The Proton Localization in Solid
2-(N-Diethylamino-N-oxomethyl)-4,6-dichlorophenol by Quantum Mechanical Calculations[*]

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One-dimensional proton potentials for O–H stretching are calculated for 2-(N-diethyl-amino-N-oxomethyl)-4,6-dichlorophenol, forming very short (2.400(5) Å) intramolecular O··H···O hydrogen bond. The calculated O–H bond length at different level of theory are compared with neutron diffraction data. The comparison of experimental IR spectra with calculated anharmonic ν(OH) band positions is performed. The problems of the basis set and appropriate structure selection as well as the role of surroundings are discussed.

The precise determination of the proton position is still a problem in X-ray crystallography, especially for a proton involved into hydrogen bonding. Theoretical methods are a potential source of such information, which can give also insight into the proton dynamics. As a rule the Born-Oppenheimer surfaces associated with hydrogen bonded systems are highly anharmonic. *Ab initio* programs like Gaussian or Gamess, on the other side, provide a harmonic approach, which is, therefore, of limited value for example in vibrational analysis. The calculated frequencies depend on the applied level of theory, but generally the agreement between calculations and experiment is much worse for the O–H vibrations than for the modes involving only heavy atoms [1]. The O–H stretching frequencies ν(OH) calculated in the harmonic approximation, as a rule, are of a few hundreds reciprocal centimeters higher than the experimental ones. *Ab initio* programs provide the r_e distances (at the minimum of the potential energy surface). On the other hand, the experiment gives, depending on temperature, the values averaged over different vibration modes (r_g). In the comparison with the experiment at not very high temperature one should take at least the value averaged over the ground vibrational ν(X-H) level – r_o. In the case of heavy atoms the differences are on the third decimal place, when distances are expressed in Å. For X–H bonds it can be up to a few hundredths of Å, which is much higher than the precision declared in different experimental techniques [2]. If one is interested in the pro-

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ton position in a hydrogen bond, where the proton potential is even more anharmonic than in the free X–H bond, then a treatment of the X–H stretching beyond the harmonic approximations is necessary in order to expect an agreement with the experiment. In order to describe the mechanical and electrical anharmonicity of a bond, one has to construct the reliable potential, and calculate the eigen values and wave functions for at least a few lowest vibrational levels.

The aim of this work is to demonstrate the use of direct outputs of Gaussian and Gamess type programs in solving such a task in relation to intramolecular hydrogen bond in solid 2-(N-diethylamino-N-oxomethyl)-4,6-dichlorophenol. The adiabatic potential for the O–H bond stretching was calculated by modulating the OH distance, while other geometric parameters keeping constant. It is based on numerous *ab initio* calculations, which show that stretching of the O–H bond is the only component of normal coordinate responsible for the $\nu_s(OH)$ absorption band in phenol derivatives, also those involved into hydrogen bonding [1,3,4].

The force field and potential energy distribution were calculated in this paper for the structure optimized at B3LYP/6-311++G** level. The mode characterized by the frequency of 2502 cm^{-1} consists entirely (99% in PED) the O–H bond stretching. The calculated frequency is much higher than the experimental one, which results from harmonic approximation in calculations and not adequate structure (too long hydrogen bond) used in the gas phase structure calculations. The obtained results demonstrate that the direction of this normal vibration is the O–H bond along. A similar procedure was used previously in literature, but mostly to describe the $\nu(OH)$ absorption, especially in strong hydrogen bonds [5–8] in the gas phase or inert gas matrices. The calculations also show that the difference between r_o and r_e in water dimer in the gas phase reaches the value up to 0.03 Å [7]. The change of the O–H bond length upon deuteration was calculated on the basis of similar gas phase O–H stretching potential in [9]. In the discussion on the anharmonic potential and the proton position in the solid state additional problems appear concerning the geometry of the rest of a molecule. The gas phase calculations, even at high levels of sophistication do not reproduce the geometry in the solid state. The most natural approach seems to take the calculated geometry, which is the nearest to the experimental one. The best solution, however, seems to be to take directly the structure from the solid state determinations. The validity of such an approach is the matter of testing in this work, by comparison the calculated expected values of O–H bond length with the best results of neutron diffraction experiment, as well as calculated $\nu(OH)$ band position with the results of direct measurements of the IR spectra in solid samples.

CALCULATIONS

The applied method of vibration levels calculations is related to Numerov method for solving one-dimensional (1D) time independent Schrödinger equation [10]. For numerically calculated proton potentials the one-dimensional Schrödinger equation was solved by using shooting method that falls into the category of solving ordinary differential equations that have to satisfy two boundary conditions. The proton wave-function should go to zero at both sites when one is approaching the hard-core part of the pro-

ton potential. The outline of the shooting method is as follows. The proton potential calculated at 20 points was interpolated using a cubic spline procedure. The time independent Schrödinger equation was rewritten as a system of two ordinary differential equations of the first order with respect to the OH distance. Some trial value of the eigen value was chosen and the wave function and its derivative were set to zero at the left site of the hard-core potential. The differential equations were integrated along the proton potential. If the numerically calculated wave function at the right part of the hard-core potential was zero (or within a small tolerance) the procedure ended, otherwise the guess for the eigen value was changed and the procedure was repeated. The procedure was implemented in a way that the wave function at the right part of the hard core region of the proton potential was assigned as a target function, which parametrically depends on the eigen value. Solving for eigen values in one dimension was performed by using numerical procedure. The program for solving 1D Schrödinger equation can be obtained from one of the authors (JM) on request. The calculations of the potential for the proton movement and vibration levels in some derivatives of picolinic acid N-oxide with the use of this program were already published [11].

RESULTS AND DISCUSSION

The object of our study is the short intramolecular hydrogen bond in 2-(N-dimethylamino-N-oxomethyl)-4,6-dichlorophenol (Figure 1).
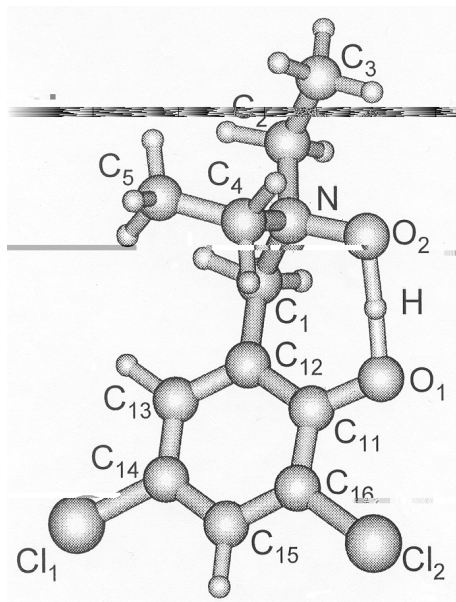

Figure 1. Structure of 2-(N-diethylamino-N-oxomethyl)-4,6-dichlorophenol.

The solid state IR spectra of O–H and O–D forms of this compound are shown in Fig. 2. The presented spectra suggest that hydrogen bond in studied system belongs to the class of proton-shared hydrogen bonds with the absorption of X–H stretching vibrations at about 1000 cm^{-1}. However, the hydrogen bond in this compound does not probably belong to A-class, according to Speakman [12] and demonstrated by HadJi *et al*. in acidic salts of carboxylic acids [13], where the centre of hydrogen bond coincides with the crystallographic symmetry element, but rather to pseudo A-class,

where there exists no symmetry element in the O...O distance centre, which are nevertheless nearly of the same strength as symmetric A-class hydrogen bonds. Such hydrogen bonds are characterized by very low sensitivity of $\nu(O..H..O)$ absorption on deuteration [14], that is seen also in Fig. 2. Such kind of very short hydrogen bonds with similar spectra were already demonstrated in salts of N-oxides of amines [15,16] and a single minimum potential was suggested [17,18]. The X-ray structure of the title compound was first time reported in [19] and two different molecules in the unit cell were found. The neutron diffraction studies of this crystal gave more precise parameters of the intramolecular hydrogen bonds [20], which are shown in Table 1. Nearly symmetrical proton distribution in a short –2.400(5) Å hydrogen bond was found. Nevertheless, the proton is clearly of the centre of homonuclear hydrogen bridge. The hydrogen bond is formed between non-equivalent oxygen atoms and there is no crystallographic symmetry at the centre of O···O distance. In such a case it was possible to distinguish the situation when the proton is distributed between two very closely located minima from the situation, when the proton is located at one minimum. The neutron diffraction experiment showed the proton distribution to be spherical and not elongated in direction of the hydrogen bridge [20], confirming a single minimum potential in our case.
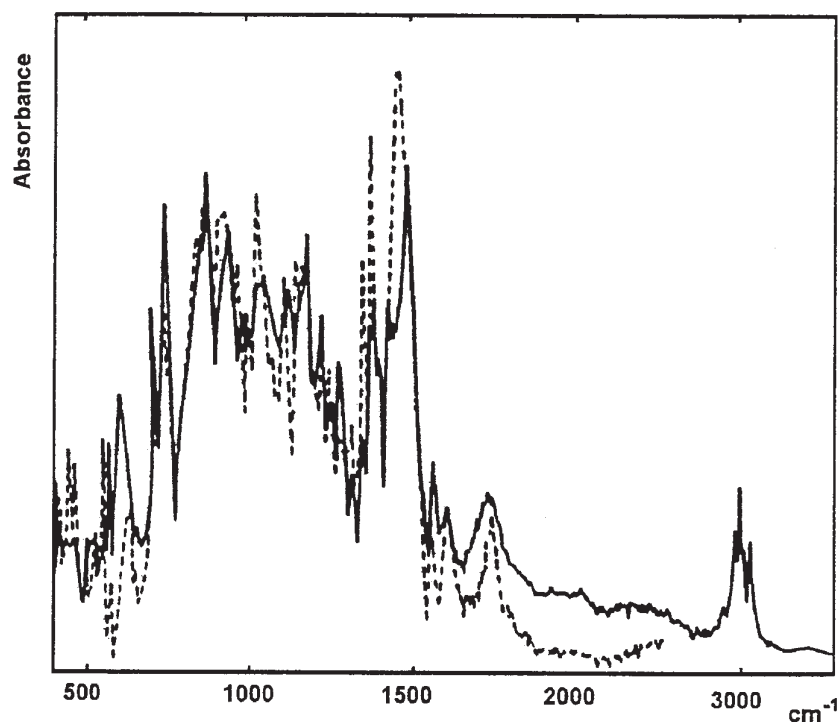

Figure 2. IR spectra of 2-(N-diethylamino-N-oxomethyl)-4,6-dichlorophenol in KBr pellets. Solid line – OH form, broken line – OD form.

Table 1. Experimental and calculated structural parameters of 2-(N-diethylamino-N-oxomethyl)-4,6-dichlorophenol.

Structure Parameters	Neutron diffraction		Calculations							
	A	B	HF 3-21G	HF 6-31G	HF 6-31G,ε	B3LYP/ 6-31G**	B3LYP/ 6-311++G**	B3LYP/ d95**,ε	B3LYP/ 6-31G**,ε	B3LYP/ 6-311++G**,ε
O1–C11	1.3191	1.3145	1.3290	1.3444	1.3440	1.3226	1.3263	1.3257	1.3193	1.3239
C11–C12	1.4191	1.4214	1.4006	1.4023	1.4038	1.4209	1.4170	1.4259	1.4231	1.4188
C12–C1	1.5043	1.5066	1.5100	1.5095	1.5107	1.5070	1.5078	1.5118	1.5087	1.5096
C1–N	1.5180	1.5166	1.5155	1.5047	1.5033	1.5325	1.5307	1.5285	1.5298	1.5279
N–C2	1.5117	1.5115	1.5078	1.5011	1.5036	1.5166	1.5202	1.5161	1.5171	1.5180
N–C4	1.5010	1.5022	1.5005	1.4966	1.4980	1.5202	1.5175	1.5201	1.5219	1.5217
C2–C3	1.4988	1.5169	1.5280	1.5194	1.5192	1.5196	1.5189	1.5242	1.5194	1.5187
C5–C4	1.5211	1.5169	1.5304	1.5231	1.5231	1.5240	1.5235	1.5288	1.5238	1.5234
C12–C13	1.4025	1.3960	1.3700	1.3908	1.3901	1.4006	1.3989	1.4043	1.3997	1.3980
C13–C14	1.3844	1.3861	1.3851	1.3762	1.3774	1.3890	1.3861	1.3953	1.3900	1.3872
C14–C15	1.3952	1.3829	1.3742	1.3788	1.3777	1.3943	1.3907	1.3991	1.3937	1.3902
C15–C16	1.3893	1.3883	1.3695	1.3783	1.3783	1.3895	1.3874	1.3950	1.3891	1.3871
Cl1–C16	1.7239	1.7363	1.8010	1.7934	1.7986	1.7495	1.7485	1.7559	1.7551	1.7544
C12–C14	1.7367	1.7393	1.8151	1.8074	1.8064	1.7606	1.7609	1.7612	1.7609	1.7606
C11–C16	1.4075	1.4116	1.3883	1.3895	1.3883	1.4149	1.4109	1.4188	1.4149	1.4103
O1···HO	1.1667(5)	1.187(6)	1.0361	0.9829	0.9871	1.0512	1.0335	1.0706	1.0704	1.0476
OH···O2	1.258(5)	1.214(6)	1.4589	1.6329	1.6093	1.4377	1.4869	1.3929	1.3924	1.4450

Table 1 (continuation)

O2–N	1.4066	1.4008	1.4696	1.4480	1.4462	1.3850	1.3851	1.3944	1.3881	1.3879
O1–O2	2.423(4)	2.400(5)	2.4828	2.5770	2.5593	2.4845	2.5113	2.4591	2.4592	2.4855
HO–O1–C11	108.6	108.8	112.2	112.6	112.1	109.1	108.7	108.1	108.8	108.3
C11–C12–C1	120.3	120.5	119.7	120.9	120.9	120.3	120.8	120.3	120.3	120.1
C12–C1–N	115.9	116.6	115.5	116.3	116.3	116.2	116.2	116.1	116.2	116.3
C1–N–O2	109.5	108.9	108.7	108.2	108.2	109.4	109.4	109.5	109.4	109.4
O1–HO–O2	175.8(5)	176.5(5)	168.5	159.6	160.0	173.1	170.5	173.1	173.7	171.2
HO–O1–C11–C12	23.6	19.2	26.7	32.2	31.9	21.8	23.9	23.6	22.3	24.1
N–C1–C12–C11	–63.8	–61.7	–69.1	–74.5	–74.1	–66.8	–68.7	–67.7	–66.9	–68.6

The calculations of the structure were performed with increasing sophistication of the quantum mechanical methods. The results of calculations are collected in Table 1 together with the experimental data. One can mention that the simple HF/3-21G method gives pretty good description of the experimental structures; the O…O distance is the shortest one among the calculated for the gas phase, but still longer than the experimental value in the solid state; the C–O distance is too long as well. The HF/6-31G calculations give worse agreement with the experiment than HF/3-21G; C–O and O···O distances are even longer. The better behaviour of HF/3-21G basis set results probably from a significant compensation of errors. Adding the polarization functions and passing to DFT methods with B3LYP functional results in decreasing the O···O distance to 2.485 Å; C–O becomes shorter (equal to 1.323 Å). Further improvement of basis set to 6-311++G** gives, however, $d_{O...O} = 2.511$ Å; the C–O distance is also too long in comparison to the experiment.

The discrepancies between calculated and experimental structures may result from the interactions between molecules in the solid state. To account the electrostatic interactions with the polar environment, the self consistent Onsager reaction field [21] method was applied as implemented in the Gaussian-94 package. The Onsager cavity radius of 4.2 Å was estimated from the volume occupied by a single molecule (*cf.* for example [22]) in the crystal structure. The electric permittivity equal to 1.9 was used, in accordance with the experimental value determined by Bator [23].

The last four columns of Table 1 present results obtained with a correction on the self consistent reaction field. Such a procedure makes generally the agreement with the experimental structures better. The O···O distances become shorter, but none of calculated values is so short as the experimental one. The proton is definitely localized at the phenolic oxygen atom. The conclusion is, that accounting the electronic interaction with surroundings, based on rational values of permittivity and radius of the Onsager sphere, is not sufficient to describe properly the experimental structure, where the proton is located nearly at the centre of the hydrogen bridge. As far as the comparison of calculation results with the experimental localization of the proton is concerned, one should account the anharmonicity of the potential for the proton movement within the hydrogen bridge. In calculations of the "adiabatic" potential for the proton movement, the rigid structures of molecules as optimized at HF/3-21G, B3LYP/6-31G** and B3LYP/6-311++G** levels were used. The O–H distances were adjusted within the range 0.65–2 Å. The rest of structural parameters were frozen. In the case of HF/3-21G structure, which contains one of the shortest calculated hydrogen bonds (*cf.* Table 1), the influence of the improvement of basis set as well as electron correlation were tested too.

Fig. 3 shows that including the electron correlation and improving the basis set, one obtains the potential wider and the proton position shifted towards the centre of the hydrogen bridge. The shape of the potential appears seriously dependent on the basis set. For all the potentials the wave functions and the vibration levels were calculated as described above. The average ("expected") values of r(OH) distance (r_o)

were calculated by using the square values of wave functions at the first vibration level as a proton distribution probability function.

The most important characteristics of the anharmonicity of the potentials are presented in Table 2. It contains also three of the first $\nu(OH)$ transitions, which demonstrate the spectroscopic anharmonicity of the obtained potentials and allows for verification of the calculated potential by the comparison with experimental spectra (Fig. 2)

Table 2. Basic characteristics of anharmonic potential for the proton movement; r in Å, ν_i in cm^{-1}.

Method	$r_e^{*)}$	r_o	ν_1	ν_2	ν_3
For optimized structures					
HF/3-21G	1.0375	1.0846	1755	3294	5146
MP2/6-31G//HF/3-21G	1.0582	1.1110	1575	3119	4935
B3LYP/6-311++G**	1.0341	1.0839	1648	3018	4703
B3LYP/6-31G**	1.0515	1.1103	1521	3083	4980
B3LYP/6-31G**,ε	1.0707	1.1452	1339	2986	4954
For solid state structure B					
MP2/6-31G	1.0765	1.1285	1700	3675	5931
B3LYP/d95**	1.0749	1.1247	1702	3666	5905
B3LYP/6-311++G**	1.0621	1.1165	1646	3539	5715
B3LYP/6-31G**	1.0710	1.1215	1694	3640	5861
For solid structure B with Onsager corrections					
MP2/6-31G	1.1405	1.1835	1498	3426	5656
B3LYP/d95**	1.1447	1.1865	1478	3396	5602
B3LYP/6-311++G**	1.1327	1.1893	1381	3229	5371
B3LYP/6-31G**	1.1392	1.1854	1457	3355	5541

$^{*)}$ r_e calculated as a minimum energy position of a given potential function.

Taking the r_o besides r_e, one obtains the extension of OH bond on 0.05–0.06 Å. It shows how important is the accounting the anharmonicity in comparing the results of calculations with the experiment, especially in strong hydrogen bonds. The calculated vibrational transitions are seriously improved in comparison to results of direct Gaussian output ($\nu_1 = 2549$ cm^{-1} in the case of HF/3-21G calculations and 2502 cm^{-1}, as calculated at B3LYP/6-311++G** level). The best agreement with the experiment was found for B3LYP/6-31G** method and MP2/6-31G method with HF/3-21G structure: the r_o values are the longest and $\nu(OH)$ frequencies are the lowest ones.

Table 2 shows simultaneously that neither O–H distance nor $\nu_1(OH)$ frequency reach the full agreement with the experiment for the four discussed above methods, which are presented at the top of Table 2.
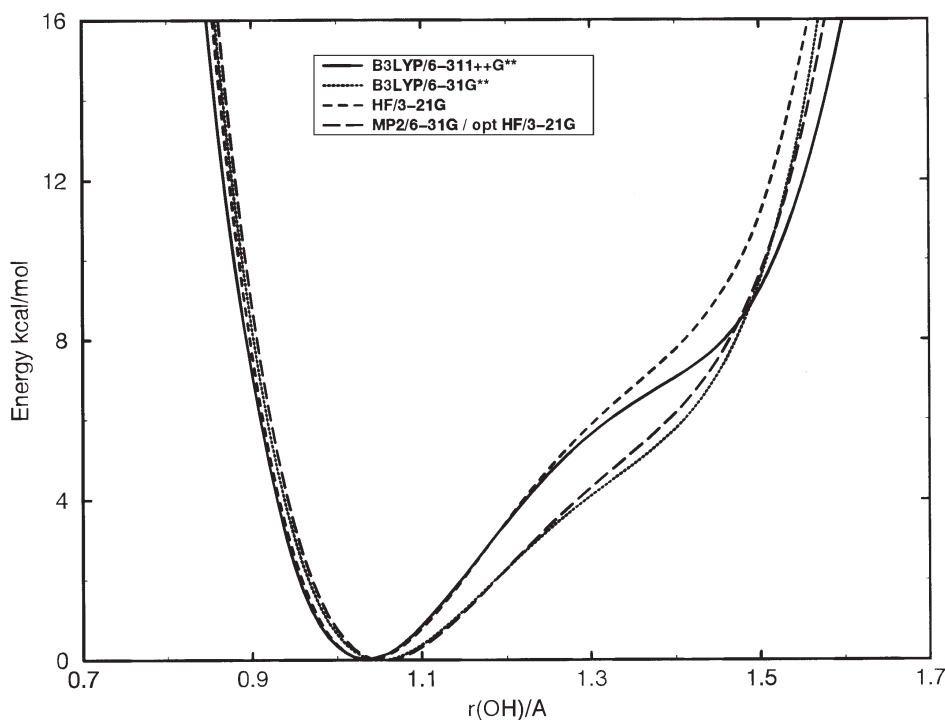
Figure 3. One-dimensional proton potentials for OH stretching in the title compound calculated at different levels of theory.

The next step of the approximation was made accounting for the dielectric (according to Onsager model) interactions in constructing the adiabatic potential for the proton movement. The calculations were performed at B3LYP/6-31G** level (*cf.* Table 2), which gave in the previous case the best approximation for both O–H distance and ν_1(OH) transition. The results are presented in Table 2 as B3LYP/6-31G**,ε variant. It is seen, that including the polarization interaction with surroundings pronouncedly improves the agreement with the experiment. The increase of r_o distance for the O–H bond is 0.035 Å in comparison to the anharmonic approximation. The ν_1(OH) decreases by nearly 180 cm^{-1} also in direction of the experimental results. Nevertheless, accounting the anharmonicity and polar interactions with surroundings is not sufficient to reproduce the experimental location of proton. Another factor influencing the results of calculations can be the structure modification resulting from crystal packing forces. This effect is not fully reproduced by only the polarization interactions. In attempt to reproduce the real potential for the proton movement, the geometry of molecule B from the crystal structure was accepted as a rigid frame. The calculations of the crystal structure effects were performed in MP2/6-31G, B3LYP/d95**, B3LYP/6-311++G** and B3LYP/6-31G** variants. An improvement of r_e and r_o values, but not the frequencies, can be mentioned for the calcula-

tions, which can be directly related to some of the previously discussed adiabatic potentials. It is seen that such an approach properly reproduces the trends in change of the geometric parameters, while the levels distribution appears to be very sensitive to the shape of the potential. From this point of view the polarization interaction with surroundings should not be excluded from considerations. Further calculations were performed, which take into account simultaneously mechanical anharmonicity, the crystal packing forces and the polarization interactions with the surroundings. Figure 4 presents graphically the gradual improvement of the potential shape upon sophistication of applied model.
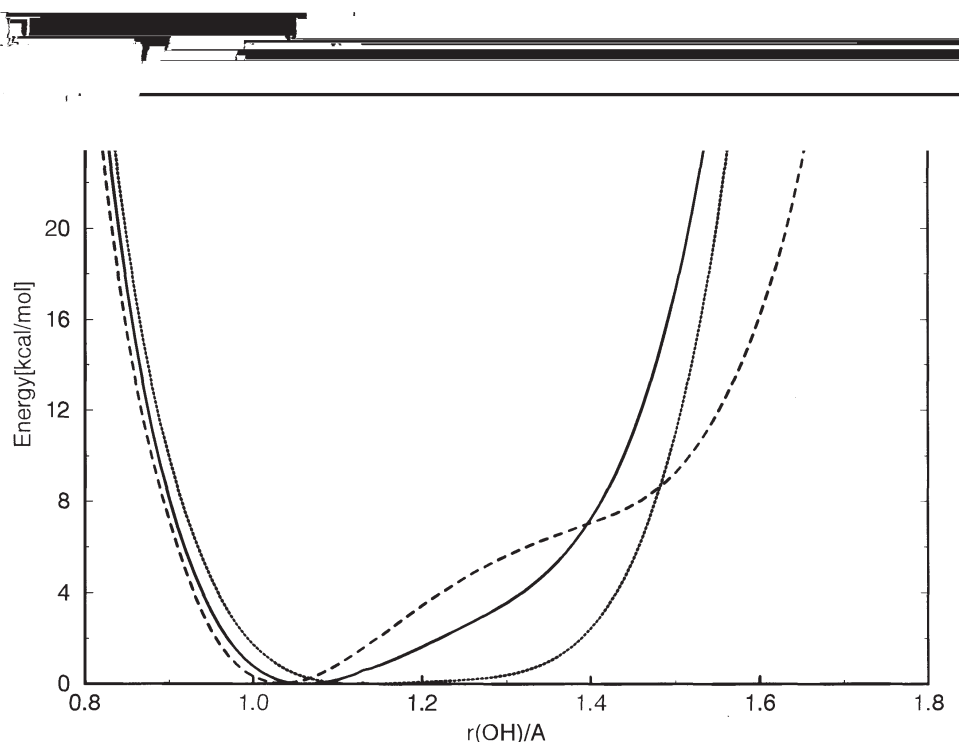

Figure 4. Influence of particular steps of improving the model of anharmonic potential for 2-(N-diethyl-amino-N-oxomethyl)-4,6-dichlorophenol on the shape of this potential.

Inspecting the related values in Table 2 one can state, that the complete agreement with the experiment was achieved, when discussing the proton localization. The frequencies of $v_1(OH)$ vibrations, even in such an approach are too high, when compared with the experimental results in the solid state. Trial calculations with permittivity equal to 3 are able to reproduce experimental both r_o and frequency values. It demonstrates that local polarization effects are stronger than it would result from bulky dielectric permittivity. Further improvement of the model calculations with direct accounting the local interactions is in progress.

CONCLUSIONS

Performed calculations demonstrate that the O–H distance, when this group is involved into hydrogen bond, cannot be reliably reproduced without the vibrational correction beyond the harmonic approximation. We also proved that the crystal field effects are not negligible. In the procedure described above, by applying the experimental O···O distance, we were able to account partially the crystal field effects and precisely reproduce the proton location within the hydrogen bridge. A substantial improvement in calculated frequencies was obtained. When harmonic, direct output of Gaussian gave $\nu(OH)$ frequency equal to 2500 cm^{-1} (experimental value is about 1000 cm^{-1}), the calculated anharmonic values obtained with the correlation on structural and polarization effects are less than 1500 cm^{-1}. A strong influence of the basis set on calculated frequencies was stated. Further improvement of basis set and possible study of overtones seem to be interesting in further testing of these effects. The approach applied can help in the discussion of the proton localization and its dynamics within the hydrogen bond, where the appropriate neutron diffraction results are not available.

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