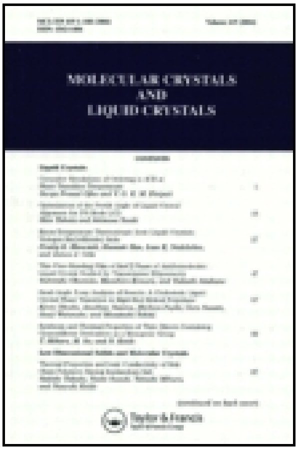

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Structural Features of Crystalline Hydrates of N'-Substituted Benzohydrazides and their Reflection in IR-Spectra

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Structural Features of Crystalline Hydrates of N′-Substituted Benzohydrazides and their Reflection in IR-Spectra

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The present paper gives a detailed discussion of the crystal structure features of *N*′-substituted benzohydrazide hydrates. The relation is found to exist between the hydration susceptibility and substituents nature, conformation and electron structure of their molecules. An assignment of the O—H stretching vibration bands of water molecules in IR-spectra is made. The condition of water in crystalline hydrates and its role in crystal stabilization is studied.

The study by single crystal X-ray diffraction analysis and IR-spectroscopy methods has shown that *N*′-derivatives of benzo-hydrazides (BH) I–IV (the Table) form crystalline hydrates of the 1:1 and 1:2 composition and/or anhydrous products depending on solvent composition and/or substituents nature.[1–9]

An amide group in all the structurally investigated BH has trans-conformation to the C_1—N_1 bond. Water molecules in crystalline hydrates participate in forming the intermolecular hydrogen bonds between amide groups of the neighbouring molecules.

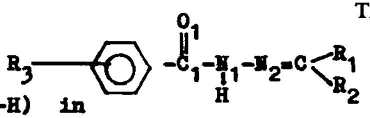
Hydrates of benzo-hydrazides in which water molecules form molecular complexes with hydrophilic centres of BH molecules resemble some biological substances.[10] Therefore, this work reports mainly the structural features of BH crystalline hydrates, the dependence of BH hydration ability on substituents nature, conformation and electronic structure of their molecules. Based on the structural analysis data, the assignment of OH stretching vibrations bands of water molecules is made. The condition of water in crystalline hydrates and its role in stabilizing the crystal structure is studied.

EXPERIMENTAL

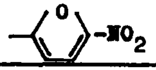
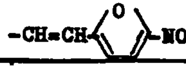
IR-spectra of I–IV BH pressed into KBr pellets were recorded on a UR-20 spectrophotometer. In order to reduce a diffusion band caused by absorption of ad-

TABLE

Benzohydrazides I-IV:



. Geometrical parameters of some H-bonds and frequencies for $\nu(O_w{-}H)$ in crystalline hydrates.

BH	Substituents R$_1$	R$_2$	R$_3$	Hydrate composition	Distances, Å $O_1 \cdots O_w$	Distances, Å $O_1 \cdots H_1$	Angle $O_1H_1O_w$, degrees	$\nu O_w{-}H_1$, cm^{-1}	Distances, Å $O_w \cdots O_{2,3}$	Distances, Å $H_2{-}O_{2,3}$	$\nu O_w{-}H_2$, cm^{-1}	Refs.
Ia		H	p-SO_2CHF_2	1:1	3.100	2.35	162	3480	3.24 3.21	2.56 2.59	3621	1
b	" - "	" - "	o-NO_2	1:1	2.969	2.34	149	3437	3.05 3.25	2.39 2.49	3606	2
c	" - "	" - "	p-Br	1:1	2.848	2.23	155	3393	3.02 3.23	2.50 2.67	3621	3
d*	" - "	" - "	H	1:1	2.784		165	3385	3.16 3.27	2.51 2.61	3600	4
				1:1	2.835	2.04	164	3483	-	-	-	4
e	" - "	" - "	di-m-NO_2	1:2	2.887	2.02	174	3463	3.06 3.13	2.51 2.43	3627	5
					2.930	2.39	135	3595	-	-	-	
f	" - "	" - "	m-Br	1:2	2.867	2.20	156	3480	3.19. 3.21	2.52 2.55	3610	6
					2.795	2.10	158	3425	-	-	-	
II		H	p-Br	1:1	2.914 2.810	2.31 2.01	147 156					7
III		CH_3	H	anhydr.								8
IV		H	H	anhydr.								9

*) Two independent molecules.

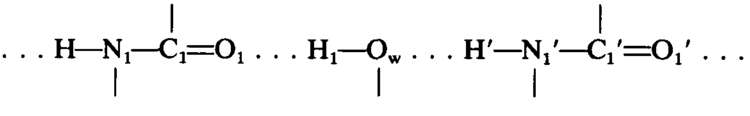
sorbed water, the spectra were recorded against KBr pellets. Full X-ray analysis data on BH are given in References 1–9. Calculation of distribution of the molecular electrostatic potential is performed using the semiempirical CNDO/2 method.[11]

DISCUSSION

The crystallization of BH from aquo-organic solvents gives clear yellow or yellow-brown crystals suitable for X-ray analysis, the BH I and II forming crystalline hydrates and BH III and IV crystallizing without water. Infrared bands of νOH for water molecules lie within the 3200–3800 cm^{-1} region. The νNH bands of amide groups in the BH spectra are in the 3200–3300 cm^{-1} region and, while BH is not a crystalline hydrate, the 3300–3800 cm^{-1} region is optically clear (Figure 1, spectrum 1). In this region, the BH II and I crystalline hydrates have νOH water bands (Figure 1, spectra 2, 3, 5, 6) disappearing on heating BH up to 90–110°C.[1] Dehydration of BH is followed by rearrangement of the crystal structure and monocrystals destruction. Anhydrous BH I produced by crystallization from dry organic solvents is also fine-crystalline. Some special conditions are evidently necessary to produce high-quality single crystals. Such crystals have not been yet produced and the structure of anhydrous BH I and II is not studied.

IR-spectra of BH Ia-f crystalline hydrates always give a very narrow intensive band in the 3600–3627 cm^{-1} region. Due to this fact the BH Ia-f are isolated into a separate group. Figure 1 gives a spectrum (3) of BH Ic. Spectra shapes of BH Ia and b in the νOH water region are similar to that of Ic. All of them consist of two bands: a very narrow one in the 3600 cm^{-1} region and a broader one within the 3400–3500 cm^{-1} interval. The frequencies of these bands maxima are listed in the Table.

X-ray analysis of BH Ia-c has shown them to be 1:1 crystalline hydrates. In crystals the BH molecules are realized in a polar syn-($O_1N_2O_2O_3$)-conformation (Figure 2). The water (w) molecule is located in the BH molecule plane and forms a hydrogen bond by one of its hydrogen atoms, $H_{1,w}$, with a carbonyl atom of oxygen, O_1. The geometrical parameters of this H-bond are listed in the Table. The second hydrogen atom, $H_{2,w}$, is directed toward oxygen atoms O_2 and O_3 of the nitrofuran fragment. Judging by distances to these atoms (the Table) which are close to upper limits of such distances in crystalline hydrates (H_w . . . . . . O ~ 2.4 Å and O_w . . . O 3.37 Å),[12] the oxygen atoms of the nitrofuran fragment can be only weakly H-bonded with O_w. An oxygen atom of the water molecule O_w is H-bonded with a nitrogen atom N_1 of the neighbouring molecule amide group (Figure 2). As a result, one-dimensional chains of amidohydrate H-bonds by the following scheme:



$$\ldots H{-}\underset{|}{N_1}{-}\overset{|}{C_1}{=}O_1 \ldots H_1{-}\underset{|}{O_w} \ldots H'{-}\underset{|}{N_1'}{-}\overset{|}{C_1'}{=}O_1' \ldots$$

are formed between BH molecules in the BH Ia-c crystals. According to the de-

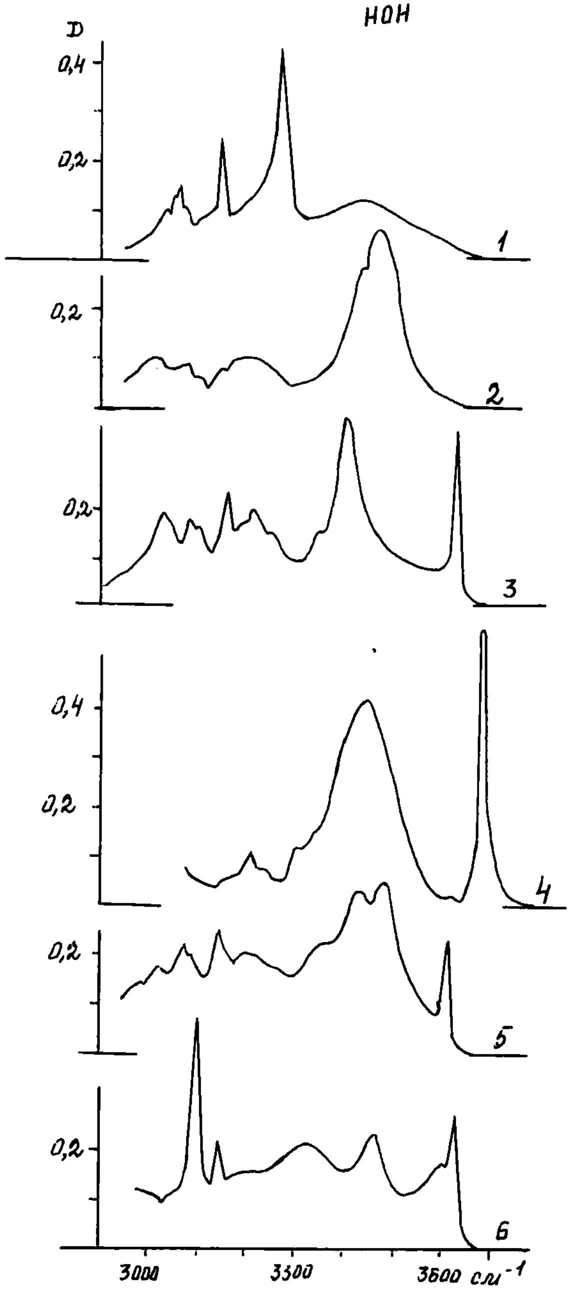


FIGURE 1 IR-spectra of BH IV (1), II (2), Ic (3), Ie (6), If (5) and a dilute solution of wet DMSO in CCl_4 (4).

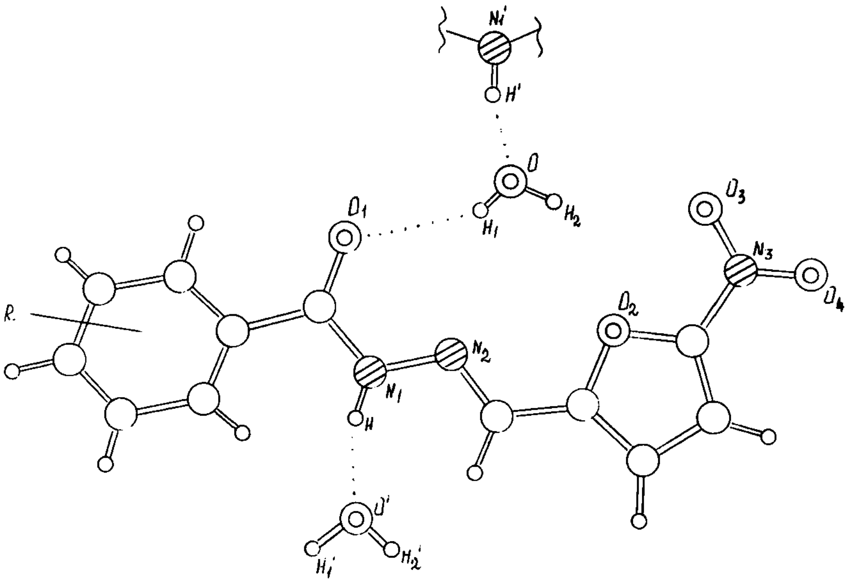


FIGURE 2 A drawing of H-bonds in monohydrates of BH I.

termined structure, the broad band in the 3400–3500 cm^{-1} region should be assigned to νOH of water participating in the H—bond $C_1{=}O_1 \ldots H_1{-}O_w$. As is seen from Figure 3, there is a linear dependence between the frequency and the $O_1 \ldots O_w$ distance in BH Ia—c. The narrow band in the 3600–3630 cm^{-1} region should be assigned to the $O_w{-}H_2$ stretching vibration. As has been mentioned above, the position of $H_{2,w}$ and the corresponding distances to O_2 and O_3 allow us to assume a weak bifurcated hydrogen bond. However, if band broadening is thought to be one of the spectral evidences of the H-bond presence, then the shape of the observed band does not suggest any disturbance of the $O_w{-}H_2$ stretching vibration by a hydrogen bond. In any case, the character of the $O_w{-}H_2$ interaction with O_2 and O_3 is the same as, for example, with CCl_4 in solutions containing

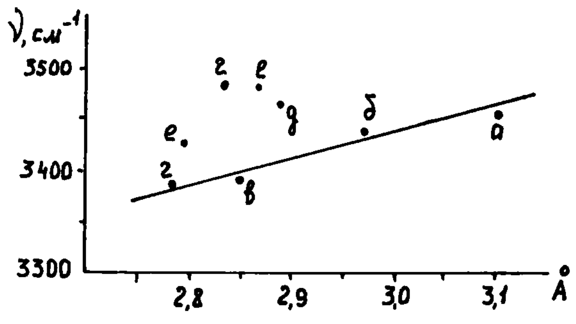


FIGURE 3 Frequencies for $\nu(O_w{-}H)$ versus the $O_w \ldots O_1$ distance for BH I.

HOH molecules that are asymmetrically H-bonded with some proton-acceptor.[13] The similarity between the water molecules spectra in such solutions and in the crystals Ia-c can be seen in Figure 1 where a spectrum (4) of a dilute solution of wet DMSO in CCl_4 is presented. In this spectrum, the narrow band due to a "free" proton vibration of the water molecule is at 3680 cm^{-1}. In more polar 1,2-dichloroethane this band is shifted toward lower frequencies (3657 cm^{-1}).[14] In BH I crystalline hydrates the electrostatic interaction of O_w—H_2 with the environment shifts this band even more, however, not altering the interaction nature. Thus we believe that the narrow band in the 3600–3630 and the broad one in the 3400–3500 cm^{-1} region in the BH I spectra testify for the presence of water molecules located in the plane of the BH molecules having a syn—($O_1N_2O_2O_3$)— conformation.

Let us examine what interactions may lead to a formation of such a hydroassociate. The syn-conformation of BH must be unfavourable from the point of view of electrostatic repulsion of the syn-located atoms $O_1N_2O_2O_3$. To denote the causes of formation of strong hydroassociates by BH I syn-conformers we have evaluated the electrostatic potential (EP) distribution about a BH model molecule in syn—($O_1N_2O_2O_3$)—and syn—(O_1N_2)—anti(N_2O_2)—conformations. Figure 4 (a,b) shows the maps of EP distribution in the plane of these molecules where, due to the program restriction,[11] the phenyl fragment is replaced by a methyl one. In the EP map of the syn-conformer (Figure 4a) in the heteroatom region, there is a negatively charged cavity whose inner size, as seen from the Figure, corresponds to the water molecule size. Such an EP distribution should apparently be responsible for the formation of the strong hydroassociates of the "key-lock" type and rigid fixation of the water molecule in the BH molecule plane. Such an interlocation of the BH and water molecules provides colinearity of their dipole moments resulting in increasing the sum dipole moment of the BH— H_2O associate. Really, the calculations by the $X\alpha$ method[15,16] have shown[4] that the dipole moment of the model syn-conformer BH I hydroassociate (the phenyl fragment is replaced by a hydrogen atom) is greater than in the absence of water (4.30 and 3.17 D, respectively). The increase of the dipole moment, in its turn, increases the energy of dipole-dipole interactions of the neighbouring molecules connected by a chain of amidohydrate H-bonds, that makes an additional contribution in stabilization of the crystalline structure as a whole.

According to the EP distribution (Figure 4b), the syn-anti-conformers should not be inclined to specific association with water, since the anti-located negative EP regions of the keto-hydrazone and nitrofuran fragments are surrounded by vast positive regions. The estimation of the dipole moment of the model syn-anti-conformer BH I has shown that its small value is practically unchanged in hydroassociation (~ 0.4 and 0.5 D, respectively). That means that the additional stabilization due to dipole-dipole interactions is absent in this case. BH III may serve as an example of a benzohydrazide where a polar syn-conformer cannot exist owing to steric hindrances (R_2=CH_3). This compound crystallizes in the form of non-polar syn-anti-conformers only that do not actually give any hydrates.

Thus, in the case of BH I crystalline hydrates we have shown the interaction of a large organic molecule with a water molecule leading to hydroassociate formation:

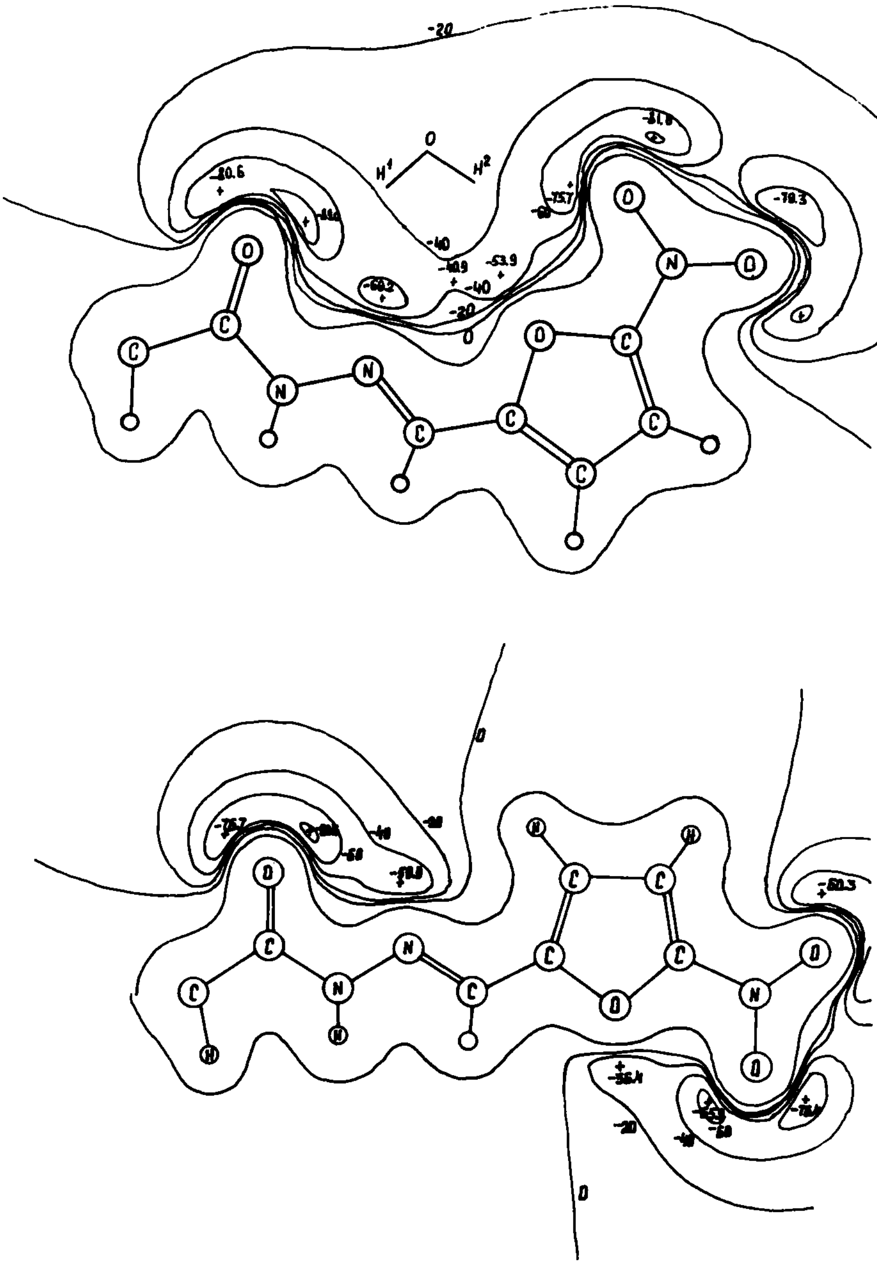


FIGURE 4 Distribution of the electrostatic potential in the plane of the syn- (a) and syn-anti-conformer (b) of the model BH I.

the syn-conformer BH I lends an energetic cavity to location of the water molecule stabilizing, in its turn, an energetically less favourable syn-conformation.

However, as our calculations have shown, the differences in energy of the syn-($O_1N_2O_2O_3$)- and syn-(O_1N_2)-anti- (N_2O_2)-conformers are not very large and the barrier of the syn → syn-anti transition of BH I evaluated by the CNDO/2 and INDO methods is sufficiently low. That suggests that in solutions the BH I conformers are in equilibrium, the shift of the latter to and fro depending on the solvent composition.

In the BH Id crystal structure we have found a proof of an unhindered syn → syn-anti transition in solution. It is a cocrystallization of the syn- and syn-anti-conformers of BH Id forming 1:1 hydroassociates. It is assumed that the formation of the non-polar syn-anti-conformer hydroassociate in this case is explained by the molecule packing effects in the crystal. Really, the BH Id molecules form uniform dense stacks of alternating parallel-arranged syn- and syn-anti-conformers packed "head-over-tail". The water molecules w and w′ are located one over another in the channels formed between the stacks, and their dipole moments vectors are antiparallel. The molecule w occupies a position typical for monohydrates in the syn-conformer plane. The w′ molecule is oriented nearly in the same way with respect to the syn-anti-conformer in the neighbouring stack, besides that the H_1—$O_{w'}$—H_2 atoms go out of the syn-anti-conformer's plane by 0.46, 0.69, and 0.26 Å, respectively. The fact that the w′ molecule goes out of the syn-anti-conformer's plane can be explained, on the one hand, by the absence of the orientating influence of the O_2 and O_3 atoms of the nitrofuran fragment and, on the other hand, by steric and electrostatic repulsions between $H_{2,w'}$ and H_4 in the furan ring. The ejection of the w′ molecule out of the syn-anti-conformer's plane results in the pairwise mutual approach of w and w′ in the channels up to a distance of 2.94 Å. (The w′ . . . w distance is 4.33 Å.) Such an arrangement of the water molecules in the channel provides an interaction of their antiparallel dipoles making an additional contribution into the energy of interactions in the crystal.

All the above-stated suggests that the formation of the syn-anti-conformer hydroassociate occurs at the crystallization stage.

Stretching vibrations of the four non-equivalent hydrogen atoms of different water molecules in the BH crystalline hydrate were to give four well-resolved bands in the IR-spectrum, since the geometry of the H-bonds C═O . . . H_1—$O_{w,w'}$ and the surroundings of $O_{w,w'}$—H_2 are considerably different. However, there are only three bands observed: the narrow one at 3600 cm^{-1} and two broader ones at 3483 and 3385 cm^{-1}. In analogy with BH Ia—c and according to the linear dependence of ν(OH) on l_{O_w} . . . O_1 the bands at 3385 and 3600 cm^{-1} should be assigned to the H_1—O_w—H_2 stretching vibrations of the water molecule located in the syn-conformer's plane. Then the band at 3483 cm^{-1} should be assigned to $\nu(O_{w'}—H_1)$ of the water molecule interacting with O_1 of the syn-anti-conformer. The high frequency, in spite of a relatively small distance $O_{w'}$ . . . O_1 (2.835 Å), is obviously due to the fact that the w′ molecule goes out of the syn-anti-conformer's plane.

A narrow band that should have been corresponding to $\nu(O_{w'}—H_2)$ is absent in the spectrum, that may be associated with the differences in the polarity of the O—H_2 bond in w and w′. The calculations have actually shown that the values of the positive (per H_2) and negative (per O_w) charges in the syn-conformer hydrate are considerably greater than in the syn-anti-conformer. In the latter case, the intensity of the $\nu(O_w—H_2)$ band is assumed to be very weak and it does not appear in the spectrum.

It has been demonstrated above that the absence of the orientating effect of the oxygen atoms O_2 and O_3 of the nitrofuran fragment leads either to the absence of BH association with water (BH III) or to the water molecule going out of the BH molecule plane (BH Id). BH II and IV are the other examples of the observed effect.

BH II, where the nitrofuran fragment is replaced by an p-nitrophenyl one, forms a 1:1 crystalline hydrate in which the BH molecules are stacked.

The absence of the specific influence of the nitrofuran fragment has led not only to the water molecule going out of the BH molecule plane but also to the $H_{2,w}$ atom rotation about the $H_1—O_w$ axis in the direction of another stack of the BH II molecules and the formation of one more H-bond $O_w—H_2 \dots O_1''{=}C_1''$ (Figure 5). Thus the water molecule has appeared to be included into two amidohydrate H-bonds between the BH molecules of the neighbouring stacks: $C_1{=}O_1 \dots H_1—O_w \dots H—N_1'$, and between pairs of molecules inside the stack: $N_1'—H \dots O_w—H_2 \dots O_1''{=}C_1''$. In the hydrogen bond system formed the water molecule is pyramidally three-coordinated and the oxygen atom of the carbonyl group is two-coordinated as distinct from the above crystalline hydrates. The water molecule hydrogen atoms are involved in the H-bonds of the same type but geometrically nonequivalent, forming a centrosymmetric cyclic structure. In the IR-spectrum of BH II (Figure 1, spectrum 2) the νOH bands merge into one broad band with a common maximum at 3480 cm^{-1}.

In the molecules of BH IV there is a vinyl group located between benzohydrazide and nitrofuran fragments of the molecule. However, BH IV does not form crystalline hydrates, although crystallizing in syn-conformation. The increase of the distance between the O_1, N_2 and O_2, O_3 is assumed to lead to decreasing the electrostatic repulsion between these atoms and, hence, to the possibility of existing of the polar syn-conformation without additional stabilization by the water molecule.

The BH IV molecules in the crystal are bonded by a linear chain of amide H-bonds in which the dipole moments vectors of the amide groups are uniformly directed. The νNH band at 3277 cm^{-1} is intensive, comparatively narrow, with a sharp peak that distinguishes it from νNH bands of the above BH whose spectra in the region of 3180–3300 cm^{-1} usually show a poorly resolved doublet with sloping peaks and optical density in the maximum (D) comparable with D of the νCH band of the furan ring (3140–3160 cm^{-1}). This character of the band is obviously accounted for by the syn-phase vibration of NH in the chain H-bonding the identical molecules.

The crystalline hydrates BH Ie,f of the 1:2 composition are interesting examples of a polar syn-conformer association with a water dimer, $O_{w1} \dots H_2—O_{w2}$. The BH Ie,f molecules in the crystal are stacked. The character of amidohydrates H-bonds formation is the same as in BH II: infinite H-bonds chains bind BH molecules of the neighbouring stacks and inside the stacks the centrosymmetric cyclic H-bond

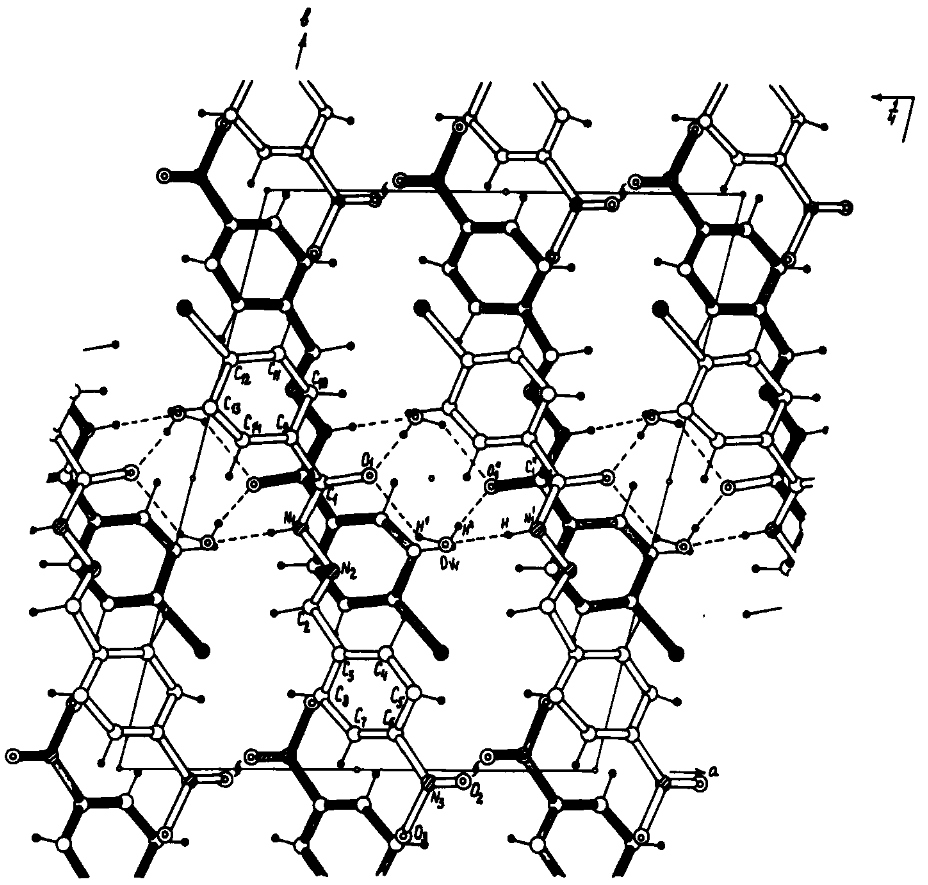


FIGURE 5 Projection of the BH II crystalline hydrate on the *ab* plane.

system pairs the BH molecules. The difference between BH Ie and If is in the fact that in BH Ie the water dimer is between the neighbouring stacks, and in BH If it is inside the stack.

In BH Ie (Figure 6) one water molecule, w_1, occupies a position typical for monohydrates of the BH I syn-conformers in the BH molecule plane and is plane-coordinated. Two bands, broad at 3463 cm^{-1} and narrow at 3627 cm^{-1}, are assigned to $\nu(O_{w1}—H_1)$ and $\nu(O_{w1}—H_2)$, respectively (Figure 1, spectrum 6). The second water molecule w_2, linearly H-bonded to w_1,$O_{w1} \ldots H_2—O_{w2}$, is turned with respect to w_1 by 68° and forms two more H-bonds with amide groups of two BH molecules of the neighbouring stack:$O_{w2} \ldots H—N_1{}'$ and $O_{w2}—H_1 \ldots O_1{}''=C_1{}''$ $(O_1=C_1)$ (Figure 6).

It has been found that in the formed system of hydrogen bonds, the $O_{w1} \ldots O_{w2}$ distance is very short (2.658Å). This value is shorter than both the theoretically calculated (2.740–3.035 Å)[11] and experimentally found (2.98 ± 0.04 Å)[17] values in an isolated dimer, $(H_2O)_2$, which is altogether not so surprising.[10]

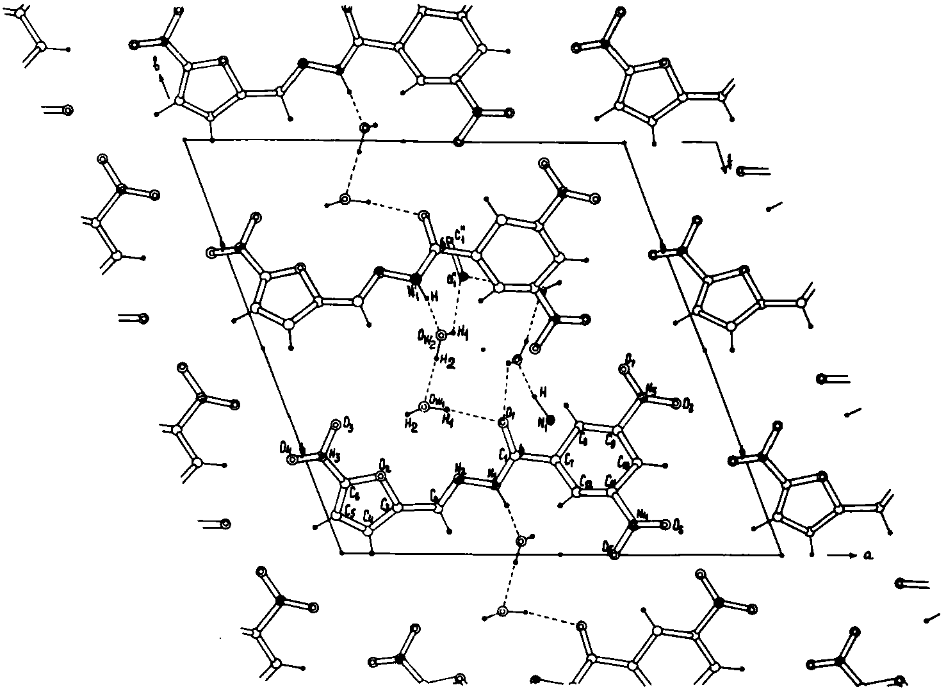


FIGURE 6 Projection of the BH Ie structure on the *ab* plane.

However, this distance has appeared to be shorter than that usually observed in proteins (2.79 ± 0.08Å).[10] In the IR-spectrum the broadest and lowest frequency band of the four νOH bands should be assigned to $\nu(O_{w2}—H_2)$. The frequency of the maximum for this band (3325 cm^{-1}) is more than 200 cm^{-1} lower than for the isolated dimer (3548 cm^{-1}),[10] that is partially caused by a shorter $O_{w1} \ldots O_{w2}$ distance.

The $O_{w2} \ldots N_1'$ distance (2.739 Å) is much shorter than in all the BH investigated (2.83–3.13 Å). The narrow intensive νNH band (3097 cm^{-1}) that is markedly shifted to the low frequency region from the typical range of 3180–3300 cm^{-1} testifies for increasing of the proton-acceptor capability of the O_{w2} atom as compared with the oxygen atom in the monomeric water molecule. Thus, the geometric and spectral data are an evidence of an increase of intermolecular interactions in the one-dimensional H-bond system with the participation of the water molecule linear dimer.

The band at 3595 cm^{-1} should be assigned to $\nu(O_{w2}—H_1)$. The geometry of the H-bond $O_{w2}—H_1 \ldots O_1''$ is such that the$H_{2,w2}$ atom is in the plane that is almost perpendicular to the carbonyl group plane, i.e. is affected by the O═C bond π-electrons. In Reference 18 it was shown that, under similar conditions, when the X—H . . . O atoms are located linearly, there appears a comparatively strong H-bond. In this case, due to the small angle $O_{w2}— H_1 \ldots O_1''$ (135°) the disturbing effect of the carbonyl group π-electrons on the electrons of the O—H bond is insignificant, despite the comparatively short $O_{w2} \ldots O_1''$ (O_1) distance of 2.93 Å. Therefore, the $\nu(O_{w2}—H_1)$ band is observed at rather high frequencies, nearly in the region of the "free"$H_{2,w1}$ stretching vibrations. However, the band broadening proves the existence of the H—bond $O_{w2}—H_1 \ldots O_1''$.

Figure 6 shows that the w_2 molecule participates in two types of amidohydrate H-bonds: in the infinite one-dimensional H-bond chain between the BH molecules stacks and in the cyclic system pairing the BH molecules inside the stack.

In the crystalline hydrate BH If the dimeric water associate $w_1 \ldots w_2$ is included in the cyclic system of the amidohydrate H-bonds inside the stack, only one w_2 water molecule participating in the chain of H-bonds between the stacks (Figure 7). The w_1 molecule occupies a position typical for BH I in the chelate cavity. The IR-spectrum shows the $\nu(O_{w1}—H_1)$ and $\nu(O_{w2}—H_2)$ bands (the Table, Figure 1, spectrum 5). The w_2 molecule bound with w_1 by the H-bond $O_{w2}—H_2 \ldots O_{w1}$ is not only turned relative to the [BH·w_1] complex plane by 89° but also goes out of it by 2.13 Å ($H_{2,w2}$), 2.88 Å (O_{w2}) and 3.25 Å ($H_{1,w2}$), respectively. As a result, the O_{w1} atom has a pyramidal coordination with the$O_{w1} \ldots O_{w2}$ distance of 2.766 Å. This distance is longer than that in the water dimer of BH Ie. Here, the maximum of the $\nu(O_{w2}—H_2)$ band is shifted toward the greater frequency region (3360 cm^{-1}). The bands at 3425 and 3480 cm^{-1} should be respectively assigned to the $\nu(O_{w2}—H_1)$ and $\nu(O_{w1}—H_1)$ in agreement with the$O_{w2} \ldots O_1$ (2.795 Å) and$O_{w1} \ldots O_1''$ (O_1) (2.867 Å) distances.

An analysis of the frequency for $\nu(O_w—H)$ plotted against the $O_w \ldots O_1$ distance displays some definite correlations. In monohydrates with a one-coordinated oxygen atom of the carbonyl group there is a linear dependence between the frequency and the $O_w \ldots O_1$ distance. In the case of the two-coordinated atom O_1 such a strict regularity is not observed, the interval $1_{O_w \ldots O_1}$ is narrower and all the frequencies for $\nu(O_w—H)$ are much higher than in the linear dependence

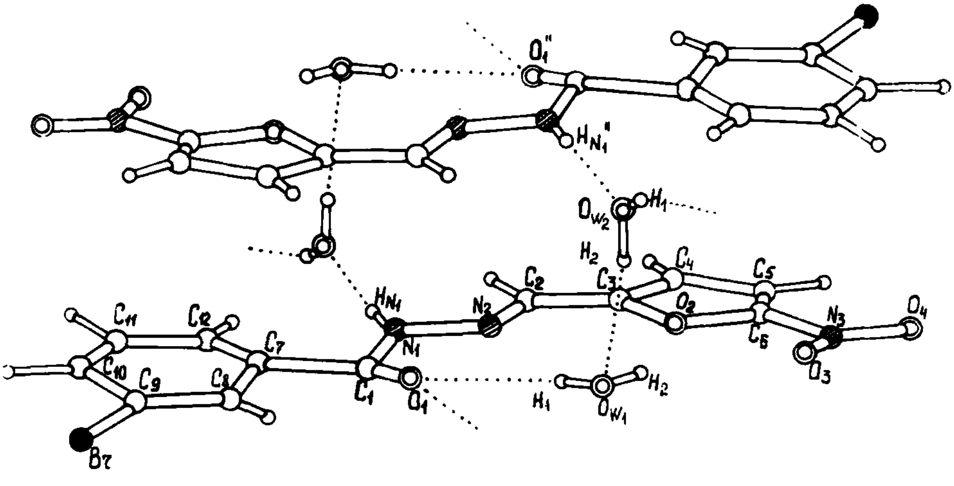


FIGURE 7 The H-bond system in the BH If crystalline hydrate.

for monohydrates. High frequencies testify for a weaker interaction of $O_w—H \ldots O_1{=}C_1$ in the case of the two-coordinated O_1 atom.

CONCLUSION

It has been mentioned in the Introduction that the investigated BH may be viewed upon as models of proteins, peptides and some other biological substances. It is known that the interaction between amides and water is stronger than amide-amide interactions and the hydrophilic character of the amide groups is provided by the presence of a carbonyl oxygen atom, rather than an NH group.[10]

The present investigation of the structures of BH crystalline hydrates has allowed us to elucidate the fact that the presence of the amide group is a necessary but insufficient condition for hydration. The existence of some peculiarities in molecular and crystal structure of BH crystalline hydrates favours their formation. Such features include the existence of several hydrophilic centres and the conformational mobility promoting the formation of chelate complexes [$H_2O{\cdot}BH$]. Stack-packing of the BH molecules, with water molecules located in channels between them, also makes a contribution into the processes of formation of crystalline hydrates. In some BH both the factors participate in crystalline hydrates formation. As in proteins,[10] the additional H-bonds in the presence of water molecules increase the stability of the crystalline structure as a whole, saturating other, than amide, acceptor centres.

The IR spectroscopic investigations of BH crystalline hydrates are of special interest as it enables us to evaluate the energetics of interactions, that is very difficult to do when studying hydrogen bonds in proteins, peptides, etc. Thus, it has been shown that some hydrophilic centres, or rather their combinations, in the BH molecule produce only an orienting effect on a water molecule, not forming H-bonds. It has also been found that very strong intermolecular interactions arise when the water dimer is involved in the linear chain of amide H-bonds.

We may conclude that the results obtained make a definite contribution into understanding the hydration of complex organic molecules.

References

1. S. M. Aldoshin, A. N. Chekhlov, E. G. Atovmyan, O. A. Kozina, V. S. Nedzvetskii, V. G. Andreev, A. S. Kulikov, L. O. Atovmyan and L. M. Yagupolskii, *Izv. Akad. Nauk SSSR* (*ser. khim.*), 1312 (1988).
2. S. M. Aldoshin, O. A. Kozina, L. O. Atovmyan, V. S. Nedzvetskii, A. S. Kulikov and V. I. Pantsyrnyi, *Izv. Akad. Nauk SSSR* (*ser. khim*), in press.
3. S. M. Aldoshin, O. A. Kozina, E. G. Atovmyan, L. O. Atovmyan and V. S. Nedzvetskii, *Izv. Akad. Nauk SSSR* (*ser. khim.*), 2308 (1988).
4. S. M. Aldoshin, O. A. Kozina, G. L. Gutsev, E. G. Atovmyan, L. O. Atovmyan and V. S. Nedzvetskii, *Izv. Akad. Nauk SSSR* (*ser. khim.*), 2301 (1988).
5. S. M. Aldoshin, E. G. Atovmyan, L. O. Atovmyan, O. A. Kozina and V. S. Nedzvetskii, *Izv. Akad. Nauk SSSR* (*ser. khim.*), in press.
6. S. M. Aldoshin, A. N. Chekhlov, E. G. Atovmyan, O. A. Kozina, L. O. Atovmyan, V. S. Nedzvetskii and A. S. Kulikov, *Izv. Akad. Nauk SSSR* (*ser. khim.*), in press.

7. S. M. Aldoshin, L. O. Atovmyan, O. A. Kozina, V. S. Nedzvetskii and V. I. Pantsyrnyi, *Izv. Akad. Nauk SSSR* (*ser. khim.*), 1773 (1988).
8. S. M. Aldoshin, L. O. Atovmyan, O. A. Kozina, V. S. Nedzvetskii and V. I. Pantsyrnyi, *Izv. Akad. Nauk SSSR* (*ser. khim.*), 1319 (1988).
9. S. M. Aldoshin, L. O. Atovmyan and O. A. Kozina, *Izv. Akad. Nauk SSSR* (*ser. khim.*), in press.
10. Molecular Interaction. V. 2. Edited by H. Ratajczak and W. J. Orville—Thomas. A Wiley—Interscienсes Publication. John Wiley and Sons. Chichester—New York—Brisbane—Toronto.
11. V. B. Luzhkov, T. S. Isichenko and T. N. Yakushchenko, IN: "7th All—Union Conference on the Use of Computers in Chemical Investigation and the Spectroscopy of Molecules," *Theses of Reports* (*in Russian*), *Riga*, 110 (1986).
12. M. J. Frish, J. E. DelBene, J. S. Binkley and H. F. Schaefer, **84**, 2279 (1986).
13. S. C. Mohr, W. D. Wilk and G. M. Barrow, *J. Amer. Chem. Soc.*, **87**, 3048 (1965).
14. D. N. Glew and N. S. Rath, *Can. J. Chem.*, **49**, 837 (1971).
15. D. E. Ellis and G. S. Painter, *Phys. Rev.*, **B7**, 2887 (1970).
16. G. L. Gutsev and A. A. Levin, *Zhurn. Strukt. Khimii*, **19**, 976 (1978).
17. T. R. Dyke and J. S. Muenter, *J. Chem. Phys.*, **60**, 2929 (1974).