Association of frustrated phosphine-borane pairs in toluene: Molecular dynamics study

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Supporting Information

1. Molecular dynamics simulations

1.1. Force-field parametrization

The MD simulations have been performed using the OPLS force-field [1]. The toluene and phosphine molecules have been treated as fully rigid bodies, whereas the borane molecule has been also parametrized for pyramidalization and aryl torsions. The functional form of the force-field consists of harmonic terms for bond stretching and angle bending, Fourier series for torsional energetics, and Coulomb plus 12-6 Lennard-Jones potentials for the nonbonded interactions as shown by the following equations:

$$E_{bond} = \sum_i K_i (r - r_{i0})^2$$

$$E_{angle} = \sum_j A_j (\alpha - \alpha_{j0})^2$$

$$E_{dihed} = \sum_l A_0 + \frac{1}{2}(A_1(1+\cos(\phi_l))) + A_2(1-\cos(2\phi_l)) + A_3(1+\cos(3\phi_l))$$

$$E_{nonb} = \sum_{i>j} 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + \frac{q_i q_j}{r_{ij}}$$

where the pair-parameters can be obtaind from the individual atomic data by using the combining rules:

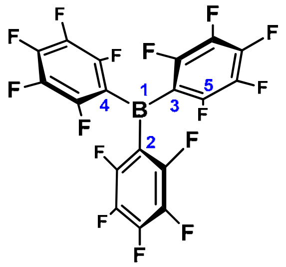
$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}; \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}.$$

In the equations above, K_i and A_j are the harmonic force constants of the ith bond and jth angle, respectively. r_{i0} and α_{io} are their corresponding equilibrium values. σ_i and ε_i are the Lennard-Jones parameters of the ith atom, and q_i is its partial charge. r_{ij} is the actual distance of the ith and jth atoms of the respective non-bonded interaction. ϕ_l is the instantaneous value of the lth dihedral angle. In the case of torsions, the 1-4 Coulombic and vdW interactions have been scaled by 0.5. The force-field parameters are listed in Table S1, whereas the partial charges are given in the Appendix along with the XYZ coordinates of the atoms.

Table S1. Force-field parameters used in MD simulations. Stretching force constant (K) is in kcal/mol/Å^2, bending force constants are in kcal/mol/deg^2, r_0 and α_0 equilibrium structural values are in Å and degree, respectively, torsional parameters are in kcal/mol, the ε and σ Lennard-Jones parameters are in kcal/mol and Å, respectively.

borane				
	K	r_0		
BC	856.0	1.567		
	A	α_0		
CCB	140.00	122.00		
CBC	140.00	120.00		
	A_0	A_1	A_2	A_3
$C_2B_1C_3C_5$ [a]	0.000	0.000	4.800	0.000
$C_2C_3C_4B_1$	0.000	0.000	7.250	0.000
$C_2B_1C_3C_4$	0.000	0.000	1.667	0.000
	ε	σ		
C	0.070	3.550		
B	0.066	3.500		
F	0.061	2.940		
phosphine				
	ε	σ		
C, methyl	0.066	3.500		
C, quaternary	0.0621	3.586		
P	0.200	3.742		
H	0.033	2.500		
toluene				
	ε	σ		
H, aromatic	0.030	2.420		
H, methyl	0.030	2.500		
C, aromatic	0.070	3.550		
C, methyl	0.066	3.500		

[a] For the numbering of atoms, see Scheme S1.



Scheme S1. Numbering of atoms for the definition of dihedral angles in $B(C_6F_5)_3$.

This setup corresponds to the "standard force-field" model in Fig. 1 of the article. For borane, some of the parameters were not directly available in the OPLS library, hence we either used analogous aromatic tertiary amine parameters (stretching and bending force constants) or derived them from quantum chemical calculations (torsional parameters, see later).

An additional term has been implemented into the force-field set to account for the partial dative bond formed via the overlap of phosphine and borane frontier orbitals. The importance of this direct P-B interaction at shorter P-B distances has been highlighted by Kim and Rhee [Ref]. The P-B interaction term has been modified so as to reproduce the gas-phase interaction energy curve predicted by SCS-MP2 calculations (see later). This has been done by aligning the two curves at the minima, taking the difference between the two curves within a given P-B range (3.50 Å - 4.21 Å, where dative bond formation is expected), and modifying the original P-B term by this difference. The analytic form of this potential term is

$$U(x) = -33077 + 63355x - 58897x^2 + 33256x^3 - 11670x^4 + 2392.9x^5 - 235.38x^6 + 1.8297x^7 + 0.98995x^8$$

where x is in Å and U(x) is in kcal/mol. The potential energy curve obtained with this improved force field for the interaction of $(^tBu)_3P$ and $B(C_6F_5)_3$ molecules is shown in Fig. 1 of the paper (solid line).

1.2 Details of MD simulations

The force-field calculations have been performed by using the DL_POLY_2.0 program package [2]. The simulation model for the MD calculations is a periodic box with an edge size of *a* = 56.69 Å, with 1011 toluene molecules and a borane-phosphine pair. The size of the box was chosen on the basis of the densitiy of toluene (0.8669 g/cm^3). Initially we have equilibrated pure toluene of 1024 molecules at 298 K for 4.5 ps, then 13 toluenes molecules have been replaced by a phosphine-borane pair kept at their equilbirium geometry. The solution was heated up to 698 K for a short period, then quenched to 298 K, and equilibrated again for 4.5 ps. The phosphine-borane dimer has been treated as a single rigid body during the equilibration, but of course, during the umbrella samplings, the two molecules have been treated separately.

The MD equations of motion have been integrated by employing the Verlet algorithm. For the equilibrations we used a time step of 15 fs. In the production runs, where the borane was flexible, a smaller time step of 5 fs has been applied. The NVT conditions have been achieved by employing the Nose-Hoover thermostat at a reference temperature of 298 K with a time constant of 0.5 ps. The Ewald summation method has been used to describe accurately the electrostatics. The real space cutoff was 9 Å.

1.3 Free energy calculations

The potential of mean force (PMF) curve (i.e. the $F(r)$ functions) has been calculated along the P-B distance as a reaction coordinate (r). The windows used in the umbrella sampling are centered at equidistant points of 1.0 Å between $r = 4.0$ Å and $r = 20$ Å. An additional window has been inserted at $r = 3.5$ Å. A harmonic restraint with force constant of 2 kcal/mol/Å^2 was applied as a bias potential within each window. The initial configurations of the umbrella sampling have been constructed by pulling apart the phosphine-borane pair using steered dynamics. In these simulations, the P-B distance was elongated by a constant velocity of 0.4 Å/ps. After reaching the desired r value, the system is equilibrated for 150 ps. The umbrella samplings have been performed for an additional 850 ps. The probability densities have been derived using bin sizes of 0.15 Å. From the individual probability distributions, the PMF curve has been constructed by using the weighted histogram analysis method (WHAM) [3]. The probability distributions for individual windows are illustrated in Figure S1. The PMF has been obtained by aligning the individual free energy sections by WHAM. It was then corrected by the $2kT\ln(r)$ term arising from the Jacobian corresponding the Cartesian-spherical coordinate transformation [4]. Four independent umbrella sampling series have been performed and the results have been averaged. The estimated error on the PMF curve is 0.2 kcal/mol.

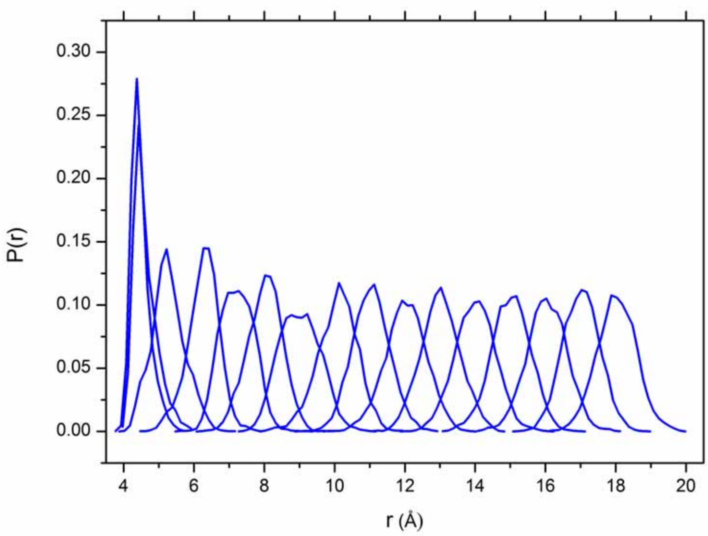


Figure S1. Individual biased distributions obtained from a typical umbrella simulation series.

In order to estimate the relative population of the associated state, one has to define a chemically meaningful region for r corresponding to the phosphine-borane dimer state. As noted in the main text (Ref. 15), this is somewhat arbitrary, but once the choice is made ($r < 6$ Å in the present case), the probability distribution is integrated over this region:

$$C(r) = \int_0^r P(\mathrm{R})\,\mathrm{dR}$$

The $C(r)$ function thus gives the probability of finding the phosphine-borane pair in states with P-B distances smaller than r.

The complete umbrella sampling region with $r = 20$ Å corresponds to a dilute solution as compared to the usual experimental conditions. The experimental concentration used in Ref. [5] is $x_{borane} = x_{phosphine} = 0.0052$, which corresponds to a box size with $a = 16$ Å. Hence, the relative populations were estimated by weighting $C(r)$ with the integrate of the probability distribution over all r values up to 16 Å.

1.4 Effect of the extra P-B term on the PMF curves

In order to estimate the importance of the short range P–B interactions (partial dative bond) in the association in toluene, we carried out MD simulations with the standard force-field model as well (i.e. without the extra P-B term). The results obtained for the probability distribution functions and the free energy curves with the two models are compared in Figure S2. Clearly, the extra P-B term gives rise only to minor differences and the two models predict very similar relative concentration of associates states.

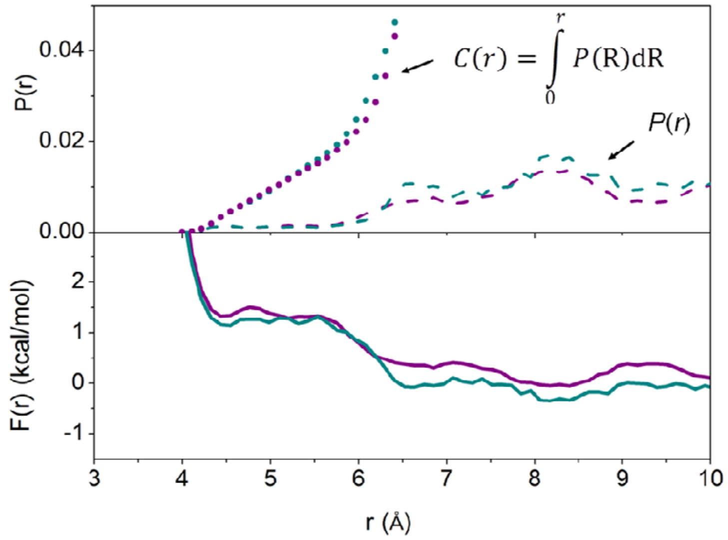


Figure S2. Comparison of the $F(r)$, $P(r)$ and $C(r)$ curves obtained by the standard (purple) and the improved (dark cyan) parametrizations. Note that these curves carry larger statistical errors than the one shown in Fig. 2 of the main text. For the present comparison we calculated a roughly one order of magnitude smaller set of configurations in the calculation of probability distributions.

2. Quantum Chemical Calculations

For the parametrization of the potentials describing possible torsional motions of the aromatic rings in borane $B(C_6F_5)_3$, as well as the facile pyramidalization of the molecule, DFT calculations at the M05-2X/6-31G* level [6] have been carried out. From the equilibrium geometry, potential energy curves have been derived along three dihedral angles $\phi_1 = \angle C_2B_1C_3C_5$, $\phi_2 = \angle C_2C_3C_4B_1$ and $\phi_3 = \angle C_2B_1C_3C_4$ (see Scheme 1 for numbering). The curves shown in Figures S3-S5 were used to obtain parameters A_2 (listed in Table S1) by a fitting procedure. First, we have derived the torsional contribution from the potential energy curves by substracting all the other force-field terms (stretching, bending, vdW and Coulomb parts) and this residual was fitted to obtain the A_2 parameters.

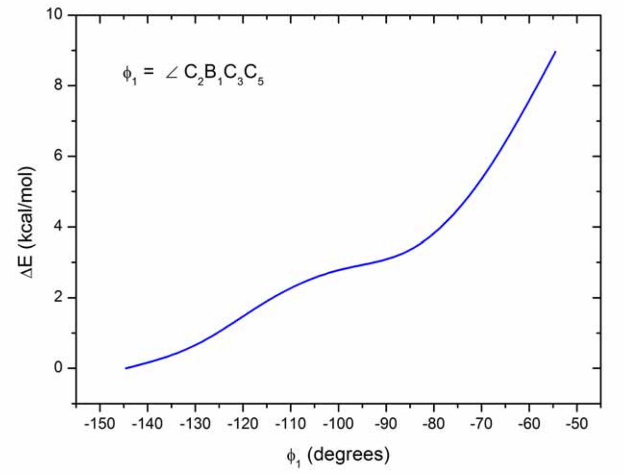


Figure S3. Potential energy curve $\Delta E(\phi_1)$ obtained for $B(C_6F_5)_3$ from M05-2X/6-31G* calculations.

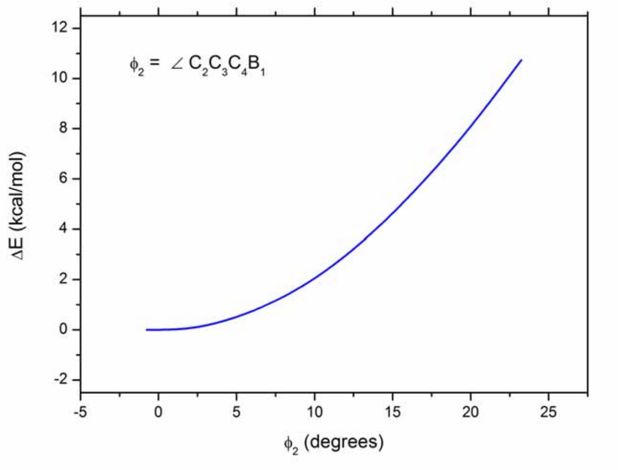


Figure S4. Potential energy curve $\Delta E(\phi_2)$ obtained for $B(C_6F_5)_3$ from M05-2X/6-31G* calculations.

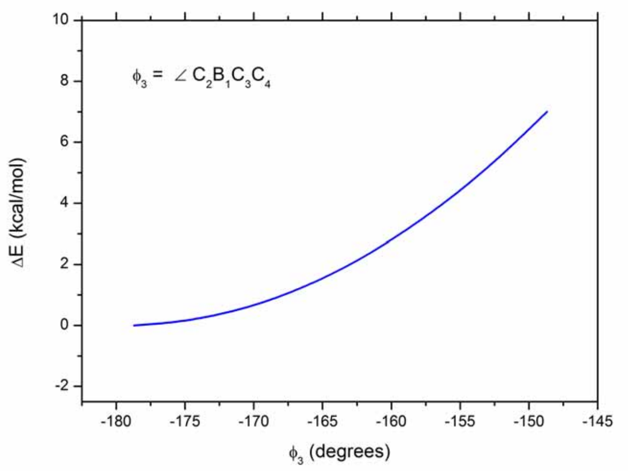


Figure S5. Potential energy curve $\Delta E(\phi_3)$ obtained for $B(C_6F_5)_3$ from M05-2X/6-31G* calculations.

The atomic charges used in the force-field calculations were derived by fitting the eletrostatic potential of the M05-2X/6-31G* optimized structures applying the CHelpG scheme [7].

The potential energy curve describing the interaction of the phosphine-borane dimer (shown in Fig. 1 of the paper) has been calculated by constraining the distance between the P and B atoms while optimizing all other degrees of freedom at the M05-2X/6-31G* level and performing additional single-point energy calculations at the SCS-MP2/cc-pVTZ level of theory [8].

The DFT calculations have been carried out by the *Gaussian09* package [9], whereas the SCS-MP2 calculations have been performed by using *Turbomole* [10]

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Appendix

Borane, XYZ coordinates and partial charges

C	-3.7502	-0.7299	-2.1661	0.1703
C	-2.9865	0.3914	-2.4544	0.0532
C	-1.8243	0.6195	-1.7366	0.3285
C	-1.3581	-0.2457	-0.7458	-0.6020
C	-2.1584	-1.3619	-0.4981	0.3298
C	-3.3358	-1.6120	-1.1791	0.0536
B	-0.0184	0.0103	0.0237	0.9799
C	0.4377	1.4738	0.3559	-0.6286
C	1.7830	1.8488	0.3681	0.3352
C	2.2078	3.1347	0.6558	0.0659
C	1.2667	4.1059	0.9626	0.1537
C	-0.0820	3.7832	0.9686	0.0680
C	-0.4696	2.4916	0.6565	0.3344
F	3.5024	3.4442	0.6412	-0.1049
F	2.7369	0.9602	0.0733	-0.1744
F	1.6553	5.3410	1.2491	-0.1010
F	-0.9875	4.7131	1.2667	-0.1050
F	-1.7844	2.2461	0.6746	-0.1760
F	-1.1276	1.7148	-2.0590	-0.1734
F	-1.8046	-2.2593	0.4281	-0.1741
F	-3.3761	1.2356	-3.4076	-0.1019
F	-4.0816	-2.6757	-0.8809	-0.1022
F	-4.8723	-0.9598	-2.8346	-0.1041
C	0.8888	-1.2028	0.4336	-0.6011
C	1.6447	-1.2075	1.6078	0.3161
C	2.4315	-2.2776	1.9957	0.0732
C	2.5035	-3.3962	1.1783	0.1545
C	1.7815	-3.4360	-0.0048	0.0698
C	0.9895	-2.3539	-0.3498	0.3176
F	3.2612	-4.4265	1.5292	-0.1020
F	3.1201	-2.2410	3.1345	-0.1061
F	1.8540	-4.5065	-0.7930	-0.1044
F	1.6135	-0.1594	2.4376	-0.1702
F	0.3206	-2.4490	-1.5035	-0.1723

Phosphine, XYZ coordinates and partial charges

C	-4.3764	0.0759	2.2338	-0.5681
C	-3.8105	0.5193	3.5978	0.8186
P	-2.0405	-0.2209	3.7206	-0.9226
C	-2.2307	-2.0356	4.3331	0.8672
C	-0.9043	-2.7493	4.0062	-0.4619
C	-3.7410	2.0543	3.5172	-0.5636
C	-4.8088	0.1597	4.7059	-0.5237
C	-1.1207	0.7452	5.1066	0.8691
C	0.1322	-0.0285	5.5531	-0.5658
C	-1.9176	1.1059	6.3668	-0.5582
C	-0.5817	2.0358	4.4580	-0.4937
C	-3.2954	-2.7735	3.5032	-0.6060
C	-2.5724	-2.2474	5.8137	-0.5301
H	-4.7364	2.4227	3.2484	0.1151
H	-5.7453	0.6977	4.5220	0.1039
H	-5.3742	0.5097	2.1082	0.1118
H	-3.4721	2.5187	4.4641	0.1242
H	-3.0499	2.3931	2.7466	0.1577
H	-4.4496	0.4501	5.6926	0.1159
H	-2.7385	1.7908	6.1614	0.1182
H	-5.0478	-0.9022	4.7284	0.1119
H	-3.7435	0.4453	1.4247	0.1454
H	-1.3643	2.6985	4.0947	0.1197
H	-4.4705	-1.0030	2.1309	0.1451
H	-1.2476	1.6068	7.0743	0.1058
H	-2.3239	0.2257	6.8634	0.1241
H	-0.0006	2.5879	5.2042	0.0882
H	-4.3092	-2.4435	3.7202	0.1348
H	0.0814	1.7927	3.6255	0.1233
H	-3.5088	-1.7645	6.0914	0.1156
H	-3.1155	-2.6848	2.4327	0.1594
H	-3.2408	-3.8372	3.7569	0.1211
H	-1.7919	-1.8872	6.4813	0.1090
H	-2.6859	-3.3215	5.9975	0.0993

H	0.7291	0.6347	6.1876	0.1107
H	-0.1008	-0.9126	6.1434	0.1206
H	0.7561	-0.3195	4.7091	0.1501
H	-0.7030	-2.7009	2.9344	0.1164
H	-0.0480	-2.3385	4.5364	0.1138
H	-0.9926	-3.8040	4.2878	0.0776

Toluene, XYZ coordinates and partial charges

C	-0.2321	1.1990	-0.0084	0.2054
C	-0.9466	0.0005	-0.0107	-0.2114
C	-0.2323	-1.1988	-0.0084	-0.0883
C	1.1587	-1.2022	0.0025	-0.1284
C	1.8602	-0.0002	0.0090	-0.0885
C	1.1594	1.2017	0.0025	-0.2115
C	-2.4545	0.0000	0.0100	-0.3126
H	-2.8294	-0.0032	1.0368	0.1244
H	-2.8541	-0.8827	-0.4907	0.1050
H	-2.8551	0.8853	-0.4854	0.1067
H	-0.7738	-2.1382	-0.0173	0.1050
H	1.6945	-2.1434	0.0019	0.1243
H	2.9428	-0.0005	0.0140	0.0900
H	1.6951	2.1429	0.0019	0.0900
H	-0.7725	2.1391	-0.0173	0.0900