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Hydrogen Complexes of *O*-Vinylacetoxime with Trifluoroacetic Acid

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Abstract—According to B3LYP/6-31G** calculations, the stable *antiperi*-, *antiperiperiplanar* and *antiperi*-, *synperiperiplanar* conformers of *O*-vinylacetoxime (**1**) form with trifluoroacetic acid strong H complexes of two types: with N···H–O and O···H–O hydrogen bonds. The former are more stable. Complexation changes N–O and C–O bond lengths in molecule **1,** as well as mutual orientation of its vinyl and azomethine groups. The structural effect depends on the orientation of the H bond, which, in its turn, is determined by the nature of the electron-donor center. When the nitrogen atom of oxime **1** is involved in complex formation, the H bond lies in the molecular plane, whereas the H bond involving the oxygen atom is directed in parallel with its lone electron pair.

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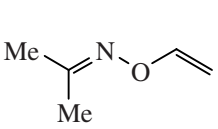
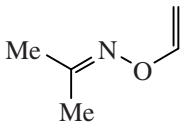
Theoretical research into rotational isomerism of *O*-vinylacetoxime (**1**) showed that in an isolated state it can exist as an ensemble of two planar conformers: *antiperi*-, *antiperiperiplanar* (*ap,ap*) and *antiperi*-, *synperiperiplanar* (*ap,sp*) [1, 2].



1 (*ap*, *ap*)

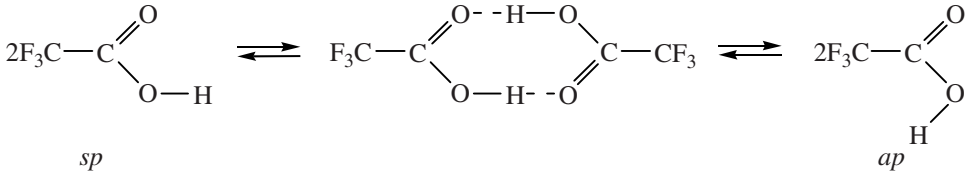


1 (*ap*, *sp*)

The difference of their total energies (HF-SCF/6-311G*) is 0.6 kcal mol^{-1}, and the ZPE-corrected value is 0.9 kcal mol^{-1}, which at 300 K corresponds to the *ap,ap/ap,sp* population ratio of 82/18 [1]. The barrier to internal rotation around the C–O bond is about 5 kcal mol^{-1}. Analysis of the IR spectra of compound **1** in the solid phase and in carbon tetrachloride, chloroform, and acetonitrile solutions revealed a little ap,sp conformer along with the *ap,ap* conformer [1]. Dielcometric study of solutions of this compound in octane showed that the dipole moment (μ) increases with temperature [3]. Similar variations in μ take place in going from octane to the polar tetrahydrofuran. Based on these observations, a conclusion was drawn that high temperatures will favor population of the more polar minor forms, since the most stable conformers of **1** (*ap,ap and ap,sp*) have practically equal dipole moments (1.94 and 2.01 D) [3]. Furthermore, the stability of the conformers can be affected by specific solvation [4]. In particular, the ability of a proton donor to form H bonds with different conformers of a protophilic molecule varies from conformer to conformer, which may affect the conformational equilibrium [4]. This effect should be especially pronounced when the dipole moments of molecules differ substantially. A previous theoretical (HF/6-31G*) study on the hydration of the stable conformers of oxime **1** [5] showed that they form with water 1 : 1 hydrogen complexes via either the nitrogen or oxygen atom. In the H complexes with the oxygen atom, the N–O bond is elongated, which may suggest a change in the conformational structure of this compound upon reaction with a stronger proton donor. Monohydrates of molecule **1** are weak H complexes with the heavy atoms arranged like in the starting *ap,ap* and *ap,sp* conformers. The present work is a continuation of investigations of interaction of *O*-vinylacetoxime with H-bond donors. As such, trifluoroacetic acid was chosen in order to elucidate the effect of the formation of a strong H complex on the

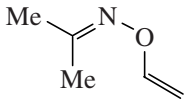
relative stability and structure of the *ap,ap* and *ap,sp* conformers of *O*-vinylacetoxime.

The dielectric constant of liquid trifluoroacetic acid is known to decrease with temperature with simultaneous increase of the effective dipole moment [6]. At the boiling point, trifluoroacetic acid is almost completely dissociated, since the effective dipole moment and the dipole moment of the monomer are approximately the same. Borovikov [6] drew a conclusion that liquid trifluoroacetic acid contains much cyclic dimers. According to our DFT (B3LYP/6-31G*) calculations, monomeric trifluoroacetic acid exists in two stable forms with *synplanar* (*sp*) and *antiplanar* (*ap*) orientations of the carbonyl and hydroxy groups.

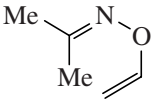


	sp		*ap*
ΔE, kcal mol^{-1}	0.0	–18.8	3.0

With the above in mind, we performed a theoretical study of N···HO or O···HO-bonded H complexes formed by the two stable conformers of trifluoroacetic acid and oxime **1** and differing in the mutual orientation of the subunits. Besides, the possibility of stabilization upon complex formation of conformers of molecule **1** with synperiplanar (*sp,ac* and *sp,sc*) orientation of the fragments with respect to the N–O bond, which are unstable in an isolated state, is also considered.



sp, *ac*



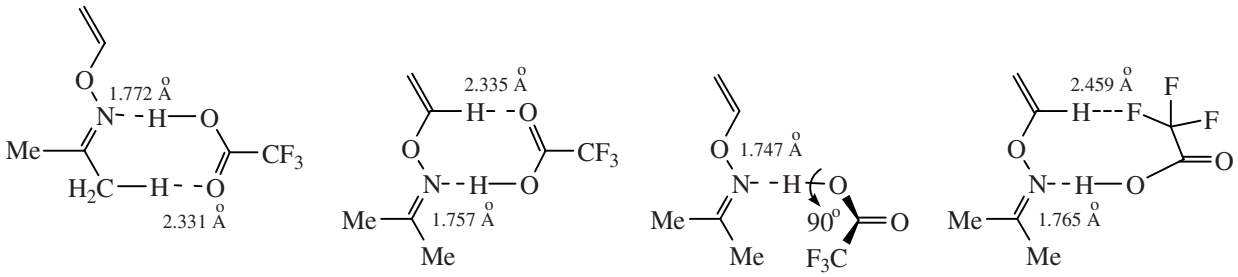
sp, *sc*

Quantum-chemical calculations of the energy of formation of the H complexes and their geometric parameters were performed by the DFT B3LYP/6-31G* method using the Gaussian-98 program package [7]. The same method was employed for calculation of monohydrates of **1**, earlier calculated at the ab initio (HF/6-31G*) level [5]. Full geometry optimization of molecular forms corresponding to the energy minima up was performed until the gradient 10^{-5} au bohr^{-1}. The energy of formation of the H complexes (ΔE_H) was estimated as the difference of their total energies and the energies of the corresponding conformers of oxime **1** and trifluoroacetic acid or water.

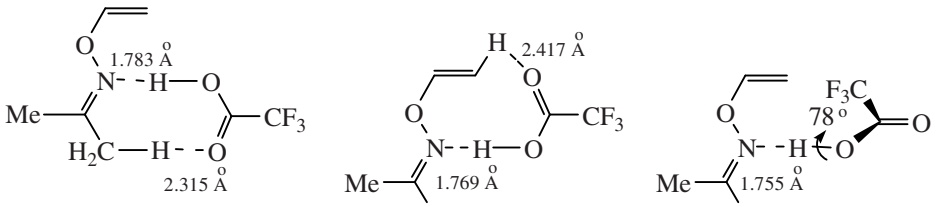
Oxime **1** forms with trifluoroacetic acid very stable H complexes (ΔE_H 7.8–12.1 kcal mol^{-1}). The H complexes of N···H–O-bonded *ap,ap* (**2a–2d**) and *ap,sp* (**2e–2g**) conformers (Scheme 1) proved to be the most favored by energy.

The energy of their formation as compared to corresponding O···H–O-bonded H complexes **3a–3h** (Scheme 2) is higher by ~3 kcal mol^{-1}.

Scheme 1.

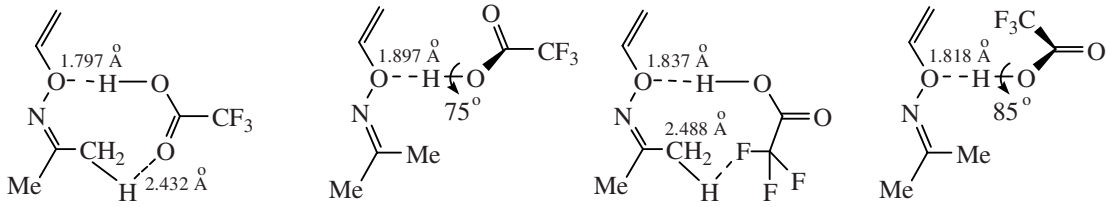


	2a	**2b**	**2c**	**2d**
ΔE_H, kcal mol^{-1}	12.0	12.1	11.1	11.2

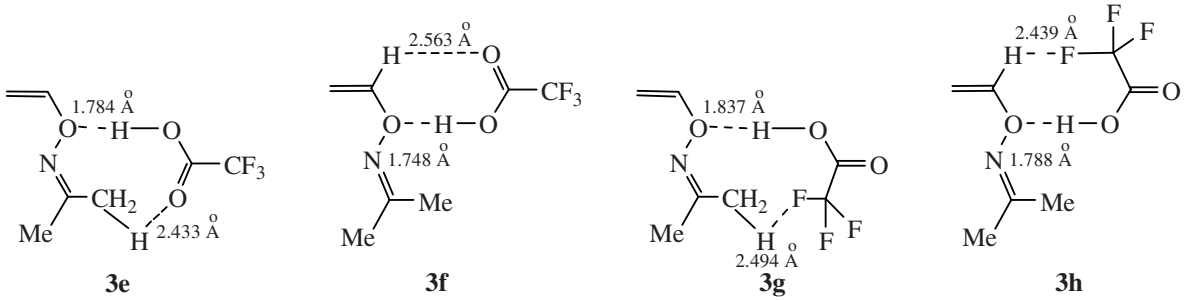


	2e	**2f**	**2g**
ΔE_H, kcal mol^{-1}	11.9	11.6	11.3

Scheme 2.



	3a	**3b**	**3c**	**3d**
ΔE_H, kcal mol^{-1}	8.9	8.7	7.9	8.1



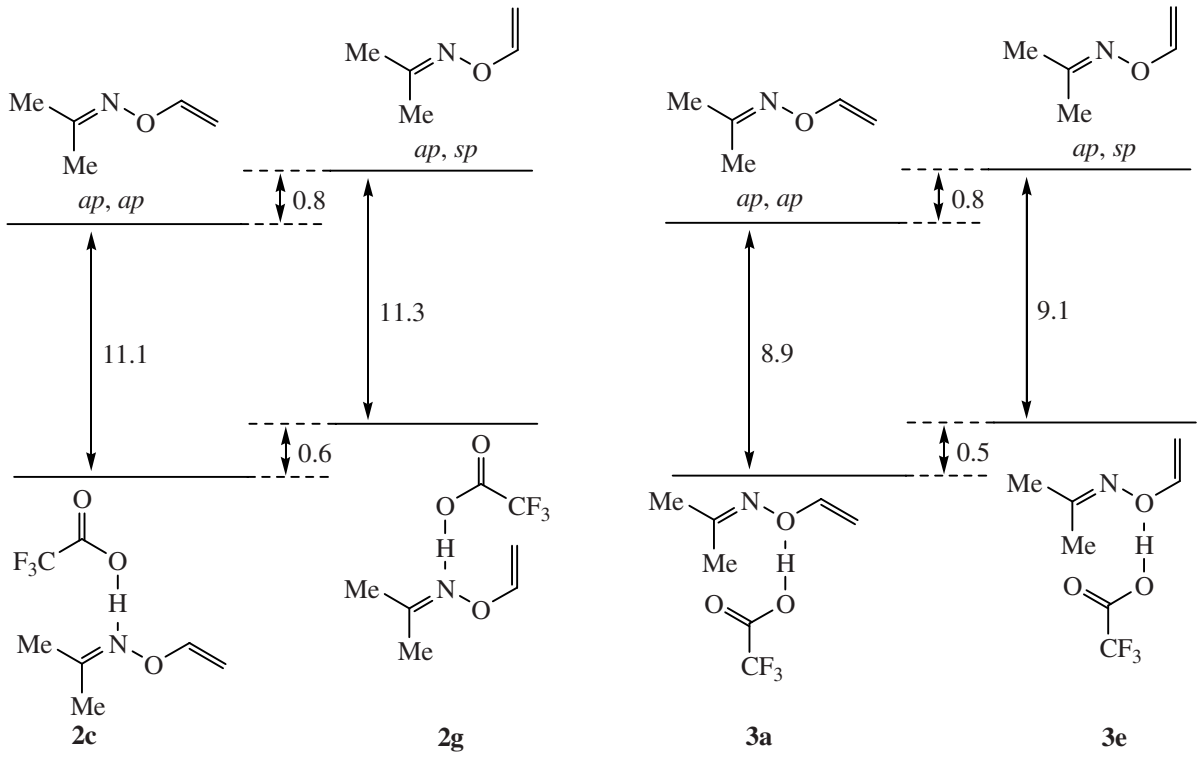
	3e	**3f**	**3g**	**3h**
ΔE_H, kcal mol^{-1}	9.1	9.1	7.8	8.6

The complexation of oxime **1** with trifluoroacetic acid only slightly affects the relative stability of its conformers. The energy gap between the *ap,ap* and *ap,sp* conformers of free **1** (0.8 kcal mol^{-1}) and of their H complexes with an N···H–O (0.6–1.3 kcal mol^{-1}) or an O···H–O bond (0.3–0.9 kcal mol^{-1}) proved to be close to each other (for examples, see Scheme 3).

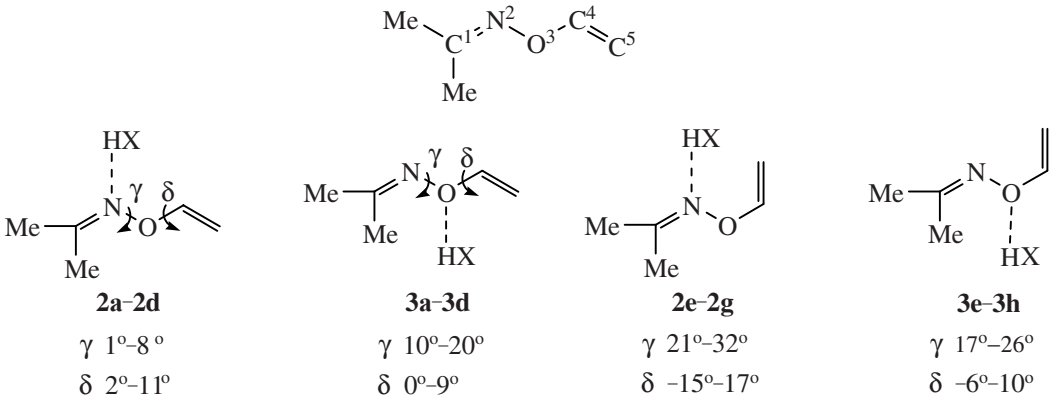
In general, the fact that the free conformers of oxime **1** and their H complexes only slightly differ in energy is, first of all, explained by small differences in the H-bond energies in molecular structures of the same type. Most complexes, along with the N···H–O or O···H–O hydrogen bonds, have additional short contacts =O···H (**2a, 2b, 2e, 2f; 3a, 3b, 3e, 3f**) or F···H (**2c, 2d, 2g; 3c, 3d, 3g, 3h**) (Schemes 1, 2) with interatomic distances no longer that the sums of the van der Waals radii of the corresponding atoms. Apparently, they contribute little in the energy of complex formation in an isolated state.

The H-complex formation disturbs the planar arrangement of the heavy atoms in the H-bond acceptor (oxime **1**). This is evidenced by changes in the $C^1{=}N^2{-}O^3{-}C^4$ (γ) and $N^2{-}O^3{-}C^4{=}C^5$ (δ) dihedral angles (Scheme 4). The largest distortions for both types of H bonds are observed in the *ap,sp* conformer.

Scheme 3.



Scheme 4.



In the complexes of the *ap,ap* conformer of oxime **1**, the dihedral angles vary no more than 20° for all types of the intermolecular hydrogen bond. Consequently, complexation does not change the molecular conformation of the H-bond acceptor. On the contrary, in the complexes of the *ap,sp* conformer, the angle vary significantly. In particular, the γ angle reaches 28° in complex **2f** and 32° in complex **2e**. Therefore, at least in the case of complex **2e**, one can speak about a change in the molecular conformation of the H-bond acceptor from *ap,sp* to *ac,sp*.

The direction of the N···HO and O···HO bonds in the H complexes in hand only slightly differs from that found earlier in monohydrates [5]. Upon N···HO bond formation, the bridging hydrogen atom (H*) lies, like in monohydrates, virtually in a plane defined by the heavy atoms of molecule **1**. In the case of O···HO bond formation, it forms an angle of about 50° with this plane. The range of variation of the dihedral angles responsible for orientation of the bridging hydrogen atom with respect to the molecular plane of oxime **1** upon N···H and O···H bond formation is 162°–174°

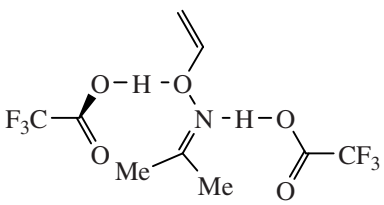
[θ($C^1O^3N^2H^*$)] and 116°–135° [φ($C^4N^2O^3H^*$)], respectively (for the atom numbering, see Scheme 4).

The changes in the geometric parameters of molecule **1**, induced by H-complex formation with trifluoroacetic acid, occur in the same direction as upon its hydration [5], but to a much greater extent. The strongest distortions are exerted by the N–O and O–C bonds in both conformers upon the formation of H complexes via the oxygen atom. The N–O–C fragment in the N···HO-bonded H complexes features weaker distortions. The bond lengths in these H complexes vary no more than 0.01 Å. Upon the formation of N···HO-bonded H complexes, the N–O valence bond in the *ap,ap* conformer is shortened by ~0.01 Å, and that in the *ap,sp* conformer, by ~0.005 Å. The O–C bonds in these conformers are elongated to the same extent. The N–O bonds in O···HO-bonded H complexes are elongated by ~0.02 Å regardless of the structure of the conformer, and the O–C bonds are longer by ~0.01 Å as compared to the isolated molecules. Consequently, the involvement of the heteroatoms of oxime **1** in a strong hydrogen bond perturbs the π system of *O*-vinylacetoxime, and the character of perturbation depends on the direction of this bond. In N···H–O-bonded complexes, the resonance interaction in the C=N–O moiety is enhanced, while in O···H–O-bonded ones, the interaction of the oxygen lone pair with the C=C and N=C, that determines the stability of the conformers of an isolated molecule **1** [3], is weakened.

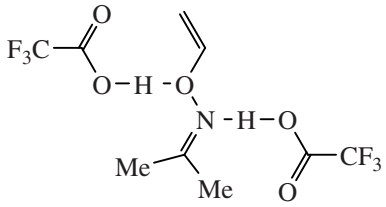
According to quantum-chemical calculations, the formation of H complexes of trifluoroacetic acid with unstable conformers of **1** with *synperiplanar* orientation of the fragments with respect to the N–O bond (*sp,ac* and *sp,sc*) does not stabilize these conformers. In geometrically optimized H complexes, their electron-donor subunits become stable conformers. Therefore, the interaction of oxime **1** with such a strong proton donor as trifluoroacetic acid only slightly affects the relative stability of conformers of **1** but has a notable influence on their geometric parameters. The character of the latter effect depends on the direction of the intermolecular hydrogen bond.

Since N···HO and O···HO hydrogen bonds often exert opposite structural effects, it was of interest to study 1 : 2 complexes, i.e. those involving both electron-donor centers (Scheme 5).

Scheme 5.

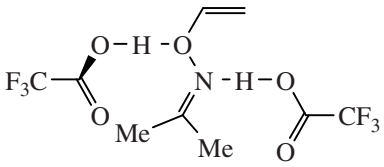


6a

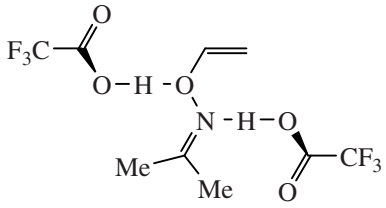


6b

$-\Delta E_H$, kcal mol^{-1} 19.7 19.8



6c



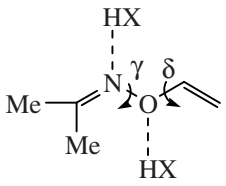
6d

$-\Delta E_H$, kcal mol^{-1} 20.0 20.0

The energy of formation of such H complexes is about 20.0 kcal mol^{-1} and practically does not depend on the conformational structure of the H-bond acceptor. Note that the ΔE_H of 1:2 complexes is very close to the energy of formation of the cyclic dimer of trifluoroacetic acid (~19 kcal mol^{-1}). Hence, in an inert medium in the presence of oxime **1**, cyclic dimers of trifluoroacetic acid will readily convert into 1 : 2 complexes. Qualitatively, the changes in the bond lengths in oxime **1** in complexes **6a–6d** are similar to those in

O···H–O-bonded 1:1 complexes, but for some bonds additivity effects are observed. Thus, the N–O bond is elongated in average by 0.01 Å, whereas the O–C bond, by 0.02 Å. The changes in the dihedral angles (γ and δ) correspond to the strongest distortion of the planar structure of oxime **1** (Schemes 4, 6).

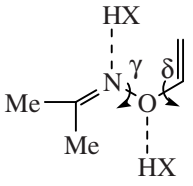
Scheme 6.



6a, 6b

γ 21°–27°

δ ≈ 6°



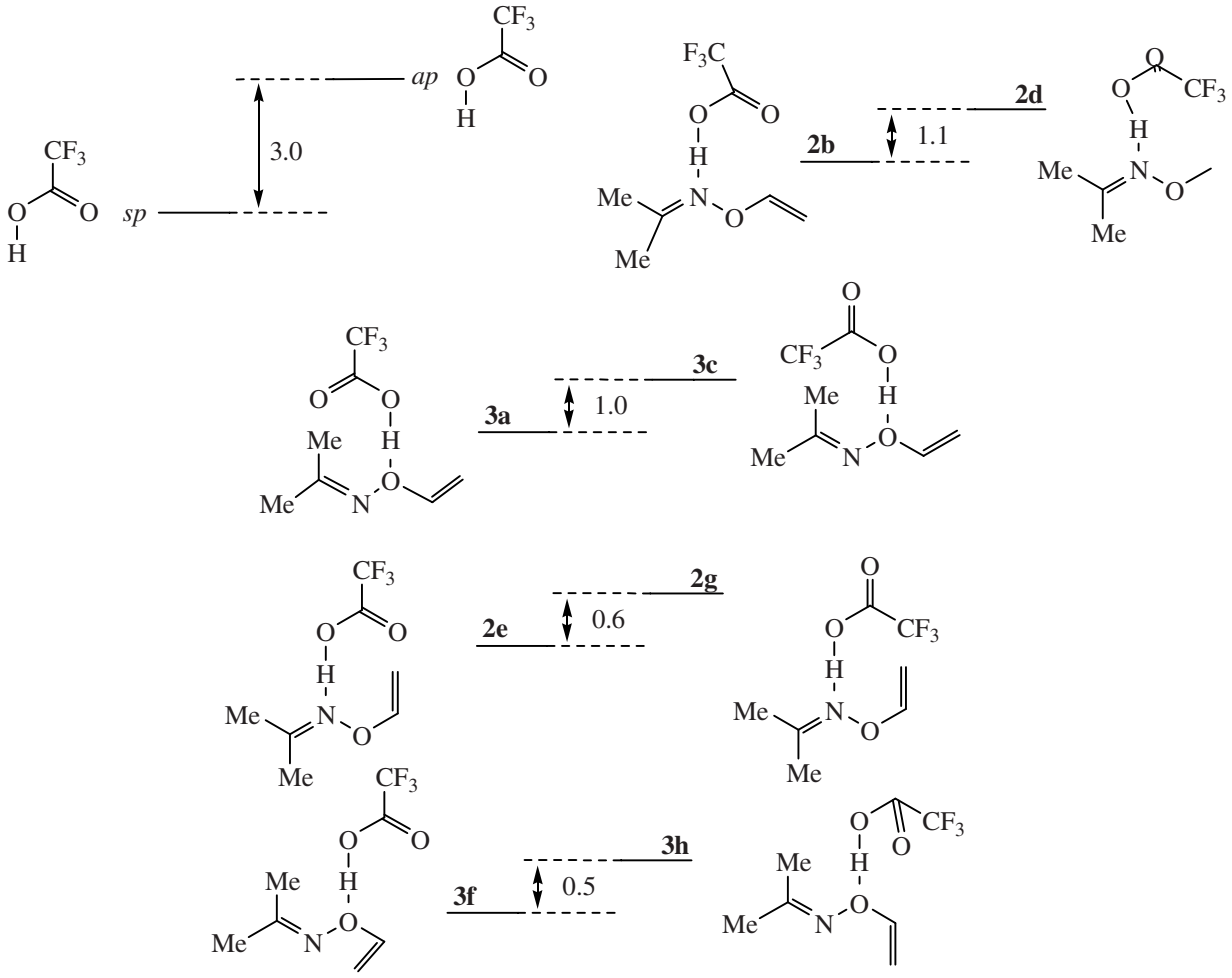
6c, 6d

γ 30°–34°

δ ≈ –18°

As noted above, the formation of H complexes of *O*-vinylacetoxime with trifluoroacetic acid slightly affects the relative stability of its conformers and, by contrast, produces a notable effect on the conformational isomerism of trifluoroacetic acid (Scheme 7).

Scheme 7.



Hydrogen complexes of both conformers of **1** with the *sp* conformer of trifluoroacetic acid are preferred by energy over those with the *ap* conformer. However, the formation of H complexes decreases the energy gap between the *sp* and *ap* conformers of trifluoroacetic acid, H-bonded with molecule **1**. This implies that complex formation stabilizes the *ap* conformer.

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