SUPPLEMENTARY INFORMATION

CRASY: Correlated Rotational Alignment Spectroscopy of Pyridine. The Rotational Raman Spectrum of Pyridine and Asymmetric Fragmentation of Pyridine Dimer Cation

Jong Chan Lee, Begüm Rukiye Özer, and Thomas Schultz

Contents

1 Line Lists and Fit Results

Pyridine rotational constants were determined through a fit of observed rotational band positions using the PGOPHER program[1]. Fits were performed assuming C_{2v} symmetry and using the Watson A-reduced Hamiltonian in the III^r representation. The assignment of rotational bands was performed by comparison of the measured spectrum with calculated line positions, based on literature constants[2]. For the 20 ns scan, band positions were determined by the peak picking algorithm in the Pgopher program. For the 100 ns and 500 ns scans, band positions were determined by Gaussian fits to the corresponding signal peaks in the spectra.

Tables S1, S2, and S3 list the observed band positions and the fitted line positions for the 20 ns, 100 ns and 500 ns scan data. Amplitudes for the experimentally observed bands are given in units of σ, based on the respective noise level in the spectrum. The noise in the power spectra was well described by an exponential distribution with P(amplitude) $\propto e^{-\sigma \cdot \text{amplitude}}$ and was readily estimated using the modified Z-score as proposed by Iglewitz and Hoaglin[3]. We expect an e^{-n} probability that an observed band with n$\cdot\sigma$ amplitude is noise (<0.1% for a 7–σ signal) and assigned only bands well above the noise level.

Small amounts of carbon disulfide were present in the sample and corresponding rotational constants were fitted to 8 (20 ns and 100 ns scan) or 7 (500 ns scan) observed lines. Comparison to literature values allowed to calculate a calibration factor, which was then used to scale pyridine rotational constants to give the values shown in Table 1 of the manuscript. Table S4 shows the uncalibrated fit results for carbon disulfide and pyridine. The calibration factors were small and we ascertained that the scaled constants agreed with fit results obtained after assigning transition lines in a scaled frequency spectrum.

The calibration against known CS_2 frequencies was necessary for the following reason: Our frequency calibration is based on the measurement of the laser oscillator repetition rate against a reference clock (refer to Ref. 4 for details). As reference time-base, we use an external GPS-locked clock (Leo Bodnar GPSDO) with $<10^{-10}$ Allan deviation between clock and laser oscillator. A faulty connection, however, caused the frequency counter (AIM-TTI TF930) to revert to its internal reference clock, which is specified with an initial oscillator adjustment error below $\pm$0.2 ppm at 21°C and an oscillator ageing rate below $\pm$1 ppm for the first year. We since re-connected the GPS-locked reference clock and removed this systematic frequency error. The error bounds for pyridine are much larger than those for CS_2 and the calibration of transition frequencies against CS2 frequencies does not add any significant uncertainties. The time-consuming re-measurement of pyridine data was therefore not warranted.

Table S1 Assigned rotational Raman transition lines in the pyridine spectrum from a 20 ns scan. Amplitudes are given as multiples of the estimated noise level (σ)) in the power spectrum. Calculated line positions and difference between observed and calculated positions (Obs.-Calc.) are based on the PGOPHER fit results.

Observed	Amplitude	Calculated	Obs.-Calc.	Upper			Lower		
(MHz)	(σ)	(MHz)	(MHz)	J	K_a	K_c	J	K_a	K_c
23210.1	17.6	23219.6	-9.5	1	1	1	2	1	1
24154.6	86.3	24156.9	-2.3	1	0	1	2	2	1
35545.3	364.1	35546.2	-0.9	2	0	2	3	2	2
		35546.3	-1.0	0	0	0	2	2	0
47343.0	66.8	47350.6	-7.6	3	0	3	4	2	3
		47346.5	-3.5	3	1	3	4	1	3
47455.6	13.7	47456.2	-0.6	3	1	2	4	3	2
58644.0	78.7	58643.7	0.2	1	0	1	3	2	1
59179.2	26.2	59189.6	-10.4	4	0	4	5	2	4
		59163.4	15.7	4	2	3	5	2	3
		59189.4	-10.2	4	1	4	5	1	4
		59181.3	-2.1	4	1	3	5	3	3
59293.9	39.1	59289.7	4.1	1	1	0	3	3	0
59818.3	65.4	59814.9	3.3	1	1	1	3	3	1
71022.2	15.7	71029.6	-7.4	5	0	5	6	2	5
		71016.4	5.7	5	2	4	6	2	4
		71029.6	-7.4	5	1	5	6	1	5
		71017.3	4.8	5	1	4	6	3	4
		71015.6	6.5	5	2	3	6	4	3
82121.9	27.1	82126.7	-4.8	2	1	1	4	3	1
82722.8	46.3	82728.3	-5.5	2	0	2	4	2	2
83101.4	168.8	83099.8	1.5	2	2	0	4	4	0
83766.7	128.4	83763.5	3.1	2	2	1	4	4	1
105642.1	45.2	105637.6	4.4	3	2	1	5	4	1
106522.2	20.8	106514.1	8.0	3	0	3	5	2	3
		106527.9	-5.7	3	1	3	5	3	3
106642.8	25.1	106638.2	4.5	3	2	2	5	4	2
106999.5	47.6	106996.4	3.0	3	3	0	5	5	0
107737.8	52.3	107732.8	4.9	3	3	1	5	5	1
129191.9	16.7	129187.2	4.6	4	3	1	6	5	1
130991.4	94.0	130988.0	3.3	4	4	0	6	6	0
131730.9	98.4	131725.8	5.0	4	4	1	6	6	1
152794.5	31.9	152789.0	5.4	5	4	1	7	6	1
155079.0	19.0	155067.0	11.9	5	5	0	7	7	0
179218.9	34.8	179212.3	6.5	6	6	0	8	8	0
179793.8	39.3	179787.1	6.6	6	6	1	8	8	1

Table S2 Assigned rotational Raman transition lines in the pyridine spectrum from a 100 ns scan. Frequency values are truncated, not rounded. Amplitudes are given as multiples of the estimated noise level (σ)) in the power spectrum. Calculated line positions and difference between observed and calculated positions (Obs.-Calc.) are based on the PGOPHER fit results.

Observed (MHz)	Amplitude (σ)	Calculated (MHz)	Obs.-Calc. (MHz)	Upper			Lower		
				J	K_a	K_c	J	K_a	K_c
23218.70	14.0	23219.96	-1.25	2	1	1	1	1	1
24157.98	62.1	24157.54	0.43	2	2	1	1	0	1
35462.52	15.9	35463.95	-1.43	3	1	2	2	1	2
35546.74	227.3	35546.98	-0.24	3	2	2	2	0	2
		35547.02	-0.28	2	2	0	0	0	0
47183.74	35.3	47182.93	0.80	4	2	2	3	2	2
47349.38	60.0	47351.61	-2.22	4	2	3	3	0	3
		47457.25	-0.54	4	3	2	3	1	2
58644.96	68.3	58644.77	0.46	3	2	1	1	0	1
59192.67	21.2	59190.81	1.85	5	2	4	4	0	4
59192.67	21.2	59190.65	2.01	5	1	4	4	1	4
59291.85	31.4	59290.90	0.94	3	3	0	1	1	0
59456.48	20.0	59457.43	-0.95	5	4	2	4	2	2
59815.12	39.4	59816.22	-1.10	3	3	1	1	1	1
71018.32	46.9	71017.06	1.25	6	4	3	5	2	3
		71017.86	0.45	6	2	4	5	2	4
		71018.72	-0.40	6	3	4	5	1	4
71031.40	12.3	71031.09	0.30	6	2	5	5	0	5
		71031.08	0.31	6	1	5	5	1	5
82128.83	32.5	82128.25	0.57	4	3	1	2	1	1
82728.21	31.1	82729.92	-1.71	4	2	2	2	0	2
82920.87	22.6	82921.21	-0.34	4	3	2	2	1	2
83101.55	164.3	83101.55	-0.00	4	4	0	2	2	0
83764.34	121.6	83765.41	-1.07	4	4	1	2	2	1
105639.38	65.9	105639.52	-0.14	5	4	1	3	2	1
106640.84	59.0	106640.37	0.46	5	4	2	3	2	2
106998.52	69.4	106998.76	-0.24	5	5	0	3	3	0
107735.00	51.0	107735.24	-0.24	5	5	1	3	3	1
129189.49	19.4	129189.65	-0.16	6	5	1	4	3	1
130181.76	12.8	130181.65	0.10	6	4	3	4	2	3
130380.16	19.9	130379.92	0.23	6	5	2	4	3	2
130990.49	92.4	130990.86	-0.37	6	6	0	4	4	0
131728.30	113.6	131728.83	-0.53	6	6	1	4	4	1
152790.27	17.4	152791.89	-1.62	7	6	1	5	4	1
154145.31	29.5	154144.12	1.18	7	6	2	5	4	2
155070.34	21.2	155070.52	-0.18	7	7	0	5	5	0
155746.75	12.2	155747.59	-0.84	7	7	1	5	5	1
179217.18	13.9	179216.42	0.75	8	8	0	6	6	0
179791.53	27.1	179791.23	0.29	8	8	1	6	6	1
201762.55	13.4	201761.46	1.08	9	8	2	7	6	2

Table S3 Assigned rotational Raman transition lines in the pyridine spectrum from a 500 ns scan. Frequency values are truncated, not rounded. Amplitudes are given as multiples of the estimated noise level (σ)) in the power spectrum. Calculated line positions and difference between observed and calculated positions (Obs.-Calc.) are based on the PGOPHER fit results.

Observed (MHz)	Amplitude (σ)	Calculated (MHz)	Obs.-Calc. (MHz)	Upper			Lower		
				J	K_a	K_c	J	K_a	K_c
23219.672	12.1	23220.140	-0.463	2	1	1	1	1	1
24156.006	17.0	24157.318	-1.313	2	2	1	1	0	1
35546.654	95.3	35546.940	-0.286	3	2	2	2	0	2
		35546.982	-0.329	2	2	0	0	0	0
47182.595	10.6	47182.939	-0.295	4	2	2	3	2	2
47351.550	13.7	47351.564	-0.002	4	2	3	3	0	3
59164.064	17.3	59164.531	-0.438	5	2	3	4	2	3
59190.328	18.6	59190.750	-0.402	5	2	4	4	0	4
		59190.592	-0.243	5	1	4	4	1	4
59290.875	20.4	59290.826	0.037	3	3	0	1	1	0
59815.982	7.5	59815.912	0.067	3	3	1	1	1	1
71017.518	17.7	71017.790	-0.239	6	2	4	5	2	4
		71018.644	-1.094	6	3	4	5	1	4
82128.356	23.3	82128.501	-0.138	4	3	1	2	1	1
83101.567	93.8	83101.413	0.122	4	4	0	2	2	0
83765.292	43.7	83764.964	0.324	4	4	1	2	2	1
105639.971	39.1	105639.820	0.155	5	4	1	3	2	1
106240.545	8.7	106240.227	0.411	5	3	2	3	1	2
106640.426	12.9	106640.236	0.200	5	4	2	3	2	2
106998.731	22.8	106998.521	0.145	5	5	0	3	3	0
107735.103	19.1	107734.640	0.457	5	5	1	3	3	1
129676.510	11.7	129676.223	0.437	6	4	2	4	2	2
130379.600	12.8	130379.738	-0.124	6	5	2	4	3	2
130990.619	31.0	130990.487	0.030	6	6	0	4	4	0
131728.022	27.1	131728.071	-0.053	6	6	1	4	4	1
152792.403	16.8	152792.244	0.139	7	6	1	5	4	1

Table S4 Fitted spectroscopic parameters (in MHz) and corresponding literature values for pyridine and carbon disulfide. Numbers in round brackets give the 1-σ standard deviation in the corresponding last digits. Square brackets indicate that a parameter was fixed to the corresponding literature value. Comparison of carbon disulfide constants to literature values allowed to calculate a calibration factor (Exp./Lit.).

	20 ns	100 ns	500 ns	Literature
carbon disulfide				
B	3271.546(23)	3271.5873(30)	3271.5983(32)	3271.5170(7)[a]
D	297(98)	346(16)	432(30)	355(3)[a]
Assigned lines	8	8	7	10[a]
Exp./Lit.	1.00000886	1.00002149	1.00002485	[1.00000000]
pyridine				
A	6039.37(17)	6039.390(29)	6039.335(23)	6039.24428(28)[b]
B	5804.85(19)	5805.004(32)	5805.047(30)	5804.91381(26)[b]
C	2980(14)	2959.1(2.7)	2961.4(1.6)	2959.21006(24)[b]
D_J	[0.00138966	[0.00138966]	1.44(33)e-3	0.00138966(21)[b]
D_K	[0.0012218]	[0.0012218]	[0.0012218]	0.00122178(30)[b]
D_JK	[-0.002498]	[-0.002498]	[-0.002498]	0.00249843(38)[b]
δ_K	[-0.002074]	[-0.002074]	[-0.002074]	0.0020740(27)[b]
δ_J	[-7.04e-6]	[-7.04e-6]	[-7.04e-6]	$7.043(84)\cdot10^{-6}$[b]
J_{max}	6	7	5	90
$K_{c,max}$	2	5	3	63
Assigned lines	36	40	26	1185[b]

[a]Schröter et al.; [b]Enyi Ye et.al.

2 Ab Initio and DFT Calculation Results

Tables S5 and S6 give dimer properties calculated at the RI-SCS-MP2/aug-cc-pVTZ and PBEh/3c levels of theory. Molecular geometries were optimized for 18 pyridine dimer geometries, starting at geometries reported in the literature[5,6]. The PBE method is described as as 'mostly free of basis-set superposition errors'[7] and binding energies were calculated directly as the difference between optimized dimer and monomer energies. Binding energies at the RI-SCS-MP2 level were corrected for basis-set-superposition errors using the counterpoise method. We accounted for the effect of zero-point energies on the binding energies using the corresponding results from the PBE thermodynamics calculations described below. Qualitative agreements between MP2 and PBE geometries and binding energies were reasonable with the biggest deviation for the case of the H-bound dimer. Apparently, the PBE method significantly over-estimates H-bonding in this system.

Thermodynamic properties were calculated at the PBE level to obtain zero-point energies and to predict the relative dimer populations at temperatures relevant to the molecular beam expansion. Note that we cannot predict at what temperature the dimer structures 'freeze out' and we therefore give results for a broad temperature range between 50 K and 300 K. The Gibbs free energy was calculated accounting for zero-point energy and thermal correction terms to the internal energy, enthalpy correction, and entropy. Results from PBE and RI-SCS-MP2 were very different because thee PBE results predicted a significantly higher stability for the H-bound dimer.

Sections 3and 4 list Cartesian coordinates and properties for dimer structures optimized at the RI-SCS-MP2/aug-cc-pVTZ and PBE-3c level. For clarity, we labeled all structures using the nomenclature in references 5,6, which supplied the starting geometries for our geometry optimizations.

Table S5 Binding energies (in kJ/mol), without (BE) and with (BE_{zpe}) zero-point energy correction and expected Boltzmann populations in thermodynamic equilibrium for 18 pyridine dimer structures, optimized at the RI-SCS-MP2 level. Binding energies were BSSE corrected and adjusted for respective zero-point energies, the latter by using results from the PBE frequency calculations. To calculate Boltzmann populations, we used the relevant thermodynamic terms from the PBE frequency calculations to obtain the relative Gibbs-free energies.

	BE	BE_{zpe}	Boltzmann population (%)			
Structure name			300 K	200 K	100 K	50 K
Piacenza1 180a	−15.3	−13.9	1.28	2.29	4.45	5.57
Piacenza2 180b	−11.3	−10.5	3.46	2.53	0.48	0.01
Piacenza3 160d	−16.1	−14.2	22.01	27.76	38.83	45.36
Piacenza4 74d	−15.4	−13.5	15.82	17.17	15.31	7.29
Piacenza5 T1	−9.0	−7.2	1.78	0.57	0.01	0.00
Piacenza6 T2	−12.4	−10.3	6.57	3.98	0.55	0.01
Piacenza7 H-bonded	−14.0	−11.3	12.55	9.44	2.45	0.09
Hohenstein P1a	−9.1	−8.1	0.14	0.07	0.00	0.00
Hohenstein P1b [a]	−15.0	−13.2	10.96	11.20	8.37	2.78
Hohenstein P2a+	−11.4	−10.6	3.89	2.89	0.57	0.01
Hohenstein P2a-	−15.4	−14.0	1.36	2.34	4.83	6.28
Hohenstein P2b	−16.1	−14.4	4.86	7.63	15.54	26.78
Hohenstein S1	−6.3	−6.0	0.04	0.02	0.00	0.00
Hohenstein S2 [b]	−15.4	−13.7	4.19	5.71	7.64	5.82
Hohenstein T1	−8.2	−7.3	0.07	0.04	0.00	0.00
Hohenstein T2	−3.5	−2.8	0.03	0.01	0.00	0.00
Hohenstein T3 [a]	−12.9	−10.8	7.11	4.71	0.86	0.02
Hohenstein T4 [a]	−10.8	−8.9	3.87	1.74	0.10	0.00

[a] Significant geometry changes. [b] Geometry converged towards the P2a- geometry.

Table S6 Binding energies (in kJ/mol), without (BE) and with (BE_{zpe}) zero-point energy correction and expected Boltzmann population for 18 pyridine dimer structures, optimized at the PBEh-3c level. Boltzmann populations were calculated based on Gibbs-free energies, obtained from frequency calculations.

	BE	BE_{zpe}	Boltzmann population (%)			
Structure name			300 K	200 K	100 K	50 K
Piacenza1 180a	−16.2	−14.8	0.7	0.8	0.5	0.1
Piacenza2 180b	−10.1	−9.3	0.8	0.3	0.0	0.0
Piacenza3 160d	−17.3	−15.5	13.5	12.6	7.1	1.3
Piacenza4 74d	−16.3	−14.5	8.7	6.6	2.0	0.1
Piacenza5 T1	−10.3	−8.6	1.1	0.3	0.0	0.0
Piacenza6 T2	−15.7	−13.7	9.2	6.2	1.2	0.0
Piacenza7 H-bonded	−19.6	−17.0	44.4	59.2	85.7	98.2
Hohenstein P1a	−10.2	−9.2	0.1	0.0	0.0	0.0
Hohenstein P1b [a]	−14.8	−13.0	3.7	2.1	0.3	0.0
Hohenstein P2a+	−10.1	−9.4	0.9	0.3	0.0	0.0
Hohenstein P2a-	−16.2	−14.8	0.7	0.8	0.6	0.1
Hohenstein P2b	−16.5	−14.9	2.2	2.2	1.2	0.1
Hohenstein S1	−4.9	−4.7	0.0	0.0	0.0	0.0
Hohenstein S2 [b]	−15.9	−14.3	1.9	1.7	0.6	0.0
Hohenstein T1	−9.8	−9.0	0.1	0.0	0.0	0.0
Hohenstein T2	−5.0	−4.3	0.0	0.0	0.0	0.0
Hohenstein T3 [a]	−15.4	−13.3	7.4	4.7	0.8	0.0
Hohenstein T4 [a]	−13.6	−11.7	4.5	2.1	0.1	0.0

[a] Significant geometry changes. [b] Geometry converged towards the P2a- geometry.

3 RI-SCS-MP2 Structures and Properties

Below, we list the calculation times, final SCF energies ("Total Energy"), final MP2 energies ("FINAL SINGLE POINT ENERGY"), dipole moments (Magnitude (Debye)), rotational constants, and Cartesian coordinates for fully optimized pyridine and pyridine dimer geometries, calculated at the RI-SCS-MP2/aug-cc-pVTZ level. Calculations were performed using the ORCA quantum mechanical calculation package[8,9]. Calculations used 4 threads on an Intel Core-i5 8500 processor with 32 GB RAM.

3.1 Hohenstein P1a

FINAL SINGLE POINT ENERGY	-495.521132 Eh
Total Energy	-493.549679 Eh
Dipole Moment	4.358 D
Rotational constants in MHz	1681.138219 692.730641 662.277403
TOTAL RUN TIME	17 hours 7 minutes for 5 geometry optimization steps

Table S7 Cartesian coordinates for geometry Hohenstein P1a, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	1.426532	0.000003	-1.106400
N	0.924073	0.000006	2.611775
C	0.832736	-1.142395	-1.481103
C	0.832736	1.142401	-1.481103
C	-0.341830	-1.195834	-2.230998
C	-0.341830	1.195841	-2.230997
C	-0.942501	0.000004	-2.617321
C	0.334335	1.142269	2.230894
C	0.334337	-1.142258	2.230894
C	-0.839963	1.195137	1.480806
C	-0.839962	-1.195128	1.480807
C	-1.442966	0.000004	1.097481
H	1.324533	-2.056309	-1.167332
H	1.324533	2.056315	-1.167331
H	-0.766925	-2.152436	-2.505723
H	-0.766924	2.152443	-2.505722
H	-1.851322	0.000004	-3.205786
H	0.825905	2.056547	2.543770
H	0.825908	-2.056536	2.543770
H	-1.265790	2.151695	1.206830
H	-1.265787	-2.151687	1.206831
H	-2.353226	0.000003	0.511587

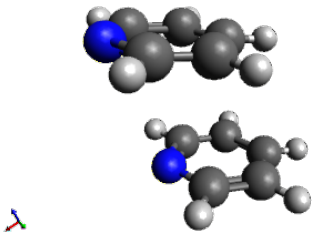

Fig. S1 Optimized molecular geometry for Hohenstein P1a.

3.2 Hohenstein P1b

FINAL SINGLE POINT ENERGY	-495.523618 Eh
Total Energy	-493.550425 Eh
Dipole Moment	3.885 D
Rotational constants in MHz	1647.129103 729.502588 692.941413
TOTAL RUN TIME	7 hours 3 seconds for 1 geometry optimization steps

Table S8 Cartesian coordinates for geometry Hohenstein P1b, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	0.456668	-2.020624	1.215126
N	-0.456660	2.020633	1.215125
C	-0.732744	-1.408072	1.109997
C	0.732752	1.408080	1.109997
C	-1.381517	-1.178209	-0.102955
C	1.381524	1.178214	-0.102954
C	-0.767847	-1.601574	-1.278827
C	0.767856	1.601580	-1.278827
C	0.468871	-2.236650	-1.188020
C	-0.468860	2.236659	-1.188021
C	1.034589	-2.422068	0.072520
C	-1.034580	2.422078	0.072519
H	-1.182002	-1.079439	2.039785
H	1.182010	1.079449	2.039786
H	-2.337930	-0.672963	-0.118375
H	2.337937	0.672968	-0.118374
H	-1.238791	-1.438875	-2.239959
H	1.238804	1.438886	-2.239958
H	0.987992	-2.584496	-2.071652
H	-0.987979	2.584508	-2.071653
H	1.994463	-2.915839	0.175231
H	-1.994453	2.915851	0.175229

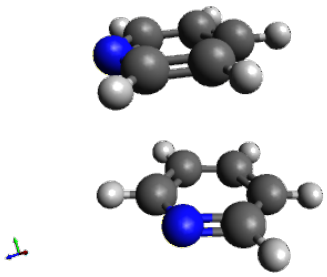

Fig. S2 Optimized molecular geometry for Hohenstein P1b.

3.3 Hohenstein P2a+

FINAL SINGLE POINT ENERGY	-495.522024 Eh
Total Energy	-493.550390 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1639.131849 718.221379 692.897900
TOTAL RUN TIME	14 hours 27 minutes for 5 geometry optimization steps

Table S9 Cartesian coordinates for geometry Hohenstein P2a+, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	-1.460269	-1.122396	0.000049
N	1.460281	1.122407	0.000050
C	-0.848688	-1.470331	-1.142188
C	-0.848630	-1.470351	1.142249
C	0.848700	1.470342	-1.142188
C	0.848640	1.470362	1.142249
C	0.361863	-2.159357	-1.195077
C	0.361926	-2.159375	1.195061
C	-0.361853	2.159365	-1.195078
C	-0.361917	2.159384	1.195061
C	0.983170	-2.511256	-0.000027
C	-0.983161	2.511263	-0.000028
H	-1.354896	-1.182159	-2.056871
H	-1.354791	-1.182200	2.056964
H	1.354910	1.182172	-2.056871
H	1.354801	1.182212	2.056964
H	0.803231	-2.407313	-2.151453
H	0.803349	-2.407344	2.151409
H	-0.803221	2.407320	-2.151454
H	-0.803339	2.407354	2.151408
H	1.927276	-3.040270	-0.000055
H	-1.927268	3.040276	-0.000056

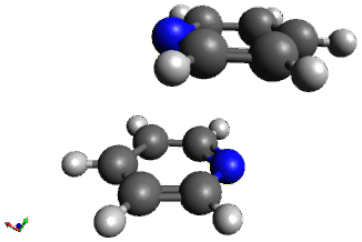

Fig. S3 Optimized molecular geometry for Hohenstein P2a+.

3.4 Hohenstein P2a-

FINAL SINGLE POINT ENERGY	-495.523665 Eh
Total Energy	-493.550500 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1607.451251 727.639206 707.542124
TOTAL RUN TIME	12 hours 7 minutes for 5 geometry optimization steps

Table S10 Cartesian coordinates for geometry Hohenstein P2a-, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	1.024045	-2.422142	0.000347
N	-1.024036	2.422148	0.000346
C	0.393430	-2.110646	1.142856
C	0.393938	-2.110743	-1.142470
C	-0.393422	2.110653	1.142855
C	-0.393928	2.110750	-1.142471
C	-0.852543	-1.486996	1.194893
C	-0.851987	-1.487047	-1.195079
C	0.852552	1.487005	1.194893
C	0.851998	1.487057	-1.195079
C	-1.490168	-1.163402	-0.000246
C	1.490179	1.163413	-0.000245
H	0.913389	-2.372561	2.057643
H	0.914285	-2.372734	-2.057014
H	-0.913382	2.372569	2.057642
H	-0.914274	2.372741	-2.057015
H	-1.305155	-1.259151	2.151112
H	-1.304167	-1.259238	-2.151512
H	1.305164	1.259163	2.151112
H	1.304180	1.259250	-2.151511
H	-2.452073	-0.667343	-0.000474
H	2.452085	0.667356	-0.000473

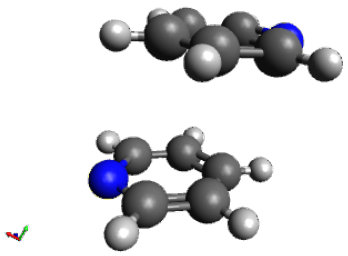

Fig. S4 Optimized molecular geometry for Hohenstein P2a-.

3.5 Hohenstein P2b

FINAL SINGLE POINT ENERGY	-495.523937 Eh
Total Energy	-493.551186 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1675.657922 719.100466 674.171413
TOTAL RUN TIME	12 hours 46 minutes for 5 geometry optimization steps

Table S11 Cartesian coordinates for geometry Hohenstein P2b, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	0.244315	-1.400036	-1.825592
N	-0.244305	1.400044	1.825601
C	-0.708476	-0.690635	-2.448601
C	0.708485	0.690643	2.448611
C	-0.743693	0.703482	-2.474149
C	0.743703	-0.703474	2.474158
C	0.261936	1.409585	-1.819070
C	-0.261927	-1.409578	1.819080
C	1.259337	0.688128	-1.167831
C	-1.259328	-0.688120	1.167841
C	1.206783	-0.704144	-1.200460
C	-1.206772	0.704153	1.200467
H	-1.476712	-1.267274	-2.951810
H	1.476721	1.267281	2.951821
H	-1.541027	1.215795	-2.996847
H	1.541035	-1.215788	2.996858
H	0.265348	2.491897	-1.808467
H	-0.265340	-2.491889	1.808477
H	2.057761	1.189234	-0.637094
H	-2.057751	-1.189226	0.637104
H	1.967356	-1.291603	-0.698837
H	-1.967345	1.291612	0.698845

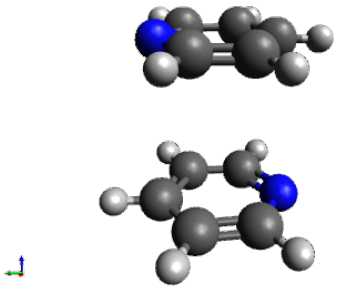

Fig. S5 Optimized molecular geometry for Hohenstein P2b.

3.6 Hohenstein S1

FINAL SINGLE POINT ENERGY	-495.519743 Eh
Total Energy	-493.550247 Eh
Dipole Moment	4.326 D
Rotational constants in MHz	1480.513396 705.949562 699.011428
TOTAL RUN TIME	1 days 6 hours for 9 geometry optimization steps

Table S12 Cartesian coordinates for geometry Hohenstein S1, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	-0.000010	-1.868505	1.395674
N	0.000017	1.868509	1.395674
C	-1.142456	-1.863397	0.693382
C	1.142448	-1.863400	0.693400
C	1.142463	1.863402	0.693382
C	-1.142441	1.863404	0.693401
C	-1.195771	-1.859395	-0.699936
C	1.195787	-1.859398	-0.699917
C	1.195778	1.859401	-0.699936
C	-1.195780	1.859403	-0.699916
C	0.000013	-1.860544	-1.413848
C	-0.000007	1.860547	-1.413847
H	-2.056195	-1.863020	1.276780
H	2.056177	-1.863024	1.276814
H	2.056202	1.863028	1.276780
H	-2.056169	1.863030	1.276816
H	-2.152012	-1.856918	-1.206531
H	2.152036	-1.856923	-1.206497
H	2.152019	1.856923	-1.206532
H	-2.152029	1.856926	-1.206495
H	0.000021	-1.860214	-2.496444
H	-0.000015	1.860219	-2.496443

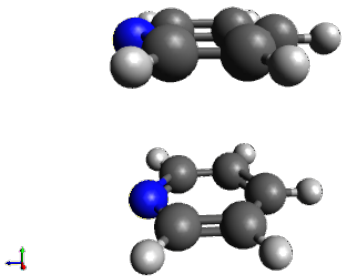

Fig. S6 Optimized molecular geometry for Hohenstein S1.

3.7 Hohenstein S2

FINAL SINGLE POINT ENERGY	-495.523685 Eh
Total Energy	-493.550455 Eh
Dipole Moment	0.004 D
Rotational constants in MHz	1625.821332 722.672469 699.400015
TOTAL RUN TIME	19 hours 22 seconds for 5 geometry optimization steps

Table S13 Cartesian coordinates for geometry Hohenstein S2, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	-2.141564	1.576923	-0.001769
N	2.141573	-1.576914	-0.001769
C	-1.976075	0.892154	-1.143658
C	-1.976273	0.894699	1.141678
C	1.976084	-0.892145	-1.143658
C	1.976281	-0.894689	1.141678
C	-1.640983	-0.460363	-1.194409
C	-1.641148	-0.457683	1.195474
C	1.640989	0.460371	-1.194410
C	1.641154	0.457693	1.195473
C	-1.465143	-1.152388	0.001317
C	1.465149	1.152397	0.001316
H	-2.118170	1.455913	-2.058950
H	-2.118521	1.460486	2.055693
H	2.118181	-1.455904	-2.058949
H	2.118529	-1.460475	2.055694
H	-1.518347	-0.952887	-2.150175
H	-1.518613	-0.948067	2.152355
H	1.518352	0.952894	-2.150176
H	1.518621	0.948077	2.152354
H	-1.191883	-2.199627	0.002493
H	1.191887	2.199636	0.002492

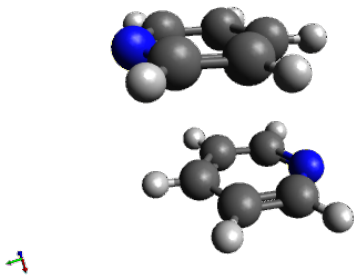

Fig. S7 Optimized molecular geometry for Hohenstein S2.

3.8 Hohenstein T1

FINAL SINGLE POINT ENERGY	-495.520541 Eh
Total Energy	-493.554632 Eh
Dipole Moment	3.621 D
Rotational constants in MHz	1986.924659 446.748769 417.221905
TOTAL RUN TIME	17 hours 2 minutes for 7 geometry optimization steps

Table S14 Cartesian coordinates for geometry Hohenstein T1, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	0.000004	1.392418	-2.440001
N	0.000004	-0.000786	3.856937
C	1.143478	0.690386	-2.448948
C	-1.143471	0.690386	-2.448947
C	1.196327	-0.703457	-2.465984
C	-1.196320	-0.703458	-2.465983
C	0.000004	-1.417531	-2.475099
C	-1.142951	0.001322	3.154417
C	1.142960	0.001322	3.154416
C	-1.195077	0.003951	1.761070
C	1.195085	0.003950	1.761070
C	0.000004	0.005012	1.046142
H	2.057300	1.273486	-2.443378
H	-2.057292	1.273486	-2.443378
H	2.152294	-1.210284	-2.473374
H	-2.152287	-1.210284	-2.473373
H	0.000005	-2.499795	-2.486319
H	-2.056905	0.001092	3.737385
H	2.056913	0.001091	3.737385
H	-2.150695	0.007005	1.253089
H	2.150703	0.007004	1.253088
H	0.000004	0.003890	-0.034561

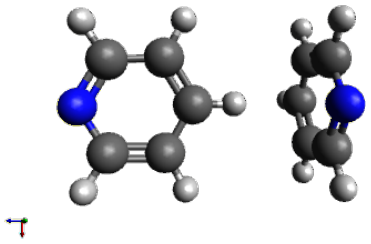

Fig. S8 Optimized molecular geometry for Hohenstein T1.

3.9 Hohenstein T2

FINAL SINGLE POINT ENERGY	-495.518552 Eh
Total Energy	-493.551208 Eh
Dipole Moment	3.406 D
Rotational constants in MHz	1989.516668 517.263824 478.245553
TOTAL RUN TIME	9 hours 34 minutes for 3 geometry optimization steps

Table S15 Cartesian coordinates for geometry Hohenstein T2, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	0.000005	1.397502	-2.248066
N	0.000002	-0.003857	0.857162
C	1.140729	0.693033	-2.246098
C	-1.140719	0.693034	-2.246099
C	1.194235	-0.699493	-2.253731
C	-1.194227	-0.699492	-2.253731
C	0.000004	-1.414253	-2.260175
C	1.140844	-0.002119	1.561208
C	-1.140839	-0.002119	1.561209
C	1.196257	0.000699	2.954042
C	-1.196249	0.000699	2.954044
C	0.000005	0.001881	3.667888
H	2.056188	1.274457	-2.247767
H	-2.056178	1.274457	-2.247768
H	2.151269	-1.204817	-2.259566
H	-2.151262	-1.204816	-2.259567
H	0.000004	-2.496634	-2.267217
H	2.054898	-0.001183	0.977185
H	-2.054894	-0.001183	0.977187
H	2.152515	0.002733	3.459900
H	-2.152506	0.002732	3.459904
H	0.000006	0.004598	4.750245

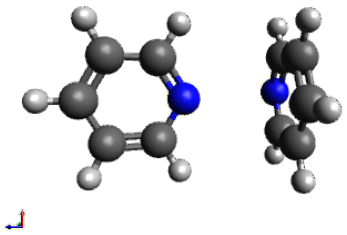

Fig. S9 Optimized molecular geometry for Hohenstein T2.

3.10 Hohenstein T3

FINAL SINGLE POINT ENERGY	-495.522345 Eh
Total Energy	-493.555403 Eh
Dipole Moment	0.581 D
Rotational constants in MHz	2018.654320 469.485737 435.883513
TOTAL RUN TIME	1 days 17 hours for 16 geometry optimization steps

Table S16 Cartesian coordinates for geometry Hohenstein T3, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	0.000004	1.178627	-2.098555
N	0.000002	-1.186065	2.136865
C	1.143830	0.490921	-2.239584
C	-1.143824	0.490922	-2.239585
C	1.196345	-0.874457	-2.517770
C	-1.196339	-0.874456	-2.517772
C	0.000003	-1.573730	-2.659927
C	0.000002	-0.695709	3.385983
C	0.000000	0.666396	3.682850
C	-0.000000	1.579475	2.630582
C	0.000001	1.089635	1.326550
C	0.000002	-0.292478	1.135214
H	2.057846	1.061518	-2.121131
H	-2.057839	1.061521	-2.121133
H	2.152223	-1.371435	-2.615448
H	-2.152218	-1.371432	-2.615453
H	0.000003	-2.635057	-2.871646
H	0.000002	-1.430182	4.183375
H	-0.000001	0.996438	4.713316
H	-0.000001	2.645092	2.821579
H	0.000001	1.749045	0.468794
H	0.000002	-0.704468	0.133028

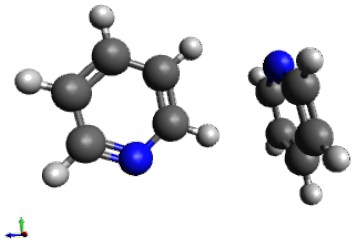

Fig. S10 Optimized molecular geometry for Hohenstein T3.

3.11 Hohenstein T4

FINAL SINGLE POINT ENERGY	-495.521518 Eh
Total Energy	-493.554697 Eh
Dipole Moment	4.596 D
Rotational constants in MHz	2024.287358 463.914713 431.349944
TOTAL RUN TIME	1 days 18 hours for 18 geometry optimization steps

Table S17 Cartesian coordinates for geometry Hohenstein T4, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	0.000003	1.181315	-2.051036
N	-0.000001	1.552743	2.643720
C	1.143909	0.496917	-2.204663
C	-1.143902	0.496917	-2.204664
C	1.196708	-0.862732	-2.510254
C	-1.196702	-0.862732	-2.510254
C	0.000003	-1.558716	-2.667328
C	-0.000000	1.028942	1.407713
C	-0.000000	-0.342686	1.150353
C	0.000000	-1.225333	2.227659
C	-0.000000	-0.697177	3.516798
C	-0.000001	0.688361	3.669996
H	2.057169	1.066145	-2.074750
H	-2.057162	1.066146	-2.074752
H	2.152521	-1.357204	-2.621336
H	-2.152514	-1.357204	-2.621336
H	0.000003	-2.614483	-2.906176
H	0.000001	1.734242	0.585025
H	0.000001	-0.701388	0.129894
H	0.000001	-2.296139	2.067456
H	-0.000000	-1.339428	4.387598
H	-0.000002	1.129229	4.660407

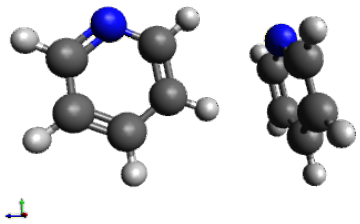

Fig. S11 Optimized molecular geometry for Hohenstein T4.

3.12 Piazenza1 180a

FINAL SINGLE POINT ENERGY	-495.523684 Eh
Total Energy	-493.550258 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1632.301759 723.023051 698.568798
TOTAL RUN TIME	1 days 1 hours for 7 geometry optimization steps

Table S18 Cartesian coordinates for geometry Piazenza1 180a, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	-0.983339	2.478716	0.000016
C	-0.365858	2.141566	-1.142651
C	0.853504	1.467329	-1.194817
C	1.478065	1.118022	0.000025
C	0.853473	1.467304	1.194860
C	-0.365813	2.141674	1.142691
H	-0.875075	2.424958	-2.057016
H	1.295412	1.220080	-2.151181
H	2.418628	0.582674	0.000030
H	1.295358	1.220023	2.151227
H	-0.874975	2.425175	2.057052
N	0.983339	-2.478716	-0.000020
C	0.365858	-2.141571	1.142649
C	-0.853501	-1.467331	1.194818
C	-1.478065	-1.118022	-0.000022
C	-0.853476	-1.467303	-1.194858
C	0.365813	-2.141669	-1.142693
H	0.875074	-2.424970	2.057012
H	-1.295401	-1.220074	2.151184
H	-2.418627	-0.582674	-0.000025
H	-1.295368	-1.220029	-2.151224
H	0.874976	-2.425162	-2.057056

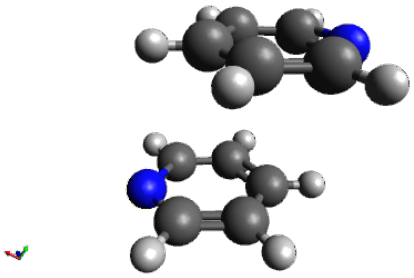

Fig. S12 Optimized molecular geometry for Piazenza1 180a.

3.13 Piazenza2 180b

FINAL SINGLE POINT ENERGY	-495.522016 Eh
Total Energy	-493.550152 Eh
Dipole Moment	0.095 D
Rotational constants in MHz	1636.543429 721.683719 696.583159
TOTAL RUN TIME	1 days 1 hours for 8 geometry optimization steps

Table S19 Cartesian coordinates for geometry Piazenza2 180b, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	-1.144600	1.475546	0.043166
C	-1.463725	0.885441	-1.118769
C	-2.126933	-0.337234	-1.211750
C	-2.483179	-0.995122	-0.037791
C	-2.161353	-0.396822	1.177394
C	-1.497037	0.828611	1.164653
H	-1.172360	1.419703	-2.016273
H	-2.351276	-0.759824	-2.182296
H	-2.991740	-1.949832	-0.068934
H	-2.413490	-0.867024	2.118768
H	-1.232667	1.317589	2.095715
N	1.096241	-1.448754	-0.019825
C	1.456150	-0.824815	-1.151781
C	2.161984	0.376806	-1.184862
C	2.519224	0.975152	0.020422
C	2.154872	0.341302	1.205227
C	1.449570	-0.858889	1.132283
H	1.162891	-1.312886	-2.074633
H	2.418617	0.828914	-2.133847
H	3.061815	1.911362	0.035992
H	2.405725	0.765119	2.168672
H	1.151270	-1.374345	2.038466

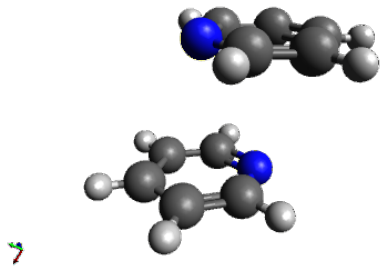

Fig. S13 Optimized molecular geometry for Piazenza2 180b.

3.14 Piazenza3 160d

FINAL SINGLE POINT ENERGY	-495.524053 Eh
Total Energy	-493.550625 Eh
Dipole Moment	0.730 D
Rotational constants in MHz	1653.751433 732.644321 691.702374
TOTAL RUN TIME	1 days 3 hours for 8 geometry optimization steps

Table S20 Cartesian coordinates for geometry Piazenza3 160d, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	2.191801	-0.349487	1.196236
C	1.521980	0.810964	1.130143
C	1.125180	1.411785	-0.064216
C	1.434429	0.779476	-1.265109
C	2.135205	-0.423914	-1.215429
C	2.488171	-0.943110	0.029145
H	1.290825	1.278880	2.080535
H	0.579646	2.345920	-0.045991
H	1.128295	1.206010	-2.211290
H	2.401335	-0.955882	-2.119497
H	3.032582	-1.878218	0.098465
N	-1.931393	-0.073074	-1.371527
C	-2.451214	0.783576	-0.479112
C	-2.330181	0.631945	0.901920
C	-1.629878	-0.466544	1.394976
C	-1.083395	-1.365829	0.482693
C	-1.262667	-1.127413	-0.879041
H	-2.990776	1.628547	-0.892135
H	-2.774447	1.360518	1.567499
H	-1.506244	-0.615578	2.459937
H	-0.521625	-2.228907	0.813835
H	-0.847631	-1.809665	-1.612038

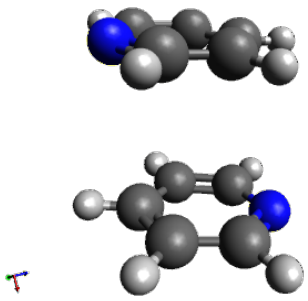

Fig. S14 Optimized molecular geometry for Piazenza3 160d.

3.15 Piazenza4 74d

FINAL SINGLE POINT ENERGY	-495.523749 Eh
Total Energy	-493.550367 Eh
Dipole Moment	3.490 D
Rotational constants in MHz	1649.931033 729.106490 693.207406
TOTAL RUN TIME	22 hours 29 minutes for 7 geometry optimization steps

Table S21 Cartesian coordinates for geometry Piazenza4 74d, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	-0.522837	-2.179646	-1.281202
C	-0.904733	-2.483451	-0.030718
C	-0.181549	-2.129539	1.107171
C	1.007331	-1.419660	0.950184
C	1.418650	-1.096938	-0.339712
C	0.624012	-1.496404	-1.414474
H	-1.832544	-3.037213	0.059534
H	-0.546623	-2.405429	2.087986
H	1.593824	-1.120914	1.809613
H	2.327588	-0.538409	-0.519027
H	0.917770	-1.254474	-2.429357
N	0.522837	2.179646	-1.281202
C	-0.624012	1.496404	-1.414474
C	-1.418650	1.096938	-0.339712
C	-1.007331	1.419660	0.950184
C	0.181549	2.129539	1.107171
C	0.904733	2.483451	-0.030718
H	-0.917770	1.254474	-2.429357
H	-2.327588	0.538409	-0.519027
H	-1.593824	1.120914	1.809613
H	0.546623	2.405429	2.087986
H	1.832544	3.037214	0.059534

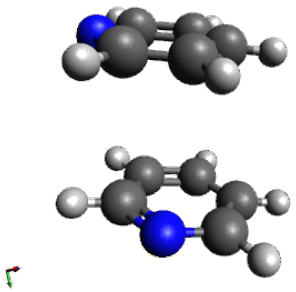

Fig. S15 Optimized molecular geometry for Piazenza4 74d.

3.16 Piazenza5 T1

FINAL SINGLE POINT ENERGY	-495.520596 Eh
Total Energy	-493.553613 Eh
Dipole Moment	2.464 D
Rotational constants in MHz	2025.260808 500.325504 462.539158
TOTAL RUN TIME	1 days 27 minutes for 14 geometry optimization steps

Table S22 Cartesian coordinates for geometry Piazenza5 T1, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	2.029148	-1.493276	-0.000000
C	2.201101	-0.811337	-1.142250
C	2.549697	0.536752	-1.194952
C	2.731594	1.226805	-0.000000
C	2.549696	0.536752	1.194952
C	2.201101	-0.811337	1.142250
H	2.053797	-1.373922	-2.057344
H	2.672668	1.026955	-2.151627
H	3.002081	2.274979	-0.000000
H	2.672667	1.026956	2.151627
H	2.053797	-1.373922	2.057344
N	-0.855466	0.288957	0.000000
C	-1.789691	1.251433	0.000000
C	-3.161532	1.001627	0.000000
C	-3.597446	-0.321263	0.000000
C	-2.640035	-1.333129	0.000000
C	-1.290391	-0.981295	0.000000
H	-1.419332	2.270706	0.000000
H	-3.863934	1.824621	0.000000
H	-4.653910	-0.557277	0.000000
H	-2.927668	-2.376208	-0.000000
H	-0.517944	-1.741363	-0.000000

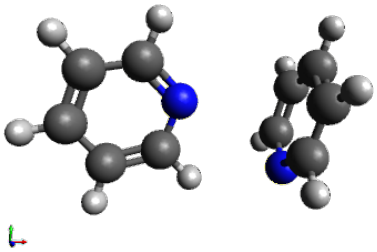

Fig. S16 Optimized molecular geometry for Piazenza5 T1.

3.17 Piazenza6 T2

FINAL SINGLE POINT ENERGY	-495.522152 Eh
Total Energy	-493.555372 Eh
Dipole Moment	4.458 D
Rotational constants in MHz	2064.353767 455.164092 425.501350
TOTAL RUN TIME	11 hours 47 minutes for 4 geometry optimization steps

Table S23 Cartesian coordinates for geometry Piazenza6 T2, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	3.912461	0.424371	0.016378
C	3.536944	-0.863312	0.008441
C	2.207003	-1.281583	-0.014741
C	1.202525	-0.316681	-0.030515
C	1.573854	1.026303	-0.022653
C	2.932212	1.340920	0.000702
H	4.340288	-1.591160	0.021254
H	1.971357	-2.337803	-0.020173
H	0.157993	-0.600223	-0.048660
H	0.825595	1.807805	-0.034209
H	3.253443	2.376259	0.007223
N	-1.792784	1.511687	-0.016957
C	-2.013758	0.866274	1.138553
C	-2.499574	-0.438502	1.215080
C	-2.774802	-1.119223	0.031146
C	-2.550657	-0.463175	-1.177259
C	-2.062730	0.842798	-1.148464
H	-1.787390	1.420742	2.042021
H	-2.655269	-0.903423	2.179398
H	-3.153454	-2.133026	0.049669
H	-2.747405	-0.947715	-2.124273
H	-1.875851	1.378668	-2.071961

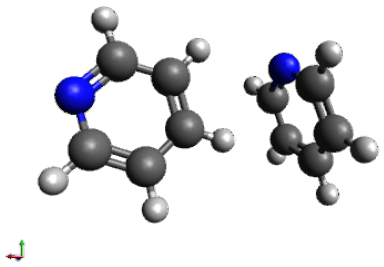

Fig. S17 Optimized molecular geometry for Piazenza6 T2.

3.18 Piazenza7 H-bonded

FINAL SINGLE POINT ENERGY	-495.522281 Eh
Total Energy	-493.558469 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	2983.181654 333.000444 299.561600
TOTAL RUN TIME	22 hours 17 minutes for 11 geometry optimization steps

Table S24 Cartesian coordinates for geometry Piazenza7 H-bonded, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
N	1.762124	0.806261	-0.000000
C	1.697478	-0.536408	-0.000000
C	2.825695	-1.356678	-0.000000
C	4.087145	-0.767371	0.000000
C	4.167604	0.623404	0.000000
C	2.984639	1.359763	-0.000000
H	0.701585	-0.965782	-0.000000
H	2.709264	-2.432307	-0.000000
H	4.983671	-1.374045	0.000000
H	5.122966	1.131106	0.000000
H	3.014388	2.443428	-0.000000
H	-0.701575	0.965792	-0.000000
N	-1.762114	-0.806252	-0.000000
C	-2.984629	-1.359754	-0.000000
C	-4.167594	-0.623395	0.000000
C	-4.087136	0.767379	0.000000
C	-2.825685	1.356687	-0.000000
C	-1.697469	0.536417	-0.000000
H	-3.014377	-2.443419	0.000000
H	-5.122955	-1.131098	0.000000
H	-4.983662	1.374054	0.000000
H	-2.709256	2.432316	-0.000000

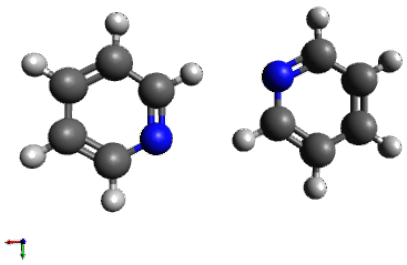

Fig. S18 Optimized molecular geometry for Piazenza7 H-bonded.

3.19 Piazenza Pyridine

FINAL SINGLE POINT ENERGY	-247.757740 Eh
Total Energy	-246.778449 Eh
Dipole Moment	2.332 D
Rotational constants in MHz	6046.057093 5803.196514 2961.068993
TOTAL RUN TIME	1 hours 6 minutes for 4 geometry optimization steps

Table S25 Cartesian coordinates for geometry Piazenza Pyridine, optimized with RI-SCS-MP2/aug-cc-pVTZ.

	x	y	z
C	0.790653	-1.247770	-0.076086
C	1.392772	0.001634	0.050267
C	-0.601515	-1.321866	-0.077889
C	0.573159	1.121296	0.169201
C	-0.809355	0.942181	0.156524
H	1.381610	-2.148905	-0.171519
N	-1.404737	-0.253671	0.035667
H	2.470603	0.100024	0.055895
H	-1.098610	-2.280136	-0.174652
H	0.990241	2.114416	0.269894
H	-1.472716	1.794512	0.247227

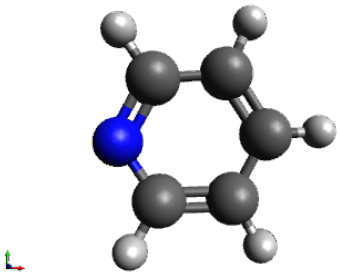

Fig. S19 Optimized molecular geometry for Piazenza Pyridine.

4 PBEh-3c Structures and Properties

Below, we list the calculation times, final SCF energies ("Total Energy"), final dispersion-corrected DFT energies ("FINAL SINGLE POINT ENERGY"), dipole moments (Magnitude (Debye)), rotational constants, and Cartesian coordinates for fully optimized pyridine and pyridine dimer geometries, calculated at the PBEh-3c level. Calculations were performed using the ORCA quantum mechanical calculation package[8,9]. Calculations used 1 thread on an Intel Core-i5 8500 processor with 32 GB RAM.

4.1 Hohenstein P1a

FINAL SINGLE POINT ENERGY	-495.463615 Eh
Total Energy	-495.480594 Eh
Dipole Moment	4.114 D
Rotational constants in MHz	1711.663326 710.185701 676.934142
TOTAL RUN TIME	16 minutes 213 msec for 12 geometry optimization steps

Table S26 Cartesian coordinates for geometry Hohenstein P1a, optimized with PBEh-3c.

	x	y	z
N	1.404005	0.000000	-1.092782
N	0.905263	-0.000000	2.589795
C	0.821937	-1.131923	-1.457718
C	0.821937	1.131923	-1.457718
C	-0.347735	-1.190455	-2.202331
C	-0.347735	1.190455	-2.202331
C	-0.944834	0.000000	-2.584704
C	0.332526	1.132524	2.212664
C	0.332526	-1.132524	2.212664
C	-0.826927	1.189775	1.452803
C	-0.826927	-1.189775	1.452803
C	-1.419711	-0.000000	1.063472
H	1.312793	-2.046085	-1.141205
H	1.312793	2.046085	-1.141205
H	-0.772963	-2.147409	-2.472750
H	-0.772963	2.147409	-2.472750
H	-1.854450	0.000000	-3.171440
H	0.823106	2.046898	2.529019
H	0.823106	-2.046898	2.529019
H	-1.245944	2.146129	1.170427
H	-1.245944	-2.146129	1.170427
H	-2.317352	-0.000000	0.459376

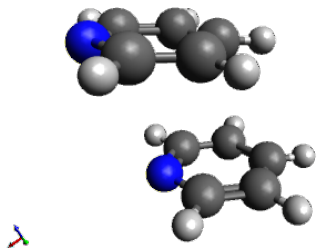

Fig. S20 Optimized molecular geometry for Hohenstein P1a.

4.2 Hohenstein P1b

FINAL SINGLE POINT ENERGY	-495.465372 Eh
Total Energy	-495.482290 Eh
Dipole Moment	3.935 D
Rotational constants in MHz	1699.748151 727.984269 685.163224
TOTAL RUN TIME	2 minutes 45 seconds for 1 geometry optimization steps

Table S27 Cartesian coordinates for geometry Hohenstein P1b, optimized with PBEh-3c.

	x	y	z
N	0.212772	-1.958711	1.304237
N	-0.212772	1.958712	1.304237
C	-0.905177	-1.324449	0.979557
C	0.905176	1.324449	0.979557
C	-1.337387	-1.156564	-0.327975
C	1.337387	1.156564	-0.327975
C	-0.560742	-1.675572	-1.350384
C	0.560742	1.675572	-1.350384
C	0.609549	-2.340633	-1.022001
C	-0.609549	2.340633	-1.022001
C	0.946803	-2.453961	0.319158
C	-0.946803	2.453961	0.319158
H	-1.483882	-0.919363	1.801852
H	1.483882	0.919363	1.801852
H	-2.252624	-0.620174	-0.535723
H	2.252624	0.620174	-0.535723
H	-0.860597	-1.559093	-2.383788
H	0.860597	1.559093	-2.383788
H	1.249049	-2.766124	-1.783578
H	-1.249049	2.766124	-1.783578
H	1.855657	-2.969601	0.611472
H	-1.855657	2.969601	0.611472

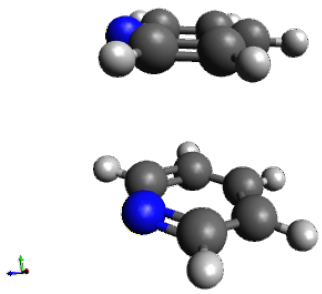

Fig. S21 Optimized molecular geometry for Hohenstein P1b.

4.3 Hohenstein P2a+

FINAL SINGLE POINT ENERGY	-495.463610 Eh
Total Energy	-495.480734 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1661.725809 727.307425 701.124722
TOTAL RUN TIME	11 minutes 39 seconds for 9 geometry optimization steps

Table S28 Cartesian coordinates for geometry Hohenstein P2a+, optimized with PBEh-3c.

	x	y	z
N	-1.443714	-1.120758	-0.000066
N	1.443714	1.120758	-0.000066
C	-0.845410	-1.460752	-1.132029
C	-0.845501	-1.460721	1.131954
C	0.845410	1.460752	-1.132029
C	0.845501	1.460721	1.131954
C	0.358263	-2.147315	-1.189917
C	0.358166	-2.147285	1.189957
C	-0.358263	2.147315	-1.189917
C	-0.358165	2.147285	1.189957
C	0.975252	-2.495186	0.000049
C	-0.975252	2.495186	0.000049
H	-1.350617	-1.167448	-2.046341
H	-1.350781	-1.167388	2.046217
H	1.350617	1.167448	-2.046341
H	1.350781	1.167388	2.046217
H	0.801743	-2.390528	-2.145710
H	0.801566	-2.390475	2.145792
H	-0.801743	2.390528	-2.145710
H	-0.801566	2.390475	2.145792
H	1.920290	-3.022267	0.000094
H	-1.920290	3.022267	0.000094

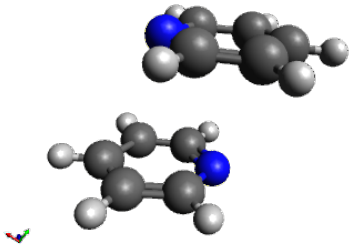

Fig. S22 Optimized molecular geometry for Hohenstein P2a+.

4.4 Hohenstein P2a-

FINAL SINGLE POINT ENERGY	-495.465925 Eh
Total Energy	-495.482644 Eh
Dipole Moment	0.004 D
Rotational constants in MHz	1681.913511 727.676443 697.848390
TOTAL RUN TIME	26 minutes 24 seconds for 21 geometry optimization steps

Table S29 Cartesian coordinates for geometry Hohenstein P2a-, optimized with PBEh-3c.

	x	y	z
N	1.016762	-2.478133	0.001717
N	-1.016762	2.478133	0.001717
C	0.413211	-2.146475	1.133869
C	0.415362	-2.147629	-1.131927
C	-0.413211	2.146475	1.133869
C	-0.415362	2.147629	-1.131927
C	-0.797063	-1.471163	1.188883
C	-0.794805	-1.472388	-1.189915
C	0.797063	1.471163	1.188883
C	0.794805	1.472388	-1.189915
C	-1.412547	-1.120505	-0.001278
C	1.412547	1.120505	-0.001278
H	0.922092	-2.430178	2.049062
H	0.926016	-2.432202	-2.045862
H	-0.922092	2.430178	2.049062
H	-0.926016	2.432202	-2.045862
H	-1.236860	-1.217944	2.143899
H	-1.232753	-1.220061	-2.146016
H	1.236861	1.217944	2.143899
H	1.232753	1.220061	-2.146016
H	-2.347636	-0.576338	-0.002431
H	2.347636	0.576338	-0.002431

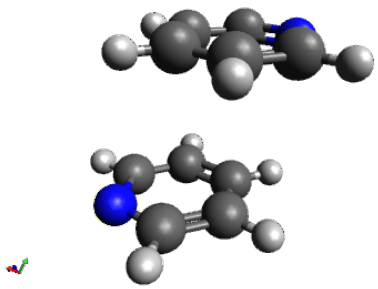

Fig. S23 Optimized molecular geometry for Hohenstein P2a-.

4.5 Hohenstein P2b

FINAL SINGLE POINT ENERGY	-495.466038 Eh
Total Energy	-495.483015 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1700.247387 717.546414 673.858038
TOTAL RUN TIME	11 minutes 12 seconds for 8 geometry optimization steps

Table S30 Cartesian coordinates for geometry Hohenstein P2b, optimized with PBEh-3c.

	x	y	z
N	0.245067	-1.382263	-1.834417
N	-0.245067	1.382263	1.834417
C	-0.698690	-0.687774	-2.452618
C	0.698690	0.687774	2.452618
C	-0.739863	0.699149	-2.477583
C	0.739863	-0.699149	2.477583
C	0.260438	1.398635	-1.821929
C	-0.260438	-1.398635	1.821929
C	1.253864	0.682485	-1.174918
C	-1.253864	-0.682485	1.174918
C	1.197301	-0.702584	-1.211160
C	-1.197301	0.702584	1.211160
H	-1.466604	-1.265706	-2.956020
H	1.466604	1.265706	2.956020
H	-1.537353	1.213339	-2.996665
H	1.537353	-1.213339	2.996665
H	0.262720	2.480601	-1.807951
H	-0.262720	-2.480601	1.807951
H	2.048866	1.183534	-0.640921
H	-2.048866	-1.183534	0.640921
H	1.955555	-1.290896	-0.706357
H	-1.955555	1.290896	0.706357

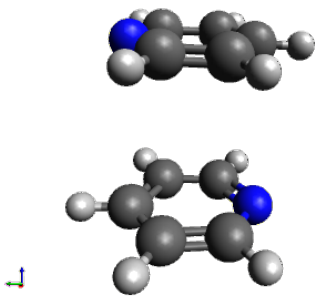

Fig. S24 Optimized molecular geometry for Hohenstein P2b.

4.6 Hohenstein S1

FINAL SINGLE POINT ENERGY	-495.461630 Eh
Total Energy	-495.479326 Eh
Dipole Moment	4.113 D
Rotational constants in MHz	1501.445576 686.654253 681.063900
TOTAL RUN TIME	6 minutes 4 seconds for 4 geometry optimization steps

Table S31 Cartesian coordinates for geometry Hohenstein S1, optimized with PBEh-3c.

	x	y	z
N	-0.000072	-1.901270	1.374583
N	0.000072	1.901270	1.374583
C	-1.133219	-1.898807	0.689398
C	1.133141	-1.898811	0.689505
C	1.133219	1.898807	0.689398
C	-1.133141	1.898811	0.689505
C	-1.190798	-1.898728	-0.696727
C	1.190849	-1.898736	-0.696615
C	1.190798	1.898728	-0.696727
C	-1.190849	1.898736	-0.696615
C	0.000058	-1.899565	-1.404265
C	-0.000058	1.899565	-1.404265
H	-2.046214	-1.898431	1.275125
H	2.046082	-1.898439	1.275317
H	2.046214	1.898431	1.275125
H	-2.046082	1.898439	1.275317
H	-2.146245	-1.898711	-1.203600
H	2.146342	-1.898726	-1.203402
H	2.146245	1.898711	-1.203600
H	-2.146342	1.898726	-1.203402
H	0.000109	-1.900820	-2.486489
H	-0.000109	1.900820	-2.486489

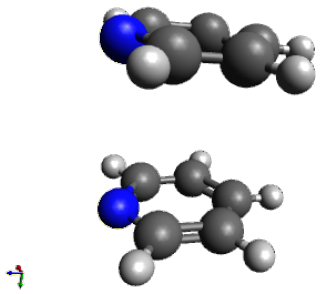

Fig. S25 Optimized molecular geometry for Hohenstein S1.

4.7 Hohenstein S2

FINAL SINGLE POINT ENERGY	-495.465813 Eh
Total Energy	-495.482564 Eh
Dipole Moment	0.006 D
Rotational constants in MHz	1683.029856 723.582918 693.849025
TOTAL RUN TIME	38 seconds 842 msec for 40 geometry optimization steps

Table S32 Cartesian coordinates for geometry Hohenstein S2, optimized with PBEh-3c.

	x	y	z
N	-2.177947	1.572095	-0.002751
N	2.177947	-1.572096	-0.002751
C	-1.996908	0.907168	-1.134533
C	-1.997184	0.911149	1.131422
C	1.996908	-0.907168	-1.134533
C	1.997184	-0.911149	1.131422
C	-1.623164	-0.427567	-1.188803
C	-1.623483	-0.423374	1.190447
C	1.623164	0.427567	-1.188803
C	1.623483	0.423374	1.190447
C	-1.426084	-1.106659	0.002041
C	1.426084	1.106659	0.002041
H	-2.155187	1.467462	-2.050072
H	-2.155604	1.474676	2.044952
H	2.155187	-1.467462	-2.050072
H	2.155604	-1.474676	2.044952
H	-1.479181	-0.916557	-2.142525
H	-1.479710	-0.908996	2.145923
H	1.479181	0.916557	-2.142525
H	1.479710	0.908996	2.145923
H	-1.117936	-2.143637	0.003900
H	1.117936	2.143637	0.003900

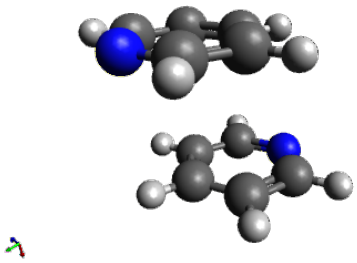

Fig. S26 Optimized molecular geometry for Hohenstein S2.

4.8 Hohenstein T1

FINAL SINGLE POINT ENERGY	-495.463489 Eh
Total Energy	-495.482812 Eh
Dipole Moment	3.323 D
Rotational constants in MHz	2012.472800 421.909874 395.613683
TOTAL RUN TIME	18 seconds 698 msec for 10 geometry optimization steps

Table S33 Cartesian coordinates for geometry Hohenstein T1, optimized with PBEh-3c.

	x	y	z
N	-0.000000	1.375699	-2.562058
N	0.000000	-0.005564	3.923256
C	1.134220	0.690132	-2.556632
C	-1.134220	0.690132	-2.556632
C	1.191703	-0.696759	-2.541253
C	-1.191703	-0.696759	-2.541254
C	0.000000	-1.404578	-2.533233
C	-1.133419	-0.002981	3.236766
C	1.133419	-0.002982	3.236766
C	-1.190444	0.000857	1.850588
C	1.190444	0.000857	1.850588
C	-0.000000	0.002731	1.141875
H	2.046652	1.276500	-2.563932
H	-2.046652	1.276499	-2.563932
H	2.146269	-1.205107	-2.537635
H	-2.146269	-1.205107	-2.537635
H	0.000000	-2.486459	-2.519204
H	-2.046659	-0.003893	3.822294
H	2.046659	-0.003894	3.822294
H	-2.144913	0.004087	1.341876
H	2.144913	0.004087	1.341876
H	-0.000000	0.002640	0.060746

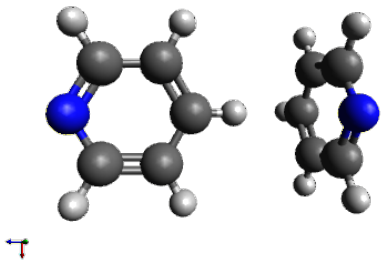

Fig. S27 Optimized molecular geometry for Hohenstein T1.

4.9 Hohenstein T2

FINAL SINGLE POINT ENERGY	-495.461644 Eh
Total Energy	-495.480088 Eh
Dipole Moment	3.151 D
Rotational constants in MHz	2014.618428 517.716051 478.719362
TOTAL RUN TIME	44 seconds 495 msec for 10 geometry optimization steps

Table S34 Cartesian coordinates for geometry Hohenstein T2, optimized with PBEh-3c.

	x	y	z
N	-0.000000	1.377431	-2.256304
N	0.000000	-0.004348	0.881283
C	1.131956	0.690998	-2.253191
C	-1.131956	0.690998	-2.253191
C	1.189992	-0.694612	-2.254087
C	-1.189992	-0.694612	-2.254087
C	-0.000000	-1.402069	-2.252646
C	1.133529	-0.003038	1.565353
C	-1.133529	-0.003038	1.565353
C	1.191384	-0.001423	2.951776
C	-1.191384	-0.001423	2.951776
C	-0.000000	-0.000887	3.659391
H	2.045552	1.276624	-2.256836
H	-2.045552	1.276624	-2.256836
H	2.145206	-1.202423	-2.256189
H	-2.145206	-1.202423	-2.256189
H	-0.000000	-2.484223	-2.250085
H	2.044753	-0.002010	0.976876
H	-2.044753	-0.002010	0.976876
H	2.146248	0.000366	3.459774
H	-2.146248	0.000366	3.459774
H	-0.000000	0.000900	4.741513

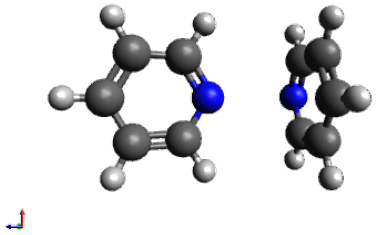

Fig. S28 Optimized molecular geometry for Hohenstein T2.

4.10 Hohenstein T3

FINAL SINGLE POINT ENERGY	-495.465627 Eh
Total Energy	-495.484963 Eh
Dipole Moment	0.720 D
Rotational constants in MHz	2070.636487 449.944424 420.539514
TOTAL RUN TIME	55 minutes 21 seconds for 54 geometry optimization steps

Table S35 Cartesian coordinates for geometry Hohenstein T3, optimized with PBEh-3c.

	x	y	z
N	-0.000004	1.127758	-2.090604
N	-0.000001	-1.155395	2.222526
C	1.134573	0.463375	-2.261470
C	-1.134579	0.463374	-2.261481
C	1.191446	-0.880557	-2.602364
C	-1.191448	-0.880558	-2.602373
C	0.000000	-1.567093	-2.774099
C	0.000001	-0.662868	3.452720
C	0.000003	0.695254	3.736201
C	0.000003	1.587708	2.675668
C	0.000002	1.085071	1.384524
C	-0.000000	-0.293090	1.215724
H	2.047919	1.028704	-2.112780
H	-2.047927	1.028703	-2.112802
H	2.146484	-1.372875	-2.723644
H	-2.146484	-1.372878	-2.723660
H	0.000002	-2.617651	-3.033447
H	0.000000	-1.388399	4.258999
H	0.000005	1.038751	4.761892
H	0.000005	2.655786	2.851084
H	0.000001	1.736433	0.521233
H	0.000000	-0.719552	0.218151

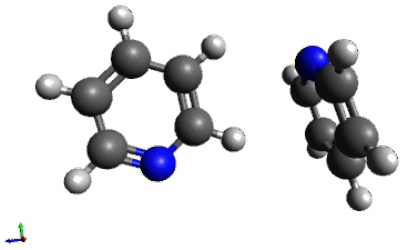

Fig. S29 Optimized molecular geometry for Hohenstein T3.

4.11 Hohenstein T4

FINAL SINGLE POINT ENERGY	-495.464915 Eh
Total Energy	-495.484204 Eh
Dipole Moment	4.383 D
Rotational constants in MHz	2080.456271 442.247123 414.213202
TOTAL RUN TIME	48 minutes 32 seconds for 47 geometry optimization steps

Table S36 Cartesian coordinates for geometry Hohenstein T4, optimized with PBEh-3c.

	x	y	z
N	-0.000000	1.132785	-2.041974
N	0.000000	1.544270	2.684449
C	1.134715	0.473968	-2.230877
C	-1.134715	0.473968	-2.230877
C	1.191656	-0.859214	-2.612239
C	-1.191656	-0.859214	-2.612239
C	0.000000	-1.539701	-2.806529
C	0.000000	1.010608	1.470647
C	0.000000	-0.358185	1.236540
C	-0.000000	-1.212476	2.327234
C	-0.000000	-0.663832	3.599927
C	0.000000	0.718360	3.720383
H	2.047645	1.035258	-2.065839
H	-2.047646	1.035257	-2.065839
H	2.146981	-1.346611	-2.750614
H	-2.146981	-1.346611	-2.750614
H	0.000000	-2.580296	-3.103911
H	0.000001	1.702419	0.635809
H	0.000000	-0.739148	0.223966
H	-0.000000	-2.285992	2.188899
H	-0.000001	-1.290268	4.481567
H	0.000000	1.180315	4.702132

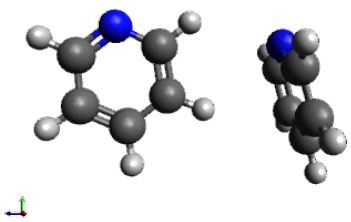

Fig. S30 Optimized molecular geometry for Hohenstein T4.

4.12 Piazenza 1 Dimer Stacked 180a

FINAL SINGLE POINT ENERGY	-495.465904 Eh
Total Energy	-495.482584 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	1662.325086 737.188220 710.135979
TOTAL RUN TIME	16 minutes 18 seconds for 10 geometry optimization steps

Table S37 Cartesian coordinates for geometry Piazenza 1 Dimer Stacked 180a, optimized with PBEh-3c.

	x	y	z
N	-0.971966	2.458272	0.000003
C	-0.369479	2.126789	-1.132726
C	0.839894	1.450223	-1.189432
C	1.456083	1.098042	0.000003
C	0.839839	1.450149	1.189432
C	-0.369450	2.126865	1.132740
H	-0.878875	2.410943	-2.047511
H	1.279356	1.198165	-2.144897
H	2.391695	0.554846	0.000009
H	1.279258	1.198010	2.144896
H	-0.878769	2.411155	2.047525
N	0.971966	-2.458272	-0.000005
C	0.369478	-2.126796	1.132725
C	-0.839890	-1.450222	1.189433
C	-1.456083	-1.098042	-0.000000
C	-0.839843	-1.450150	-1.189431
C	0.369450	-2.126858	-1.132741
H	0.878871	-2.410961	2.047508
H	-1.279347	-1.198156	2.144898
H	-2.391695	-0.554846	-0.000004
H	-1.279267	-1.198019	-2.144895
H	0.878773	-2.411137	-2.047527

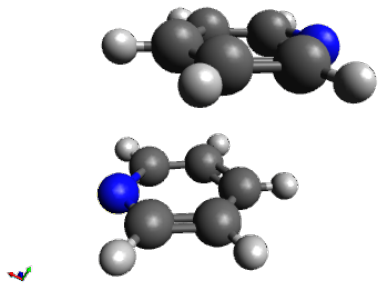

Fig. S31 Optimized molecular geometry for Piazenza 1 Dimer Stacked 180a.

4.13 Piazenza 2 Dimer Stacked 180b

FINAL SINGLE POINT ENERGY	-495.463604 Eh
Total Energy	-495.480732 Eh
Dipole Moment	0.097 D
Rotational constants in MHz	1657.887697 726.974155 701.459117
TOTAL RUN TIME	11 minutes 27 seconds for 9 geometry optimization steps

Table S38 Cartesian coordinates for geometry Piazenza 2 Dimer Stacked 180b, optimized with PBEh-3c.

	x	y	z
N	-1.154377	1.461803	0.043018
C	-1.462266	0.883954	-1.108443
C	-2.119143	-0.333759	-1.206310
C	-2.470208	-0.987850	-0.037381
C	-2.153879	-0.393141	1.172570
C	-1.495770	0.827546	1.154782
H	-1.168701	1.418975	-2.005547
H	-2.339014	-0.758757	-2.176057
H	-2.976437	-1.943692	-0.068834
H	-2.401420	-0.865558	2.113284
H	-1.229016	1.316860	2.085701
N	1.100831	-1.432274	-0.019832
C	1.452179	-0.822321	-1.141948
C	2.156439	0.371941	-1.180031
C	2.510078	0.965752	0.020050
C	2.148642	0.336974	1.199785
C	1.444926	-0.855721	1.122003
H	1.155158	-1.309734	-2.064649
H	2.410030	0.825507	-2.128371
H	3.053346	1.901441	0.035722
H	2.396056	0.762601	2.162554
H	1.142544	-1.370548	2.027931

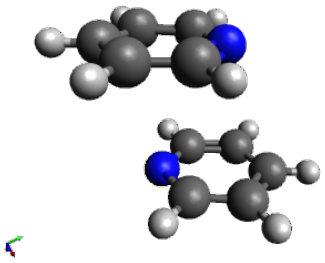

Fig. S32 Optimized molecular geometry for Piazenza 2 Dimer Stacked 180b.

4.14 Piazenza 3 Dimer Stacked 160

FINAL SINGLE POINT ENERGY	-495.466348 Eh
Total Energy	-495.483124 Eh
Dipole Moment	0.692 D
Rotational constants in MHz	1681.295588 738.585279 697.533971
TOTAL RUN TIME	17 minutes 24 seconds for 9 geometry optimization steps

Table S39 Cartesian coordinates for geometry Piazenza 3 Dimer Stacked 160, optimized with PBEh-3c.

	x	y	z
N	2.187840	-0.344029	1.178978
C	1.517796	0.797627	1.124319
C	1.116026	1.398808	-0.059636
C	1.427285	0.771053	-1.253376
C	2.130807	-0.422471	-1.209551
C	2.486005	-0.933705	0.029646
H	1.283522	1.260983	2.076793
H	0.562388	2.327222	-0.040725
H	1.118833	1.195993	-2.199121
H	2.393619	-0.950901	-2.115859
H	3.035630	-1.866587	0.098786
N	-1.923804	-0.073965	-1.353450
C	-2.440483	0.777668	-0.479689
C	-2.322067	0.633669	0.895057
C	-1.623116	-0.458376	1.383479
C	-1.080658	-1.356458	0.479569
C	-1.261580	-1.117285	-0.874334
H	-2.978397	1.622955	-0.895972
H	-2.765672	1.361715	1.560675
H	-1.496983	-0.606043	2.448119
H	-0.520478	-2.218064	0.814275
H	-0.846516	-1.799810	-1.607983

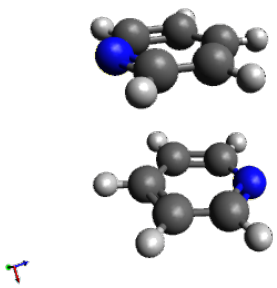

Fig. S33 Optimized molecular geometry for Piazenza 3 Dimer Stacked 160.

4.15 Piazenza 4 Dimer Stacked 74

FINAL SINGLE POINT ENERGY	-495.465969 Eh
Total Energy	-495.482761 Eh
Dipole Moment	3.303 D
Rotational constants in MHz	1676.681775 735.146227 698.702742
TOTAL RUN TIME	13 minutes 13 seconds for 9 geometry optimization steps

Table S40 Cartesian coordinates for geometry Piazenza 4 Dimer Stacked 74, optimized with PBEh-3c.

	x	y	z
N	-0.511826	-2.175871	-1.266447
C	-0.897912	-2.476374	-0.034708
C	-0.186209	-2.120079	1.101068
C	0.994465	-1.411239	0.942685
C	1.407787	-1.091696	-0.338874
C	0.617924	-1.497459	-1.405266
H	-1.824813	-3.033353	0.054043
H	-0.551190	-2.392126	2.082161
H	1.578254	-1.109944	1.802723
H	2.313118	-0.528477	-0.516567
H	0.912091	-1.256023	-2.420819
N	0.511826	2.175871	-1.266447
C	-0.617924	1.497459	-1.405266
C	-1.407787	1.091696	-0.338874
C	-0.994465	1.411239	0.942685
C	0.186209	2.120079	1.101068
C	0.897912	2.476374	-0.034708
H	-0.912091	1.256023	-2.420819
H	-2.313118	0.528477	-0.516567
H	-1.578254	1.109944	1.802723
H	0.551190	2.392126	2.082161
H	1.824813	3.033352	0.054043

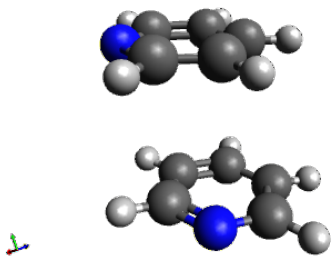

Fig. S34 Optimized molecular geometry for Piazenza 4 Dimer Stacked 74.

4.16 Piazenza 5 Dimer T-shaped1

FINAL SINGLE POINT ENERGY	-495.463665 Eh
Total Energy	-495.482867 Eh
Dipole Moment	2.110 D
Rotational constants in MHz	2079.297520 493.036431 458.223150
TOTAL RUN TIME	22 minutes 29 seconds for 16 geometry optimization steps

Table S41 Cartesian coordinates for geometry Piazenza 5 Dimer T-shaped1, optimized with PBEh-3c.

	x	y	z
N	1.976022	-1.420129	0.000000
C	2.178681	-0.764086	-1.132839
C	2.599370	0.555795	-1.190167
C	2.815803	1.229580	-0.000000
C	2.599369	0.555795	1.190166
C	2.178680	-0.764085	1.132839
H	1.997517	-1.318577	-2.047320
H	2.749331	1.039083	-2.145854
H	3.144192	2.260965	-0.000000
H	2.749328	1.039085	2.145853
H	1.997514	-1.318576	2.047320
N	-0.894605	0.230338	0.000000
C	-1.795002	1.201564	0.000001
C	-3.164742	0.978503	0.000001
C	-3.617064	-0.331324	0.000000
C	-2.682437	-1.354223	-0.000000
C	-1.335016	-1.020215	-0.000000
H	-1.406883	2.214785	0.000001
H	-3.854856	1.811101	0.000001
H	-4.677198	-0.549494	0.000000
H	-2.985687	-2.392462	-0.000001
H	-0.572319	-1.791207	-0.000000

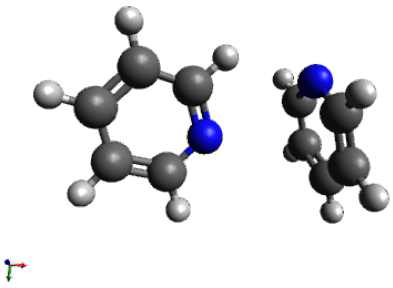

Fig. S35 Optimized molecular geometry for Piazenza 5 Dimer T-shaped1.

4.17 Piazenza 6 Dimer T-shaped2

FINAL SINGLE POINT ENERGY	-495.465726 Eh
Total Energy	-495.485057 Eh
Dipole Moment	4.318 D
Rotational constants in MHz	2112.945459 437.784401 411.551178
TOTAL RUN TIME	981 msec for 9 geometry optimization steps

Table S42 Cartesian coordinates for geometry Piazenza 6 Dimer T-shaped2, optimized with PBEh-3c.

	x	y	z
N	3.943110	0.456789	0.016419
C	3.618016	-0.827640	0.008105
C	2.309182	-1.287727	-0.016577
C	1.283276	-0.356174	-0.033376
C	1.611273	0.990552	-0.024846
C	2.954188	1.339243	0.000117
H	4.443650	-1.531114	0.021797
H	2.105510	-2.350047	-0.022392
H	0.247502	-0.670621	-0.053078
H	0.840853	1.749608	-0.036836
H	3.245384	2.384246	0.007534
N	-1.795117	1.474630	-0.015002
C	-2.041202	0.855411	1.131049
C	-2.582332	-0.419900	1.211412
C	-2.884128	-1.083008	0.032318
C	-2.630973	-0.443410	-1.170940
C	-2.087781	0.833188	-1.137663
H	-1.791101	1.400442	2.034499
H	-2.759729	-0.877054	2.175071
H	-3.307623	-2.078865	0.050908
H	-2.846859	-0.919177	-2.117595
H	-1.875100	1.360628	-2.060922

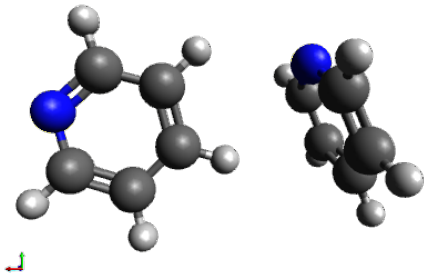

Fig. S36 Optimized molecular geometry for Piazenza 6 Dimer T-shaped2.

4.18 Piazenza 7 Dimer H-bonded

FINAL SINGLE POINT ENERGY	-495.467209 Eh
Total Energy	-495.487868 Eh
Dipole Moment	0.000 D
Rotational constants in MHz	3027.904050 334.615187 301.316545
TOTAL RUN TIME	11 minutes 56 seconds for 10 geometry optimization steps

Table S43 Cartesian coordinates for geometry Piazenza 7 Dimer H-bonded, optimized with PBEh-3c.

	x	y	z
N	1.738083	0.681012	0.000000
C	1.723994	-0.646777	0.000000
C	2.879994	-1.415118	0.000000
C	4.106196	-0.770518	-0.000000
C	4.126708	0.615186	-0.000000
C	2.915052	1.289778	-0.000000
H	0.743303	-1.111481	0.000000
H	2.813919	-2.494454	0.000000
H	5.028257	-1.337397	0.000000
H	5.058116	1.164869	-0.000000
H	2.894504	2.374256	-0.000000
H	-0.743303	1.111481	0.000000
N	-1.738083	-0.681011	-0.000000
C	-2.915052	-1.289778	-0.000000
C	-4.126708	-0.615186	-0.000000
C	-4.106196	0.770517	0.000000
C	-2.879994	1.415118	-0.000000
C	-1.723994	0.646777	0.000000
H	-2.894503	-2.374256	-0.000000
H	-5.058116	-1.164869	-0.000000
H	-5.028258	1.337396	0.000000
H	-2.813919	2.494454	0.000000

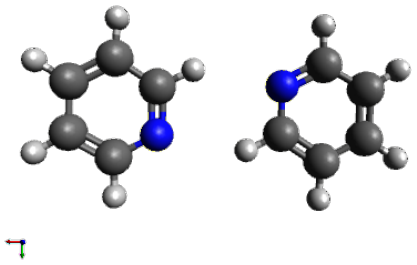

Fig. S37 Optimized molecular geometry for Piazenza 7 Dimer H-bonded.

4.19 pyridine PBEh-3c

FINAL SINGLE POINT ENERGY	-247.729874 Eh
Total Energy	-247.740334 Eh
Dipole Moment	2.185 D
Rotational constants in MHz	6112.164206 5896.192014 3001.118240
TOTAL RUN TIME	54 seconds 361 msec for 3 geometry optimization steps

Table S44 Cartesian coordinates for geometry pyridine PBEh-3c, optimized with PBEh-3c.

	x	y	z
C	0.779693	-1.247831	-0.081099
C	1.440022	-0.036087	0.043397
C	-0.608048	-1.245778	-0.071255
C	0.685970	1.119288	0.172053
C	-0.696894	1.006523	0.170341
H	1.324211	-2.176413	-0.185386
N	-1.337733	-0.147002	0.051496
H	2.521276	0.007209	0.039940
H	-1.156551	-2.176619	-0.168102
H	1.154862	2.088672	0.272895
H	-1.318155	1.889920	0.270729

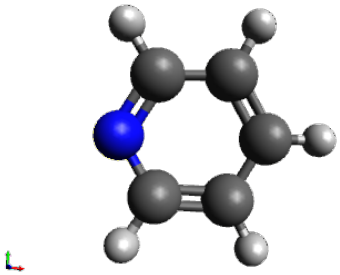

Fig. S38 Optimized molecular geometry for pyridine PBEh-3c.

5 References

1 C. M. Western and B. E. Billinghurst, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10222–10226.

2 E. Ye, R. P. A. Bettens, F. C. De Lucia, D. T. Petkie and S. Albert, *Journal of Molecular Spectroscopy*, 2005, **232**, 61–65.

3 B. Iglewicz and D. Hoaglin, in *The ASQC Basic References in Quality Control: Statistical Techniques*, ed. E. Mykytka, American Society for Quality Control, 1993, vol. 16 of The ASQC Basic References in Quality Control: Statistical Techniques.

4 C. Schröter, J. C. Lee and T. Schultz, *Proc. Natl. Acad. Sci. USA*, 2018, **115**, 5072–5076.

5 M. Piacenza and S. Grimme, *Chemphyschem*, 2005, **6**, 1554–1558.

6 E. G. Hohenstein and C. D. Sherrill, *Journal of Physical Chemistry A*, 2009, **113**, 878–886.

7 S. Grimme, J. G. Brandenburg, C. Bannwarth and A. Hansen, *The Journal of Chemical Physics J. Chem. Phys.*, 2015, **143**, 054107.

8 F. Neese, *WIREs Computational Molecular Science*, 2012, **2**, 73–78.

9 F. Neese, *WIREs Computational Molecular Science*, 2018, **8**, e1327.