Supporting information

Intermolecular Interactions of a Chiral Amine Borane Adduct Revealed by VCD Spectroscopy

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Contents

1. Concentration dependence of IR spectra

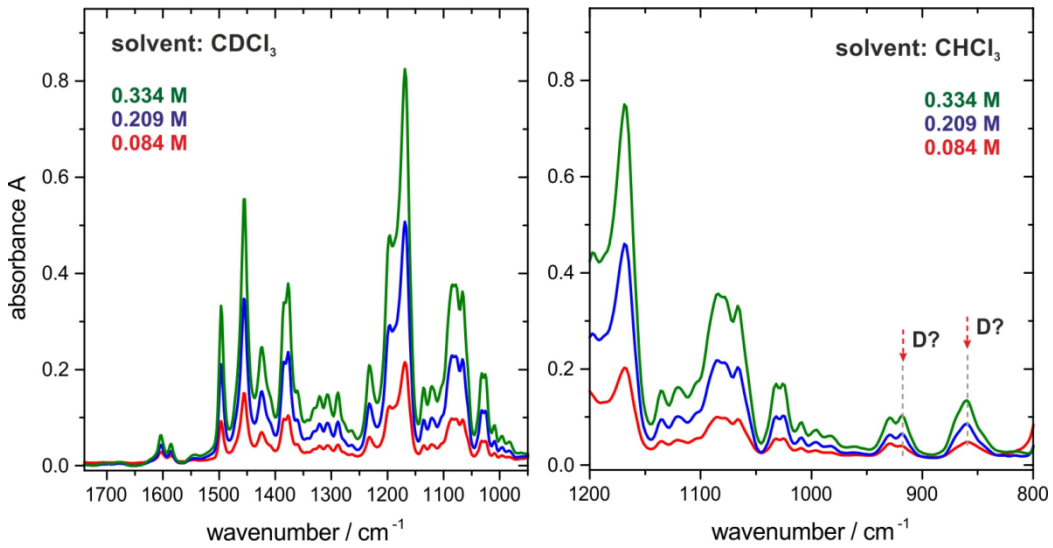


Figure S1. Concentration dependence of the IR spectra of **1** in $CDCl_3$ (1750-950 cm^{-1}) respectively $CHCl_3$ (1200-800 cm^{-1}). Bands marked with ***D*** indicate possible dimer bands.

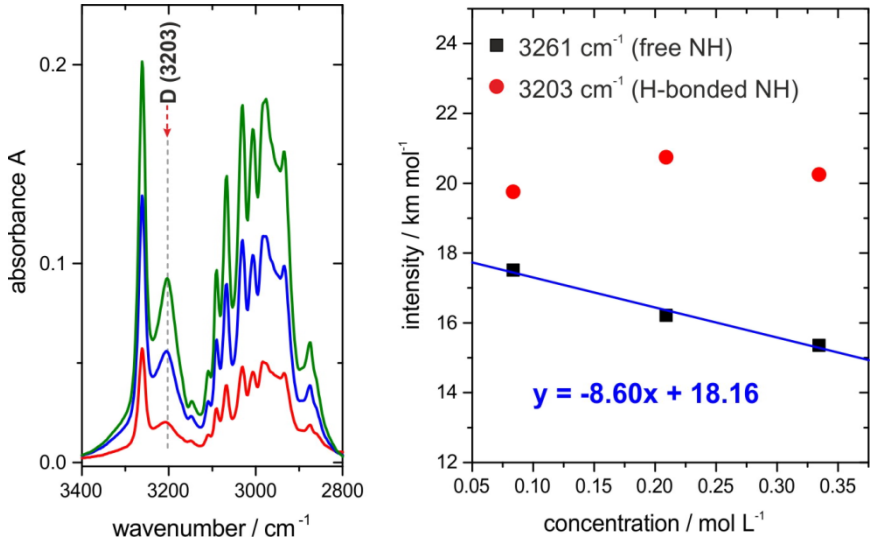


Figure S2. Linear correlation of the free NH stretching mode intensity with concentration.

The amount of monomers present at room temperature was estimated based on spectra taken for solutions of different concentrations. First, the IR bands of the N-H stretching modes of free and hydrogen-bonded NH-groups were integrated by fitting Lorentzian band shapes to the experimental data. These integrated intensities were subsequently converted to molar intensities (in units of km/mol) and plotted against the concentration (Fig. S2). Using this data, the intensity of the free NH vibration at infinite dilution can be approximated by linear regression to 18.16 km/mol.

Table S1. Concentration dependent intensity of the IR band at 3261 cm^{-1} and the corresponding amounts of monomeric **1**.

c / mg ml^{-1}	**c / M**	**I (3261) / km/mol**	**monomers / %**
80	0.334	15.356	84.6
50	0.209	16.216	89.3
20	0.084	17.514	96.4

2. Monomeric BisPEA-BH_3

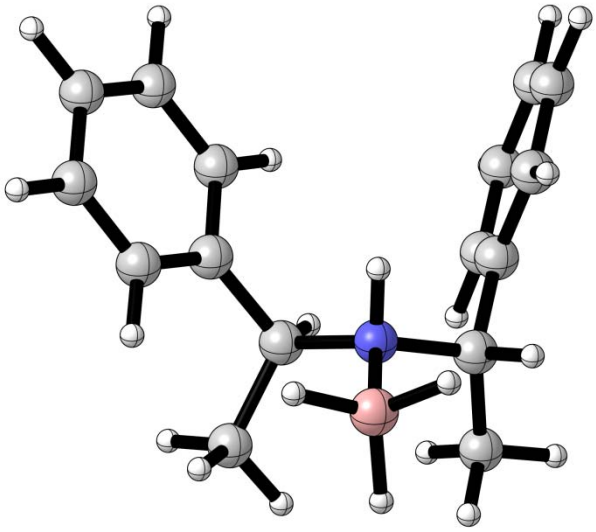


Table S2. Optimized torsion angles of the eight conformers of *(S)*-BisPEA-BH_3 obtained at the B3LYP/6-311++G(2d,p) level of theory.

Conf.	B-N-C^{α}-C_{Ar}	B-N-C^{α}-C_{Ar}	Short
1	168.53	60.08	t g+
2	92.17	-152.64	g+ t
3	-84.24	27.77	g- g+
4	82.22	-63.87	g+ g-
5	88.8	70.16	g+ g+

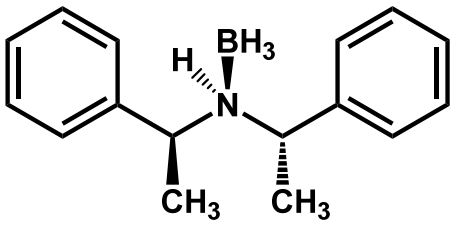


Table S3. Calculated relative zero-point corrected (ΔE) and Gibbs free energies (ΔG) of the five conformers of BisPEA-BH_3 (in kcal/mol) together with the corresponding Boltzmann populations at 298 K (in %).

	B3LYP / 6-311++G(2d,p)				B3PW91 / 6-311++G(2d,p)				B3LYP-*GD3* / 6-311++G(2d,p)			
conf.	**ΔE**	**ΔG**	**popE**	**popG**	**ΔE**	**ΔG**	**popE**	**popG**	**ΔE**	**ΔG**	**popE**	**popG**
1	0.02	0.11	47.90	44.45	0.00[b]	0.00[b]	55.21	51.56	0.18	0.31	42.13	36.81
2	0.00[a]	0.00[a]	49.65	53.85	0.15	0.05	42.77	47.07	0.00[c]	0.00[c]	56.86	62.20
3	1.83	2.10	2.28	1.56	2.02	2.21	1.82	1.24				
4	3.44	3.63	0.15	0.12	3.39	3.58	0.18	0.12				
5	4.51	4.56	0.02	0.02	4.71	5.25	0.02	0.01				

[a] Referenced to the ZPC-energy of conformer 2, E_h = -702.418444 hartree, and the Gibbs free energy G_h= -702.464255 hartree
[b] Referenced to the ZPC-energy of conformer 1, E_h = -702.137661 hartree, and the Gibbs free energy G_h= -702.183299 hartree
[c] Referenced to the ZPC-energy of conformer 2, E_h = -702.462874 hartree, and the Gibbs free energy G_h= -702.507690 hartree

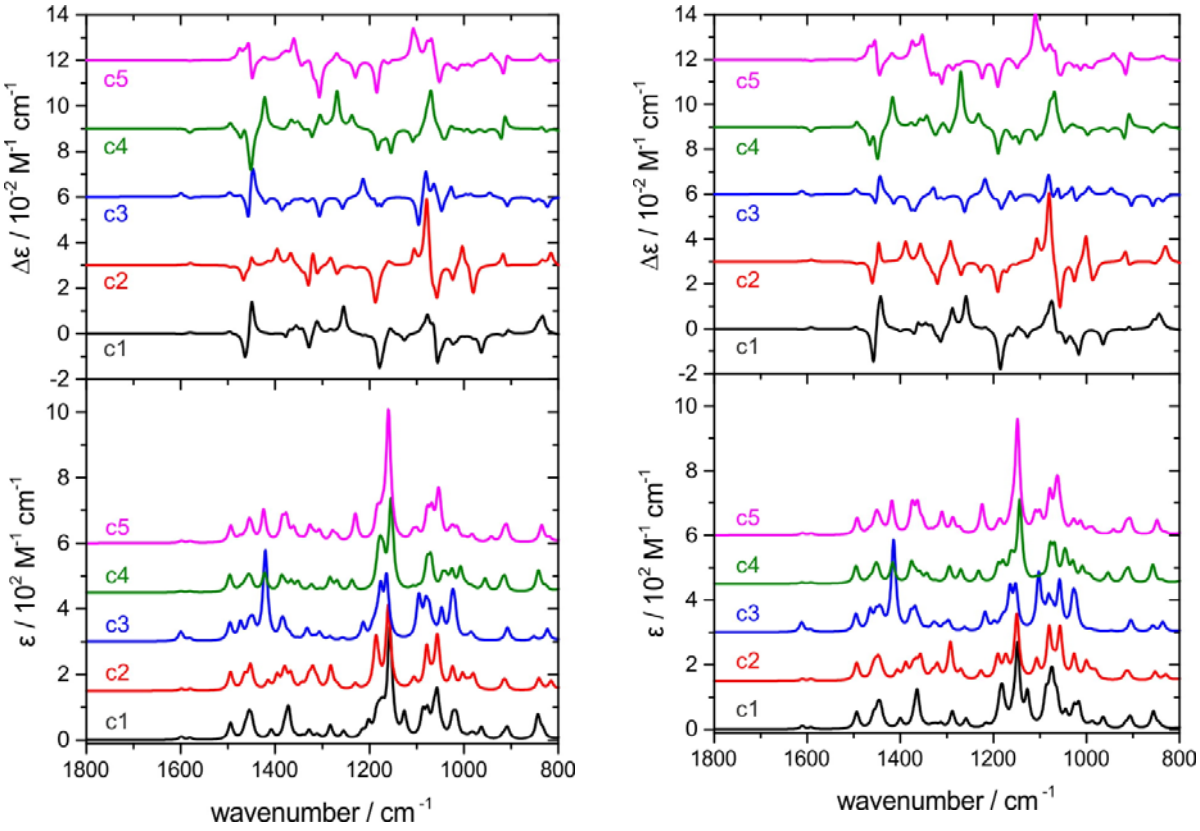


Figure S3. Single conformer IR and VCD spectra obtained with the B3LYP (left) and B3PW91 (right) functionals, the 6-311++G(2d,p) basis set and applying the IEFPCM of chloroform.

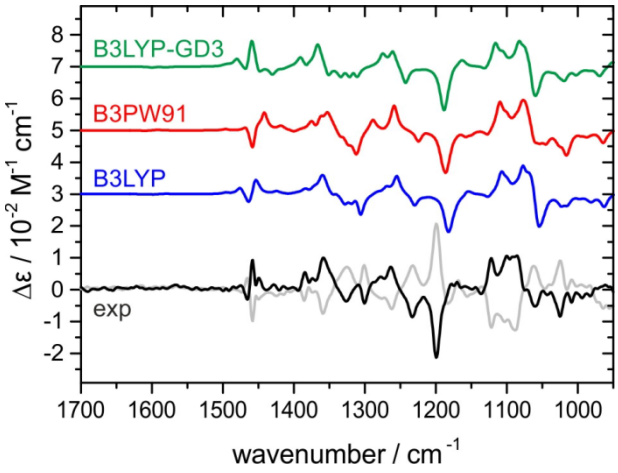


Figure S4. Comparison of the Boltzmann weighted VCD spectra of monomeric **1** obtained from B3LYP, B3PW91, and B3LYP-GD3 calculations with the experimental data.

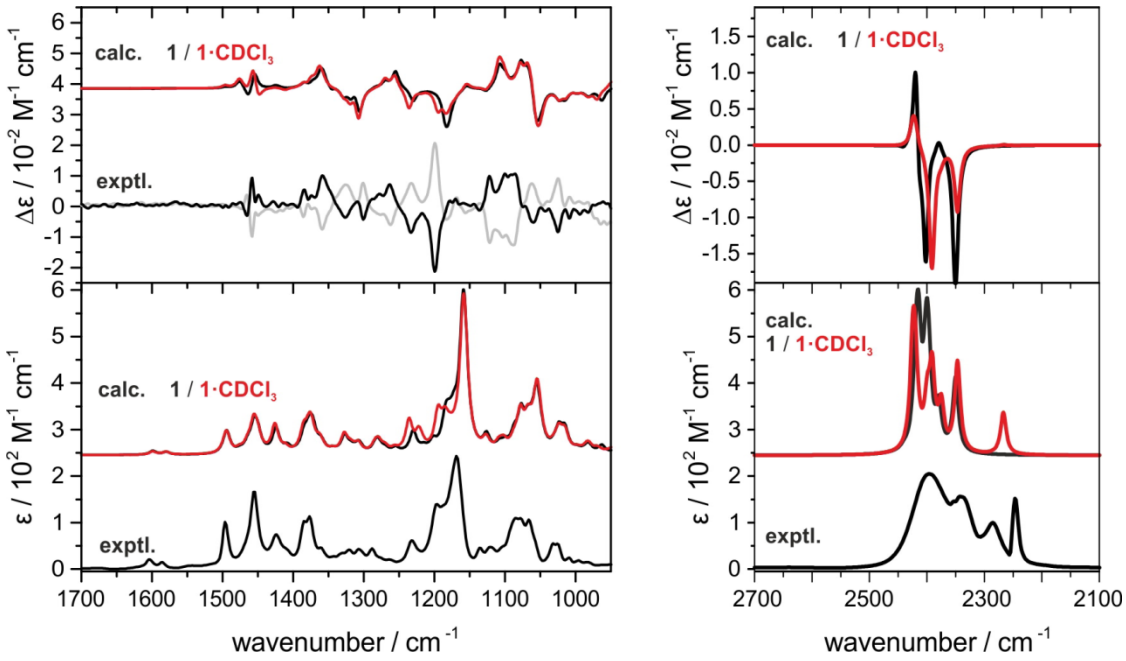


Figure S5. Comparison of the experimental spectra of **1** in $CDCl_3$ in the fingerprint (left) and BH stretching region (right) with the calculations of monomeric **1** and mono-solvated **1**·$CDCl_3$.

3. Acetonitrile measurements

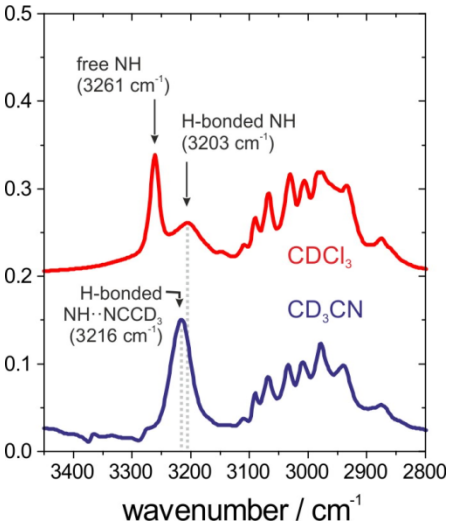


Figure S6. Comparison of the NH stretching region of 1 in chloroform-d_1 and acetonitrile-d_3 at 0.2 M.

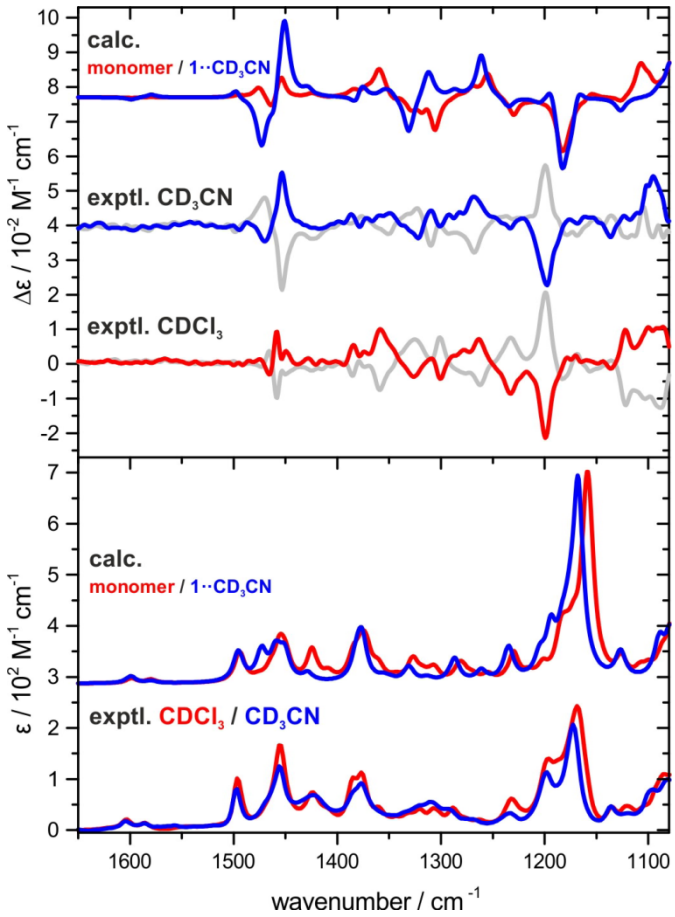


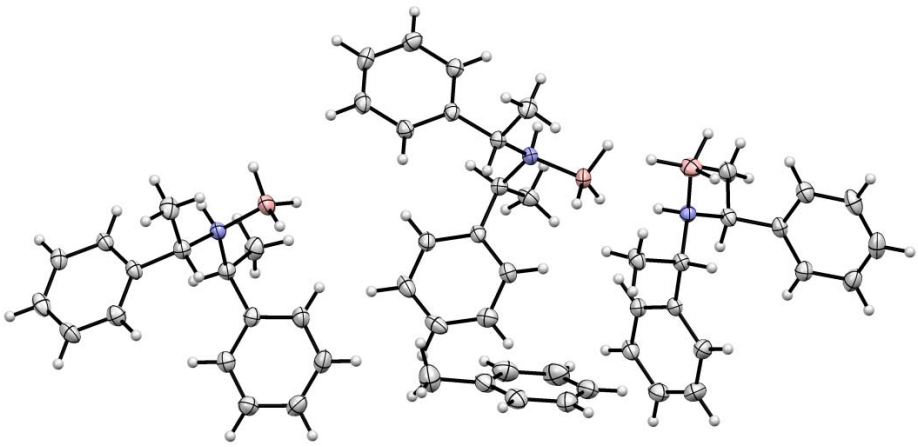
Figure S7. Comparison of experimental spectra of **1** in $CDCl_3$ and CD_3CN with the calculated spectra of the monomeric form and the solvated form [**1**··CD3CN].

4. Crystal structure data of *(S)*-1

Table S4. Crystal data and details of structure refinement for $[BH_3 \bullet HN(CH(Me)\text{-}C_6H_5)_2]_3 \cdot$Toluol

formula	$C_{55}H_{74}B_3N_3$
formula weight[g/mol]	809.6
temperature [K]	173(2)
crystal system	orthorhombic
space group	$P2_12_12_1$
a	9.8161(3)
b	14.3640(4)
c	34.7658(8)
V [Å^3]	4901.9(2)
Z	4
calc. density [g cm^{-3}]	1.097
F (000)	1760
no. of rflns. measured	39074
no. of unique rflns.	10066
μ [mm^{-1}]	0.460
$2Q_{max}$ (deg)	76.00
parameters	593
S (F^2)	1.017
R1 [$I > 2\sigma(I)$]	0.0469
wR2 (all rflns.)	0.1109

Deposited in Cambridge Crystallographic Data Centre under CCDC 1473010.



5. Thermochemistry

The IR spectra of a 0.209 M solution of **1** in chloroform-d_1 measured at different temperatures are shown in Figure S8 (left). The spectra clearly show an increase of the dimeric species with decreasing in temperature. Accordingly, the band assigned to the monomeric species decreases and sharpens. Background correction was carried out by subtraction of a chloroform-d_1 spectrum taken at the same temperature. However, as can be seen in the range from 3500-3300 cm^{-1}, this background correction did not yield a perfectly overlapping background, in particular for the spectra taken above 0 °C.

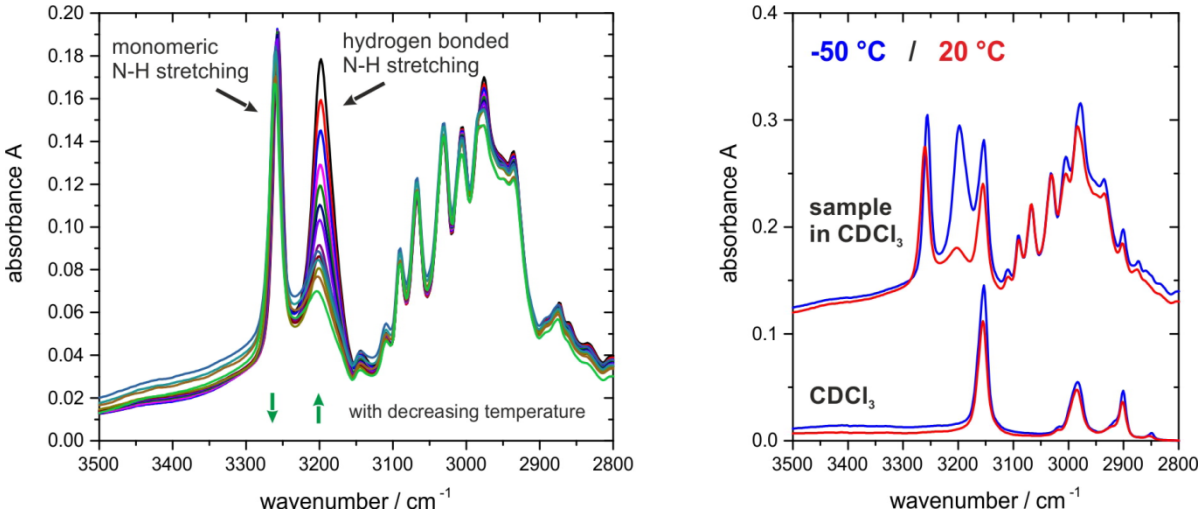


Figure S8. Temperature-dependent IR spectra of **1**. Left: Superposition of all background corrected spectra; Right: Raw spectra of sample and solvent at -50 °C and +20 °C.

With decreasing temperature, not only the band assigned to the dimeric species increased, but a solvent band at ~3150 cm^{-1} increases linearly in intensity due to the temperature-dependent change in density of chloroform (Fig. S8, right). Therefore, instead of fitting the background corrected spectra, the intensities of the free and H-bonded NH stretching mode were determined relative to the intensity of the solvent band by fitting all three bands in the raw spectra.

From the analysis of the concentration dependent measurements, it is known for a 0.209 M solution at room temperature that about 89% of the molecules are found in a monomeric form. With this value, it is possible to convert the molar IR intensities of the monomeric and dimeric NH stretching modes obtained at different temperatures to concentrations. Taking into account that $2\,M \rightleftharpoons D$, the concentrations of monomers and dimers can be calculated according to:

$$I_{3261cm^{-1}} = c_M \quad \Longrightarrow \quad c_D = \frac{1}{2}(1 - c_M).$$

With these concentrations, the mole fractions and equilibrium constants can be determined for all temperatures, and a van't Hoff plot can be prepared. According to the equation

$$\ln(K) = -\frac{\Delta G}{RT}$$

the binding enthalpy can be extracted from linear regression analysis. The corresponding correlation plot is shown in Figure S9.

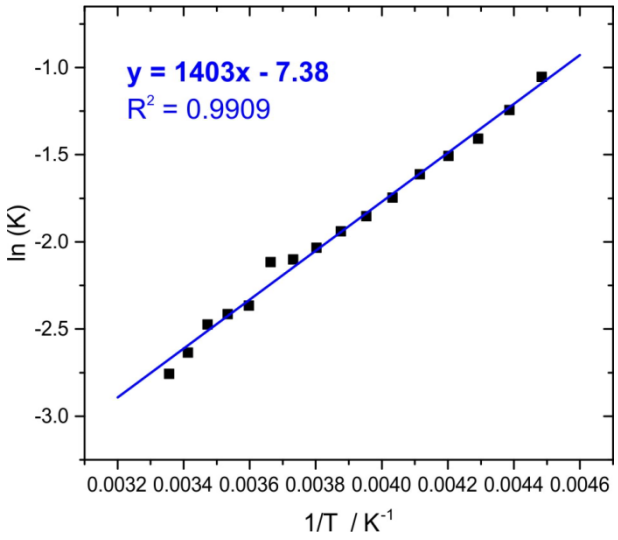


Figure S9. Van't Hoff plot for the temperature dependent dimer formation of **1** in chloroform-d_1.

6. Calculations on the dimeric species

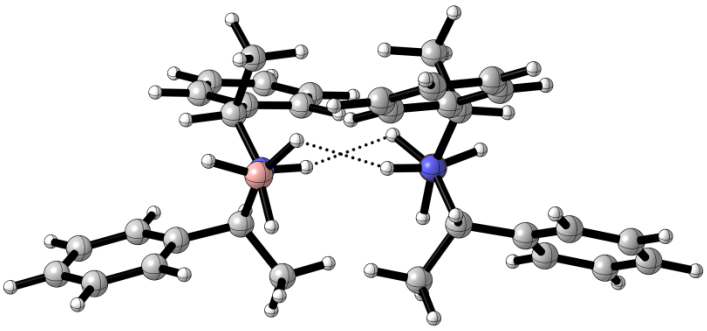


Table S5. Calculated relative zero-point corrected (ΔE) and Gibbs free energies (ΔG) of the two dimers of BisPEA-BH_3 (in kcal/mol) together with the corresponding Boltzmann populations at 298K (in %).

	B3LYP / 6-311++G(2d,p)				**B3PW91 / 6-311++G(2d,p)**				**B3LYP-*GD3* / 6-311++G(2d,p)**			
conf.[a]	**ΔE**	**ΔG**	**popE**	**popG**	**ΔE**	**ΔG**	**popE**	**popG**	**ΔE**	**ΔG**	**popE**	**popG**
HT(c1-c1)	0.00[b]	0.00[b]	70.01	66.88	0.00[c]	1.10	72.11	11.22	0.00[d]	0.18	50.29	42.43
HT(c1-c2)	0.50	0.42	29.99	33.12	0.89	0.98	15.91	13.78	0.01	0.00[d]	49.71	57.57
open(c1-c1)	1.30	0.63	6.63	23.24	1.50	0.00[c]	5.69	71.82	3.22	2.23	0.22	1.29
open(c1-c2)	1.12	0.00	8.94	67.42	1.45	1.85	6.28	3.18	3.57	2.03	0.12	1.80

[a] Dimers with c2-c2 are not possible due to strong steric interactions.
[b] Referenced to the ZPC-energy of HT(c1-c1), E_h = -1404.840446 hartree, and the Gibbs free energy G_h= -1404.912627 hartree
[c] Referenced to the ZPC-energy of HT(c1-c1),, E_h = -1404.27854 hartree, and the Gibbs free energy of open(c1-c2), G_h= -1404.352548 hartree
[d] Referenced to the ZPC-energy of HT(c1-c1),, E_h = -1404.944025 hartree, and the Gibbs free energy of HTc1-c2), G_h= -1405.014015 hartree

7. Cartesian coordinates of selected optimized structures

Conformer 1

C	2.65909300	2.33429200	-0.29091400
C	3.91180100	1.77600100	-0.51677100
C	4.11637400	0.42353200	-0.25580400
C	3.07737500	-0.36685600	0.22225300
C	1.80838600	0.17850600	0.44070200
C	1.62002500	1.53909400	0.18498100
C	0.65650200	-0.62648100	1.01892100
N	0.02100100	-1.60577500	0.02639600
H	-0.64140100	-2.13696300	0.59068500
H	2.48824800	3.38753800	-0.48004700
H	4.72471000	2.38935400	-0.88715400
H	5.09127200	-0.01908700	-0.42314700
H	3.25313100	-1.41529200	0.41577400
H	0.65015100	1.98694500	0.36896000
H	-0.13470600	0.08479500	1.25594900
C	-0.80020400	-0.87394900	-1.02284200
C	1.01190600	-1.34858000	2.31849600
H	1.81642800	-2.06820200	2.18589300
H	0.14150600	-1.87485000	2.72048200
H	1.32411700	-0.60939100	3.05774500
C	-1.89696100	-0.01140300	-0.41329700
C	-2.84364500	-0.54332000	0.46661100
C	-3.87330800	0.24535200	0.96860100
C	-3.98348700	1.57926800	0.58578400
C	-3.05695600	2.11596100	-0.30173000
C	-2.02163300	1.32559300	-0.79307700
C	-1.40671700	-1.83131100	-2.05286500
H	-0.08509500	-0.22652800	-1.53070300
H	-2.79351600	-1.58520500	0.76506700
H	-4.59419200	-0.18484000	1.65358200
H	-4.78720700	2.19310300	0.97407500
H	-3.13555500	3.15168800	-0.61020100
H	-1.30313200	1.75363100	-1.48320700
H	-0.63690600	-2.36823900	-2.60024600
H	-1.99977200	-1.24517300	-2.75684600
H	-2.07027200	-2.55892600	-1.58062100
B	1.00773800	-2.76527500	-0.59837700
H	1.59373900	-2.28812700	-1.54126400
H	1.75660300	-3.11493600	0.28020600
H	0.28483700	-3.67868900	-0.92216000

conformer 2

C	-2.28559700	-2.46949600	0.32848900
C	-3.55641700	-2.22343500	-0.18053100
C	-3.95590300	-0.91281200	-0.42505800
C	-3.09238800	0.14616600	-0.16329500
C	-1.81168600	-0.08811200	0.34477300
C	-1.42297600	-1.40884500	0.58731000
C	-0.83011000	1.03697000	0.64086300
N	-0.07990000	1.42060000	-0.64283700
C	1.43556300	1.55880200	-0.46495900
C	2.08082300	0.19807500	-0.23812800
C	2.24645500	-0.65354900	-1.33630200
C	2.81246900	-1.91419400	-1.18919300
C	3.23338600	-2.34598900	0.06573800
C	3.08828700	-1.50551200	1.16363800
C	2.51834400	-0.24345200	1.01215800
H	-1.96496300	-3.48518600	0.52760800
H	-4.23200600	-3.04605200	-0.38277800
H	-4.94459900	-0.71185500	-0.82038700

H	-3.41960800	1.15722500	-0.36345100
H	-0.43452400	-1.61020500	0.98543500
H	-0.07603200	0.61653000	1.30611200
H	-0.18304600	0.60554500	-1.24447600
C	1.81288800	2.62688400	0.55321200
H	1.93815300	-0.32185100	-2.32276400
H	2.93293800	-2.55487400	-2.05454300
H	3.67924400	-3.32625200	0.18408700
H	3.42239100	-1.82807800	2.14263900
H	2.42930400	0.39648300	1.88064600
C	-1.46800500	2.23457800	1.33893500
H	1.75729100	1.90948100	-1.44580600
H	1.52231100	2.37018400	1.57210200
H	1.35265000	3.57814700	0.29250700
H	2.89628900	2.75577000	0.54101100
H	-2.23966500	2.69958200	0.72953900
H	-0.73050600	2.99757000	1.58083900
H	-1.92098800	1.88991000	2.27066300
B	-0.70828000	2.62525600	-1.55711600
H	-0.52792200	3.68269800	-1.00379600
H	-0.10395500	2.55329200	-2.60747500
H	-1.88285900	2.38498400	-1.70817800

Dimer HT-(c1-c1)

C	6.40024700	-1.59342000	1.63444600
C	6.07215900	-2.84713500	2.13710900
C	4.73300300	-3.18329000	2.31796700
C	3.72925700	-2.27665400	1.99592600
C	4.04440700	-1.01747900	1.47500100
C	5.39238000	-0.68995000	1.30808200
C	2.98912800	0.03385000	1.17068600
N	2.13728000	-0.27272700	-0.06513700
H	1.44114100	0.47739200	-0.09276200
H	7.43845100	-1.31442100	1.49787500
H	6.85194500	-3.55500700	2.39225200
H	4.46752700	-4.15576700	2.71585900
H	2.69546600	-2.55426700	2.14346800
H	5.65951100	0.28790700	0.92430600
H	3.52322600	0.94930200	0.91746300
C	2.95853800	-0.15232400	-1.33998000
C	2.10058800	0.35373400	2.37274900
H	1.57542700	-0.52346500	2.74377100
H	1.36056900	1.11570000	2.11797200
H	2.72887900	0.74539800	3.17456900
C	3.61849800	1.21085300	-1.49735200
C	2.88084700	2.39684700	-1.43787100
C	3.49555100	3.62688300	-1.64777300
C	4.85590700	3.69152400	-1.93671100
C	5.59650600	2.51673100	-2.01316400
C	4.98062700	1.28812000	-1.79144200
C	2.13223600	-0.47088200	-2.58987700
H	3.73770500	-0.90795600	-1.23809800
H	1.81657900	2.37174600	-1.22959600
H	2.90819200	4.53565000	-1.59106700
H	5.33316500	4.64983900	-2.10294900
H	6.65530200	2.55437500	-2.24078800
H	5.56679500	0.37766600	-1.84939500
H	1.75348600	-1.48941500	-2.57055300
H	2.77387900	-0.35016200	-3.46424900
H	1.29102500	0.21651400	-2.69435900
B	1.22811000	-1.63531200	-0.00737200
H	1.90685700	-2.56729500	-0.36669100
H	0.82719200	-1.76933500	1.12119900
H	0.29729200	-1.45203600	-0.76219200
C	-6.40024800	1.59343600	1.63443900
C	-6.07215700	2.84715200	2.13709600
C	-4.73300000	3.18330400	2.31795300

C	-3.72925600	2.27666400	1.99591600
C	-4.04440800	1.01748800	1.47499700
C	-5.39238300	0.68996100	1.30807900
C	-2.98913200	-0.03384600	1.17068700
N	-2.13728200	0.27272500	-0.06513700
H	-1.44114500	-0.47739700	-0.09275600
H	-7.43845200	1.31443800	1.49786900
H	-6.85194100	3.55502600	2.39223600
H	-4.46752100	4.15578200	2.71583900
H	-2.69546400	2.55427600	2.14345600
H	-5.65951600	-0.28789600	0.92430700
H	-3.52323200	-0.94929700	0.91746700
C	-2.95853800	0.15231600	-1.33998000
C	-2.10059400	-0.35372800	2.37275100
H	-1.57543300	0.52347200	2.74377200
H	-1.36057500	-1.11569500	2.11797700
H	-2.72888700	-0.74538900	3.17457100
C	-3.61849800	-1.21086100	-1.49734800
C	-2.88084700	-2.39685400	-1.43785700
C	-3.49554900	-3.62689200	-1.64775400
C	-4.85590400	-3.69153500	-1.93669600
C	-5.59650400	-2.51674300	-2.01315800
C	-4.98062600	-1.28813100	-1.79144200
C	-2.13223300	0.47087000	-2.58987700
H	-3.73770500	0.90794900	-1.23810300
H	-1.81657900	-2.37175200	-1.22958000
H	-2.90819000	-4.53565800	-1.59104200
H	-5.33316100	-4.64985100	-2.10293000
H	-6.65529800	-2.55438900	-2.24078500
H	-5.56679400	-0.37767700	-1.84940200
H	-1.75348300	1.48940200	-2.57055700
H	-2.77387400	0.35014600	-3.46425000
H	-1.29102200	-0.21652700	-2.69435500
B	-1.22811200	1.63530800	-0.00737700
H	-0.82719400	1.76933600	1.12119400
H	-0.29729400	1.45202900	-0.76219600
H	-1.90685700	2.56729100	-0.36669900

Solvated [1·CD3CN]

C	-4.19595900	0.05969800	-0.53262100
C	-4.76999900	-1.12960800	-0.09885400
C	-3.95597200	-2.23174900	0.14976000
C	-2.57974000	-2.14610000	-0.02915000
C	-1.98697000	-0.95148300	-0.45074500
C	-2.81693900	0.14307600	-0.70627100
C	-0.49666900	-0.82511000	-0.72553600
N	0.37687400	-0.81575400	0.53036600
H	1.33803900	-0.80098200	0.17648500
H	-4.81788400	0.92288100	-0.73907100
H	-5.84251300	-1.20068800	0.03909200
H	-4.39471000	-3.16530400	0.48227200
H	-1.96247500	-3.01032900	0.16944600
H	-2.38057200	1.07328800	-1.05131500
H	-0.34582600	0.15464800	-1.17815300
C	0.18070500	0.45763500	1.33465700
C	0.01524800	-1.86065200	-1.72813400
H	-0.14764200	-2.88072600	-1.38792400
H	1.08326100	-1.72513400	-1.91224700
H	-0.51233900	-1.72146100	-2.67341000
C	0.37874800	1.73185900	0.52400200
C	1.53725000	1.96119300	-0.22422500
C	1.72125100	3.16563200	-0.89589600
C	0.75800600	4.16795900	-0.81974200
C	-0.39262700	3.95508300	-0.06789700
C	-0.57898600	2.74485200	0.59435800
C	1.08776400	0.49340500	2.56966200

H	-0.85653300	0.41725500	1.66825500
H	2.30444800	1.19857400	-0.29166400
H	2.62264100	3.32255800	-1.47675300
H	0.90423200	5.10641300	-1.34111300
H	-1.14894400	4.72814300	0.00105300
H	-1.48135200	2.58642100	1.17450200
H	0.86993400	-0.32659500	3.24839500
H	0.92441900	1.43829500	3.09057100
H	2.14145000	0.44312800	2.28722100
B	0.32853300	-2.16751300	1.46527700
H	-0.61541800	-2.06874900	2.21583500
H	0.22981000	-3.12147100	0.73284700
H	1.37881900	-2.20763700	2.06245900
C	4.44837900	-1.71058800	-0.44025100
N	3.48337400	-1.08571000	-0.43137300
C	5.66612400	-2.50623500	-0.44789500
H	6.01501100	-2.64188300	-1.47210100
H	6.44201400	-2.00271700	0.12971700
H	5.47002200	-3.48330500	-0.00507800

Dimer open(c1-c1)

C	3.95055200	-4.00727700	-0.51259100
C	2.70641500	-4.62058100	-0.60363000
C	1.56946900	-3.92838500	-0.19509700
C	1.67124600	-2.63034800	0.29245100
C	2.91446500	-1.99609300	0.37491100
C	4.04920100	-2.70761200	-0.02365200
C	3.08427900	-0.60055400	0.95079100
N	2.73655900	0.52273900	-0.03729100
H	2.75687500	1.36757200	0.53273600
H	4.84537500	-4.53912900	-0.81384200
H	2.62283900	-5.63309300	-0.98063100
H	0.59646300	-4.40187100	-0.25041900
H	0.77490900	-2.11575300	0.60877200
H	5.02635300	-2.24603500	0.06138000
H	4.14701000	-0.47057300	1.15526800
C	3.82682500	0.69120900	-1.08418600
C	2.34266600	-0.38466900	2.26921200
H	1.26687900	-0.51133100	2.16990900
H	2.53902700	0.61615100	2.66445700
H	2.70761900	-1.10706100	3.00077200
C	5.17736200	1.02388200	-0.46471500
C	5.33654200	2.10345800	0.40859500
C	6.58855900	2.42866200	0.91950700
C	7.70829600	1.68746900	0.55260600
C	7.56527100	0.62061100	-0.32799800
C	6.30853900	0.29216700	-0.82850500
C	3.46784400	1.74133800	-2.13961000
H	3.89284200	-0.28032300	-1.57404700
H	4.48467200	2.71148000	0.69560800
H	6.69006100	3.26614900	1.59936000
H	8.68400300	1.94212000	0.94837900
H	8.43046800	0.03924300	-0.62369700
H	6.20733100	-0.54164200	-1.51425200
H	2.57169600	1.46581600	-2.68909600
H	4.30167000	1.81919400	-2.83937100
H	3.31452900	2.72527900	-1.69162400
B	1.22021200	0.50372500	-0.65623700
H	1.19299200	-0.27321800	-1.57957100
H	0.47329800	0.17531800	0.23619800
H	0.98210100	1.63700000	-1.00235300
C	-7.09776500	-0.83118000	-0.68863600
C	-7.31378300	-2.13441700	-0.25622600
C	-6.22330000	-2.93877000	0.06476800
C	-4.92795200	-2.44467100	-0.04043600
C	-4.69640900	-1.13076000	-0.46020100
C	-5.79930500	-0.33858300	-0.78918000

C	-3.29913500	-0.56346900	-0.65435800
N	-2.56318300	-0.25184100	0.65180500
H	-1.62450700	0.02804300	0.35605300
H	-7.93624600	-0.19690000	-0.95149700
H	-8.32190600	-2.52367700	-0.17548200
H	-6.38119200	-3.95827500	0.39677900
H	-4.09367100	-3.08209500	0.21484600
H	-5.64175400	0.67620000	-1.13596100
H	-3.41993600	0.40253100	-1.14388200
C	-3.17573100	0.94131700	1.36495700
C	-2.42292700	-1.41993700	-1.56895100
H	-2.28916200	-2.42911400	-1.18619900
H	-1.43659200	-0.96801600	-1.69848400
H	-2.89756400	-1.48096000	-2.54981600
C	-3.26830400	2.18746600	0.49468700
C	-2.15934200	2.69807000	-0.18569800
C	-2.25723500	3.87687800	-0.91808100
C	-3.46078000	4.57458600	-0.97001100
C	-4.56711100	4.08238500	-0.28554500
C	-4.46931000	2.89642600	0.43672500
C	-2.42828200	1.27675400	2.65991700
H	-4.18553900	0.61993700	1.62124200
H	-1.20604300	2.18169600	-0.15666400
H	-1.38854300	4.25150600	-1.44658600
H	-3.53477300	5.49372500	-1.53886500
H	-5.50915300	4.61712500	-0.31683100
H	-5.33846500	2.51784200	0.96333900
H	-2.46553600	0.45348500	3.36799800
H	-2.89681000	2.15346000	3.11014100
H	-1.38258600	1.52064600	2.46072500
B	-2.28744700	-1.52300400	1.65772800
H	-2.04623200	-2.48767300	0.97516500
H	-1.32093800	-1.22762400	2.32099000
H	-3.27451000	-1.67927300	2.33908800