

Supporting information on:

## Strained hydrogen bonding in imidazole trimer: A combined infrared, Raman, and theory study

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### List of Tables

S1	Experimental anharmonic constants and relative band intensities for the imidazole monomer from Raman spectra based on comparison with B3LYP-D3(BJ)/VTZ – VPT2 calculations . . . . .	2
S2	Anharmonic shifts and diagonal contributions to them for imidazole monomer XH stretching fundamentals and their dimer acceptor and donor counterparts $\nu_i^a$ and $\nu_i^d$ from the harmonic value based on comparison with B3LYP-D3(BJ)/VTZ – VPT2 calculations . . . . .	2
S3	Vibrational transitions for imidazole and its clusters observed in Raman and FTIR jet spectra . . . . .	3
S4	Calculated harmonic wavenumbers and results of the normal mode 1D scans for the NH stretch fundamentals in the imidazole monomer, dimer, and trimer (based on the B3LYP-D3(BJ)/def2-TZVP structures) . . . . .	4
S5	Calculated harmonic wavenumbers and results of the normal mode 1D scans for the NH stretch fundamentals in the imidazole monomer, dimer, and trimer (based on the SCS-MP2/def2-TZVP structures) . . . . .	5
S6	Calculated harmonic wavenumbers and results of the normal mode 1D scans for the NH stretch fundamentals in the imidazole monomer, dimer, and trimer (based on the B2PLYP/def2-QZVP structures) . . . . .	6
S7	Cartesian coordinates for the imidazole monomer (M) from B3LYP-D3(BJ)/def2-TZVP geometry optimization . . . . .	7
S8	Cartesian coordinates for the imidazole monomer (M) from B3LYP/def2-TZVP geometry optimization . . . . .	7
S9	Cartesian coordinates for the imidazole dimer (D) from B3LYP-D3(BJ)/def2-TZVP geometry optimization . . . . .	8

S10	Cartesian coordinates for the imidazole dimer (D) from B3LYP/def2-TZVP geometry optimization . . . . .	9
S11	Cartesian coordinates for the cyclic imidazole trimer ( $T_{\text{cyclic}}$ ) from B3LYP-D3(BJ)/def2-TZVP geometry optimization . . .	10
S12	Cartesian coordinates for the cyclic imidazole trimer ( $T_{\text{cyclic}}$ ) from B3LYP/def2-TZVP geometry optimization . . . . .	11
S13	Cartesian coordinates for the linear imidazole trimer ( $T_{\text{linear}}$ ) from B3LYP-D3(BJ)/def2-TZVP geometry optimization . . .	12
S14	Cartesian coordinates for the linear imidazole trimer ( $T_{\text{linear}}$ ) from B3LYP/def2-TZVP geometry optimization . . . . .	13
S15	Comparison of the internal coordinates of the imidazole monomer as optimized by different levels of theory . . . . .	14
S16	Calculated corrections for the vibrational wavenumbers for the NH stretch fundamentals in the imidazole dimer and trimer in dependence of excluded off-diagonal terms . . . . .	15

Table S1: Experimental anharmonic constants  $x_{1,k}$  and  $x_{2,k}$  and relative band intensities  $I_k/I_i$  for the imidazole monomer from Raman spectra (Figures 1,2) based on comparison with VPT2 calculations (B3LYP-D3(BJ)/VTZ). The deviations from the def2-TZVP results are quite small.

$i$	$k$	$\tilde{\nu}_k^{\text{VPT2}}/\text{cm}^{-1}$	$x_{i,k}^{\text{VPT2}}/\text{cm}^{-1}$	$x_{i,k}^{\text{exp}}/\text{cm}^{-1}$	$I_k/I_i$
1	12	1070	-8	-9	0.01 <sup>a</sup>
1	21	521	-20	-21	0.14 <sup>a</sup>
1	2×21	1053	-40	-39	0.01 <sup>a</sup>
2	13	1056	-7	-6	$\geq 0.005^b$
2	16	862	-5	-6	$\geq 0.01^b$
2	18	724	-13	-11	$\geq 0.01^b$

<sup>a</sup>: from Raman spectrum in Figure 1; <sup>b</sup>: lower bounds from spectrum (a) in Figure 2 due to overlap.

Table S2: Anharmonic shifts  $\Delta(\nu_i)/\text{cm}^{-1}$  and diagonal contributions  $2x_{i,i}/\text{cm}^{-1}$  to them for imidazole monomer XH stretching fundamentals  $\nu_i$  and their dimer acceptor and donor counterparts  $\nu_i^a$  and  $\nu_i^d$  from the harmonic value based on comparison with VPT2 calculations (B3LYP-D3(BJ)/VTZ). The deviations from the def2-TZVP results are quite small.

mode	$i$	$2x_{i,i}$	$\Delta(\nu_i)$	$2x_{i,i}^a$	$\Delta(\nu_i^a)$	$2x_{i,i}^d$	$\Delta(\nu_i^d)$
NH	1	-141	-166	-140	-165	-242	-151
CH <sub>s</sub>	2	-91	-131	-98	-131	-92	-134
CH <sub>a</sub>	3	-52	-132	-56	-132	-74	-134
CH <sub>a</sub>	4	-54	-133	-74	-131	-86	-134

Table S3: Vibrational transitions in  $\text{cm}^{-1}$  for imidazole and its clusters observed in Raman and FTIR jet spectra with monomer hot band intensities relative to their respective X-H stretch fundamental (in parentheses)<sup>a</sup>. Results from earlier Argon matrix and Helium nano droplets experiments as well as band assignments are also included.

Raman jet	FTIR jet <sup>1</sup>	Ar matrix <sup>2</sup>	He nano <sup>3</sup>	Assignment
3518 (1)	3518 (1)	3500 <sup>b</sup>	3518	monomer: N-H stretch ( $\nu_1$ )
3516	-	-	3516	dimer acceptor: N-H ( $\nu_1^a$ + monomer hot band: ( $\nu_1 + \nu_{20}$ ) - $\nu_{20}$ ) (shoulder of N-H stretch monomer)
3509 (0.01)	-	-	-	monomer hot band: ( $\nu_1 + \nu_{12}$ ) - $\nu_{12}$
3497 (0.14)	3497 (0.11)	-	-	monomer hot band: ( $\nu_1 + \nu_{21}$ ) - $\nu_{21}$
3479 (0.01)	-	-	-	monomer hot band: ( $\nu_1 + 2\nu_{21}$ ) - $2\nu_{21}$
3381	3381	-	-	cyclic trimer: N-H ( $\nu_1'$ )
3322	3322	-	-	cyclic trimer: N-H ( $\nu_1''$ )
3214	3214	-	3200	dimer donor: N-H (upper Fermi) + cyclic trimer: N-H ( $\nu_1'''$ )
3206	3206	-	3195	dimer donor: N-H (shoulder)
3164	-	-	-	dimer: C-H stretch ( $\nu_2^a$ )
3159 (1)	3160	-	-	monomer: C-H stretch ( $\nu_2$ )
3153 (0.005)	-	-	-	monomer hot bands: ( $\nu_2 + \nu_{16}$ ) - $\nu_{16}$ and ( $\nu_2 + \nu_{13}$ ) - $\nu_{13}$
3151	-	-	-	dimer: C-H stretch ( $\nu_2^d$ )
3148 (0.01)	-	-	-	monomer hot band: ( $\nu_2 + \nu_{18}$ ) - $\nu_{18}$
3133	3133/3127	3114 <sup>c</sup>	-	monomer: C-H stretch ( $\nu_3$ )
3054	-	-	-	dimer donor: N-H stretch (lower Fermi)
3044	-	-	-	monomer overtone: $2\nu_5$

<sup>a</sup> NH and CH hot band intensities from spectrum in Fig. 1 and spectrum (b) in Fig. 2, respectively. The  $\nu_2/\nu_1$  band intensity ratio is 2.1 from integration of a survey spectrum.

<sup>b</sup> 3400  $\text{cm}^{-1}$  in an earlier Ar matrix study (Ref. 4).

<sup>c</sup> marked with "??" in the reference without further explanation.

Table S4: Calculated harmonic wavenumbers  $\omega$  and results of the normal mode 1D scans for the NH stretch fundamentals in the imidazole monomer, dimer, and trimer (in  $\text{cm}^{-1}$ ). Optimisations and harmonic frequency calculations have been performed using B3LYP-D3(BJ)/def2-TZVP. The normal mode 1D scans based on the B3LYP-D3(BJ)/def2-TZVP structures and normal modes are performed using the different methods listed in the table. The harmonic wavenumbers  $\omega_{\text{fit}}$  are derived from octic polynomial fits to the 1D scans. The single-mode contributions to the anharmonic shift  $\Delta_{1\text{M(d)}}$  are obtained by comparing the anharmonic wavenumber  $\tilde{\nu}_{\text{fit}}$  to the harmonic wavenumber  $\omega$ . All calculations were carried out with the Orca program package. The B3LYP functional used is the one defined in the original publication,<sup>5</sup> while the Gaussian calculations use a different exchange kernel.

method		monomer	dimer	trimer			
		$\nu_1$	$\nu_1^a$	$\nu_1^d$	$\nu_1^t$	$\nu_1''$	$\nu_1'''$
B3LYP-D3(BJ)	$\omega$	3646	3645	3303	3525	3460	3355
B3LYP-D3(BJ)/ def2-TZVP	$\omega_{\text{fit}}$	3646	3646	3302	3526	3461	3357
	$\tilde{\nu}_{\text{fit}}$	3508	3509	3092	3375	3292	3172
	$\Delta_{1\text{M(d)}}$	-138	-137	-210	-152	-169	-184
	$\omega + \Delta_{1\text{M(d)}}$	3508	3509	3093	3374	3292	3171
M06-2X/ def2-TZVP	$\omega_{\text{fit}}$	3710	3702	3401	3600	3549	3454
	$\tilde{\nu}_{\text{fit}}$	3581	3574	3172	3458	3390	3270
	$\Delta_{1\text{M(d)}}$	-129	-128	-229	-142	-159	-184
	$\omega + \Delta_{1\text{M(d)}}$	3517	3517	3074	3384	3301	3171
SCS-MP2/ def2-TZVP	$\omega_{\text{fit}}$	3668	3660	3365	3560	3503	3408
	$\tilde{\nu}_{\text{fit}}$	3536	3528	3163	3418	3346	3235
	$\Delta_{1\text{M(d)}}$	-132	-131	-202	-143	-157	-174
	$\omega + \Delta_{1\text{M(d)}}$	3514	3514	3101	3383	3303	3181
B2PLYP/ def2-QZVP	$\omega_{\text{fit}}$	3718	3714	3397	3587	3526	3444
	$\tilde{\nu}_{\text{fit}}$	3577	3574	3182	3433	3356	3257
	$\Delta_{1\text{M(d)}}$	-142	-140	-215	-154	-170	-187
	$\omega + \Delta_{1\text{M(d)}}$	3504	3505	3087	3371	3290	3168
DLPNO- CCSD(T)/ cc-pVTZ	$\omega_{\text{fit}}$	3743	3735	3523	3637	3595	3530
	$\tilde{\nu}_{\text{fit}}$	3601	3594	3312	3492	3436	3357
	$\Delta_{1\text{M(d)}}$	-142	-141	-211	-145	-159	-174
	$\omega + \Delta_{1\text{M(d)}}$	3504	3505	3092	3380	3301	3182

Table S5: Calculated harmonic wavenumbers  $\omega$  and results of the normal mode 1D scans for the NH stretch fundamentals in the imidazole monomer, dimer, and trimer (in  $\text{cm}^{-1}$ ). Optimisations and harmonic frequency calculations have been performed using SCS-MP2/def2-TZVP. The normal mode 1D scans based on the SCS-MP2/def2-TZVP structures and normal modes are performed using the different methods listed in the table. The harmonic wavenumbers  $\omega_{\text{fit}}$  are derived from octic polynomial fits to the 1D scans. The single-mode contributions to the anharmonic shift  $\Delta_{1\text{M(d)}}$  are obtained by comparing the anharmonic wavenumber  $\tilde{\nu}_{\text{fit}}$  to the harmonic wavenumber  $\omega$ . All calculations were carried out with the Orca program package. The B3LYP functional used is the one defined in the original publication,<sup>5</sup> while the Gaussian calculations use a different exchange kernel.

method		monomer	dimer		trimer		
		$\nu_1$	$\nu_1^{\text{a}}$	$\nu_1^{\text{d}}$	$\nu_1'$	$\nu_1''$	$\nu_1'''$
SCS-MP2	$\omega$	3656	3651	3350	3547	3492	3392
SCS-MP2/ def2-TZVP	$\omega_{\text{fit}}$	3656	3652	3350	3549	3495	3394
	$\tilde{\nu}_{\text{fit}}$	3525	3522	3150	3410	3343	3224
	$\Delta_{1\text{M(d)}}$	-131	-131	-201	-139	-153	-169
	$\omega + \Delta_{1\text{M(d)}}$	3525	3520	3150	3408	3340	3223
M06-2X/ def2-TZVP	$\omega_{\text{fit}}$	3698	3693	3395	3589	3537	3440
	$\tilde{\nu}_{\text{fit}}$	3570	3566	3167	3450	3385	3262
	$\Delta_{1\text{M(d)}}$	-128	-127	-228	-139	-153	-177
	$\omega + \Delta_{1\text{M(d)}}$	3528	3523	3122	3408	3340	3214
B3LYP-D3(BJ)/ def2-TZVP	$\omega_{\text{fit}}$	3635	3638	3287	3519	3457	3344
	$\tilde{\nu}_{\text{fit}}$	3498	3502	3077	3370	3293	3165
	$\Delta_{1\text{M(d)}}$	-137	-136	-210	-148	-164	-180
	$\omega + \Delta_{1\text{M(d)}}$	3519	3515	3141	3399	3329	3212
B2PLYP/ def2-QZVP	$\omega_{\text{fit}}$	3707	3707	3374	3578	3519	3429
	$\tilde{\nu}_{\text{fit}}$	3566	3567	3160	3427	3354	3247
	$\Delta_{1\text{M(d)}}$	-141	-140	-214	-151	-165	-183
	$\omega + \Delta_{1\text{M(d)}}$	3515	3511	3136	3396	3327	3209
DLPNO- CCSD(T)/ cc-pVTZ	$\omega_{\text{fit}}$	3729	3723	3492	3612	3646	3512
	$\tilde{\nu}_{\text{fit}}$	3589	3585	3287	3475	3460	3343
	$\Delta_{1\text{M(d)}}$	-140	-138	-205	-137	-186	-169
	$\omega + \Delta_{1\text{M(d)}}$	3516	3513	3145	3410	3306	3223

Table S6: Calculated harmonic wavenumbers  $\omega$  and results of the normal mode 1D scans for the NH stretch fundamentals in the imidazole monomer, dimer, and trimer (in  $\text{cm}^{-1}$ ). Optimisations and harmonic frequency calculations have been performed using B2PLYP/def2-QZVP. The normal mode 1D scans based on the B2PLYP/def2-QZVP structures and normal modes are performed using the different methods listed in the table. The harmonic wavenumbers  $\omega_{\text{fit}}$  are derived from octic polynomial fits to the 1D scans. The single-mode contributions to the anharmonic shift  $\Delta_{1\text{M(d)}}$  are obtained by comparing the anharmonic wavenumber  $\tilde{\nu}_{\text{fit}}$  to the harmonic wavenumber  $\omega$ . All calculations were carried out with the Orca program package. The B3LYP functional used is the one defined in the original publication,<sup>5</sup> while the Gaussian calculations use a different exchange kernel.

method		monomer	dimer	trimer			
		$\nu_1$	$\nu_1^{\text{a}}$	$\nu_1^{\text{d}}$	$\nu_1'$	$\nu_1''$	$\nu_1'''$
B2PLYP	$\omega$	3683	3680	3343	3559	3494	3384
B2PLYP/ def2-QZVP	$\omega_{\text{fit}}$	3684	3682	3344	3560	3494	3390
	$\tilde{\nu}_{\text{fit}}$	3545	3544	3126	3408	3326	3205
	$\Delta_{1\text{M(d)}}$	-139	-138	-218	-152	-168	-185
	$\omega + \Delta_{1\text{M(d)}}$	3544	3543	3125	3407	3326	3199
M06-2X/ def2-TZVP	$\omega_{\text{fit}}$	3675	3672	3350	3572	3517	3399
	$\tilde{\nu}_{\text{fit}}$	3549	3549	3119	3433	3360	3216
	$\Delta_{1\text{M(d)}}$	-126	-123	-231	-139	-157	-183
	$\omega + \Delta_{1\text{M(d)}}$	3557	3557	3112	3420	3337	3200
B3LYP-D3(BJ)/ def2-TZVP	$\omega_{\text{fit}}$	3612	3613	3254	3499	3429	3301
	$\tilde{\nu}_{\text{fit}}$	3477	3480	3041	3350	3263	3120
	$\Delta_{1\text{M(d)}}$	-135	-133	-212	-149	-166	-182
	$\omega + \Delta_{1\text{M(d)}}$	3548	3547	3130	3410	3328	3202
SCS-MP2/ def2-TZVP	$\omega_{\text{fit}}$	3634	3628	3320	3532	3472	3353
	$\tilde{\nu}_{\text{fit}}$	3505	3500	3115	3393	3317	3182
	$\Delta_{1\text{M(d)}}$	-130	-128	-204	-140	-155	-171
	$\omega + \Delta_{1\text{M(d)}}$	3554	3553	3138	3419	3339	3212
DLPNO- CCSD(T)/ cc-pVTZ	$\omega_{\text{fit}}$	3706	3698	3478	3612	3577	3495
	$\tilde{\nu}_{\text{fit}}$	3568	3564	3263	3469	3414	3314
	$\Delta_{1\text{M(d)}}$	-138	-134	-215	-144	-163	-181
	$\omega + \Delta_{1\text{M(d)}}$	3545	3547	3128	3415	3331	3203

Table S7: Cartesian coordinates for the imidazole monomer (M) from B3LYP/def2-TZVP geometry optimization with D3(BJ) dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -226.3188127 \cdot E_h$ )

Atom	X	Y	Z
N	-0.101 147	-1.223 180	-0.000 018
C	1.001 488	-0.515 096	-0.000 003
N	0.733 974	0.821 197	0.000 016
C	-0.634 870	0.965 589	-0.000 015
C	-1.129 080	-0.309 745	0.000 017
H	2.006 519	-0.904 856	-0.000 006
H	1.409 198	1.565 784	0.000 028
H	-1.110 701	1.929 973	-0.000 025
H	-2.160 039	-0.621 509	0.000 026

Table S8: Cartesian coordinates for the imidazole monomer (M) from B3LYP/def2-TZVP geometry optimization without dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -226.307477 E_h$ )

Atom	X	Y	Z
N	0.113 358	-1.222 470	0.000 000
C	-0.994 881	-0.524 325	0.000 001
N	-0.741 910	0.814 189	-0.000 001
C	0.624 815	0.971 522	0.000 001
C	1.130 713	-0.298 855	0.000 000
H	-1.996 337	-0.924 165	0.000 001
H	-1.425 207	1.551 684	-0.000 002
H	1.092 318	1.940 318	0.000 001
H	2.165 208	-0.599 921	-0.000 001

Table S9: Cartesian coordinates for the imidazole dimer (D) from B3LYP/def2-TZVP geometry optimization with D3(BJ) dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -452.6540828 E_h$ )

Atom	X	Y	Z
N	3.595 290	-0.457 388	-0.617 746
C	2.322 283	-0.541 256	-0.937 975
N	1.528 101	0.093 090	-0.036 883
C	2.355 669	0.616 977	0.925 250
C	3.626 465	0.267 353	0.549 281
H	1.923 623	-1.043 773	-1.804 659
H	0.506 470	0.156 938	-0.063 214
H	1.976 400	1.175 408	1.762 931
H	4.554 373	0.494 956	1.047 619
N	-1.414 828	0.117 026	-0.043 781
C	-2.087 698	-0.866 234	0.508 401
N	-3.424 700	-0.669 996	0.379 087
C	-3.610 051	0.513 829	-0.298 892
C	-2.353 200	0.985 392	-0.551 629
H	-1.663 717	-1.724 344	1.003 184
H	-4.149 367	-1.279 779	0.716 906
H	-4.587 491	0.896 796	-0.530 443
H	-2.068 137	1.888 318	-1.063 673



Table S10: Cartesian coordinates for the imidazole dimer (D) from B3LYP/def2-TZVP geometry optimization without dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -452.6284851 E_h$ )

Atom	X	Y	Z
N	3.633 568	-0.380 198	-0.661 059
C	2.359 378	-0.493 208	-0.962 854
N	1.557 899	0.042 902	-0.006 382
C	2.383 757	0.532 153	0.974 825
C	3.658 518	0.261 680	0.552 336
H	1.964 027	-0.950 577	-1.856 058
H	0.535 536	0.071 064	-0.013 155
H	2.001 449	1.015 044	1.857 226
H	4.586 454	0.492 074	1.050 043
N	-1.439 886	0.050 889	-0.006 506
C	-2.189 919	-0.916 389	0.467 990
N	-3.507 811	-0.632 567	0.312 627
C	-3.599 369	0.595 411	-0.300 891
C	-2.309 086	1.000 771	-0.489 535
H	-1.836 274	-1.826 134	0.925 129
H	-4.277 753	-1.215 065	0.594 429
H	-4.543 701	1.051 539	-0.538 627
H	-1.955 801	1.912 366	-0.940 976

Table S11: Cartesian coordinates for the cyclic imidazole trimer ( $T_{\text{cyclic}}$ ) from B3LYP/def2-TZVP geometry optimization with D3(BJ) dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -678.9984288 E_h$ )

Atom	X	Y	Z
N	2.727 846	-0.635 425	0.960 458
C	1.588 470	-1.293 720	1.046 565
N	1.304 938	-1.960 428	-0.096 566
C	2.324 288	-1.704 363	-0.980 129
C	3.200 324	-0.893 406	-0.308 496
H	0.925 633	-1.301 532	1.896 016
H	0.389 317	-2.364 823	-0.306 013
H	2.336 891	-2.114 965	-1.973 957
H	4.135 988	-0.487 989	-0.655 587
N	-1.555 089	-1.841 596	-0.413 579
C	-1.423 600	-0.532 808	-0.499 503
N	-2.545 286	0.103 662	-0.094 494
C	-3.454 657	-0.856 816	0.280 040
C	-2.826 900	-2.055 330	0.070 935
H	-0.550 222	-0.002 121	-0.838 130
H	-2.603 017	1.109 697	0.012 049
H	-4.433 232	-0.610 208	0.650 891
H	-3.209 309	-3.047 677	0.239 133
N	-0.967 455	2.639 244	0.252 538
C	-0.109 724	2.074 472	1.078 777
N	1.089 306	1.861 957	0.483 854
C	0.989 759	2.309 438	-0.810 413
C	-0.284 680	2.796 102	-0.933 304
H	-0.310 856	1.788 593	2.097 936
H	1.857 011	1.314 666	0.864 171
H	1.809 571	2.239 017	-1.502 235
H	-0.747 277	3.244 038	-1.796 576

Table S12: Cartesian coordinates for the cyclic imidazole trimer ( $T_{\text{cyclic}}$ ) from B3LYP/def2-TZVP geometry optimization without dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -678.9491016 E_h$ )

Atom	X	Y	Z
N	2.745 767	-0.609 123	0.911 817
C	1.596 722	-1.244 842	1.007 495
N	1.363 282	-2.035 980	-0.065 959
C	2.435 373	-1.894 178	-0.911 762
C	3.282 379	-1.017 714	-0.288 636
H	0.893 954	-1.160 130	1.820 280
H	0.462 022	-2.465 721	-0.271 950
H	2.499 769	-2.416 727	-1.849 787
H	4.241 952	-0.664 115	-0.628 054
N	-1.590 119	-1.928 527	-0.446 094
C	-1.486 416	-0.622 462	-0.576 236
N	-2.593 882	0.013 995	-0.132 592
C	-3.467 214	-0.947 572	0.314 905
C	-2.832 058	-2.141 776	0.107 912
H	-0.638 598	-0.089 359	-0.973 268
H	-2.665 338	1.020 490	-0.044 310
H	-4.430 406	-0.704 996	0.727 352
H	-3.192 804	-3.133 495	0.323 805
N	-1.017 202	2.681 348	0.263 170
C	-0.133 869	2.097 339	1.045 026
N	1.089 048	2.034 058	0.463 898
C	0.978 724	2.611 379	-0.776 935
C	-0.325 557	3.013 180	-0.879 511
H	-0.329 484	1.697 811	2.026 858
H	1.881 654	1.501 785	0.809 300
H	1.812 918	2.683 005	-1.451 972
H	-0.802 386	3.520 934	-1.701 474

Table S13: Cartesian coordinates for the linear imidazole trimer ( $T_{\text{linear}}$ ) from B3LYP/def2-TZVP geometry optimization with D3(BJ) dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -678.992639 E_h$ )

Atom	X	Y	Z
N	-1.175 819	0.995 056	-0.023 480
C	-0.107 693	0.227 134	0.065 864
N	1.031 306	0.950 993	-0.019 595
C	0.666 808	2.265 884	-0.173 826
C	-0.701 881	2.276 590	-0.174 096
H	-0.113 955	-0.843 067	0.191 933
H	1.990 177	0.579 222	0.016 337
H	1.393 164	3.053 525	-0.266 041
H	-1.367 421	3.117 377	-0.272 188
C	-4.626 915	-0.386 997	1.128 351
N	-3.839 589	-0.160 667	0.027 629
C	-4.499 434	-0.676 258	-1.040 553
H	-4.333 093	-0.072 784	2.114 488
H	-2.918 871	0.298 688	0.015 203
H	-4.098 909	-0.632 219	-2.040 691
N	3.711 507	-0.158 234	0.038 878
C	4.357 455	-0.644 511	-0.996 781
N	5.566 665	-1.133 538	-0.624 299
C	5.695 398	-0.945 892	0.733 264
C	4.535 948	-0.340 439	1.125 633
H	4.001 247	-0.666 375	-2.013 292
H	6.246 539	-1.558 851	-1.231 191
H	6.571 740	-1.251 511	1.275 616
H	4.245 593	-0.027 894	2.113 898
N	-5.651 372	-1.214 086	-0.698 786
C	-5.740 023	-1.037 023	0.660 913
H	-6.593 076	-1.383 719	1.220 881

Table S14: Cartesian coordinates for the linear imidazole trimer ( $T_{\text{linear}}$ ) from B3LYP/def2-TZVP geometry optimization without dispersion correction. Calculations were carried out in Gaussian 09 Rev. E.01<sup>6</sup> under the conditions mentioned in the main publication. ( $E = -678.9525142 E_h$ )

Atom	X	Y	Z
N	-1.165 564	0.872 785	-0.020 968
C	-0.078 985	0.131 208	0.054 456
N	1.043 670	0.881 071	-0.023 123
C	0.647 639	2.188 432	-0.157 125
C	-0.720 114	2.165 810	-0.153 870
H	-0.058 476	-0.940 869	0.165 084
H	2.009 714	0.532 613	0.006 631
H	1.353 714	2.995 730	-0.239 676
H	-1.403 912	2.993 852	-0.238 253
C	-4.716 840	-0.381 411	1.129 726
N	-3.922 768	-0.189 301	0.027 666
C	-4.628 498	-0.630 299	-1.044 450
H	-4.394 696	-0.112 794	2.120 767
H	-2.974 205	0.205 042	0.016 267
H	-4.234 018	-0.593 759	-2.047 641
N	3.803 259	-0.161 437	0.029 622
C	4.488 283	-0.595 441	-1.003 676
N	5.713 056	-1.036 637	-0.624 119
C	5.812 244	-0.872 563	0.737 976
C	4.620 365	-0.329 760	1.123 409
H	4.150 091	-0.612 095	-2.026 837
H	6.420 408	-1.416 800	-1.229 907
H	6.693 285	-1.148 846	1.289 016
H	4.303 259	-0.052 670	2.114 447
N	-5.813 737	-1.088 810	-0.705 221
C	-5.877 599	-0.936 237	0.657 641
H	-6.749 543	-1.231 532	1.218 586

Table S15: Comparison of the internal coordinates of the imidazole monomer as optimized by different levels of theory. Bond distances  $r$  are provided in Å, angles  $\angle$  in degrees. The CCSD(T)-F12C values are taken from Ref.<sup>7</sup>. The numbering of the atoms follows the nomenclature of the latter publication. The B3LYP and B2PLYP values were computed with the def2-TZVP basis set, as mentioned in the main manuscript.

	CCSD(T)-F12C	B3LYP	B2PLYP
$r(7\ 2)$	1.075	1.075	1.072
$r(2\ 1)$	1.369	1.368	1.367
$r(1\ 6)$	1.077	1.077	1.074
$r(1\ 3)$	1.380	1.375	1.374
$r(3\ 5)$	1.313	1.310	1.311
$r(5\ 8)$	1.077	1.078	1.074
$r(5\ 4)$	1.362	1.363	1.360
$r(4\ 9)$	1.003	1.005	1.003
$r(4\ 2)$	1.377	1.376	1.374
$\angle(4\ 2\ 1)$	105.1	105.2	105.2
$\angle(2\ 1\ 3)$	110.7	110.4	110.5
$\angle(1\ 3\ 5)$	105.1	105.7	105.5
$\angle(3\ 5\ 4)$	111.9	111.4	111.5
$\angle(5\ 4\ 2)$	107.2	107.3	107.4
$\angle(4\ 2\ 7)$	122.3	122.3	122.3
$\angle(7\ 2\ 1)$	132.6	132.6	132.6
$\angle(2\ 1\ 6)$	127.9	128.0	128.0
$\angle(6\ 1\ 3)$	121.4	121.5	121.5
$\angle(3\ 5\ 8)$	125.8	126.1	126.0
$\angle(8\ 5\ 4)$	122.3	122.5	122.5
$\angle(5\ 4\ 9)$	126.3	126.5	126.4

Table S16: Calculated corrections for the vibrational wavenumbers (in  $\text{cm}^{-1}$ ) for the NH stretch fundamentals in the imidazole dimer and trimer in dependence of excluded off-diagonal terms. These values give a rough estimate of the dependence of the latter on the computed low frequency intermolecular modes (which are hard to calculate on the basis of VPT2 theory). The ‘full’ results are those computed as detailed in the main manuscript and featured in Table 4 at the B3LYP-D3(BJ)/def2-TZVP level of theory. The ‘no inter  $x_{ij}$ ’ values are computed excluding the off-diagonal coupling constants resulting from the intermolecular modes. The ‘no inter’ values result from the removal of all intermolecular off-diagonal terms. The latter affect also the diagonal correction as shown in Eq. (3). The different terms contributing to the anharmonic shift are discussed in detail in the text. The main effect of the neglect of the intermolecular modes is, as expected, on the off-diagonal correction. The corrections are otherwise stable, particularly the Fermi  $\Delta_{\text{F}}$  term. The main differences are observed in the trimer case, whereby the different contributions accumulate resulting in large deviations.

approach	$\Delta_{\text{IM(d)}}$	$\Delta_{\text{MM(d)}}$	$\Delta_{\text{off}}$	$\Delta_{\text{F}}$
dimer $\nu_1^{\text{a}}$				
full	-138	-1	-19	
no inter $x_{ij}$	-138	-1	-24	
no inter	-138	-1	-25	
dimer $\nu_1^{\text{d}}$				
full	-201	-37	+51	+31
no inter $x_{ij}$	-201	-37	+36	+35
no inter	-201	-13	+19	+34
trimer $\nu_1^{\text{'}}$				
full	-152	-32	-6	
no inter $x_{ij}$	-152	-32	-11	
no inter	-152	-11	-21	
trimer $\nu_1^{\text{''}}$				
full	-166	-36	+12	
no inter $x_{ij}$	-166	-36	+1	
no inter	-166	-16	-7	
trimer $\nu_1^{\text{'''}}$				
full	-180	-86	+59	
no inter $x_{ij}$	-180	-86	+40	
no inter	-180	-34	+5	

## References

- [1] J. Zischang, *PhD thesis*, Georg-August Universität, Göttingen, 2014.
- [2] M. K. Van Bael, J. Smets, K. Schoone, L. Houben, W. McCarthy, L. Adamowicz, M. J. Nowak and G. Maes, *J. Phys. Chem. A*, 1997, **101**, 2397–2413.
- [3] M. Y. Choi and R. E. Miller, *J. Phys. Chem. A*, 2006, **110**, 9344–9351.
- [4] S. T. King, *J. Phys. Chem.*, 1970, **74**, 2133–2138.
- [5] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- [6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Montgomery, J. A., Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, 2009.
- [7] J. C. Mullaney, D. P. Zaleski, D. P. Tew, N. R. Walker and A. C. Legon, *ChemPhysChem*, 2016, **17**, 1154–1158.