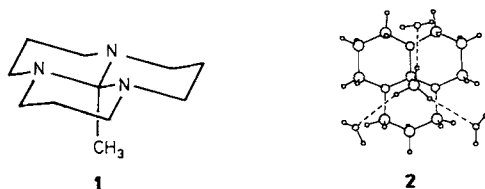


On the Strength of the C–H···O Hydrogen Bond and the Eclipsed Arrangement of the Methyl Group in a Tricyclic Orthoamide Trihydrate**

By Juan J. Novoa,* Pere Constans, and Myung-Hwan Whangbo*

In the thousands of compounds whose crystal structures have been determined by X-ray or neutron diffraction the conformation about the C_{sp^3} –CH₃ bonds is staggered. The only exception was reported for a crystalline trihydrate of tricyclic orthoamide **1** (i.e., **1** · 3H₂O), in which the conformation about the C_{sp^3} –CH₃ bond is nearly eclipsed (N–C–C–H dihedral angle of 8.0°).^[1,2] Since in a single crystal of *anhydrous 1* the conformation about the C_{sp^3} –CH₃ bond is staggered, the eclipsed arrangement in **1** · 3H₂O is attributed to the three C–H···O hydrogen bonds between the methyl group of **1** and the three water molecules surrounding **1**.^[1] (In the schematic representation **2** the H···O contacts are represented by dashed lines. In addition to the C–H···O hydrogen bond, each water molecule makes a O–H···N hydrogen bond with one of the nitrogen atoms of an adjacent molecule **1**.)



To explain this striking observation, Seiler et al.^[1] carried out theoretical evaluations of the rotational barrier of the methyl group in **1** and the energy of the C–H···O hydrogen bond. Their *ab initio* SCF calculations for CH₃–C(NH₂)₃ (with the N lone pair antiperiplanar (*app*) to the C–CH₃ bond, structural parameters from the crystallographic study) show the staggered conformation to be more stable than the eclipsed by 5.52 kcal mol⁻¹. Thus, the minimum strength of each of the three C–H···O hydrogen bonds in **1** · 3H₂O must be about 1.8 kcal mol⁻¹ to produce the eclipsed conformation (under the implicit assumption that the energies of the C(methyl)–H···O hydrogen bonds are additive). On the basis of their MP2-level calculations on model complexes CH₄···OH₂ and CH₄···OH₂···NH₃, Seiler et al.^[1] concluded that the C–H···O hydrogen bond has this strength. In this evaluation, however, the basis set superposition errors^[3] (BSSEs) were not corrected. According to our recent study,^[4] the energy of the C–H···O hydrogen bond is at most 0.59 kcal mol⁻¹ (based on MP2-level calculations for CH₄···OH₂ with a near Hartree–Fock limit (NHFL) basis set), and the large values reported by Seiler et al.^[1] (1.45–1.94 kcal mol⁻¹) are due mainly to the BSSEs. Consequently, the explanation for the eclipsed conformation about the C_{sp^3} –CH₃ bond of **1** · 3H₂O remains a challenge to theoreticians, which prompted us to carry out systematic theoretical

calculations aimed at understanding this unusual observations.

To estimate the rotational barrier for the methyl group of **1**, *ab initio* 6-31 + +G** SCF calculations were performed for the model compounds CH₃–C(NH₂)₃ and CH₃–C[N(CH₃)₂]₃ (with the N lone pair *app* to the C–C bond) with full geometry optimizations. These calculations show that the staggered conformation is more stable than the eclipsed by 5.44 kcal mol⁻¹ in CH₃–C(NH₂)₃, and by 5.48 kcal mol⁻¹ in CH₃–C[N(CH₃)₂]₃. These values are very close to that estimated by Seiler et al.^[1] In addition, *ab initio* 6-31 + +G** SCF calculations for CH₃–CH₃ predict a rotational barrier of 2.98 kcal mol⁻¹, in good agreement with experiment. As already pointed out by Seiler et al., therefore, the rotational barrier of the methyl group in **1** is 5.4–5.5 kcal mol⁻¹, and this barrier should be overcome in **1** · 3H₂O by the stabilization energy associated with the three C–H···O hydrogen bonds.

The most accurate estimate of the energy of the C–H···O hydrogen bond, 0.59 kcal mol⁻¹, is based on the model CH₄···OH₂ in which one methane hydrogen atom forms a C–H···O hydrogen bond.^[4] In **1** · 3H₂O all three hydrogen atoms of the methyl group participate in C–H···O hydrogen bonds. Thus, one might speculate that the energy of the C–H···O hydrogen bonding in **1** · 3H₂O is enhanced by a cooperative effect of the three C–H···O bonds of the methyl group. To test this hypothesis, we carried out MP2 calculations on the model compounds CH₄···OH₂, CH₄···(OH₂)₂ and CH₄···(OH₂)₃, whose geometries were chosen to have one, two, and three C–H···O hydrogen bonds, respectively.^[5] According to our previous study of CH₄···OH₂,^[4] use of diffuse functions is crucial in reducing the BSSEs. Our 6-31 + +G** MP2 calculations show that after correction of the BSSEs by the counterpoise method,^[6] the energies of the hydrogen-bonding in CH₄···OH₂, CH₄···(OH₂)₂, and CH₄···(OH₂)₃ are 0.37,^[7] 0.61, and 0.86 kcal mol⁻¹, respectively. Thus, the total energy of the hydrogen bonds of CH₄···(OH₂)_n ($n = 2, 3$) is not larger but rather somewhat smaller than the value predicted by n times the C–H···O hydrogen-bond energy of CH₄···OH₂. Our 6-31 + +G** MP2 calculations for CH₄···OH₂···NH₃ (geometry of the C–H···O–H···N arrangement as found in **1** · 3H₂O) show that the energy of the C–H···O hydrogen bond in CH₄···OH₂···NH₃ is 0.52 kcal mol⁻¹ after BSSE correction; this is larger than that of CH₄···OH₂ by about 40% (0.52 vs. 0.37 kcal mol⁻¹). Thus, even if C–H···O–H···N hydrogen bonding is assumed to increase the energy of the C–H···O hydrogen bond by about 40%, the stabilization energy expected from the three C–H···O hydrogen bonds in **1** · 3H₂O (roughly 2.5 = 3 × 0.59 × 1.4 kcal mol⁻¹) is much smaller than the rotational barrier of the methyl group in **1**.

Another estimate of the stabilization energy for the three C–H···O hydrogen bonds in **1** · 3H₂O was made by determining the rotational barriers of the methyl groups in **1** and **1** · 3H₂O (the three H₂O molecules were arranged around **1** as in crystalline **1** · 3H₂O) on the basis of semiempirical AM1 SCF-MO calculations.^[8] (AM1 calculations for CH₃–C(NH₂)₃ give a rotational barrier of 2.62 kcal mol⁻¹, which is about 2.8 kcal mol⁻¹ lower than the *ab initio* value.) For the rigid rotation of the methyl group based on the experimental geometries, AM1 calculations show that the staggered conformation about the C_{sp^3} –CH₃ bond is more stable than the eclipsed by 1.53 kcal mol⁻¹ in **1**, and by 0.27 kcal mol⁻¹ in **1** · 3H₂O. Namely, the three C–H···O hydrogen bonds in **1** · 3H₂O provide the stabilization energy of about 1.3 kcal mol⁻¹. The latter suggests a stabilization energy of about 1.8 kcal mol⁻¹ for crystalline **1** · 3H₂O if we allow for

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a 40% increase as a result of the cooperative C–H⋯O–H⋯N hydrogen bonding effect. This estimate is consistent with the results of our ab initio calculations.

In the above estimates of the stabilization energy associated with the three C–H⋯O hydrogen bonds in $1 \cdot 3\text{H}_2\text{O}$, possible crystal effects were not taken into consideration. To remedy this situation, we calculated the energies of crystalline $1 \cdot 3\text{H}_2\text{O}$ by employing empirical atom–atom potentials.^[9] The structure found in the crystal and the hypothetical structure resulting from it when the conformation about the $\text{C}_{\text{sp}^3}\text{--CH}_3$ bond is made staggered by rigid rotation are of interest. Our atom–atom potential calculations employed the potential parameters of Williams and Houpt^[10] and those of Mirsky.^[11] The Madelung energy was calculated by employing the point charges of the atoms that best simulate the electrostatic potentials^[12] of **1** and H_2O calculated by the AM1 method. In addition to the usual atom–atom potential terms,^[10, 11] the C–H⋯O hydrogen bond potentials of Cox et al.^[13] were employed to calculate the energies of the C–H⋯O hydrogen bonds for all the H⋯O contacts shorter than 2.7 Å. Our calculations show that the energy of the interaction between one methyl group and the rest of the crystal is more favorable for the eclipsed than for the staggered arrangement by 2.97 kcal mol⁻¹ with the parameters of Williams and Houpt, and by 1.87 kcal mol⁻¹ with the parameters of Mirsky. These values are comparable with the stabilization energies estimated by the present ab initio and AM1 calculations on model compounds.

To maintain the eclipsed arrangement about the $\text{C}_{\text{sp}^3}\text{--CH}_3$ bond of $1 \cdot 3\text{H}_2\text{O}$, the stabilization energy associated with the three C–H⋯O hydrogen bonds of each methyl group should be larger than 5.4–5.5 kcal mol⁻¹, but all our calculations suggest that this energy does not exceed 3 kcal mol⁻¹. Our results do not support the explanation of Seiler et al.^[1] for the eclipsed conformation of $1 \cdot 3\text{H}_2\text{O}$ and lead us to wonder why an eclipsed arrangement is found about the $\text{C}_{\text{sp}^3}\text{--CH}_3$ bond of $1 \cdot 3\text{H}_2\text{O}$. It is possible that the observed structure of $1 \cdot 3\text{H}_2\text{O}$ is not a global but a local energy minimum. It is noted that organic conducting salts often have different phases with identical chemical compositions.^[14]

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[1] P. Seiler, G. R. Weisman, E. D. Glendening, F. Weinhold, V. B. Johnson, J. D. Dunitz, *Angew. Chem.* **1987**, *99*, 1216; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1175.

[2] P. Seiler, J. D. Dunitz, *Helv. Chim. Acta* **1989**, *72*, 1125.

[3] B. Liu, A. D. McLean, *J. Chem. Phys.* **1989**, *91*, 2348, and references therein.

[4] J. J. Novoa, B. Tarron, M.-H. Whangbo, J. M. Williams, *J. Chem. Phys.* **1991**, *95*, 5179.

[5] The C–H bond of each C–H⋯O bond was aligned along the bisecting line of the H–O–H angle of H_2O for $\text{CH}_4\cdots\text{OH}_2$, $\text{CH}_4\cdots(\text{OH}_2)_2$, and $\text{CH}_4\cdots(\text{OH}_2)_3$. The C_{2v} and C_{3v} point group symmetries were assumed for $\text{CH}_4\cdots(\text{OH}_2)_2$ and $\text{CH}_4\cdots(\text{OH}_2)_3$, respectively. All fragment geometries were fixed.

[6] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.

[7] With the same geometrical constraints, the MP2 calculations with a NHFL basis set gave 0.52 kcal mol⁻¹ for the C–H⋯O bond energy in $\text{CH}_4\cdots\text{OH}_2$ [4].

[8] M. J. S. Dewar, E. G. Zoebisch, E. F. Healey, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[9] For a recent review, see A. J. Pertin, A. I. Kitaigorodsky, *The Atom-Atom Potential Method*, Springer, Berlin, **1987**.

[10] D. E. Williams, D. J. Houpt, *Acta Crystallogr. Sect. B* **1986**, *42*, 286.

[11] K. Mirsky, *Acta Crystallogr. Sect. A* **1976**, *32*, 199.

[12] J. J. P. Stewart, Quantum Chemistry Program Exchange, p. 455.

[13] S. R. Cox, L.-Y. Hsu, D. E. Williams, *Acta Crystallogr. Sect. A* **1981**, *37*, 293.

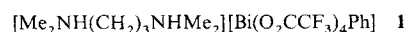
[14] For a review, see: J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, M.-H. Whangbo, *Prog. Inorg. Chem.* **1987**, *35*, 51.

Structural Variations Observed in the $[\text{Bi}(\text{O}_2\text{CCF}_3)_4\text{Ph}]^{2-}$ Anion: Selective Cation–Anion Interactions through Hydrogen Bonds**

By Steven R. Breeze* and Suning Wang*

Hydrogen bonds are known to play an essential role in determining the shape and function of molecules,^[1] and their influence on the structures of solids is widely recognized.^[2] The controlled assembly of molecules by hydrogen bonding is a frequently used strategy in the synthesis of supramolecules and inorganic precursor compounds for solid-state materials.^[3] However, systematic examinations on the effect of hydrogen bonds on the geometry and stability of inorganic complexes are scarce. We report here on the anionic bismuth complex $[\text{Bi}(\text{O}_2\text{CCF}_3)_4\text{Ph}]^{2-}$, whose solid-state structure can be dramatically influenced by interactions with its counterion by the formation of hydrogen bonds.

The reaction of BiPh_3 with trifluoroacetic acid and *N,N,N',N'*-tetramethyl-1,3-propanediamine (tmpda) in a 1:4:1 ratio produced **1** in good yield. The anion in com-



pound **1** displays an cuplike structure^[4] in the solid state as shown in Figure 1. The Bi^{3+} ion is coordinated by one car-

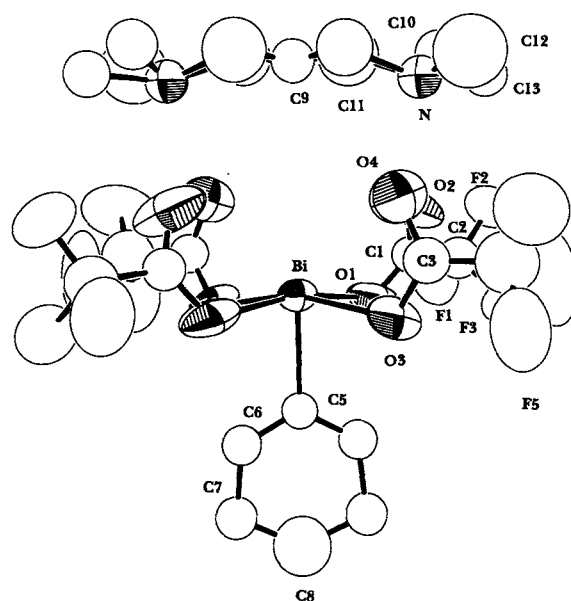


Fig. 1. Crystal structure of **1**; ellipsoids at the 50% probability level. Selected distances [Å] and angles [°]: Bi–O1 2.38(3), Bi–O3 2.42(2), Bi–C5 2.28(4); O1–Bi–O1' 169(1), O3–Bi–O3' 165(1).

bon atom of the phenyl group and four oxygen atoms of the acetate ligands with normal bond lengths and a square-pyramidal geometry. The lone pair of electrons probably occupies the vertex of the octahedron. The bismuth atom is 0.27 Å above the O1–O3–O1'–O3' plane. Compound **1** has a twofold proper rotation axis; the diammonium cation is disordered over this axis. The most unusual feature of the anion is the orientation of the four trifluoroacetate ligands—they

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