ground-state equilibrium geometries of complexes of W(VI) and V(V) with DNC found at the BLYP/CEP-31G level

($K_{unst}=1.8\times10^{-21}$) and can be expressed with the formula $(H^+)_2[W^{VI}O_2(DNC)_2]$. In this formula, DNC is an anion with a charge of two (DNC^{2-}) and WO_2^{2+} is the complex-forming ion.

Systems containing V(V) and DNC have been investigated by Marczenko and Lobinski [17, 18]. They reported the formation of binary ($\lambda_{max}=428$ nm) and ternary complexes in the pH range 1–3. The general formula of the ternary complexes was found to be $(R^+)_2[V^VO(OH)(DNC)_2]$ (where R^+ represents cations deriving from the cationic ion-association reagents, such as Rhodamine B and Brilliant Green). The binary complex was not described in detail in [17] and [18]; however, we can assume that it is a complex acid with a similar formula: $(H^+)_2[V^VO(OH)(DNC)_2]$.

In the present study, the complex acids of W(VI) and V(V) were optimized at the BLYP/CEP-31G level (Fig. 6). Two complex structures were obtained for each of the metals (W1, W2, V1 and V2). The results showed that structures with mutually perpendicular DNC ligands (W2 and V2) are more stable than those with coplanar ligands (W1 and V1). In the second case, one of the DNC ligands (left-handed) seems to be monodentate [the distance between the metal (M) and one of the catecholate oxygen atoms is too long: 3.447 Å (M=V) and 3.500 Å (M=W)]. In the most stable structures W2 and V2, both DNC ligands are bidentate (with a metal–catecholate oxygen distance≤2.504 Å) and the complexes can be regarded as octahedral.

The results of our investigations on W(VI)-DNC and V(V)-DNC systems under long-time UV-irradiation showed that the tungsten complex is more stable than the vanadium one. The relative instability of the vanadium complex acid can be explained by the following peculiarities: (1) one of the catecholate oxygen atoms in the vanadium complex V2 is protonated in both DNC ligands (while in the tungsten complex W2 only one of the DNC ligands has a protonated oxygen atom); (2) the complex-forming ion in the vanadium complex is $VO(OH)^+$. Under the optimum pH interval (pH 1–3) the most common vanadium species should be VO_2^+ [33]. One can expect that $VO(OH)^+$ would be stabile only in the presence of bulky organic cations, which are able to ensure complete transfer of the vanadium complex in a different phase (e.g., CCl_4, cyclohexane), as Marczenko and Lobinski have shown in their extraction-spectrophotometric [17] or flotation-spectrophotometric [18] investigations.

It should be reminded that a low DNC concentration was maintained in our systems ($C_{DNC}=C_M$). The lack of DNC-excess enhances the possibility of formation of 1:1 vanadium-to-DNC species instead of the postulated 1:2 vanadium-to-DNC ones. The observed hipsochromic shift (from 419 nm to 403–401 nm) after several minutes of UV-irradiation indicates the presence of at least two different complexes in the vanadium-DNC system (and supports the supposition that

1:1 species exist under the specified conditions). For comparison, there is no shift in the absorption maximum of the tungsten-DNC complex ($\lambda_{max}=383$ nm) even after 60 min of irradiation. This fact confirms the conclusion [16] that only one complex is formed in the W(VI):DNC system.

Conclusions

The present theoretical and experimental study of DNC and its complexes with W(VI) and V(V) led to the following major conclusions: (1) conformer C of the DNC ligand should be the most stable since it forms two intramolecular H-bonds that stabilize the molecule; (2) irradiation of the DNC ligand is accompanied by a parallel proton migration from the hydroxy group to the neighboring NO_2 group. This effect causes a large Stokes shift of the absorption and emission bands; (3) W(VI) forms more stable DNC complexes than V(V).

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