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Nitroso-naphthol quinone-monooxime tautomeric equilibrium revisited: evidence for oximo group isomerization

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Abstract

An ab initio and DFT treatment of the nitroso-naphthol/quinone-monooxime tautomeric equilibrium revealed that the proton transfer process within the intramolecular hydrogen bond cannot be responsible for the observed doubling of NMR signals. Our analysis demonstrates that the barrier associated with geometric isomerization of the C=N bond is the likely cause of the signal doubling phenomenon. The conclusion of our study would suggest the need for re-interpretation of the dynamics in tautomeric equilibria of this type. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Proton transfer in a hydrogen bond is an elementary process present in many systems of biological interest. Recently many experimental and computational studies addressed proton dynamics in hydrogen bonds [1–5].

Nitroso-hydroxy compounds are an example of systems that possess an intramolecular hydrogen bond. They are the key reagents in the production of azo dyes. Since they are good chelating agents [6], they have found a place in many analytical [7], synthetic [8] and other applications [9,10]. In solution, nitrosonaphthols as well as nitrosophenols generally exist in tautomeric equilibria with the corresponding quinone-monooxime forms (Fig. 1). The nitroso-oxime tautomeric equilibrium was extensively studied by spectroscopic methods including UV [11], IR [12,13] and NMR [14–18]. The latter is a particularly powerful method for studying the structure and dynamics of such hydrogen-bonded (H-bonded) systems [19]. Spectroscopic studies confirmed the presence of two distinct species that were interpreted as forms **1** and **2** that are related through an intramolecular proton transfer through the existing intramolecular H-bond.

Theoretical studies of this equilibrium [20–23] concentrated on total energies of tautomers with an intramolecular H-bond but related no information concerning the proton transfer process and its activation energy. Very recently Enchev et al. [18] reported results of ab initio calculations on

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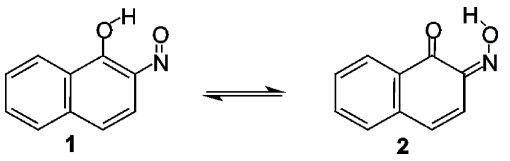

Fig. 1. Nitrosonaphthol/quinone-monooxime tautomeric equilibrium.

acenaphthene–quinone-monooxime, involving the same type of tautomeric system. The authors found the barrier associated with the intramolecular proton transfer to be approximately 2.5 kcal mol^{-1}. Using NMR, they observed three species present in DMSO (*cis*- and *trans*-quinonoid forms and a nitroso-hydroxy species) and two in CCl_4. A further thorough NMR and computational study of nitrosonaphthol revealed the presence of two rotamers of the quinone-oxime form.

Here, we present the results of ab initio and density functional theory (DFT) calculations on the tautomeric equilibrium in 2-nitroso-1-naphthol (2NNP). The calculated barrier associated with the proton transfer was found to be too low to allow observation of the two sets of NMR signals associated with the two tautomers. Based on our results, we propose internal rotation about the C–N bond as the cause for the potential barrier separating the two experimentally observed species.

2. Results and discussion

Ab initio Hartree Fock (HF) and Møller Plesset second-order perturbation theory (MP2) as well as DFT full geometry optimizations using the 6-31G(d) basis set were performed for all studied species, apart from the structure approximating the transition state (form **7**). The MP2 and DFT calculations proved to predict reliable proton potentials [24]. The applied DFT level includes the calculation of the exchange functional by the method proposed by Becke [25] and the correlation functional suggested by Lee et al. [26] The B3LYP functional combined with the 6-31G(d) basis set was used by Nagy and coworkers [27] and gave good estimates of proton potentials in H bonded systems. To verify the results the Møller Plesset method MP2 was applied to the same systems. Our calculations were performed using the Gaussian-98 suite of programs [28] implemented on a Hewlett-Packard C180 workstation.

Solvation effects were included through two methods. In the first method, a solvent reaction field was introduced using the method of Miertuš et al. [29] as implemented in Gaussian-98. The solute cavity was composed of interlocking spheres with Van der Waals atomic radia scaled up by a factor of 1.2. In the second method, we considered one discrete DMSO molecule in relevant explicit contact with the 2NNP molecule. Chemical shieldings were calculated using the GIAO method as implemented in Gaussian-98. The shift values are relative to calculated shieldings for tetramethylsilane obtained by the same method.

The one-dimensional (1D) Schrödinger equation for the DFT calculated proton potential was solved by using an iterative shooting method that falls into the category of solving ordinary differential equations that need to satisfy two boundary conditions. The proton wavefunction should equal zero when approaching the hard-core region of the proton potential. The program for solving the 1D Schrödinger equation can be obtained from one of the authors (JM) on request.

The optimized geometries of 2NNP isomers **1** and **2** gave characteristic quinonoid and aromatic ring bond distances. Calculated total energies indicate the quinonoid form to be more stable by 2.68 and 2.64 kcal mol^{-1} by DFT and MP2, respectively. Ivanova and Enchev obtained an energy difference from 2.6 to 5.4 kcal mol^{-1} depending on the level of theory. The relative stability of the quinonoid form is in agreement with the reported predominance of this form in a wide range of solvents.

It is worth stressing that during the geometry optimizations of 1 and 2 no constraints were imposed. In order to obtain the potential curve for the proton transfer process constraints were then imposed on the O–H distance in forms **1** and **2**. However, the O–O distance was not kept frozen; its optimized value ranged from 2.350 to 2.568 Å. The potential curve is shown in Fig. 2. In vacuo the classical potential barrier of 1.47 kcal mol^{-1} was found with the maximum at an O–H distance

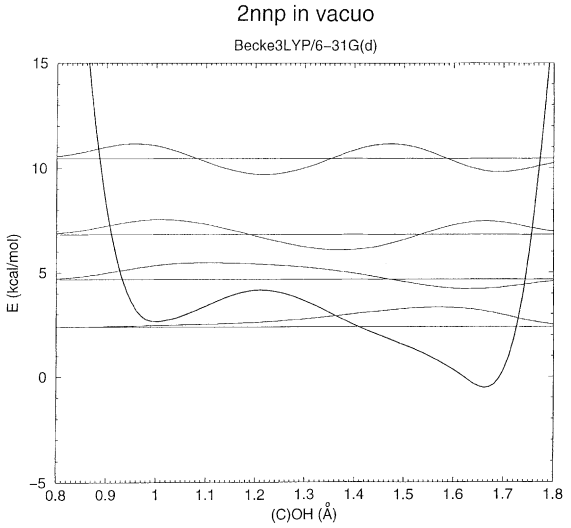

Fig. 2. Potential curve (B3LYP/6-31G(d)) for proton transfer between the 2NNP and 1,2-quinone-2-monooxime tautomers with intramolecular H-bonding. Shown are also eigenvalues and wavefunctions of the system.

of 1.209 Å. The potential curve for the process in DMSO is very similar to that in vacuum including the potential barrier value.

Solving the 1D Schrödinger equation based on the DFT potential curve gave an estimate of the wavefunction and associated eigenvalues. Population analysis of the obtained proton ground state vibrational eigenfunctions predicted 98.2%, 98.6% and 98.7% of the quinone-monooxime form in vacuum, chloroform and DMSO, respectively. These results are in full agreement with the reported 100% of the quinonoid form in DMSO but less so with the 80% found in carbon tetrachloride with a 10% addition of chloroform. The lowest experimentally determined presence of the quinonoid form was found in chloroform at 67% [17].

It is difficult to explain the observed splitting of signals in both ^{1}H and ^{13}C NMR [17,18] by the low potential barrier for the proton transfer. For our system, we can suppose that we have two isomeric molecular forms of approximately the same free energy. The forward and backward rate constants are the same and their ratio determines the equilibrium constant, while the rate of the interconversion is associated with the barrier height. Transition state theory shows an exact correspondence between the barrier height in terms of free energy and the rate constant. Conventional NMR experiment takes place on the millisecond time scale. To apply the NMR time scale to our system we selected the chemical shift associated with the C1 carbon atom. The original assignments [17] of signals for this atom gave a 43 ppm difference in ^{13}C chemical shieldings between the two isomers. On a 50 MHz NMR spectrometer used for ^{13}C measurements the above signal separation equals a 2150 Hz difference. By combining the transition state formula with basic NMR line shape equations it is possible to calculate the free energy of activation for the rate process associated with coalescence of the signals [30,31]:

$$\Delta G^{\#} = k_B T_c \cdot \ln \frac{\sqrt{2} k_B T_c}{\pi h |\nu_A - \nu_B|}, \quad (1)$$

where ν_A and ν_B correspond to signal frequencies in Hz, k_B is the Boltzmann constant, h is Planck's constant and T_c is the coalescence temperature. By inserting the values for frequencies and the room temperature value into the above equation, we can calculate the required free energy of activation associated with coalescence. This free energy of activation was 12.7 kcal mol^{-1} and the associated rate constant was approximately 4800 s^{-1}. The C1 carbon would thus give a single signal if 2NNP were involved in a process with an activation energy lower than 12.7 kcal mol^{-1}, and a doubled signal if the activation energy were higher than 12.7 kcal mol^{-1}. In other words, the NMR experiment should yield one signal or one set of signals if the rate constant for the interconversion is faster than 4800 s^{-1} and two signals for slower processes. However, the required value is much higher than the free energy of activation for the proton transfer within the existing intramolecular H-bond in 2NNP. Therefore, we should find an alternative isomerization process responsible for doubling the NMR signals of 2NNP. An isomer that would solve this apparent contradiction should be of comparable free energy to other isomers and moreover, should be separated from other isomers by a barrier of more than 12.7 kcal mol^{-1}.

In our search for a solution to the question, we considered the isomerization of the nitroso and oximo group by internal rotation about the C–N as well as C–O and N–O bonds. The HF and MP2 energy profile for internal rotation about the C–N bond is depicted in Fig. 3. The conformations of 2NNP considered and the energies calculated under different conditions are shown in Fig. 4 and Table 1, respectively. Full optimizations were done in vacuo, after which the DMSO effect was added as a solvent reaction field contribution. Finally, the most interesting structures were reoptimized with the addition of one explicit DMSO solvent molecule at the B3LYP level.

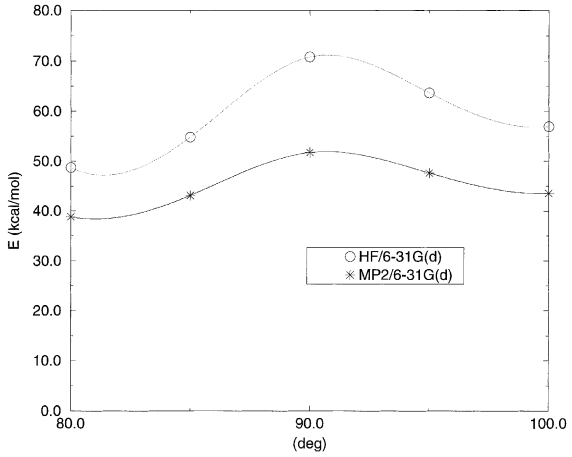

Fig. 3. HF and MP2 /6-31G(d) energy profile for internal rotation about the C–N bond of 1,2-quinone-2-monooxime. Potential energy functions were calculated with a fixed dihedral angle while all other degrees of freedom were optimized.

Results indicated that the *trans*-quinonoid form **6** with an intermolecular H-bond fit the criteria for the appreciably populated species involved in the equilibrium. The barrier of the process requiring C–N bond rotation was modeled by structure **7** with an imposed constraint of the CCNO dihedral angle to 90°. The HF, MP2 and B3LYP/6-31G(d) calculated barrier heights are 70.8, 51.8, and 49.4 kcal mol^{-1}, respectively, are consistent with the experimentally observed splitting of the NMR signals. The choice of transition state (90°) was demonstrated to be correct by the HF and MP2 energy profile for the internal rotation of the nitroso group (Fig. 3). The important role of structure **6** in the equilibrium is supported by the fact that *trans*-structures were found in a number of X-ray structures of *o*-nitroso phenols and naphthols [32–34] and their metal complexes [35,36]. An important consequence of the presence of structure **6** is that it demonstrates that intramolecular H-bonding is not as preferential to intermolecular as is commonly (intuitively) believed for this system.

Further support for form **6** as a component of the 2NNP tautomeric equilibrium was obtained by agreement between experimental ^{13}C NMR chemical shifts and the calculated values shown in Table 2. However, good agreement should not come as a surprise since structure **6** differs from the normally proposed quinone-monooxime structure **2** only in the orientation of the oximo group.

To be thorough we considered an alternative pathway including a proton transfer from the oximo group to the solvent followed by an isomerization of the deprotonated oximo group and

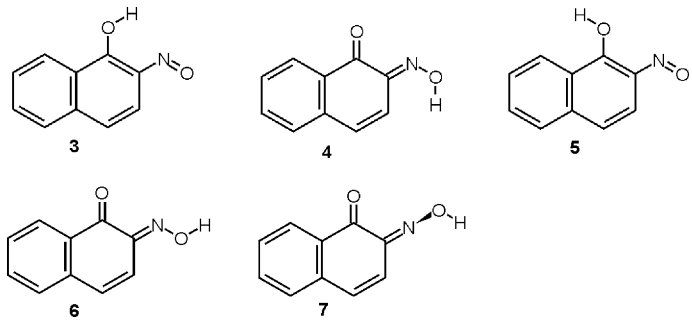

Fig. 4. Investigated isomers of 2NNP.

Table 1
HF, MP2 and B3LYP 6-31G(d) relative total energies of 2NNP isomers

Method/environment	Structure, relative energy (kcal mol^{-1})						
	1	**2**	**3**	**4**	**5**	**6**	**7**
HF	3.598	0	3.762	10.092	12.466	0.408	70.817
MP2	2.639	0	3.831	12.953	13.686	4.535	51.751
B3LYP	2.679	0	5.852	14.142	16.273	6.556	49.437
B3LYP DMSO (SCRF)	0.001	−1.899	4.349	6.703	11.741	0.573	44.855
B3LYP DMSO molecule	8.246	7.515	–	–	–	0	–

The lowest energy in vacuo (B3LYP) was used as 0 for SCRF DMSO values. In series with one DMSO molecule the lowest value was used as 0.

Table 2
Calculated ^{13}C NMR shifts for *trans* 1,2-naphthoquinone-2-monooxime in vacuo (ppm) compared with experimental literature data [17]

Structure	Atom, ^{13}C NMR shift (ppm)					
	C1	C2	C3	C4	C5	C6
1 (exp)	137.5	136.8	115.6	127.2	128.5	128.7
6[a] (exp)	180.5	146.9	126.9	135.8	128.3	127.5
1 (calc)	128.2	148.6	127.6	110.5	128.6	118.5
2 (calc)	167.5	139.8	123.6	115.3	130.1	123.8
6 (calc)	172.0	139.3	110.6	120.0	129.0	124.5

Data are given for C atoms of ring bearing hetero groups. Labeling follows that used in naming. Data for C atoms 7–10 are not listed since little difference between forms is seen in second ring.
[a] In [17] the data was assigned to structure **2**.

reprotonation from the solvent. We limited our study to the second step since the first and last, in principle, require a quantum dynamical treatment [3,37]. The calculated barrier for isomerization of the deprotonated species is approximately 20 kcal mol^{-1}. The barrier for this isomerization pathway is sufficient to cause doubling of NMR signals, however, based on our calculations we are unable to determine the isomerization pathway.

In summary, the low potential barrier for the proton transfer process in the tautomeric equilibrium of 2NNP, coupled with total energy calculations, indicates that the experimentally observed species are unlikely to be the normally proposed forms **1** and **2** with intramolecular H bonding. Our results suggest C–N internal bond rotation as the process connecting the two observed species, and the quinonoid form to be in the *trans*-conformation. Still, further support could be obtained by ab initio molecular dynamics combined with the path integrated treatment of the protons [38].

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