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Hydrogen Bonding between Phenol and Acetonitrile

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The present work aims to resolve theoretically the puzzling effect of downshifting of the ν_{OH} stretching mode of phenol, complexed with acetonitrile, as the latter concentration increases, via performing a thorough search of the potential energy surface of the interaction of phenol with acetonitrile at the modest MP2/6-31+G(d,p), MP2/6-31G(d), and B3LYP/6-31+G(d,p) computational levels. We postulate and firmly approve that, besides the conventional σ hydrogen-bonded structure of phenol with one acetonitrile molecule, there exists the novel, although less favorable, structure with π-type hydrogen bonding. Such bonding becomes crucial as the second acetonitrile molecule is added to the 1:1 complex of phenol and acetonitrile, and furthermore, its substantial stabilization in polar solvents provides an explanation of the mentioned controversial issue that has stood unclear during the last four decades.

1. Introduction

Acetonitrile (ACN) possesses some unique properties such as a high dielectric constant (35.95) and the solubilization of many inorganic and organic materials.[1] It is actually one of the few simple aprotic solvents miscible in water at any ratio. X-ray diffraction studies of pure acetonitrile revealed that ACN molecules do not strongly interact with themselves and are only weakly associated via dipole−dipole interaction.[2] The IR spectrum of pure acetonitrile includes two major bands placed at 2257 and 2295 cm^{-1}.[2] The former one, called ν_2, originates from the C≡N stretching mode while the latter is a combination band composed of the CCH bend (ν_3) and C−C stretch (ν_4) modes.[3]

For the last 40 years the acetonitrile molecule was, and still is, a "workhorse" in many laboratories worldwide, in experimental studies of hydrogen bonding with nitriles. It is obvious that ACN possesses two sites for accepting a hydrogen bond: one on the lone-pair electrons of the nitrogen atom (σ bonding) and the other on the C≡N triple bond (π bonding). Hydrogen-bond formation in phenol−nitrile systems were initially examined by White and Thompson,[4] Sousa Lopes and Thompson,[5] Mitra,[6] and Allerhand and Schleyer[7] in inert solvents such as CCl_4 or C_2Cl_4 (see also ref 8), who all recorded that their IR spectra contain an additional band placed on the low-frequency side of the free phenol O−H stretching band ν_{OH} as the concentration of nitrile increases. The $\Delta\nu_{OH}$ shift varies from 148.5 cm^{-1} at 0.119 mol/L ACN to 156.5 cm^{-1}, when the ACN concentration reaches 0.687 mol/L.[4] They then suggested that this new band results from the O−H stretching mode of a hydrogen-bonded complex involving the OH group of phenol and the nitrogen atom of the nitrile. Mitra[6] and Sousa Lopes and Thompson[5] postulated the existence of a 1:1 complex between phenol and nitrile in inert solvents. White and Thompson[4] pointed out the appearance of an unusual blue shift of the C≡N stretching vibration by about 12.5 cm^{-1} when the nitrogen atom of the nitrile group is complexed with the OH group of phenol, implying thus a σ-type hydrogen bonding between the nitrogen lone pair and this group of phenol. The increased frequency of the C≡N stretching vibration in the complex gave rise to a shoulder on the high-frequency side of the C≡N peak.

Nearly at the same time, based on the well-known Buckingham formula describing the frequency shift in a medium,[9] Horak et al.[10] deduced that if the fundamental stretching mode ν_{OH} of the free phenol in the gas-phase is fitted at 3655 cm^{-1}, it must be extrapolated in the phenol−acetonitrile complex to 3540 cm^{-1}, and therefore, the red shift, due to complexation, becomes equal to 115 cm^{-1}. That appears much smaller than we would expect,[11] although, as we already mentioned, White and Thompson[4] revealed the red shift of 148.5−156.5 cm^{-1} (similar red shifts of 152 and 160 cm^{-1} were detected in refs 7 and 8a, respectively). Yarwood[11] also noticed that the origin of the frequency shift of the ν_{OH} mode of phenol in the phenol−ACN complex from 3460 to 3409 cm^{-1} under increasing concentrations of acetonitrile from 0.19% to 100% acetonitrile in CCl_4 (interestingly, it goes stepwise: between 0.19% and 0.39%, no shift was detected; between 0.78% and 1.8%, it is equal to −5 cm^{-1}; a further concentration to 4% results in −10 cm^{-1}; etc.) is not entirely clear and suggested a possible formation of 2:1 phenol−acetonitrile complexes due to the increased basicity of the oxygen atom of phenol. A similar trend has been been recently observed by Zeegers-Huyskens and co-workers for the pentachlorophenol−acetonitrile complex.[12] Paradoxically, such a puzzling effect has not been so well appreciated by theoreticians despite the fact that it still annoys experimentalists (see refs 13a−e and particularly the current review, ref 13f). It is nevertheless worth recollecting the mid-1980s theoretical work by Figeys and co-workers,[13a] who suggested that the most favorable hydrogen-bond formation with nitriles occurs via σ-type hydrogen bonding (for the other works on this topic see refs 13b−f and the recent B3LYP/6-31G(d,p) study by Koll and co-workers[14] of the phenol−acetonitrile and phenol−pyridine complexes, which was mainly focused on anharmonicity contributions to their dipole moments).

Summarizing, what else can we tell the readers from a theoretical point of view? There are certainly some points still

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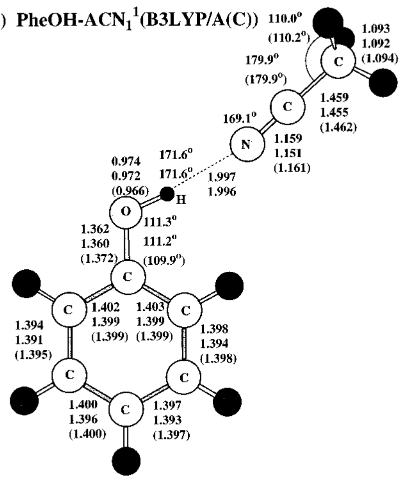
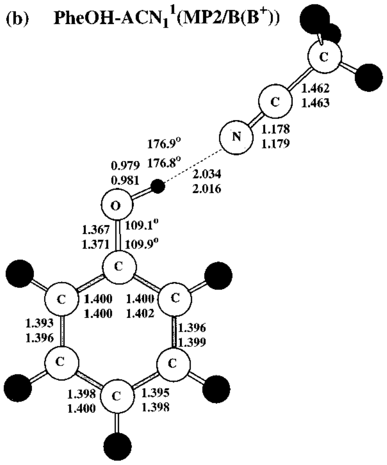
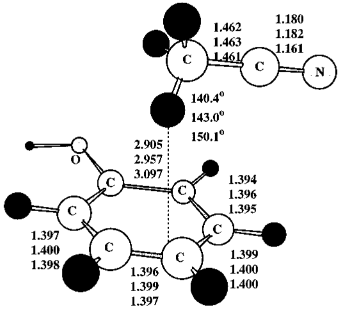
(a) PheOH-ACN$_1^1$(B3LYP/A(C))



(b) PheOH-ACN$_1^1$(MP2/B(B$^+$))



(c) PheOH-ACN$_1^2$(MP2/B(B$^+$) vs. B3LYP/A)



(d) PheOH-ACN$_1^3$(B3LYP/A)

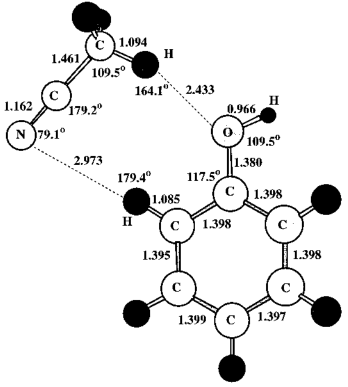


Figure 1. Complexes of phenol with acetonitrile. The bond lengths (in angstroms) and bond angles correspond to B3LYP/A (upper values) and B3LYP/C (lower values) in panel a and to MP2/B (upper values) and MP2/B$^+$ (lower values) in panel b. The values in parentheses (in panel a) correspond to the B3LYP/A optimized geometries of the free phenol and acetonitrile molecules.

unclear and just related to a quite routine usage of quantum chemical programs of getting the optimized structure of the 1:1 complex between phenol and acetonitrile and exploring somehow the calculated frequencies to discuss, again routinely, an agreement between the experiment and the theory. It looks as though really nothing is left, except the existence of a 1:2 complex suggested by Yarwood and its structure, and what is more, the puzzling dependence of the shift of the ν_{OH} mode of phenol on the ACN concentration, although impressed by the rampant experimentalists' arguments, this was likely a way to almost nowhere and would not ever deserve to be published. Nevertheless, in our naïve endeavor of putting “all ends together”, we have performed a rather exhaustive search of the potential energy surface (PES) of the phenol−acetonitrile interaction, and the results of this search and the way of thinking developed in this work to explain the experiments are presented here for the readers' consideration.

2. Computational Methodology

It was not actually our intention to explore the PES using a large basis set and more sophisticated computational level, so we have confined our PES search to the use of a rather simple density functional hybrid B3LYP computational level in conjunction with a split-valence double-ζ 6-31+G(d,p) ($\equiv$ A) basis set with the help of the GAUSSIAN 98 program.[15] The chosen computational level, which by no means could not be considered as rather inaccurate, was nevertheless further refined via the second-order perturbation Møller−Plesset method, taken together with the 6-31+G(d) ($\equiv$ B$^+$) and 6-31G(d) ($\equiv$ B) basis sets, and B3LYP in conjunction with a larger basis set 6-311++G(d,p) ($\equiv$ C). The B3LYP/A(C) and MP2/B computational levels were also employed for calculating harmonic frequencies (with the computational uncertainty of ±3−5 cm^{-1}) and, therefore, for identifying the stationary points on the studied PES, and for obtaining enthalpy and entropy and zero-point vibrational energy (ZPVE) as well. The latter was further used to deduce the binding energy of the complex AB as $E_f(AB) \equiv -\{[E(AB) - ZPVE(AB)] - ([E(A) - ZPVE(A)] + [E(B) - ZPVE(B)])\}$, expressed throughout the present work in kilocalories per mole, although the uncorrected binding energy $E_f(AB) \equiv -[E(AB) - E(A) - E(B)]$ will be used also. The effect of the basis-set superposition error (BSSE) was only tested for the phenol−acetonitrile complexes by the standard counterpoise procedure.

3. Phenol−Acetonitrile Complex

The PES of the interaction of the phenol and acetonitrile molecules consists only of three lower-energy minimum structures at the B3LYP/A computational level, which are further reduced to two under the MP2/B$^+$ method refinement. They are displayed in Figure 1. The first complex, named herein as PheOH−ACN$_1^1$, is the conventional cliché structure, which exists at both chosen levels and which has been explored by experimentalists for four decades. It occupies the global energetic minimum on that PES with the B3LYP/A binding energy $E_f^{B3LYP/A}$(PheOH−ACN$_1^1$) = 5.3 kcal/mol and the B3LYP/A enthalpy of formation $H_f^{B3LYP/A}$(PheOH−ACN$_1^1$) of 4.1 kcal/mol (see Table 1). The latter fairly agrees with the experimental value H_f^{expt}(PheOH−ACN$_1^1$) = 4.5 kcal/mol, reported in refs 8a and 13b despite the fact that the theoretical value is taken within the harmonic approximation. Notice also that the BSSE correction, estimated via the B3LYP/A method, comprises only 0.1 kcal/mol and is hereafter neglected. The MP2/B$^+$ and MP2/B binding energies and enthalpies of forma-

TABLE 1: Some Key Features of the Phenol−Acetonitrile Complexes PheOH−ACN$_1$[a]

	PheOH−ACN$_1{}^1$				PheOH−ACN$_1{}^2$			
feature[a]	B3LYP/A	B3LYP/C	MP2/B$^+$	MP2/B	B3LYP/ A	B3LYP/ C	MP2/B$^+$	MP2/B
$-E$	440.26969	440.36486	438.87007	438.84189	440.26179	440.35697	438.86645	438.83623
ZPVE	94.9	94.4	95.2	95.3	94.3	94.0	95.3	91.5
E_f	5.3	5.4	7.1	7.0	0.9	0.9	3.8	4.7
$-H$	440.10746	440.20326	438.70804	438.67864	440.09990	440.19561	438.70465	438.67338
S	113.5	113.4	121.2	116.1	118.4	119.7	109.4	109.5
dipole	6.8	6.7	6.9	6.7	5.1	5.1	5.5	5.3
ν(IR)[b]								
τ_{OH}	645 [596[c]]	635	621	580	338	315	281	342
ν_{CN}	2378	2377	2231	2245	2362	2359	2211	2229
ν_{OH}	3673 [3679[c]]	3669	3641	3673	3828	3834	3727	3754
	(873) (850[c])	(886)	(700)	(665)	(59)	(65)	(63)	(59)

[a] Total electronic energy E and enthalpy H are in hartrees; zero-point vibrational energy (ZPVE) and binding energy E_f are in kilocalories per mole; entropy S is in cal/mol·T; total dipole moment is in debyes; frequencies ν are in reciprocal centimeters and their IR activities (IR) are in kilometers per mole. [b] In the free phenol, the $\boldsymbol{\tau_{OH}}$ mode is placed at 330 (B3LYP/A), 311 (B3LYP/C), 277 (MP2/B$^+$), and 334 (M2/B) cm^{-1} while $\boldsymbol{\nu_{OH}}$ is placed at 3831 (57 km/mol; B3LYHP/A), 3733 (62; B3LYP/C), 3733 (61; MP2/B$^+$), and 3755 (56; MP2/B) cm^{-1}. The ν_{CN} mode of the free acetonitrile is centered at 2364 (B3LYP/A), 2362 (B3LYP/C), 2215 (MP2/B$^+$), and 2229 (MP2/B) cm^{-1}. [c] Theoretical B3LYP/6-31G(d,p) results.[14]

tion are larger, compared to those at the B3LYP/A level, and vary within the intervals of 7.0−7.1 and 5.7−5.9 kcal/mol, respectively.

The second minimum-energy structure, PheOH−ACN$_1{}^2$, is novel; that is, reported in the present work for the first time and, one might say, unthinkable. Relative to PheOH−ACN$_1{}^1$, it is placed higher by 4.4 (B3LYP/A), 2.3 (MP2/B$^+$), and 3.3 (MP2/B) kcal/mol, and therefore its binding energy E_f(PheOH−ACN$_1{}^2$) amounts to 0.9 (B3LYP/A), 4.7 (MP2/B$^+$), and 3.8 (MP2/B) kcal/mol. A considerable discrepancy between the binding energies, evaluated at the MP2/B$^+$ and B3LYP/A computational levels for this complex PheOH−ACN$_1{}^2$, which is even larger than that of 1.7 kcal/mol found for PheOH−ACN$_1{}^1$, likely originates from a poorer B3LYP/A(C) description of the acetonitrile molecule. This is clearly seen not only from its energy of dimerization, which will be discussed in the next section, but also from a shorter, by 0.03 Å, triple CN bond compared to MP2/B(B$^+$). It is worth mentioning as well the Gibbs free energy difference between PheOH−ACN$_1{}^1$ and PheOH−ACN$_1{}^2$, which, at the MP2/B$^+$ level, amounts to −5.6 kcal/mol whose ≈60% contribution is due to their relatively large entropy effect, as shown in Table 1.

If the cliché structure PheOH−ACN$_1{}^1$ is formed via the typical medium-strength σ-type O−H···N hydrogen bond between the OH group of phenol and the lone electron pair of the nitrogen atom of acetonitrile, respecting all canonical although still somewhat loosely defined rules,[16] the other one, PheOH−ACN$_1{}^2$, is quite peculiar in the sense that it has not been expected due to a certain belief that the π cloud of phenol is unable to form a relatively strong (at the MP2 level only) π hydrogen bond compared, e.g., to that of benzene. Let us follow now a quite routine procedure and first analyze what are the substantial changes in the geometries of the monomers[17] and their characteristic vibrational modes, accompanied the formation of the hydrogen bond in PheOH−ACN$_1{}^1$. This is primarily the elongation of the O−H bond by 0.008 (0.006, 0.006) Å (the ordering B3LYP/A, MP2/B, MP2/B$^+$ is taken hereafter) manifested, say in spectroscopic terms, in a red shift of the ν_{OH} stretching vibration by 158 (92, 82) cm^{-1}. We observe a fair enough agreement of the B3LYP value with the experimental red shifts of White and Thompson[4] and Allerhand and Schleyer[7] and a significant enhancement of its IR activity, viz., from 57 (61, 56) km/mol in the free phenol to 873 (700, 665) km/mol in PheOH−ACN$_1{}^1$ (Table 1). The formed hydrogen bond has a typical length of 1.997 (2.016, 2.034) Å and is actually rather linear with a bond angle ∠OHN of 171.6° (176.8°, 176.9°). The hydrogen-bond stretching vibration ν_σ(O−H···N) appears at 112 (119, 119) cm^{-1}. It is also worth noticing two lower-frequency modes, centered at 59 (58, 43) and 70 (83, 79) cm^{-1}, referring to the hydrogen-bond bending motions and originating from the molecular dipole rotation, by analogy with the band at 90 cm^{-1}, which is observed in the phenol−pyridine complex.[19]

The out-of-plane bending mode, mimicking the τ_{OH} of the free phenol, upshifts to 645 (580, 621) cm^{-1}. Less substantial changes are predicted by the present ab initio methods in the phenol geometrical patterns in the vicinity of the OH group. For instance, the COH bond angle of phenol just slightly increases by 2.2° (0.7°, 0.7°). Nearly nothing special, to be pointed out, occurs in the phenol-bonded counterpart, except likely the blue-shifted ν(CN) mode by 14 (16, 16) cm^{-1} related to a shortening of the C≡N triple bond by 0.002 (0.002, 0.002) Å. The present value fairly matches the experimental blue shift of 12.5 cm^{-1} detected by White and Thompson.[4]

As mentioned, in the PheOH−ACN$_1{}^2$ complex, the acetonitrile molecule abuts the phenolic ring, forming the anchor π hydrogen bond between the C−H of acetonitrile and the π cloud of the phenol ring, mainly localized in the vicinity of its para carbon atom. The corresponding (C)H···C bond length varies from 2.905 (MP2/B) to 2.957 (MP2/B$^+$) and 3.097 (B3LYP/A) Å. The formation of π hydrogen bond is accompanied by the elongation of the C−C bonds close to the para carbon by 0.002−0.004 Å. Such π hydrogen is quite weak and likely cannot be responsible for its rather large binding energy of about 4 kcal/mol. However, the relative disposition of phenol and ACN in PheOH−ACN$_1{}^2$ shows that their dipole−dipole interaction serves as an extra stabilization factor.

The third minimum-energy structure, PheOH−ACN$_1{}^3$, only appears at the B3LYP level and straightforwardly converts to PheOH−ACN$_1{}^2$ under the MP2 refinement of the B3LYP optimization.

4. Phenol Bonding with Two Acetonitrile Molecules

After discovering in the preceding section the existence of two lower-energy structures of phenol and acetonitrile, we feel quite capable to explain the experiments via modeling an increase of the acetonitrile concentration microscopically. Although before we embark on that, it would be worth making a short excursion to the acetonitrile dimer because it is likely to anticipate that combining the locations of acetonitrile molecules in the PheOH−ACN$_1{}^1$ and PheOH−ACN$_1{}^2$ structures

ACN$_2$

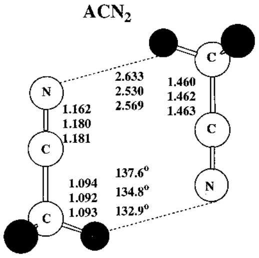
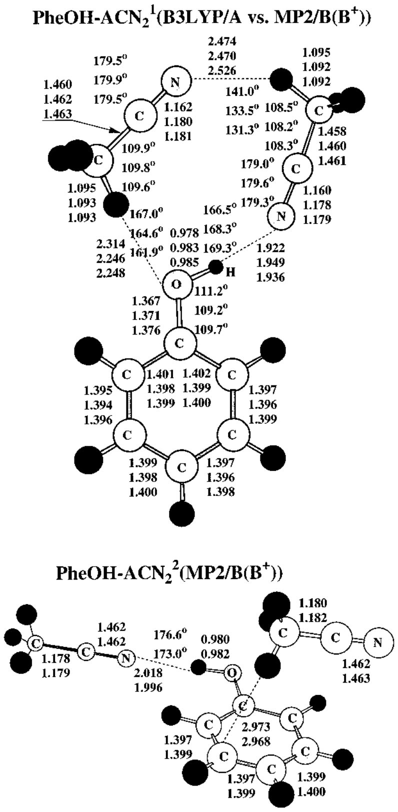


Figure 2. Acetonitrile dimer. The bond lengths (in angstroms) are indicated from top to bottom for the B3LYP/A, MP2/B, and MP2/B$^+$ computational levels, respectively.

leads to their partial dimerization, whenever another acetonitrile molecule is added to either PheOH−ACN$_1$^{1} or PheOH−ACN$_1$^{2}. There are two possible structures of the acetonitrile dimer: one is cyclic and the other one is built in a so-called “head-to-tail” manner (see, e.g., the recent references 18 and 20). Regarding the phenol−acetonitrile complexes, the latter ACN dimer structure seems to be not so important and actually plays a role beyond the second solvation shell and is nearly twice as weak compared to the cyclic dimer.[21] That is why we confine ourselves in the present study to the cyclic ACN dimer and provide its short description by demonstrating first its optimized structure in Figure 2, which looks similar to that drawn in Figure 2 of ref 20 and in Figure 7 of ref 18. The binding energy of the cyclic ACN dimer amounts to 4.1 (6.4, 6.3) kcal/mol and 3.4 (5.6, 5.5) kcal/mol after ZPVE. These values support, on one hand, the aforementioned suggestion of the relative poorness of the B3LYP description of the acetonitrile molecule, such that even a larger basis set C gives a binding energy of 3.4 kcal/mol after ZPVE. On the other hand, the present MP2 values agree satisfactorily with the MP2/cc-pVDZ and MP2/6-311+G(d) ones reported in refs 18 and 20.

The ACN dimer possesses two bonds of the C−H···N type, characterized by N···H lengths of 2.633 (2.530, 2.567) Å and bond angles of 137.6° (134.8°, 132.9°). Two CN stretch vibrations are tiny, split into the symmetric and asymmetric bands at 2358.1 (2228.5, 2213.7) and 2358.9 (2228.6, 2213.8) cm^{-1}. This demonstrates that its formation spectroscopically results in a small red-shifting of the ν(C≡N) by 1−6 cm^{-1}, compared to the free acetonitrile molecule.


PheOH-ACN$_2$^{1}(B3LYP/A vs. MP2/B(B$^+$))

PheOH-ACN$_2$^{2}(MP2/B(B$^+$))

Figure 3. Complexes of phenol with two acetonitrile molecules (bond lengths in angstroms).

TABLE 2: Some Key Features of the Phenol−Acetonitrile Complexes PheOH−ACN$_2$

	PheOH−ACN$_2$^{1}			PheOH−ACN$_2$^{2}	
feature^a	B3LYP/A	MP2/B$^+$	MP2/B	MP2/B$^+$	MP2/B
$-E$	573.04533	571.22920	571.19499	571.22573	571.18830
ZPVE	124.1		125.1		124.8
$-H$	572.83216		570.97950		570.97246
S	133.7		134.0		149.3
dipole	2.0	1.9	1.8	10.8	10.9
ν(IR)^b					
τ_{OH}	681		597		607
$\nu_{CN}{}^{l}$	2357		2229		2228
$\nu_{CN}{}^{h}$	2370		2247		2246
ν_{OH}	3587 (958)		3610 (793)		3660 (719)

^{a} Total electronic energy E and enthalpy H are in hartrees; zero-point vibrational energy (ZPVE) and binding energy E_f are in kilocalories per mole; entropy S is in cal/mol·T; total dipole moment is in debyes; frequencies ν are in reciprocal centimeters and their IR activities (IR) are in kilometers per mole. ^{b} $\nu_{CN}{}^{l,h}$ indicates the lower- and higher-frequency bands of the CN stretch.

Let us now consider the two lower-energy stable structures, PheOH−ACN$_2$^{1} and PheOH−ACN$_2$^{2}, of phenol with two acetonitrile molecules (the B3LYP analogue of the latter does not exist; rather, B3LYP predicts the another complex where the second acetonitrile molecule is located similarly to PheOH−ACN$_1$^{3}). They are displayed in Figure 3 and supplied therein by the optimized geometrical parameters. As seen in this figure, PheOH−ACN$_2$^{1} consists of a partially dimerized acetonitrile (cf. Figure 2). Relative to the asymptotically separated PhOH−ACN$_1$^{1} + ACN, the former structure appears to be the most stable, with binding energy E_f(PheOH−ACN$_2$^{1}) = 6.1 (8.6, 9.0) kcal/mol (5.3 and 8.1 kcal/mol after ZPVE at B3LYP/A and MP2/B, respectively), compared to the latter, whose binding energy comprises only 6.5 and 5.1 (4.4 after ZPVE) kcal/mol at MP2/B$^+$ and MP2/B, respectively. This is valid at 0 K. Temperature reverses this order due to the entropy effect, since the entropy of PheOH−ACN$_2$^{2} exceeds that of the complex PheOH−ACN$_2$^{1} by 15.0 cal/mol·T at MP2/B. It turns then out that at $T > 281$ K, that is, precisely the temperature when their enthalpy difference is canceled by their difference in entropy, the complex PheOH−ACN$_2$^{2} becomes more favorable in terms of Gibbs free energy. Particularly, at room temperature, the Gibbs free energy difference between the former and the latter complexes amounts to 0.2 kcal/mol. There is still another effect favoring a higher stability of PheOH−ACN$_2$^{2}. It plays mostly a role in polar solvents such as, e.g., acetonitrile inasmuch as this complex has a huge total dipole moment equal to 10.9 D, larger than in PheOH−ACN$_2$^{1} by a factor of 5.5 (their MP2/B polarizabilities and quadrupole moments are nearly the same: 152.9, 117.9, and 54.8 au vs 143.6, 85.7, and 88.7 au and 72.1, 59.6, and 88.5 D·A vs 52.0, 79.3, and 76.5 D·A, respectively).

Having cleared up the role that the complex PheOH−ACN$_2$^{2} might play in modeling an experimental setup with increasing acetonitrile concentration, let us now consider whether it looks somewhat peculiar in comparison to the other complex of phenol with two acetonitrile molecules. Surprisingly, it has precisely the feature we are looking for. As follows from Table 2, the MP2/B ν_{OH} stretch of phenol shifts further by 115 cm^{-1} toward lower wavenumbers compared with the free phenol and by −13 cm^{-1} compared to its frequency in PheOH−ACN$_1^1$. This is precisely in line with a stepwise effect of dilution on the shift[11] noticed in the Introduction. This is on one hand. On the other hand, the same stretch mode in PheOH−ACN$_2^1$ shifts more strongly, namely, red-shifting by 145 cm^{-1} compared to PheOH and by 63 cm^{-1} compared to PheOH−ACN$_1^1$. Both red shifts could be explained by the fact that the C−H···O bond, formed between the methyl group of acetonitrile and the lone pair of the oxygen atom of phenol, weakens the O−H bond in PheOH−ACN$_2^1$ and pushes the proton participating in the O−H···N hydrogen bonding toward N. This is readily seen in Figure 3 where the O−H bond in PheOH−ACN$_2^1$ is longer by 0.003 Å compared to that in PheOH−ACN$_2^2$. It is also worth mentioning the location of the ν(CN) bands in both complexes. As already discussed, this mode shifts to higher frequencies in the complex PheOH−ACN$_1^1$ by 16 cm^{-1} (MP2/B) that matches the expeimental shift of 12.5 cm^{-1}.[4] A similar shift of 17 cm^{-1} is predicted in the complex PheOH−ACN$_2^2$ where it also appears in the lower-frequency wing with the red shift equal to only 1 cm^{-1}, mimicking that found in the complex PheOH−ACN$_1^2$. In the complex PheOH−ACN$_2^1$, the higher frequency band is placed by 18 cm^{-1} aside that in the free acetonitrile molecule. Apparently, the other characteristic frequencies gathered in Table 2 might be of use to differentiate both complexes of phenol with two acetonitrile molecules.

5. Rather Concise Discussion

What have we to summarize after all? Primarily, we have found the novel structure by which phenol complexes with the acetonitrile molecule despite the widespread belief of the experimentalists. Such structure has an absolutely different hydrogen-bonding pattern, which certainly makes it less favorable compared with the conventional one attributed to the σ-type hydrogen bonding. We have shown that the novel, π hydrogen-bonding formation between phenol and acetonitrile plays a role under increasing concentration of acetonitrile molecules. Postulating and firmly approving its existence under such conditions, when phenol interacts with two acetonitrile molecules, we were able to explain the experimental data, which seem to have been rather unclear during the last four decades.

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References and Notes

(1) Riddick, J. A.; Bungh, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley: New York, 1986.

(2) Takamuku, T.; Tabata, M.; Yamaguchi, M.; Nishimoto, J.; Kumamoto, M.; Wakita, H.; Yamaguchi, T. *J. Phys. Chem. B* **1998**, *102*, 8880 and references therein.

(3) Jamroz, D.; J. Stangret, J.; Lingdren, J. *J. Am. Chem. Soc.* **1993**, *115*, 6165.

(4) White, S. C.; Thompson, H. W. *Proc. R. Soc. London* **1966**, *A 291*, 460.

(5) Sousa Lopes, M. S.; Thompson, H. W. *Spectrochim. Acta* **1968**, *24A*, 1367.

(6) Mitra, S. S. *J. Chem. Phys.* **1962**, *36*, 3286.

(7) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 371.

(8) (a) Gramstadt, T.; Sandström, J. *Spectrochim. Acta* **1969**, *25A*, 31. (b) Couzi, M.; Huong, P. V. *Spectrochim. Acta* **1970**, *26A*, 49. (c) Campbell, J. M.; Park, Y. S.; Shurvell, H. F. *Can. J. Spectrosc.* **1991**, *36*, 6. (d) Ng, J. C. F.; Park, Y. S.; Shurvell, H. F. *J. Raman Spectrosc.* **1992**, *23*, 229. (e) Ng, J. C. F.; Park, Y. S.; Shurvell, H. F. *Spectrochim. Acta* **1992**, *48A*, 1137. (f) Quadri, S. M.; Shurvell, H. F. *Spectrochim. Acta* **1995**, *51A*, 1355.

(9) Buckingham, D. A. *Proc. R. Soc. London A* **1958**, *248*, 169.

(10) (a) Horak, M.; Polakova, J.; Jakoubkova, M.; Moravec, J.; Pliva, J. *Collect. Czech. Chem. Commun.* **1966**, *31*, 622. (b) Horak, M.; Moravec, J. *Collect. Czech. Chem. Commun.* **1971**, *36*, 2757.

(11) Yarwood, J. In *Spectroscopy and Structure of Molecular Complexes*; Yarwood, J., Ed.; Plenum: London, 1973; p 182ff.

(12) Czarnik-Matusewicz, B.; Zeegers-Huyskens, Th. *J. Phys. Org. Chem.* **2000**, *13*, 237.

(13) (a) Figeys, H.; Geerlings, P.; Berckmans, D.; Van Alsenoy, C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 721. (b) Gramstadt, T.; Tjessem, K. *J. Mol. Struct.* **1977**, *41*, 231. (c) Baraton, M.-I. *J. Mol. Struct* **1971**, *10*, 231. (d) Abramczyk, H.; Reimschüssel, W.; Barańska, H.; Labudzińska, A. *Chem. Phys.* **1985**, *94*, 435. (e) Kryachko, E. S.; Nguyen, M. T. *J. Chem. Phys.* **2001**, *115*, 833. (f) Nguyen, M. T.; Kryachko, E. S.; Vanquickenborne, L. G. In *The Chemistry of Phenols*; Rappoport, Z., Ed.; Wiley: New York, 2002.

(14) Melikova, S.; Shchepkin, D.; Koll, A. *J. Mol. Struct. (THEOCHEM)* **1998**, *448*, 239.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98* (Revision A.5); Gaussian, Inc.: Pittsburgh, PA, 1998.

(16) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960.

(17) The B3LYP/6-31+G(d,p) optimized geometry of the acetonitrile molecule shown parenthetically in Figure 1 is fairly consistent with the microwave data (Demaison, J.; Dubrelle, A.; Boucher, D.; Burie, J.; Typke, V. *J. Mol. Spectrosc.* **1979**, *76*, 1; Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864): r(C−N) = 1.157 Å, r(C−C) = 1.462 (1.458) Å, r(C−H) = 1.095 (1.102) Å, and ∠C−C−H = 109.8° (109.5°) and appears to be more accurate than that obtained at the B3LYP/DZVP2 level (Barich, D. H.; Xu, T.; Song, W.; Wang, Z.; Deng, F.; Haw, J. F. *J. Phys. Chem. B* **1998**, *102*, 7163). See also Reimers, J. R.; Zeng, J.; Hush, N. S. *J. Phys. Chem.* **1996**, *100*, 1498, and compare with the values in Table 1 in ref 18. It becomes there evident that the MP2/6-311++G(d,p) level[19] overestimates the C−N and C−C bond lengths by ca. 0.005−0.017 Å and underestimates the C−H bond length by 0.010 Å.

(18) Cabaleiro-Lago, E. M.; Ríos, M. *J. Phys. Chem. A* **1997**, *101*, 8327 and references therein.

(19) Agarwal, U. P.; Green, R. S.; Yarwood, J. *Chem. Phys.* **1983**, *74*, 35.

(20) Reimers, J. R.; Hall, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 3730.

(21) According to the MP2/cc-pVDZ calculations,[20] the antiparallel dimer (ACN)$_2$ has a binding energy of 4.48 kcal/mol, whereas the "head-to-tail" dimer has a binding energy of 2.09 kcal/mol. The HF/STO-3G computational level substantially underestimates the former value by a factor of 2.6, as quoted by Wakisaka, A.; Shimizu, Y.; Nishi, N.; Tokumaru, K.; Sakuragi, H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1129, based on the incorrect ref 11. For the recent study of the acetonitrile dimer see Ford, T. A.; Glasser, L. *Int. J. Quantum Chem.* **2001**, *84*, 226.