SHORT COMMUNICATION

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Tautomerism in Bis(oxazoline)s

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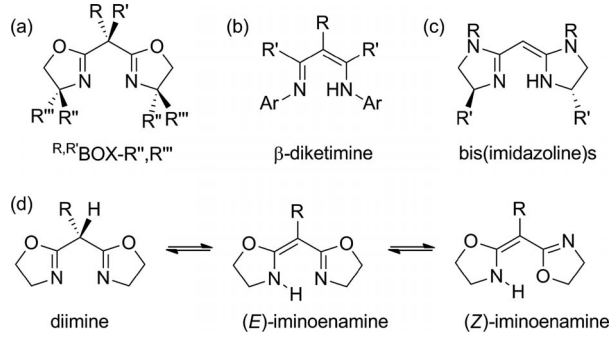
Bis(oxazoline)s (BOXs) are a privileged ligand class and have found widespread use in catalysis. Herein, the tautomerism of selected BOX ligands was evidenced by X-ray diffractometry as well as by NMR and IR spectroscopy and supported by DFT calculations. In $CDCl_3$ solution at room temperature, the new 1,1-bis(4,4-dimethyl-1,3-oxazolin-2-yl)-1-phenylmethane (^{Ph,H}BOX-Me_2) ligand is present as a 1:1 mixture of the diimine and iminoenamine tautomers. Thermodynamic and kinetic data for the tautomeric equilibrium were determined, which allowed comparison with related bidentate ligand classes. The other BOXs studied, ^{H,H}BOX-Me_2, ^{Me,H}BOX-Me_2, and ^{tBu,H}BOX-Me_2, are largely present in the diimine form under similar conditions. IR spectroscopy was identified as a valuable tool for detecting the presence of the iminoenamine form as a minor component.

Introduction

Since bis(oxazoline) (BOX) ligands were first developed by several groups around 1990,[1–5] their metal complexes have found use in a variety of metal-mediated catalytic reactions, in particular in asymmetric synthesis. BOXs have quickly developed into a high-performance ligand platform and are now classified among the so called "privileged ligands". Some BOXs are commercially available, such as methylene- and isopropylidene-bridged ones (R = R′ = H or Me; Scheme 1a). Most common are metal complexes of neutral bis(oxazoline) ligands[6–12] that have two alkyl substituents at the bridging backbone C atom (R = R′ ≠ H), but complexes with deprotonated monoanionic bis(oxazolinate) are also well established.[13] The latter are closely related to the bidentate β-diketiminate ligands (Scheme 1b) that are extremely popular in coordination chemistry.

In view of the widespread use of BOX ligands, it is somewhat surprising that little is known about the tautomerism of BOXs containing a single substituent R at the backbone bridge, or BOXs with the parent methylene spacer. In these systems, the H atom may shift from the bridge C atom to one of the oxazoline N atoms to give the iminoenamine form; the latter may have *E* or *Z* configuration (Scheme 1d). For β-diketones the enol isomer is usually far more stable than the keto isomer, and β-diketimines are always regarded as iminoenamines (Scheme 1b), but BOXs are mostly encountered and described in the form of the diimine. The same is true for the closely related ligand class of azabis(oxazoline)s,[14] which also exist in the diimine form with the proton at the bridge N atom. Exceptions are the ^{CN}BOXs and related semicorrins,[15] which feature strongly electron-withdrawing cyano groups at the bridge C atom. Some azasemicorrins have also been reported to exist in their iminoenamine form.[16]



Scheme 1. Structural motives of (a) bis(oxazoline)s (BOXs), (b) the related β-diketimines, (c) methylenebis(imidazoline)s, and (d) the potential tautomeric BOX isomers. This work: R = Ph, *t*Bu, Me, H; R′ = H; R″ = R‴ = Me.

On the basis of UV/Vis spectra, Kovač et al. assumed that a small amount of an iminoenamine isomer was also present in solutions of ^{H,H}BOX-*t*Bu,H, but ^{1}H NMR and ^{13}C NMR spectroscopy did not confirm this, and photoelectron spectroscopy (PES) revealed no such tautomer in the gas phase.[17] Just recently, the protonated bis(oxazoline)s $[H\{^{Me,H}BOX\text{-}Me_2\}]^+$[18] and $[H\{^{Me,H}BOX\text{-}Ph,H\}]^+$,[19] which were serendipitously isolated, were found to exist in the (*Z*)-enamine form in the solid state. Even more recently, the bis(oxazoline) $^{p\text{-}CF_3C_6H_4CH_2,H}$BOX-$H_2$ was crystallized as the iminoenamine tautomer, and, furthermore, two tautomers were observed in solution.[20] Related methylene-bridged bis(imidazoline)s were found to undergo tautomer-

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ism depending on the solvent and protonation state,[21,22] and the conjugated iminoenamine tautomer is thermodynamically more favorable (Scheme 1c).[22] Herein, we report a detailed NMR and IR spectroscopic and crystallographic study of the tautomeric equilibrium of the neutral bis(oxazoline) ^{Ph,H}BOX-Me$_2$, and we present relevant thermodynamic and kinetic parameters, accompanied by DFT calculations. This is important and fundamental information for understanding and rationalizing the reactivity of this prominent class of compounds.

Results and Discussion

Synthesis

The bis(oxazoline)s used in this work, ^{R,H}BOX-Me$_2$ (R = Ph, *t*Bu, Me, H), were prepared in close analogy to procedures reported previously (see the Supporting Information). The simple methylene-bridged ^{H,H}BOX-Me$_2$ and the homologous 1,1-ethylene-bridged ^{Me,H}BOX-Me$_2$ and 1,1-neopentylene-bridged ^{tBu,H}BOX-Me$_2$ were prepared for comparison. ^{Me,H}BOX-Me$_2$ is often applied as a ligand for several metal ions.[23] Although the preparation of ^{H,H}BOX-Me$_2$ was previously reported,[24] we found no published analytical data. ^{Ph,H}BOX-Me$_2$ and ^{tBu,H}BOX-Me$_2$ had not been previously reported. We fully characterized all four BOXs (see the Supporting Information). Contrary to other bis(oxazoline)s, which were obtained as well-soluble colorless liquids, ^{Ph,H}BOX-Me$_2$ precipitated in the course of its synthesis from the reaction solution. We attribute this to the presence of the iminoenamine tautomer in the case of ^{Ph,H}BOX-Me$_2$, which apparently is insoluble under the applied conditions.

Solid-State Structure of ^{Ph,H}BOX-Me$_2$ and ^{H,H}BOX-Me$_2$

Small colorless needles of ^{Ph,H}BOX-Me$_2$ were obtained by slow concentration of a CH_2Cl_2/methanol (9:1) solution; a single crystal was analyzed by X-ray diffraction. The molecular structure of ^{Ph,H}BOX-Me$_2$, which crystallizes in the monoclinic *P*2/*n* space group, is depicted in Figure 1a (see also Table 1). Clearly, ^{Ph,H}BOX-Me$_2$ exists in its (*E*)-iminoenamine form in the solid state.

The two oxazoline rings in ^{Ph,H}BOX-Me$_2$ are roughly coplanar (the torsion angle between the C6–N1 and C6′–N1′ distances of 1.40 and 1.31 Å differ strongly from those found for oxazolines in their diimine form[7] but are between typical values for C–C and C=C bonds and for C–N and C=N bonds, respectively, and thus reflect delocalization or crystallographic disorder.[25] The cavity between both oxazoline rings is widened at the front with an angle between both C–N bonds of 14.3°; the N···N separation is 2.73 Å. The backbone phenyl ring at C1 is rotated by approximately 71° relative to the plane defined by the two oxazoline rings. The enamine H1 proton lies in the latter plane [0.1(1) Å distance] and forms a moderate to weak, resonance-assisted[26] N–H···N hydrogen bond with a length of 2.15 Å and an angle of 131° (cf. Table 2 for additional hydrogen-bonding parameters). The averaged C–C and C–N bond lengths within the C1(–C6=N1···H1–N1′–C6=) ring of ^{Ph,H}BOX-Me$_2$ suggest complete delocalization, but the localized positions of the two enamine hydrogen atoms (H1, H1′) indicate that an overlay of an enamine–imine and an imine–enamine structure is more likely (Scheme 2).

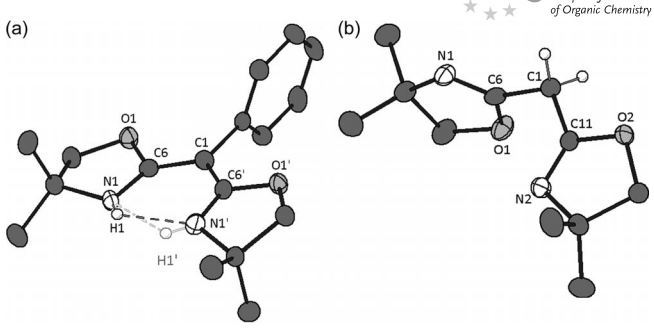


Figure 1. X-ray solid-state molecular structures of (a) the iminoenamine ^{Ph,H}BOX-Me$_2$ and (b) the diimine ^{H,H}BOX-Me$_2$ with selected atoms labeled. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms except the enamine H1 (a) and the H atoms at the backbone C1 (b) are omitted for clarity; symmetry transformation used to generate equivalent atoms (′) in (a): 1.5 – *x*, *y*, 1.5 – *z*. The dotted line represents the hydrogen-bonding interaction between H1 and N1′. Selected interatomic distances and angles are listed in Table 1.

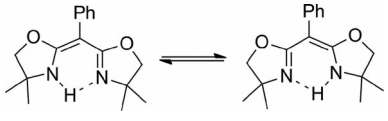
Table 1. Selected metric parameters (bond lengths [Å] and angles [°]) of the ^{Ph,H}BOX-Me$_2$ and ^{H,H}BOX-Me$_2$ bis(oxazoline)s.[a]

	^{Ph,H}BOX-Me$_2$[b]	^{H,H}BOX-Me$_2$
N1–C6, N2–C11	1.313(3)	1.264(1), 1.260(1)
C1–C6, C1–C11	1.403(3)	1.493(1), 1.497(1)
C6–C1–C6′/11	117.7(3)	113.88(8)

[a] Additional parameters are provided in the text and the Supporting Information. [b] Bonds are symmetrically equivalent.

Table 2. Hydrogen-bonding parameters (bond lengths [Å] and angles [°]) of the iminoenamine form of ^{Ph,H}BOX-Me$_2$.

	D–H	D···A	H···A	D–H···A
N1–H1···N1′	0.78(10)	2.15(10)	2.726(5)	131(9)



Scheme 2. Autotrope interconverted tautomers disordered in the solid-state structure of ^{Ph,H}BOX-Me$_2$.

The nature of the crystallographic disorder remains unclear: the structure is either statically or dynamically disordered. However, dynamic disorder seems reasonable, as related compounds were found to show such phenomenon (see below). It should be emphasized that the two disordered structures are identical tautomers (autotrope in-

terconverted, Scheme 2).[27] Prototropic tautomerization in the solid state is a relatively rare phenomenon found in, for example, cyclic hydrogen-bonded pyrazole derivatives, which have been intensively studied by solid-state CPMAS (cross polarization, magic angle spinning) NMR techniques.[28] More closely related to ^{Ph,H}BOX-Me$_2$ are dibenzoylmethane and analogous 1,3-diketones,[29–31] the degenerate, intramolecular hydrogen-bridged tautomers of which resemble the situation found here. However, the solid-state tautomerism of ^{Ph,H}BOX-Me$_2$ was not further investigated as part of the present study.

For comparison, we also determined the solid-state molecular structure of ^{H,H}BOX-Me$_2$. Large single crystals were obtained by vacuum sublimation. ^{H,H}BOX-Me$_2$ crystallizes in the orthorhombic *Pbca* space group; the molecular structure is shown in Figure 1b. ^{H,H}BOX-Me$_2$ is clearly present in its diimine from; the two oxazoline rings are tilted by around 78.4°. The C2–C1–C7 angle at the bridging CH_2 group is 113.9°, which reflects sp^3 hybridization. Accordingly, the C1–C6/11 (1.49/1.50 Å) bonds are distinctly longer and the C6/11=N1/2 (both 1.26 Å) bonds are shorter than those in ^{Ph,H}BOX-Me$_2$, as expected for the diimine tautomer.

A search in the Cambridge Structural Database (CSD)[32] revealed over 100 deposited structures containing a bis(oxazoline) moiety, most of which have BOXs as coordinating ligands. Only about 10 structures of free bis(oxazoline)s are known, including the iminoenamine and the two protonated (*Z*)-iminoenamines mentioned above. However, the rest are diimines, and only one of them has a CH_2 spacer between the oxazoline rings,[33] whereas all of the others are bridged by a dialkylmethylene group.

Characterization of ^{Ph,H}BOX-Me$_2$ in Solution

NMR spectroscopy is the method of choice for studying tautomerism.[34] Its main drawback is its limited sensitivity, as it is not possible to detect minority tautomers that are present in less than 1–2%. In chloroform solution, in which ^{Ph,H}BOX-Me$_2$ is only slightly soluble, it exists as a mixture of both tautomers, (*E*)-iminoenamine (*N*-protonated) and diimine (*C*-protonated, Figure 2a), with a ratio of about 1:1 at around room temperature. Although the formation of a (*Z*)-iminoenamine tautomer is, in principle, feasible, we did not observe any indication of its presence during the course of this work.

The ^{1}H and ^{13}C NMR resonances of the different tautomeric forms of ^{Ph,H}BOX-Me$_2$ are well resolved at 25 °C (Figure 2b; see also Figure S2 in the Supporting Information), and this is evidence of rather slow interconversion. Unambiguous assignment was facilitated by the isolation of the pure iminoenamine tautomer: by dissolving an isomerically pure crystalline sample at low temperature, we were able to record the NMR spectra of the pure (*E*)-iminoenamine tautomer. A single set of signals and apparent C_{2v} symmetry reflect rapid proton exchange between both oxazoline N atoms and the degenerate autotrope tautomerism.

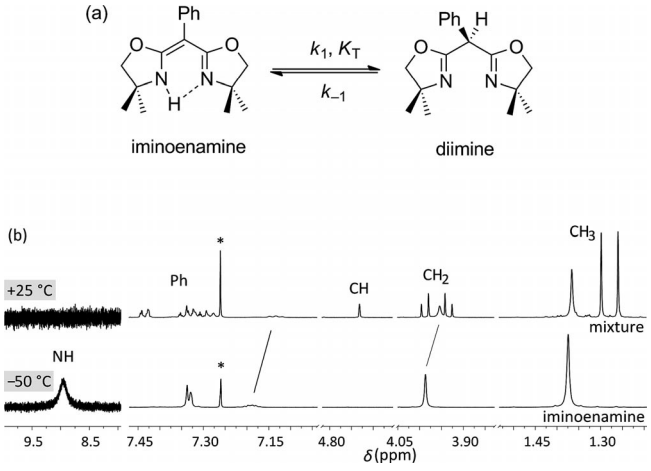


Figure 2. (a) Equilibrium of diimine and iminoenamine tautomers of ^{Ph,H}BOX-Me$_2$. (b) Parts of the ^{1}H NMR spectrum of the pure iminoenamine tautomer at –50 °C and an equilibrated mixture after warming to 25 °C; the NH regions are magnified, and resonance-free regions are omitted for the sake of clarity; the asterisks indicate the residual chloroform solvent peaks. See text for details and Figures S1–S5 in the Supporting Information for the ^{1}H NMR, ^{13}C NMR, and {^{15}N,^{1}H} HMBC NMR spectra for all four BOXs as well as the {^{13}C,^{1}H} HSQC NMR spectrum of ^{Ph,H}BOX-Me$_2$.

The enamine NH proton is observable at –50 °C as a broad peak ($\delta_H \approx 9.0$ ppm); no NH resonance signal could be detected at 25 °C. The diimine tautomer, seen at elevated temperatures after equilibration, is C_s-symmetric, and, hence, its oxazoline CH_2 protons are diastereotopic (and anisochronous) and give a typical AX spin system. Also, the methyl carbon atoms at each oxazoline are diastereotopic, which leads to two ^{1}H and ^{13}C resonances. The sp^3 hybridization of the bridge C atom in the diimine tautomer is reflected in its ^{13}C NMR spectrum by a shift of δ_C = 46 ppm and a cross-peak with the *C*-bound proton that appears at δ_H = 4.74 ppm in the {^{13}C,^{1}H} HSQC spectrum (cf. Figure S3). {^{15}N,^{1}H} HMBC NMR analysis (Figure S4) confirmed the assignment and the identity of both isomers: only two distinct ^{15}N resonances are observed in the expected regions at δ_N = –132 (ketimine N of the diimine isomer) and –216 ppm (averaged signal for the iminoenamine isomer).[35] The obvious tautomerism of ^{Ph,H}BOX-Me$_2$ appears to be unique so far, as NMR spectroscopy of ^{H,H}BOX-Me$_2$, ^{Me,H}BOX-Me$_2$, and ^{tBu,H}BOX-Me$_2$ bis(oxazoline)s did not show any indication of the presence of an iminoenamine tautomer in solution (Figures S1, S2, and S5).

IR spectroscopy can be used as a complementary tool to examine the tautomeric state of bis(oxazoline)s. Whereas the diimine tautomer gives rise to a single broad distinctive band at around 1660 cm^{-1}, which we assigned to the asymmetric and symmetric stretching modes (ν_a and ν_s) of the (N=C–C–C=N) group, the iminoenamine tautomer in the crystalline material of ^{Ph,H}BOX-Me$_2$ is identified by two prominent and very strong bands at 1646 and 1558 cm^{-1}

(Figure 3). We assigned both bands to ν_a and ν_s of the C=C–C=N group, accompanied with in-plane bending (δ) of the N–H bond (Figure S7 represents the characteristic computed modes); they resemble a similar mode found in the enol form of acetylacetone.[36] DFT-calculated spectra of both tautomers of ^{H,H}BOX-Me$_2$ and ^{Ph,H}BOX-Me$_2$ show good agreement with experiment (see the Supporting Information for details). Whereas ^{tBu,H}BOX-Me$_2$ (which cannot convert into the planar iminoenamine form because of the bulky *t*Bu group) exists solely as the diimine tautomer as expected, the IR spectra of ^{H,H}BOX-Me$_2$ and ^{Me,H}BOX-Me$_2$ interestingly suggest the presence of some iminoenamine tautomer as a minor component. See Figure S6 for a comparison of all experimental and computed spectra.

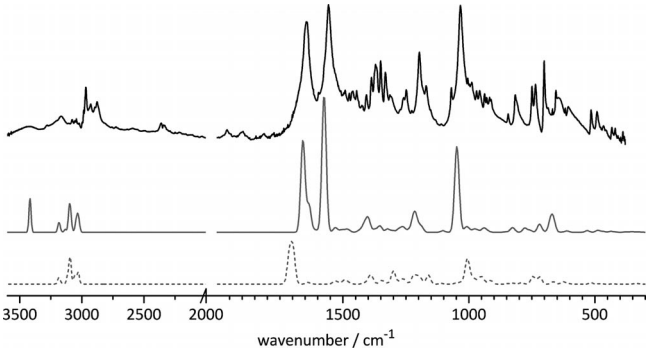


Figure 3. Experimental FTIR spectrum (black line) and DFT-calculated vibrational spectra (grey) of ^{Ph,H}BOX-Me$_2$. Spectra were computed from the geometry-optimized structures of the diimine (grey dashed line) and iminoenamine structure (grey solid line) at the B3LYP/def2-TZVPP level of theory. See the Supporting Information for details and spectra of all BOXs (Figure S6). The characteristic modes of the iminoenamine are represented in Figure S7.

Thermodynamic and Kinetic Parameters of the Equilibrium

From the ratio of the two tautomers of ^{Ph,H}BOX-Me$_2$ (determined by integration of the signals in the ^{1}H NMR spectrum) we estimated equilibrium constants K_T (pK_T) between 0.93 (0.03) and 1.92 (–0.28) in the temperature range 268–323 K [K_T = *c*(diimine)/*c*(iminoenamine)]. Thermodynamic parameters were derived from a van't Hoff plot (Figure S9, Table 3) and reveal only small energy differences between the two tautomers: the diimine has a $\Delta H°$ of 2.33(6) kcal mol^{-1} and a weakly positive $\Delta S°$ of 8.5(2) cal K^{-1} mol^{-1}. These parameters are comparable to those of recent DFT calculations[18] for ^{Me,H}BOX-Me$_2$ (BP86/TZVP level, Table 3). However, under the conditions applied in that study, only the diimine tautomer was observed experimentally. In comparison, our DFT calculations resulted in similar thermodynamic parameters for ^{Ph,H}BOX-Me$_2$ and ^{H,H}BOX-Me$_2$ (B3LYP/def2-TZVPP level, Table S4). Finally, these parameters are reminiscent of those of acetylacetone (equilibrium ca. 90% on the enol side)[37] and also of acetoacetates.[38]

Table 3. Thermodynamic data of the equilibrium of iminoenamine and diimine tautomers.[a] See Table S4 for additional DFT-calculated parameters.

	$\Delta H°$ [kcal mol^{-1}]	$\Delta S°$ [cal K^{-1} mol^{-1}]	$\Delta G°_{298}$ [kcal mol^{-1}]	K_T^{298}
^{Ph,H}BOX-Me$_2$[b]	2.33±0.06	8.5±0.2	–0.21±0.08	1.43
^{Me,H}BOX-Me$_2$[c]	3.8	–	0.7	0.31

[a] Parameters refer to the equilibrium (*E*)-iminoenamine ⇄ diimine. [b] In $CDCl_3$ solution, derived from the van't Hoff plot shown in Figure S9; this work. [c] DFT calculation at the BP86/TZVP level; ref.[18]

In the ^{1}H NMR spectrum of ^{Ph,H}BOX-Me$_2$, no signal broadening owing to proton exchange was observed over the examined temperature range, and this reflects rather slow exchange ($k < 1$ s^{-1}). Kinetic parameters of the tautomerization were determined by the equilibration method. After dissolving the crystalline material of the pure iminoenamine tautomer, the time dependence of the equilibration was monitored by ^{1}H NMR spectroscopy in the range between 25 and –5 °C (Figure 4, see also Figure S8). Values for the first-order rate constant $k_{obs} = k_1 + k_{-1}$ (with k_1 and k_{-1} denoting the forward and the backward reaction, respectively) at 298 K are $(6.90 \pm 0.62) \times 10^{-3}$, with $k_1 = (4.14 \pm 0.37) \times 10^{-3}$ and $k_{-1} = (2.76 \pm 0.25) \times 10^{-3}$ s^{-1} (see Table S1). Activation parameters were determined from the temperature dependence of the respective rate constants (Eyring plot shown in Figure S10) and are compiled in Table 4.

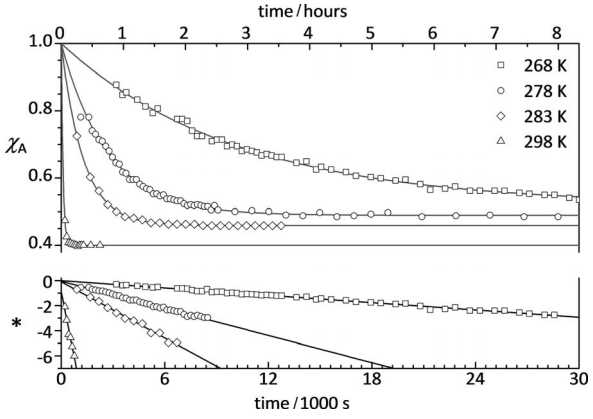


Figure 4. Time course of the equilibration of the iminoenamine form of ^{Ph,H}BOX-Me$_2$ to the respective diimine at various temperatures (top). Linearized form with solid lines showing fits to the integrated rate law to obtain rate constants from the slope $k_{obs} = k_1 + k_{-1}$ (bottom). The asterisk stands for $\ln[(\chi_A - \chi_A^\infty)/(\chi_A^0 - \chi_A^\infty)]$ in which χ_A is the fraction of iminoenamine at time *t*, χ_A^0 at $t = 0$ and χ_A^∞ at equilibrium.

The first-order rate and the relatively small and positive entropy of activation for the iminoenamine → diimine transformation, $\Delta S^‡ = (12 \pm 3)$ cal K^{-1} mol^{-1}, suggest a unimolecular reaction in the rate-determining step.[39] The experimental activation barrier ($\Delta G^‡$) of (20.7 ± 1.3) kcal mol^{-1} for ^{Ph,H}BOX-Me$_2$ is in the expected

Table 4. Activation parameters of the equilibration of iminoenamine tautomers.[a] See Table S5 for additional parameters and DFT-calculated values.

	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [cal K^{-1} mol^{-1}]	$\Delta G^{\ddagger}_{298}$ [kcal mol^{-1}]
^{Ph,H}BOX-Me$_2$[b]	24.1±0.9	12±3	20.7±1.3
^{Me,H}BOX-Me$_2$[c]	55.7		

[a] Parameters refer to the reaction: (*E*)-iminoenamine → diimine (k_1). [b] In $CDCl_3$ solution, derived from the Eyring plot shown in Figure S10; this work. [c] Zero-point energy corrected energies from DFT calculations at the BP86/TZVP level; ref.[18]

range if tautomer interconversion can be observed ($\Delta G^{\ddagger} <$ 25 kcal mol^{-1}). However, it is significantly lower than the barrier (zero-point energy corrected, $\Delta E^{\ddagger}$) of 55.7 kcal mol^{-1} that was calculated for the analogous intramolecular tautomerization reaction of ^{Me,H}BOX-Me$_2$.[18] The latter value is likely too high, as possible solvent assistance or tunneling effects were not considered.

In the case of ^{Ph,H}BOX-Me$_2$ and ^{H,H}BOX-Me$_2$, our DFT computations afforded two different transition states per BOX, and all four states are of equal energy of about 60 kcal mol^{-1} (Figure S14, Table S5). This is quite comparable to the above results for ^{Me,H}BOX-Me$_2$ and suggests that more complicated transition states should be considered upon inspecting the mechanism in greater depth. Noteworthy is the analogous tautomerization of malonaldehyde (and the similar acetylacetone and malonic acid), for which it could be shown by DFT calculations that the inclusion of four water molecules can lower the transition-state energy of the highly strained four-membered ring significantly from 60 to approximately 7 kcal mol^{-1};[40] this is in agreement with experimental energies.[41,42] It is likely that the aromatic phenyl ring in ^{Ph,H}BOX-Me$_2$ has a significant stabilizing effect on such solvent aggregates.

Conclusions

Tautomerism in the prominent BOX ligand class was evidenced and studied in detail by X-ray diffractometry as well as by NMR and IR spectroscopy, which provided thermodynamic and kinetic data for ^{Ph,H}BOX-Me$_2$. The phenyl group at the backbone spacer clearly favors the iminoenamine form in ^{Ph,H}BOX-Me$_2$ and may also lower the activation barrier for tautomerization, whereas other bis(oxazoline)s that lack the stabilizing effect of the phenyl residue are mostly observed in their diimine forms. However, the iminoenamine tautomer may be present as a minor component in certain cases, as suggested by IR spectroscopy for ^{H,H}BOX-Me$_2$ and ^{Me,H}BOX-Me$_2$. The iminoenamine form of ^{Ph,H}BOX-Me$_2$ is reminiscent of β-diketimines that are extensively used as anionic ligands, and a similarly rich coordination chemistry is indeed emerging.[13]

Supporting Information (see footnote on the first page of this article): Synthetic procedures, full experimental details and physical data, as well as details on DFT calculations, spectra for all compounds and further background material.

Acknowledgments

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[1] R. E. Lowenthal, A. Abiko, S. Masamune, *Tetrahedron* **1990**, *46*, 6005–6008.
[2] D. A. Evans, K. A. Woerpel, M. M. Hinman, M. M. Faul, *J. Am. Chem. Soc.* **1991**, *113*, 726–728.
[3] E. J. Corey, N. Imai, H.-Y. Zhang, *J. Am. Chem. Soc.* **1991**, *113*, 728–729.
[4] D. Müller, G. Umbricht, B. Weber, A. Pfaltz, *Helv. Chim. Acta* **1991**, *74*, 232–240.
[5] J. Hall, J.-M. Lehn, A. DeCian, J. Fischer, *Helv. Chim. Acta* **1991**, *74*, 1–6.
[6] A. K. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron: Asymmetry* **1998**, *9*, 1–45.
[7] M. Gómez, G. Muller, M. Rocamora, *Coord. Chem. Rev.* **1999**, *193–195*, 769–835.
[8] K. A. Jørgensen, M. Johannsen, S. Yao, H. Audrain, J. Thorhauge, *Acc. Chem. Res.* **1999**, *32*, 605–613.
[9] J. S. Johnson, D. A. Evans, *Acc. Chem. Res.* **2000**, *33*, 325–335.
[10] H. A. McManus, P. J. Guiry, *Chem. Rev.* **2004**, *104*, 4151–4202.
[11] G. Desimoni, G. Faita, K. A. Jørgensen, *Chem. Rev.* **2011**, *111*, PR284–PR437.
[12] R. Rasappan, D. Laventine, O. Reiser, *Coord. Chem. Rev.* **2008**, *252*, 702–714.
[13] S. Dagorne, S. Bellemin-Laponnaz, A. Maisse-François, *Eur. J. Inorg. Chem.* **2007**, 913–925.
[14] H. Werner, R. Vicha, A. Gissibl, O. Reiser, *J. Org. Chem.* **2003**, *68*, 10166–10168.
[15] H. Fritschi, U. Leutenegger, K. Siegmann, A. Pfaltz, W. Keller, C. Kratky, *Helv. Chim. Acta* **1988**, *71*, 1541–1552.
[16] U. Leutenegger, G. Umbricht, C. Fahrni, P. von Matt, A. Pfaltz, *Tetrahedron* **1992**, *48*, 2143–2156.
[17] B. Kovač, L. Klasinc, Z. Raza, V. Šunjić, *J. Chem. Soc. Perkin Trans. 2* **1999**, *3*, 2455–2459.
[18] S. Milione, V. Bertolasi, *Tetrahedron Lett.* **2011**, *52*, 3570–3574.
[19] H. Arii, F. Nakadate, K. Mochida, *Organometallics* **2011**, *30*, 4471–4474.
[20] J.-P. Qu, Y. Liang, H. Xu, X.-L. Sun, Z.-X. Yu, Y. Tang, *Chem. Eur. J.* **2012**, *18*, 2196–2201.
[21] D. Akalay, G. Dürner, J. W. Bats, M. Bolte, M. W. Göbel, *J. Org. Chem.* **2007**, *72*, 5618–5624.
[22] A. E. Sheshenev, E. V. Boltukhina, A. A. Grishina, I. Cisařova, I. M. Lyapkalo, K. K. Hii, *Chem. Eur. J.* **2013**, *19*, 8136–8143.
[23] S. Dagorne, S. Bellemin-Laponnaz, R. Welter, *Organometallics* **2004**, *23*, 3053–3061.
[24] G. K. Jnaneshwara, V. H. Deshpande, M. Lalithambika, T. Ravindranathan, A. V. Bedekar, *Tetrahedron Lett.* **1998**, *39*, 459–462.
[25] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19.
[26] G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023–1028.
[27] I. Alkorta, P. Goya, J. Elguero, S. Singh, *Natl. Acad. Sci. Lett.* **2007**, *30*, 139–159.
[28] O. Klein, F. Aguilar-Parrilla, J. M. Lopez, N. Jagerovic, H.-H. Limbach, *J. Am. Chem. Soc.* **2004**, *126*, 11718–11732.
[29] A. J. Vila, C. M. Lagier, A. C. Olivieri, *J. Chem. Soc. Perkin Trans. 2* **1990**, 1615–1618.
[30] A. J. Vila, C. M. Lagier, A. C. Olivieri, *J. Mol. Struct.* **1992**, *274*, 215–222.
[31] R. M. Cravero, M. González-Sierra, C. Fernández, A. C. Olivieri, *J. Chem. Soc., Chem. Commun.* **1993**, 1253.
[32] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380–388.
[33] M. Jiang, S. Dalgarno, C. A. Kilner, M. A. Halcrow, T. P. Kee, *Polyhedron* **2001**, *20*, 2151–2162.

[34] R. M. Claramunt, C. López, M. D. Santa María, D. Sanz, J. Elguero, *Prog. Nucl. Magn. Res. Sp.* **2006**, *49*, 169–206.
[35] S. Berger, S. Braun, H.-O. Kalinowski, *NMR Spectroscopy of the Non-Metallic Elements*, John Wiley & Sons, New York, **1996**.
[36] S. F. Tayyari, F. Milani-nejad, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **2000**, *56*, 2679–2691.
[37] J. N. Spencer, E. S. Holmboe, M. B. Kirshenbaum, D. B. Firth, P. B. Pinto, *Can. J. Chem.* **1982**, *60*, 1178–1182.
[38] M. M. Folkendt, B. E. Weiss-Lopez, J. P. Chauvel, N. S. True, *J. Phys. Chem.* **1985**, *89*, 3347–3352.
[39] K. Connors, *Chemical Kinetics: The Study of Reaction Rates in Solution*, VCH, Weinheim, **1990**.
[40] S. Yamabe, N. Tsuchida, K. Miyajima, *J. Phys. Chem. A* **2004**, *108*, 2750–2757.
[41] N. C. Søndergaard, P. E. Sørensen, J. Ulstrup, *Acta Chem. Scand.* **1975**, *29a*, 709–712.
[42] H. Watarai, N. Suzuki, *J. Inorg. Nucl. Chem.* **1974**, *36*, 1815–1820.

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