

Molecular Structure of Complexes with Bifurcated Hydrogen Bond: I. *N*-(4-Methyl-2-nitrophenyl)acetamide

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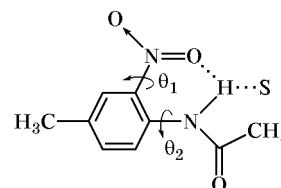
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Abstract—According to the results of HF/6-31G* and B3LYP/6-31G* nonempirical calculations, *N*-(4-methyl-2-nitrophenyl)acetamide in the synperiplanar and antiperiplanar conformations gives stable complexes with protophilic solvents, which are stabilized by bifurcated (three-center) hydrogen bond. The complexes are characterized by (1) opposite variations of the interatomic distances and angles corresponding to intra- and intermolecular components of the bifurcated hydrogen bond, (2) extension of the intramolecular component and a more pronounced shortening of the intermolecular component with increase in the strength of the three-center H-complex, and (3) nonlinear and nonmonotonic relation between the NH stretching vibration frequency and the energy of complex formation.

The concept of bifurcated hydrogen bond [1–5] has been developed with the goal of interpreting specific structure of some H-complexes in crystal. Most frequently, such bonds have been found in biogenic materials [6, 7]. During a certain period, it was presumed that the formation of bifurcated hydrogen bond is forced by solid phase effects. The first indications to the existence of such bonds in solution were obtained in 1960–1970 [8, 9]. However, as compared to common two-center H-bond, the properties of bifurcated hydrogen bond have been studied very poorly by both experimental and theoretical methods. The available information (except for a few data reported in [2, 10–14]) consists mainly of mere statement of the fact that a three-center H-bond exists [1, 8, 15–17], though it should be regarded as a factor determining a new type of specific solvation.

In the present communication we report the results of nonempirical calculations of the molecular structure of 1:1 solvate complexes formed by *N*-(4-methyl-2-nitrophenyl)acetamide and protophilic solvents (S), which are stabilized by a fairly strong bifurcated (three-center) hydrogen bond. The proton-donor fragment in these complexes was synperiplanar conformer of *N*-(4-methyl-2-nitrophenyl)acetamide (*sp,ap*-MH; here, the second index refers to rotation about the amide N–C bond), whose structure involves intramolecular hydrogen bond N–H···O [18–21]. The

presence of the latter is a necessary condition for formation of three-center H-complexes (according to the number of the neighboring heavy atoms).



Among protophilic solvents, we selected only those which are sufficiently strong hydrogen acceptors, for there are no distinct criteria to distinguish between three-center and van der Waals complexes of weak proton acceptors in the liquid phase. We also analyzed the energy parameters characterizing formation of solvate complexes and their vibrational spectra. The calculations were performed using two nonempirical methods, HF/6-31G* and B3LYP/6-31G*.

Table contains the most characteristic parameters of the solvate H-complexes formed by *N*-(4-methyl-2-nitrophenyl)acetamide. The following geometric parameters are given: $l_{N\cdots O}$ and $l_{N\cdots O(S)}$ are the lengths of intra- and intermolecular hydrogen bonds, respectively; $l_{H\cdots O}$ and $l_{H\cdots O(S)}$ are nonvalence distances corresponding to the intra- and intermolecular components of these bonds; θ_1 and θ_2 are the angles of

Calculated parameters of *N*-(4-methyl-2-nitrophenyl)acetamide and its solvate H-complexes with three-center hydrogen bond^a

No.	Hydrogen bond acceptor	$-\Delta E_{\text{H}}$, kcal \times mol ⁻¹	ν_{NH} , cm ⁻¹	$l_{\text{N}\cdots\text{O}}$	$l_{\text{H}\cdots\text{O}}$	$l_{\text{N}\cdots\text{O}(\text{S})}$	$l_{\text{H}\cdots\text{O}(\text{S})}$	$l_{\text{N}\cdots\text{H}}$	$\angle\text{N}-\text{H}\cdots\text{O}$	$\angle\text{N}-\text{H}\cdots\text{O}(\text{S})$	θ_1	θ_2	q_{H}
HF/6-31G*													
1	–	0	3878	2.640	1.874	–	–	0.994	131.5	–	5.9	10.8	0.467
2	Dioxane	3.55	3866	2.674	1.995	3.326	2.510	0.996	123.2	138.9	24.1	21.2	0.487
3	DMSO	7.99	3794	2.787	2.349	2.954	2.009	1.000	105.4	156.7	19.8	38.8	0.502
4	THF	4.18	3847	2.685	2.011	3.335	2.462	0.997	122.8	145.9	24.2	23.2	0.494
5	Tetra-methyl-urea	5.53	3834	2.686	2.039	3.219	2.337	0.998	120.4	146.8	27.1	22.6	0.502
6	DMF	6.32	3802	2.765	2.258	3.043	2.105	1.000	110.0	155.5	15.4	35.6	0.493
B3LYP/6-31G*													
7	–	0	3506	2.633	1.811	–	–	1.017	135.4	–	0.0	0.0	0.384
8	Dioxane	4.83	3538	2.671	1.904	3.296	2.536	1.016	130.0	131.3	1.3	20.2	0.399
9	DMSO	8.37	3469	2.720	2.071	3.027	2.116	1.020	119.3	147.5	7.3	24.4	0.417

^a Bond lengths are given in Å, and angles, in deg.

rotation of the nitro and amide groups relative to the benzene ring plane. The length of the N–H covalent bond is denoted as $l_{\text{N-H}}$; the oxygen atom in the solvent molecule, which acts as proton acceptor, is denoted as O(S); and q_{H} is the charge on the bridging hydrogen atom.

The data in table show that the donor component in the solvate H-complexes retains its molecular conformation (*sp,ap*-MH, $\theta_1 < 30^\circ$). The distance $l_{\text{H}\cdots\text{O}(\text{S})}$ between the solvent oxygen atom, which mediates interaction between the proton-donor and proton-acceptor components, and the bridging hydrogen atom is shorter than the sum of their van der Waals radii. The oxygen atom deviates by $\sim 25^\circ$ from the bisector of the external N–H \cdots O angle. The angle N–H \cdots O(S) is, on the average, $140 \pm 8^\circ$ (B3LYP/6-31G* and $149 \pm 6^\circ$ (HF/6-31G*), which is not typical of two-center hydrogen bonds. In other words, the structure of the coordination entity unambiguously indicates that the hydrogen bond is bifurcated. According to the calculations, three-center solvate complexes are stable. This follows from fairly high values of their formation energies (ΔE_{H} , see table). The coordination number of the bridging hydrogen atom in solvate complexes is equal to 3.

The coordination entity in the three-center complex is fairly labile from the geometric viewpoint. The appearance of intermolecular component leads to

weakening of the intramolecular hydrogen bond: it becomes longer, and the angle between the valence (N–H) and nonvalence (H \cdots O) bonds decreases (see table). As the intermolecular component strengthens, the intramolecular component further weakens: the corresponding nonvalence interatomic distances change in the opposite directions (Fig. 1). The relation between the intra- and intermolecular hydrogen bonds in the isolated solvate complexes is qualitatively consistent with the analogous relation obtained by Taylor and Kennard [22], who performed statistical analysis of structural information on multicenter hydrogen bonds in crystals.

An unexpected structural correlation was revealed while considering the calculated angles N–H \cdots O and N–H \cdots O(S) between the valence and nonvalence bonds in the coordination entity of the three-center complexes. We have found that these angles also change in the opposite directions (Fig. 2) for the complexes whose energy of formation is greater than 3.5 kcal/mol. Therefore, the orientation of the O(S) atom therein is determined mainly by fine details of the structure of the six-membered ring which is closed through the intramolecular N–H \cdots O bond. This fact must be taken into account in the statistical analysis, since the most probable $\angle\text{N}-\text{H}\cdots\text{O}(\text{S})$ values [4] are likely to make no significant sense for complexes with a variable proton acceptor.

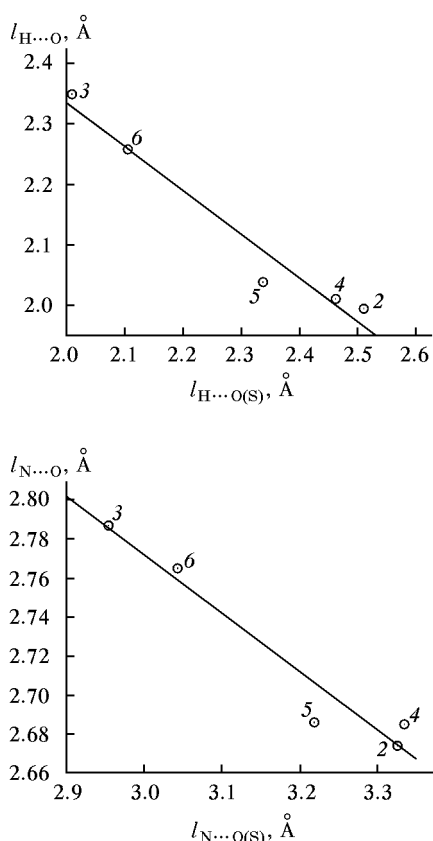


Fig. 1. Correlations between nonvalence distances corresponding to intra- and intermolecular components of the bifurcated hydrogen bond in solvate complexes of *N*-(4-methyl-2-nitrophenyl)acetamide according to the results of HF/6-31G* calculations. Hereinafter (Figs. 1–6), the numbering of proton acceptors is the same as in table.

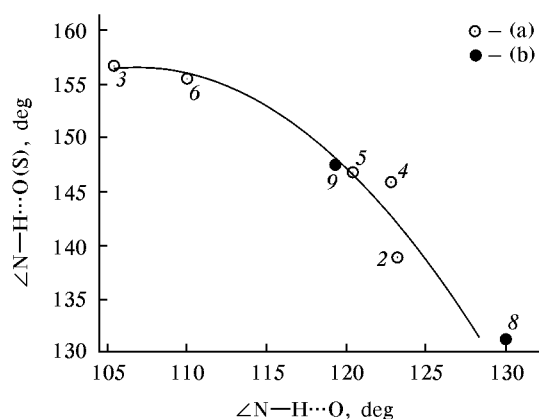


Fig. 2. Correlation between the angles formed by valence and nonvalence bonds in the coordination entity of three-center solvate complexes of *N*-(4-methyl-2-nitrophenyl)acetamide according to the results of (a) HF/6-31G* and (b) B3LYP/6-31G* calculations.

It was interesting to elucidate the relation between the energy of formation of solvate complex and geometric parameters of bifurcated hydrogen bond. The results are illustrated by Figs. 3 and 4. The two calculation methods revealed the same tendency: as $|\Delta E_H|$ rises, the intramolecular hydrogen bond weakens, while the intermolecular component becomes stronger; the first of these changes to a lesser extent. Insofar as solvate complexes, whose energy of formation $-\Delta E_H$ falls into the range from 3 to 8 kcal/mol, show nearly linear relations between the geometric parameters of the coordination entity (Fig. 1), we presumed that ΔE_H is proportional to the strength of the intermolecular component, expressed through the nonvalence distance $l_{N...O(S)}$. Analysis of the most reliable HF/6-31G* data showed that the correlation coefficient is not high and that an additional factor should be taken into account.

$$-\Delta E_H \text{ (kcal/mol)} = (23 \pm 2) - (8 \pm 1)l_{H...O(S)} \text{ (\AA)};$$

$$r = 0.972, s = 0.5, n = 5.$$

As with two-center hydrogen bonds, the formation of a three-center H-complex is accompanied by reduction of electron density on the bridging hydrogen atom (see table). Therefore, we made an attempt to correlate ΔE_H not only with geometric parameters of bifurcated hydrogen bond but also with variation of excess positive charge (Δq_H) on that atom upon complex formation. The following two-parameter equation is characterized by an acceptable correlation coefficient and statistically significant regression coefficients:

$$-\Delta E_H \text{ (kcal/mol)} = (19 \pm 2) - (6.6 \pm 0.6)l_{H...O(S)} \text{ (\AA)}$$

$$+ (72 \pm 22)\Delta q_H \text{ (a.u.);}$$

$$r = 0.983, s = 0.2, n = 5.$$

Using this equation, we estimated the interatomic distance $H...O(S)$, at which proton acceptor no longer affects charge distribution and ΔE_H tends to zero, and obtained a reasonable $l_{H...O(S)}$ value of 2.88 Å.

Calculation of the vibration frequencies of the isolated molecule of *N*-(4-methyl-2-nitrophenyl)acetamide and its solvate complexes revealed another interesting specific feature of the bifurcated hydrogen bond. According to the HF/6-31G* data, the frequency of N–H stretching vibrations (ν_{NH}) shows a nonlinear dependence on the energy of formation of three-center H-complexes. The results of B3LYP/6-31G* calculations demonstrated that this dependence is not only

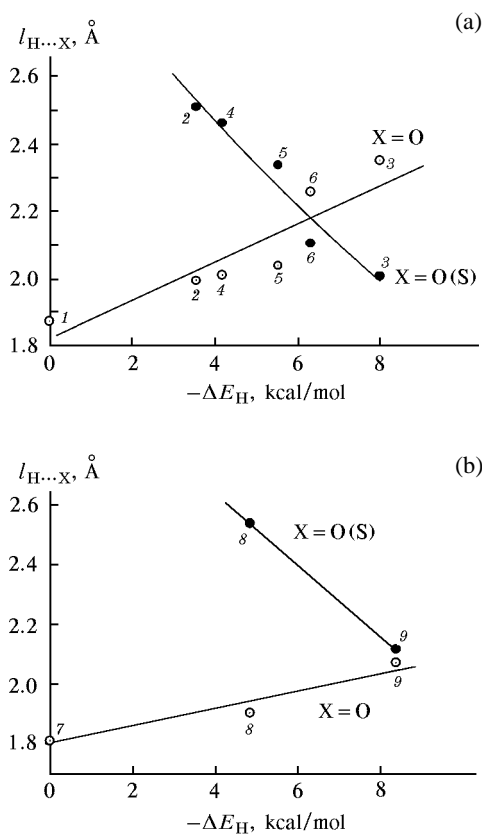


Fig. 3. Correlations between the geometric parameters of the intra- and intermolecular H-bond components in 1:1 solvate complexes of *N*-(4-methyl-2-nitrophenyl)acetamide and their energies of formation according to the results of (a) HF/6-31G* and (b) B3LYP/6-31G* calculations.

nonlinear but is also characterized by a clearly defined maximum (Fig. 5). Therefore, stretching vibration frequencies of the N–H bond in the nonspecifically solvated molecule and in the three-center H-complex may coincide with each other, which is impossible in the case of two-center H-bonding. From the viewpoint of hydrogen bond effect on ν_{NH} , this may be due to incomplete compensation of two oppositely acting factors. Weakening of the intramolecular N–H...O bond upon formation of a three-center H-complex leads to increase in ν_{NH} , whereas appearance and further strengthening of the intermolecular component reduces this frequency. Undoubtedly, in experimental studies more attractive are the results of calculations performed with account taken of electron correlation effects. Empirical confirmation of the predicted nonmonotonic dependence $\nu_{\text{NH}} = f(\Delta E_{\text{H}})$ could make it a fundamental spectroscopic criterion for formation of a bifurcated hydrogen bond in solution. However, it seems to be premature to directly extend theoretical predictions to real solutions for

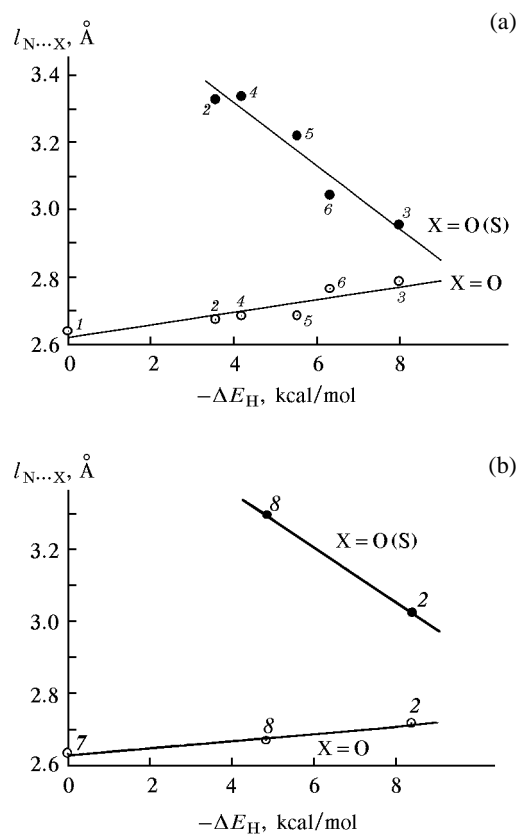


Fig. 4. Correlations between the lengths of the intra- and intermolecular hydrogen bonds in 1:1 solvate complexes of *N*-(4-methyl-2-nitrophenyl)acetamide and their energies of formation according to the results of (a) HF/6-31G* and (b) B3LYP/6-31G* calculations.

the following two reasons. First, three-center complexes with bifurcated hydrogen bond are very labile with respect to their geometry; therefore, the effect of nonspecific solvation on the structure of the coordination entity must be taken into account, and no predictions could be made without detailed examination of the solvate shell effect. Second, comparison of the results obtained by the two theoretical methods shows that the behavior of the function $\nu_{\text{NH}} = f(\Delta E_{\text{H}})$ is determined by the strength of the intramolecular hydrogen bond in the isolated molecule (cf. $l_{\text{N...O}}$ and $l_{\text{H...O}}$ in table). Therefore, we cannot rule out that, depending on the environment (pure protophilic solvents or their binary mixtures with an inert solvent), different relations between ν_{NH} and ΔE_{H} could be obtained for the same substrate.

Despite the above stated, there are no reasons to have some doubt as to spectroscopic criterion for formation of complexes with bifurcated hydrogen bond in solution will be found experimentally. This follows from numerous (though disembodied) data on

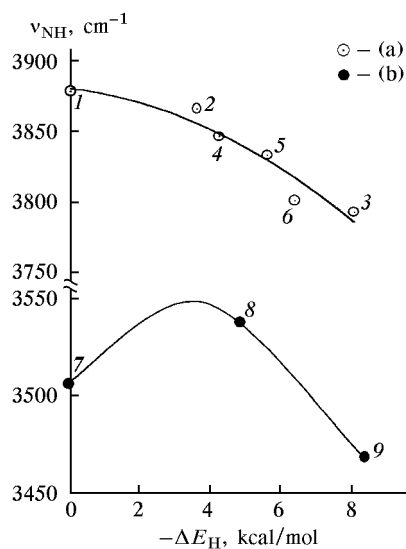


Fig. 5. Plot of the N–H stretching vibration frequency versus energy of formation of 1:1 solvate complexes of *N*-(4-methyl-2-nitrophenyl)acetamide according to the results of (a) HF/6-31G* and (b) B3LYP/6-31G* calculations.

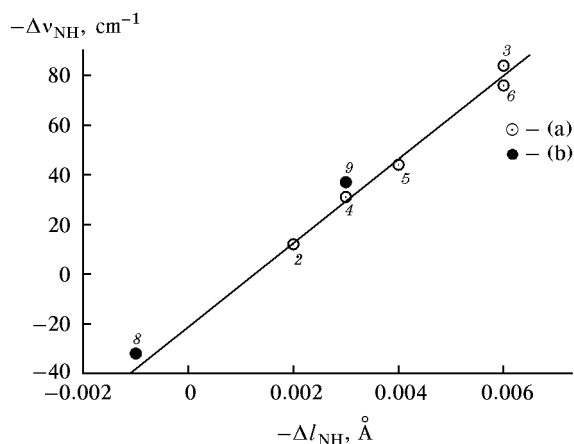


Fig. 6. Correlation between the changes on ν_{NH} and l_{NH} upon complex formation (with respect to the isolated molecule) according to the results of (a) HF/6-31G* and (b) B3LYP/6-31G* calculations.

the high-frequency shift of X–H stretching vibrations in solutions of compounds with very strong intramolecular hydrogen bond, such as *ortho*-substituted phenols [23–28].

In the case of two-center H-complexes, decrease in ν_{XH} results from weakening of the covalent X–H bond. Therefore, reasons for the anomalous behavior of ν_{NH} upon formation of a three-center complex should be sought for in the state of the N–H bond.

Figure 6 shows the relation between $\Delta\nu_{\text{NH}}$ and Δl_{NH} . It is seen that the variation of ν_{NH} for three-center solvate complexes is linearly related to the change of the N–H bond length, which is very typical for compounds with intramolecular hydrogen bond (see, e.g., [29–31]). Hence the gain in ν_{NH} observed for some complexes with bifurcated hydrogen bond is caused by shortening of the corresponding N–H bond (see table).

It should be emphasized that the above conclusions refer only to proton donors with intramolecular hydrogen bond. A different kind of bifurcated (three-center) hydrogen bond is likely to be characterized by different spectroscopic relations.

Nonempirical calculations of the energy, geometric parameters, and vibrational spectra of the isolated molecule of *N*-(4-methyl-2-nitrophenyl)acetamide and its 1:1 solvate complexes with proton acceptors were performed with the use of GAUSSIAN-98 software package [32].

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