Electronic Supplementary Information

Cations brought together by hydrogen bonds: The protonated pyridine-boronic acid dimer explained

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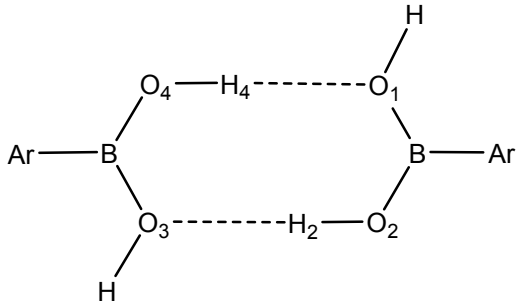
Table S1. Intermolecular parameters (Å) of the neutral aromatic boronic acid dimers found in the CSD.



Refcode	O1-O4	O2-O4	O1-H4	O3-H2	Aromatic
YOQZIO	2.465	2.465	1.647	1.647	Phenyl
LIYHOR	2.482	2.482	1.526	1.526	Phenyl
ROBJID	2.543	2.507	1.704	1.659	Phenyl
ROBJAV	2.678	2.788	1.845	1.954	Phenyl
XUVBAR	2.691	2.691	1.867	1.867	Phenyl
ZUCSIB	2.695	2.743	1.859	1.905	Phenyl
MIDZAB	2.697	2.697	1.915	1.915	Phenyl
QEKSIL	2.697	2.697	1.859	1.859	Phenyl
DAPCOP	2.702	2.702	1.879	1.879	Phenyl
USALAC	2.704	2.704	1.908	1.908	Phenyl
RORMES	2.706	2.842	1.892	2.024	Phenyl
WIYNAU	2.706	2.894	1.919	2.016	Phenyl
FEJGIL	2.711	2.711	1.871	1.871	Phenyl
MULQER	2.711	2.711	1.896	1.896	Phenyl
AZASOL	2.712	2.798	1.882	1.994	Phenyl
EJAGAZ	2.717	2.717	1.949	1.949	Phenyl
FAKTER	2.717	2.756	1.883	1.919	Phenyl
OLIDOC	2.719	2.719	1.883	1.883	Phenyl
YIPJIS	2.720	2.720	1.894	1.894	Phenyl
PHBORA01	2.721	2.734	1.804	1.888	Phenyl
FUQBOK	2.722	2.722	1.878	1.878	Phenyl
GODGUC	2.722	2.722	1.898	1.898	Phenyl
PAXSUD	2.724	2.724	1.804	1.804	Phenyl
EHIZOM	2.725	2.725	1.898	1.898	Phenyl
XUVBEV	2.725	2.725	1.910	1.910	Phenyl
QADKIQ	2.727	2.727	1.911	1.911	Phenyl
NIQYUI	2.728	2.728	1.860	1.860	Phenyl
DOVHUT	2.729	2.759	1.912	1.940	Phenyl
FETZUA	2.729	2.729	1.964	2.158	Phenyl
FETZUA	2.729	2.729	2.158	1.964	Phenyl
KUGBUK	2.731	2.731	1.938	1.938	Phenyl
LABMIN	2.731	2.759	1.902	1.914	Phenyl
RUYTEM	2.731	2.798	1.950	1.997	Phenyl

WAJXEL	2.733	2.733	1.810	1.810	Phenyl
BAGYOZ	2.734	2.734	1.849	1.849	Phenyl
PHBORA01	2.734	2.721	1.888	1.804	Phenyl
PEJZEM	2.734	2.781	1.923	1.973	Phenyl
BEWYAE	2.735	2.735	1.896	1.896	Phenyl
GESLAT	2.735	2.735	1.927	1.927	Phenyl
OHAZOO	2.735	2.735	1.949	1.949	Phenyl
PEJZEM	2.735	2.770	1.924	1.969	Phenyl
IGERAO	2.736	2.736	1.952	1.952	Phenyl
MUWYUZ01	2.738	2.738	1.842	1.842	Phenyl
BEWYAE01	2.739	2.739	1.922	1.922	Phenyl
ISANOH	2.739	2.750	1.852	1.862	Phenyl
TIRXUP	2.739	2.739	1.757	1.757	Phenyl
BEWYAE	2.740	2.740	1.904	1.904	Phenyl
FUZLES	2.740	2.740	1.919	1.919	Phenyl
GISVIO	2.740	2.740	1.881	1.881	Phenyl
GODHAJ	2.741	2.751	1.876	1.852	Phenyl
ISANOH01	2.741	2.741	1.846	1.846	Phenyl
QEKSIL	2.741	2.741	1.902	1.902	Phenyl
EFIDIH	2.742	2.742	1.909	1.909	Phenyl
MUWYUZ	2.742	2.742	1.778	1.778	Phenyl
TENRUB	2.742	2.742	1.900	1.900	Phenyl
WIYMUN	2.742	2.742	1.921	1.921	Phenyl
BEWYAE01	2.743	2.743	1.927	1.927	Phenyl
ZILBEB	2.743	2.743	1.913	1.913	Phenyl
ZUCSIB	2.743	2.695	1.905	1.859	Phenyl
DEWYEK	2.744	2.744	1.926	1.926	Phenyl
EJUXAK	2.745	2.745	1.909	1.909	Phenyl
WEJCIY	2.745	2.745	1.871	1.871	Phenyl
FEJGUX	2.746	2.746	1.906	1.906	Phenyl
TIRXUP	2.746	2.746	1.765	1.765	Phenyl
VEFCOZ	2.746	2.746	1.823	1.823	Phenyl
PEJYUB01	2.746	2.757	1.925	1.935	Phenyl
NEBTEV	2.748	2.748	1.928	1.928	Phenyl
PHBORA	2.748	2.758	1.965	2.058	Phenyl
QACYIE	2.748	2.748	1.909	1.909	Phenyl
UJACIT01	2.748	2.748	1.933	1.933	Phenyl
PEJYUB	2.748	2.756	1.948	1.951	Phenyl
PEJZIQ	2.748	2.748	1.934	1.934	Phenyl
DOVJEF	2.749	2.749	1.949	1.949	Phenyl
WIYMUN	2.749	2.749	1.934	1.934	Phenyl
PEJZAI	2.749	2.749	1.935	1.935	Phenyl
TASCEW	2.750	2.750	1.905	1.905	Phenyl

TECCEL	2.750	2.750	1.921	1.921	Phenyl
VOSZOU	2.750	2.839	1.919	1.998	Phenyl
WIYMOH01	2.750	2.750	1.962	1.962	Phenyl
UJACUF	2.752	2.840	1.877	1.962	Phenyl
BPHBAC01	2.753	2.753	2.085	2.085	Phenyl
WIYPEA	2.753	2.753	1.923	1.923	Phenyl
BASQOD	2.754	2.754	1.866	1.866	Phenyl
GODHAJ	2.754	2.754	1.836	1.836	Phenyl
DOVJOP	2.755	2.755	1.943	1.943	Phenyl
KEZDOK	2.755	2.757	1.942	1.941	Phenyl
ROGMEF	2.755	2.755	1.939	1.939	Phenyl
RORMES	2.755	2.755	1.938	1.938	Phenyl
VIVQAT	2.755	2.755	1.926	1.926	Phenyl
ZUCREW	2.756	2.756	1.894	1.894	Phenyl
PEJYUB	2.756	2.748	1.951	1.948	Phenyl
PHBORA02	2.756	2.746	1.937	1.928	Phenyl
GESLAT	2.757	2.757	1.938	1.938	Phenyl
ROGKUU	2.757	2.757	1.960	1.960	Phenyl
XOSFAN	2.757	2.757	1.868	1.868	Phenyl
TUNNEW	2.758	2.758	1.922	1.922	Phenyl
VEFCIT	2.758	2.758	1.805	1.805	Phenyl
ETOLAA	2.759	2.759	1.869	1.869	Phenyl
QEKSIL	2.759	2.751	1.922	1.919	Phenyl
FAKTER	2.760	2.763	1.922	1.925	Phenyl
RORNIX	2.760	2.760	2.006	2.006	Phenyl
RORPOF	2.760	2.760	1.915	1.915	Phenyl
BASQET	2.761	2.761	1.849	1.849	Phenyl
IYAXAH	2.761	2.761	1.930	1.930	Phenyl
YICHIB01	2.761	2.761	1.947	1.947	Phenyl
ZAPDAV	2.761	2.761	1.885	1.885	Phenyl
GISVIO	2.762	2.762	1.878	1.878	Phenyl
NUPZAB	2.762	2.762	1.900	1.900	Phenyl
EFIDON	2.763	2.763	1.925	1.925	Phenyl
HUXXII	2.763	2.763	1.884	1.884	Phenyl
KUGBOE	2.763	2.763	1.965	1.965	Phenyl
RORMUI	2.763	2.763	1.932	1.932	Phenyl
DECROT	2.764	2.764	1.929	1.929	Phenyl
KOJQAC	2.764	2.764	1.931	1.931	Phenyl
RORPUL	2.764	2.764	2.002	2.002	Phenyl
FOVMOT	2.765	2.765	1.890	1.890	Phenyl
KEZDOK	2.765	2.765	1.947	1.947	Phenyl
VIVPUM	2.765	2.765	1.872	1.872	Phenyl
XOSDOZ	2.765	2.765	1.890	1.890	Phenyl

DOVHON	2.766	2.766	1.965	1.965	Phenyl
VOSZUA	2.768	2.768	2.024	2.024	Phenyl
WIYMOH	2.768	2.768	1.961	1.961	Phenyl
ZUCRIA	2.768	2.768	1.941	1.941	Phenyl
NEYVIX	2.769	2.769	1.891	1.891	Phenyl
PELMIF	2.771	2.771	1.898	1.898	Phenyl
BASQIX	2.772	2.772	1.852	1.852	Phenyl
XOSDUF	2.772	2.804	1.864	1.894	Phenyl
AZATAY	2.773	2.773	1.873	1.873	Phenyl
GETPAY	2.773	2.773	1.941	1.941	Phenyl
IRASIF	2.773	2.773	1.831	1.831	Phenyl
DEWYAG	2.774	2.774	1.916	1.916	Phenyl
WIYMUN01	2.774	2.774	1.962	1.962	Phenyl
XOSDUF	2.774	2.774	1.898	1.898	Phenyl
EBIXIZ	2.775	2.775	1.938	1.938	Phenyl
TENROV	2.775	2.813	1.932	1.984	Phenyl
GITLAX	2.778	2.778	1.871	1.871	Phenyl
RORMES	2.778	2.778	1.962	1.962	Phenyl
PEJZOW	2.779	2.779	1.963	1.963	Phenyl
UJADAM	2.780	2.780	1.896	1.896	Phenyl
UJADEQ	2.781	2.781	1.923	1.923	Phenyl
ROBJAV	2.782	2.724	1.947	1.891	Phenyl
LABCUM	2.783	2.783	1.956	1.956	Phenyl
WIYMUN01	2.783	2.783	1.968	1.968	Phenyl
TUNGAK01	2.786	2.786	1.975	1.975	Phenyl
RORQAS	2.787	2.787	1.977	1.977	Phenyl
GESKEW	2.788	2.788	1.896	1.896	Phenyl
HOXPIU01	2.789	2.789	1.709	1.709	Phenyl
BUDREY	2.789	2.789	1.937	1.937	Phenyl
TITDEG	2.790	2.790	1.897	1.897	Phenyl
MOKKON01	2.792	2.792	1.989	1.989	Phenyl
DOVJIJ	2.793	2.793	1.968	1.968	Phenyl
HOXPIU	2.794	2.794	1.907	1.907	Phenyl
OCEFAF	2.794	2.794	1.956	1.956	Phenyl
SAFSID	2.795	2.795	1.985	1.985	Phenyl
AZASIF	2.796	2.796	1.937	1.937	Phenyl
WENZUL	2.796	2.796	2.061	2.061	Phenyl
JESXIR	2.796	2.796	1.984	1.984	Phenyl
MUCJUQ	2.797	2.797	1.969	1.969	Phenyl
RUYTEM	2.798	2.731	1.997	1.950	Phenyl
TUNGAK	2.798	2.798	1.975	1.975	Phenyl
DOVJOP01	2.799	2.799	2.028	2.028	Phenyl
GETPEC	2.799	2.799	2.047	2.047	Phenyl

OLEXAF	2.799	2.799	2.052	2.052	Phenyl
VOSZOU	2.799	2.732	1.988	1.896	Phenyl
REHDOY	2.800	2.800	1.964	1.964	Phenyl
YUTQEL	2.800	2.800	1.964	1.964	Phenyl
UCETUS	2.803	2.803	1.855	1.855	Phenyl
REHDOY	2.804	2.804	1.970	1.970	Phenyl
CIQHAN	2.805	2.805	1.967	1.967	Phenyl
NEBTAR	2.806	2.806	1.982	1.982	Phenyl
UZUMEI	2.806	2.806	1.928	1.928	Phenyl
RORNOD	2.808	2.808	2.040	2.040	Phenyl
MOKKON	2.809	2.809	1.972	1.972	Phenyl
TILLUX	2.809	2.809	2.000	2.000	Phenyl
RONLIP	2.817	2.817	1.931	1.931	Phenyl
OLEXOT	2.824	2.824	1.998	1.998	Phenyl
ZUCROG	2.824	2.824	2.017	2.017	Phenyl
TAZBEE	2.831	2.831	1.927	1.927	Phenyl
OCAJUY	2.834	2.834	1.971	1.971	Phenyl
KERQOP	2.836	2.836	2.054	2.054	Phenyl
RORMES	2.842	2.706	2.024	1.892	Phenyl
MELGES	2.845	2.845	2.045	2.045	Phenyl
XECHUJ	2.846	2.846	2.000	2.000	Phenyl
MELGES	2.851	2.851	2.049	2.049	Phenyl
MELGIW	2.865	2.865	2.084	2.084	Phenyl
KEGNAM	2.875	2.875	2.046	2.046	Phenyl
MELGAO	2.901	2.901	2.090	2.090	Phenyl
VUWHAY	2.960	2.960	2.209	2.209	Phenyl
QUSPUQ	2.748	2.779	1.982	2.010	4-Pyridyl
BAJTEM	2.790	2.790	2.076	2.076	3-Pyridyl
BAJTEM01	2.766	2.766	2.050	2.050	3-Pyridyl
BAJTEM02	2.780	2.780	1.965	1.965	3-Pyridyl
BAJTIQ	2.761	2.761	1.962	1.962	3-Pyridyl
DIXTIO	2.769	2.787	1.985	1.950	3-Pyridyl
DIXTOU	2.710	2.710	1.875	1.875	3-Pyridyl
FECSEM	2.780	2.780	1.910	1.910	3-Pyridyl
FECSEM	2.749	2.749	1.939	1.939	3-Pyridyl
FUBKOD	2.775	2.775	1.956	1.956	3-Pyridyl
QUSQAX	2.697	2.748	1.887	2.045	3-Pyridyl
SARQOU	2.740	2.740	1.917	1.916	5-Pyrimidyl
ZOQVEI	2.762	2.762	1.914	1.914	5-Pyrimidyl

Fig. S1. CSD Refcode and structure of the protonated pyridine derivative dimers.

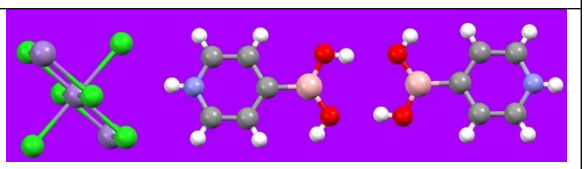
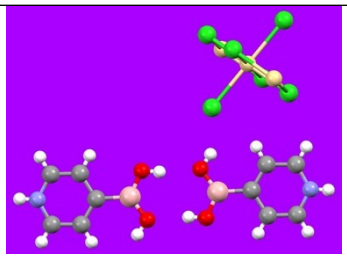
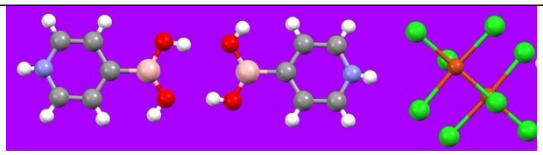
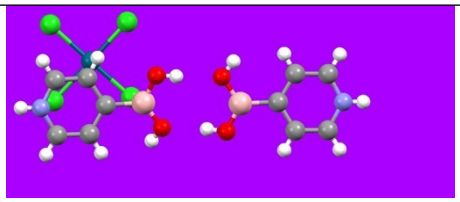
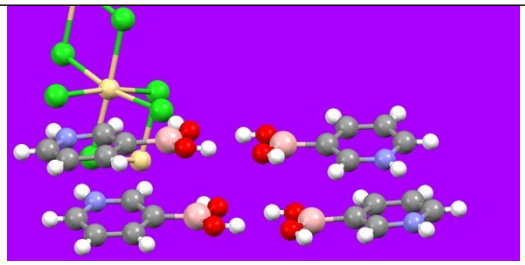
Refcode	Structure
DUKJOK	
DUKJUQ	
DUKKAX	
DUKKEB	
DUKKIF	

Fig. S2. Histogram of the angle between the planes defined by the aromatic ring in all the complexes found in the CSD database for dimers with a double hydrogen bond interaction.

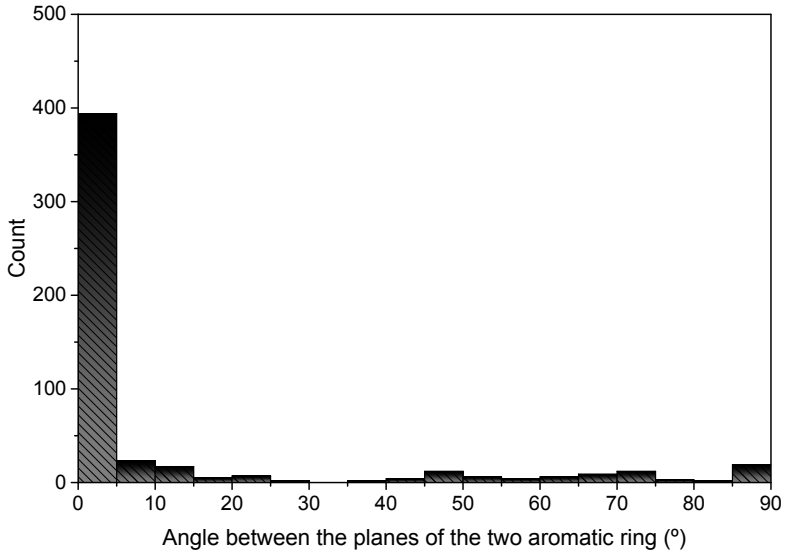
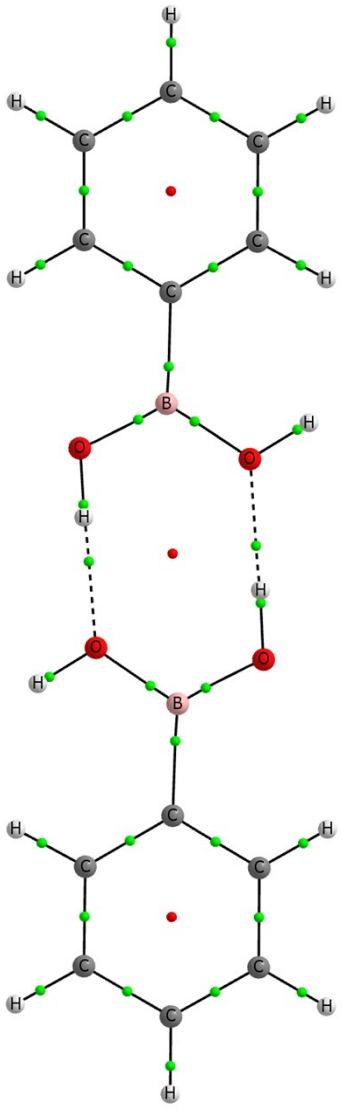


Table S2. Molecular graph (small green and red spheres indicate the position of the bond and ring critical points, respectively), Electronic energy and geometry of the optimized $(R–B(OH)_2)_2$ and $[(RH–B(OH)_2)_2]^{2+}$dimers in gas phase (R can be Ph = phenyl, Py = pyridine, Py(H+) = protonated pyridine) at M06-2x/6-311++G(d,p) level.



dBO2H2.ph
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O,1.4759146694,1.2684759823,0.0304160906
O,-1.3213761271,1.0635039865,0.2641590068
O,1.3213761271,-1.0635039865,0.2641590068
O,-1.4759146694,-1.2684759823,0.0304160906
H,0.5086791413,1.2195525487,0.1123331954
H,-1.8274335513,1.873463097,0.3569956097
C,5.762509303,-1.2052152546,-0.1174937051
H,-0.5086791413,-1.2195525487,0.1123331954
C,4.373538632,-1.1904107994,-0.0506514819
C,3.6614288414,0.0117200842,0.0216972382
C,4.3892961417,1.2078945527,0.0178410973
C,5.7775672895,1.2032038043,-0.0456942903
C,6.4658370888,-0.0049649406,-0.1129213307
H,6.2947373208,-2.1472862265,-0.175684149
H,3.8520496255,-2.1444477099,-0.0675261164
H,3.8484918377,2.1464135131,0.0666934842
H,6.3247035122,2.1386784046,-0.0445777031
H,7.5484833821,-0.0116270002,-0.1638162256
H,1.8274335513,-1.873463097,0.3569956097
C,-3.6614288414,-0.0117200842,0.0216972382
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C,-4.373538632,1.1904107994,-0.0506514819
C,-5.7775672895,-1.2032038043,-0.0456942903
H,-3.8484918377,-2.1464135131,0.0666934842
C,-5.762509303,1.2052152546,-0.1174937051
H,-3.8520496255,2.1444477099,-0.0675261164
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H,-6.3247035122,-2.1386784046,-0.0445777031
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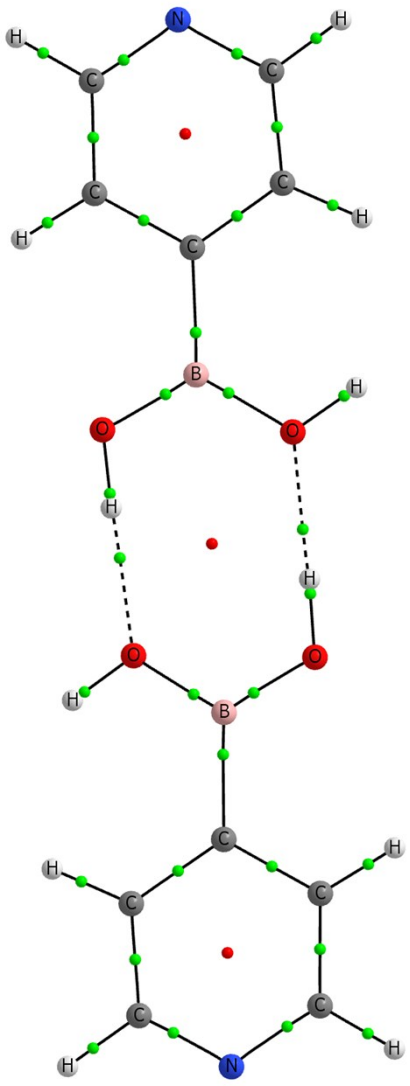
H,-7.5484833821,0.0116270002,-0.1638162256



dBO2H2.4py
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O,-1.32041641,-1.07500638,0.2754528
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H,-0.51097231,1.22296209,0.12763057
H,1.82478777,1.88835142,0.34978068
H,-1.82478777,-1.88835142,0.34978068
H,0.51097231,-1.22296209,0.12763057
C,-5.77224516,-1.14633969,-0.14228626
C,-4.38422741,-1.18981209,-0.05570451
C,-3.65801123,0.00058498,0.00587469
C,-4.39499504,1.1859497,-0.02886309
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N,-6.47006606,-0.01265908,-0.16936517
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H,-3.90018969,-2.1623551,-0.04746904
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C,5.78168712,-1.1279413,-0.11345819
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C,5.77224516,1.14633969,-0.14228626
H,3.90018969,2.1623551,-0.04746904
N,6.47006606,0.01265908,-0.16936517
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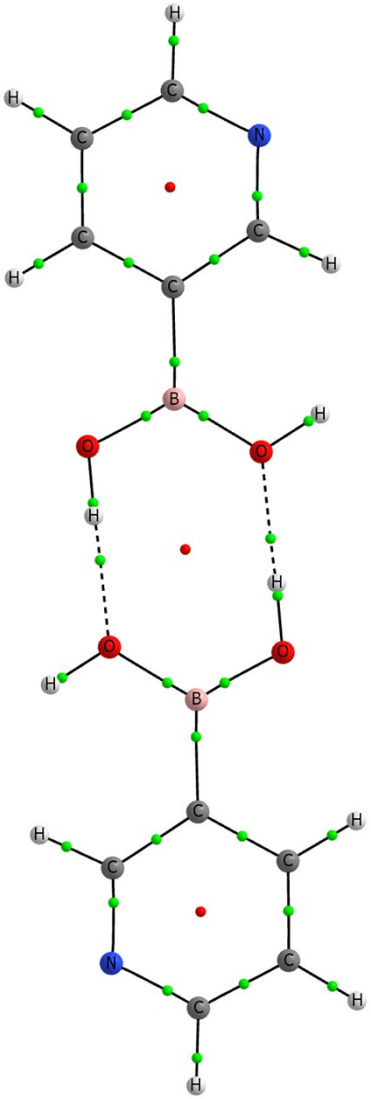

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O,-1.3207844431,1.0850406044,0.
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H,1.8170521634,-1.9065504562,0.
H,-1.8170521634,1.9065504562,0.
H,0.5165093827,1.2178178703,0.
N,5.732399223,-1.2502839604,0.
C,4.4029526781,-1.1755002208,0.
C,3.665920564,0.0114374501,0.
C,4.400512896,1.2014975824,0.
C,5.7859877479,1.1507075819,0.
C,6.4017486829,-0.0981725059,0.
H,7.4846812843,-0.1772970814,0.
H,3.9019117767,-2.1433083976,0.
H,3.8746624251,2.1500032545,0.
H,6.3852623276,2.0525582937,0.
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N,-5.732399223,1.2502839604,0.
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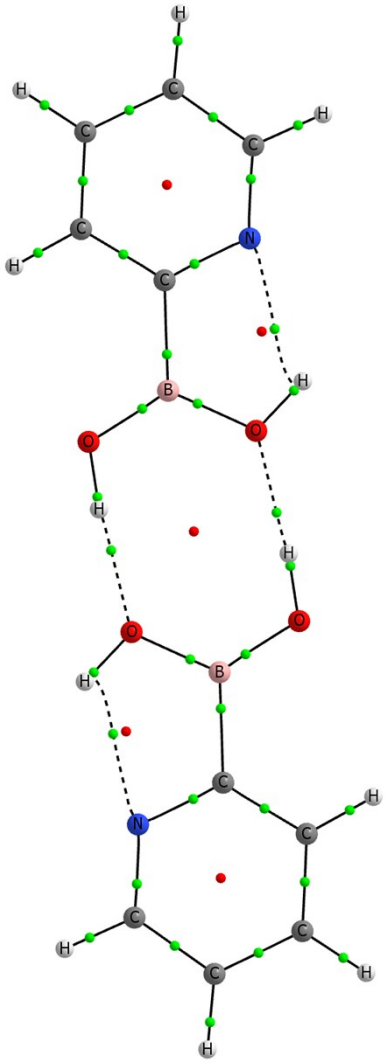

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O,-1.64930222,0.35102067,0.
O,0.70451085,1.83723012,0.
H,0.15288839,-1.37441377,0.
H,2.53938611,-0.73667664,0.
C,-5.4748477,-1.05679738,0.
H,-0.1529026,1.37430215,0.
N,-4.2061182,-0.65853138,0.
C,-3.2385993,-1.5960546,0.
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C,-5.85155154,-2.3977898,0.
H,-6.22695045,-0.27392777,0.
H,-5.11492898,-4.42049878,0.
H,-6.90063912,-2.6659866,0.
H,-2.53939396,0.73666771,0.
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H,6.22690775,0.273859,0.
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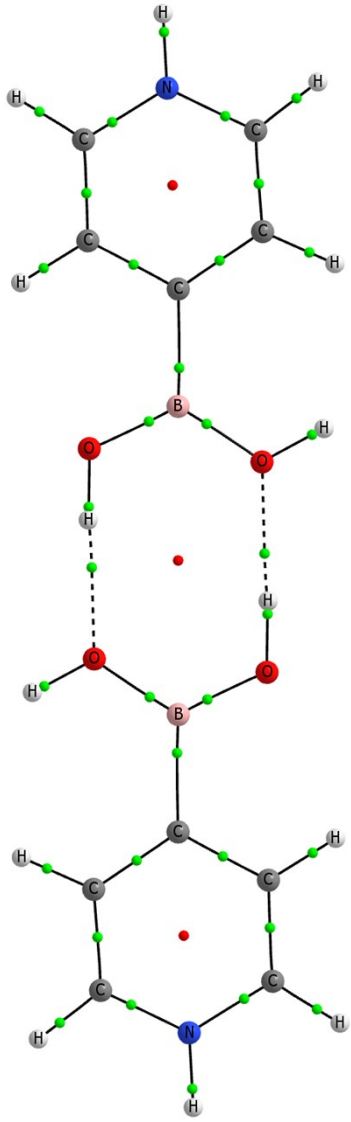
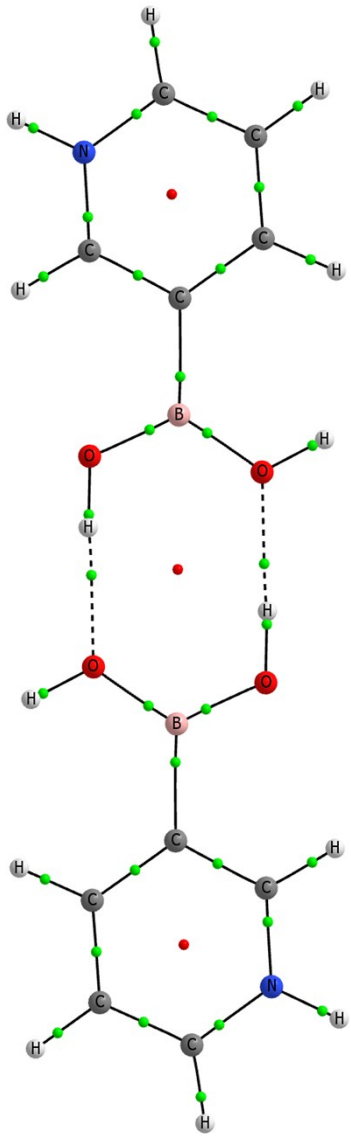
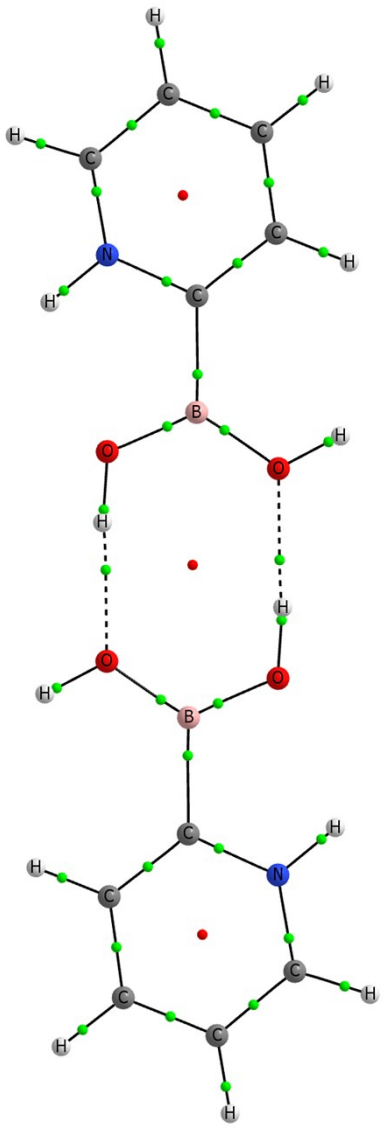
	dBO2H2.4py+ Electronic Energy= -849.219551097 Hartree, NIMAG= 0 B,-2.0989072634,0.0299569703,-0.0378856698 B,2.0989072634,-0.0299569703,-0.0378856698 O,-1.5416501759,-1.1850826642,-0.0190149699 O,1.3241657178,-1.1592698888,-0.0874965234 O,-1.3241657178,1.1592698888,-0.0874965234 O,1.5416501759,1.1850826642,-0.0190149699 H,-0.5705911069,-1.2140047737,-0.0462970185 H,1.7673954035,-2.0086845205,-0.1580988435 H,-1.7673954035,2.0086845205,-0.1580988435 H,0.5705911069,1.2140047737,-0.0462970185 C,-5.8400618438,1.141019815,0.2009274785 C,-4.4618813776,1.2140437498,0.1766731494 C,-3.6975440194,0.0563373007,-0.0020266604 C,-4.3723536933,-1.1628839093,-0.1457380845 C,-5.7503990132,-1.2004091627,-0.1208643612 N,-6.4353532246,-0.054271034,0.0496966889 H,-6.4888181499,1.9962480459,0.3373327024 H,-4.011733637,2.1902042198,0.31059658 H,-3.8159876334,-2.0826425121,-0.2751057928 H,-6.3340612708,-2.105258746,-0.2289508668 H,-7.4519129635,-0.0949343985,0.0681831221 C,3.6975440194,-0.0563373007,-0.0020266604 C,4.3723536933,1.1628839093,-0.1457380845 C,4.4618813776,-1.2140437498,0.1766731494 C,5.7503990132,1.2004091627,-0.1208643612 H,3.8159876334,2.0826425121,-0.2751057928 C,5.8400618438,-1.141019815,0.2009274785 H,4.011733637,-2.1902042198,0.31059658 N,6.4353532246,0.054271034,0.0496966889 H,6.3340612708,2.105258746,-0.2289508668 H,6.4888181499,-1.9962480459,0.3373327024 H,7.4519129635,0.0949343985,0.0681831221

	dBO2H2.3py+, Electronic Energy= -849.224315364 Hartree, NIMAG= 0 B,-2.10185825,-0.05556675,0. B,2.10185825,0.05556675,0. O,-1.55848342,1.16939411,0. O,1.30863459,1.17293694,0. O,-1.30863459,-1.17293694,0. O,1.55848342,-1.16939411,0. H,-0.58742312,1.20857305,0. H,1.73861265,2.03201883,0. H,-1.73861265,-2.03201883,0. H,0.58742312,-1.20857305,0. C,-5.87849271,-1.17416482,0. C,-4.4863671,-1.24984006,0. C,-3.69145923,-0.09963129,0. C,-4.35399266,1.11978205,0. N,-5.69648288,1.16686863,0. C,-6.47508019,0.06715186,0. H,-6.49617816,-2.06214743,0. H,-4.03172985,-2.23553861,0. H,-3.82824911,2.06694369,0. H,-6.14911786,2.07811347,0. H,-7.54576263,0.22463131,0. C,3.69145923,0.09963129,0. C,4.35399266,-1.11978205,0. C,4.4863671,1.24984006,0. N,5.69648288,-1.16686863,0. H,3.82824911,-2.06694369,0. C,5.87849271,1.17416482,0. H,4.03172985,2.23553861,0. C,6.47508019,-0.06715186,0. H,6.14911786,-2.07811347,0. H,6.49617816,2.06214743,0. H,7.54576263,-0.22463131,0.



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O,-1.2817161757,-1.2163299634,0.
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C,-3.6777710513,-0.1642740691,0.
N,-4.2755644458,1.0531599329,0.
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C,-6.4465939405,0.1527458632,0.
H,-6.5331976103,-1.9922886278,0.
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H,-7.5176217987,0.3052811039,0.
H,-1.7027512773,-2.081223422,0.
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N,4.2755644458,-1.0531599329,0.
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C,5.6000643975,-1.2477438871,0.
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H,7.5176217987,-0.3052811039,0.

Table S3. Intermolecular O···H distances (Å) in the $(R–B(OH)_2)_2$ and $[(RH–B(OH)_2)_2]^{2+}$dimers in gas phase (R can be Ph = phenyl, Py = pyridine, Py(H+) = protonated pyridine) in the different PCM solvent environments.

Ar	gas	N-hexane	$CHCl_3$	Acetone	Water
Ph	1.843	1.839	1.834	1.831	1.830
4-Py	1.843	1.838	1.834	1.834	1.831
3-Py	1.842	1.838	1.834	1.831	1.829
2-Py	1.813	1.811	1.806	1.805	1.803
4-Py(H^+)	1.896	1.870	1.843	1.831	1.830
3-Py(H^+)	1.896	1.860	1.842	1.834	1.829
2-Py(H^+)	1.900	1.862	1.840	1.827	1.822

Fig. S3. Electric field maps of the neutral and protonated 2- and 3-pyridine dimers. The region in grey corresponds to the volume of the $B(OH)_2$ group in one of the molecules. The electric field lines are colored based on the atom of origin (grey for carbon, black for hydrogen, red for oxygen, blue for nitrogen and orange for boron).

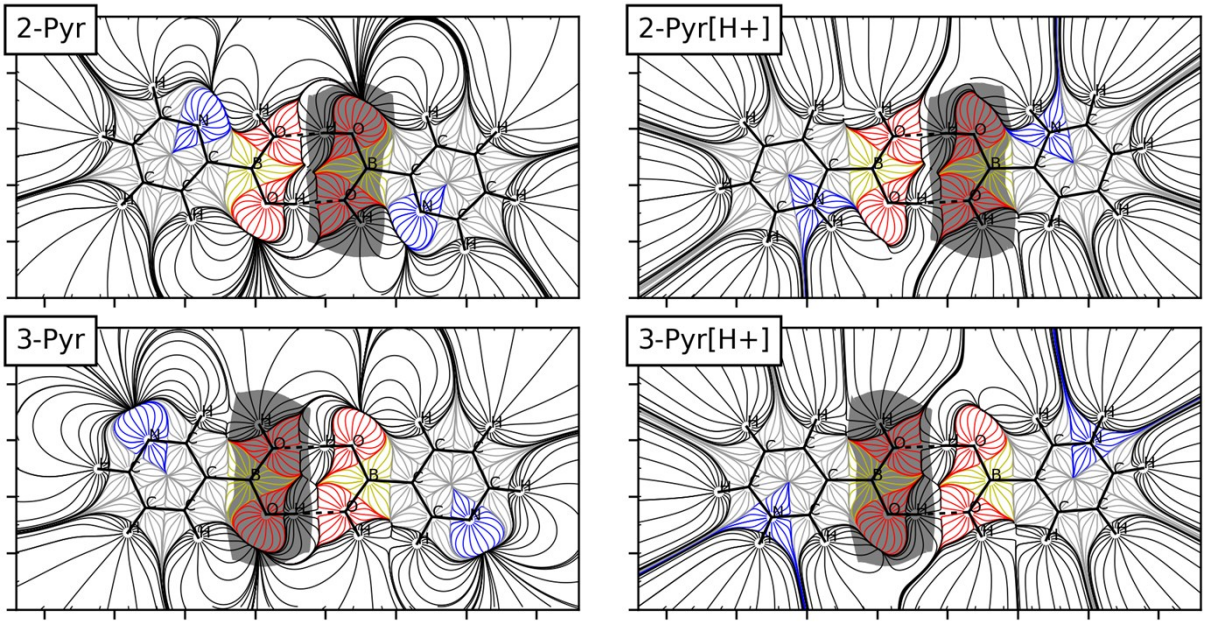

Fig. S4. Relationships between the electron density properties at the O···H BCP (au) and the interatomic distance (Å) for all the dimers studied in the present article. The values corresponding to the neutral molecules calculated in gas phase are shown with red squares.