Supplementary Information

Accurate Equilibrium Structure of 3-Aminophthalimide from Gas Electron Diffraction and Coupled-Cluster Computations and Diverse Structural Effects due to Electron Density Transfer

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Table S1. Relative intensities of ions in mass spectrum of the vapor over solid 3-APhI

Ions [a]	m/e, u [a]	I_{rel}, %
$C_6H_3NH(C=O)_2NH_2^+$	162	85
$C_6H_4NH(C=O)^+$	119	12
$C_6H_3NH(C=O)^+$	118	25
$C_6H_2NH(C=O)^+$	117	8
$C_6H_3NH_2^+$	91	100
$C_6H_2NH_2^+$	90	10
$C_5H_5^+$	65	23
$C_5H_4^+$	64	27
$C_5H_3^+$	63	31
$C_5H_2^+$	62	16
$C_4H_4^+$	52	15

[a] Ions with relative intensity higher than 5%.

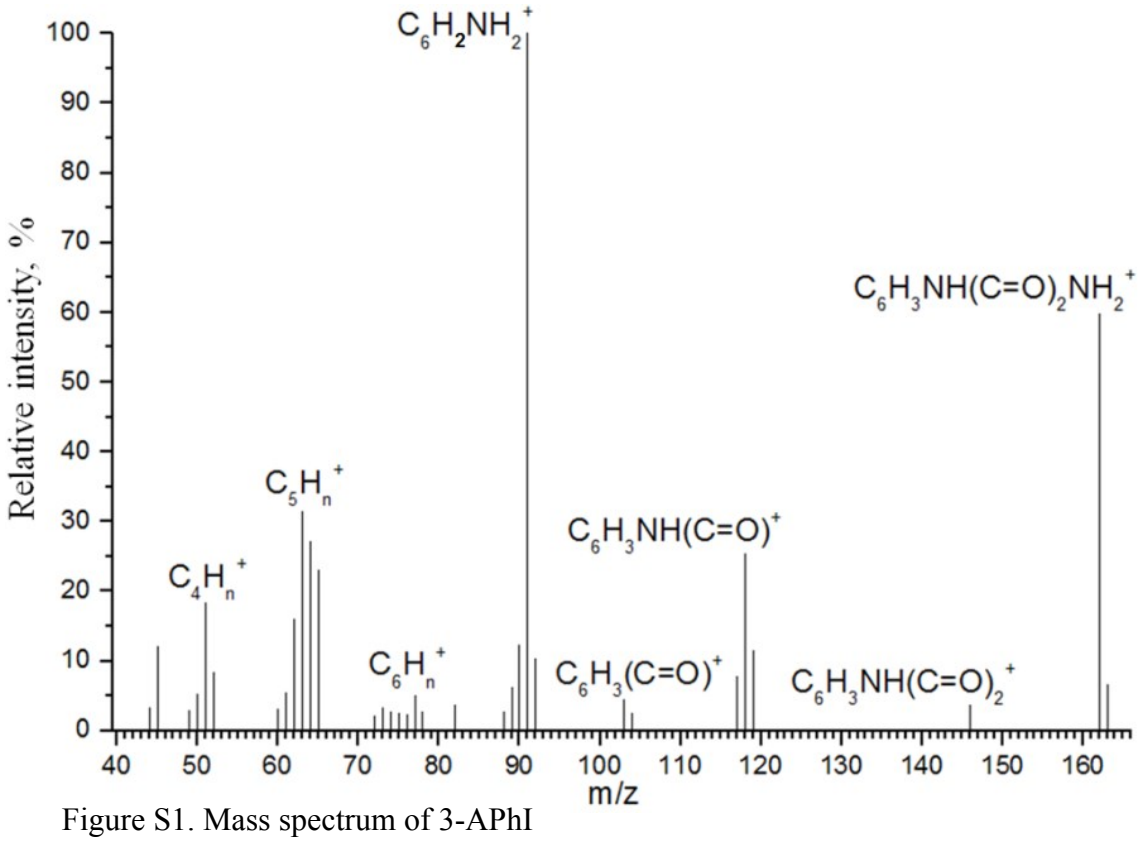

Figure S1. Mass spectrum of 3-APhI

Table S2. Experimental intensities $I(s)$ of 3-aminophthalimide (3-APhI) with background $G(s)$.

a) Long nozzle-to-film distance (L = 598 mm)

s, Å^{-1}	$I(s)$	$G(s)$
1.2	2.78913	2.17047
1.3	2.37112	1.9168
1.4	1.97594	1.69815
1.5	1.68626	1.52121
1.6	1.47316	1.37035
1.7	1.28837	1.25083
1.8	1.13465	1.15115
1.9	1.00792	1.06581
2.0	0.90261	0.99112
2.1	0.81521	0.92742
2.2	0.74644	0.87295
2.3	0.69266	0.82395
2.4	0.65493	0.78032
2.5	0.63157	0.74361
2.6	0.6137	0.70981
2.7	0.6047	0.68342
2.8	0.59832	0.66141
2.9	0.59332	0.64423
3.0	0.59054	0.63053
3.1	0.58326	0.61998
3.2	0.57126	0.61073
3.3	0.55347	0.60304
3.4	0.53458	0.59573
3.5	0.51124	0.58947
3.6	0.48767	0.58396
3.7	0.46999	0.57931
3.8	0.45357	0.57473
3.9	0.44115	0.57064
4.0	0.43156	0.56648
4.1	0.42424	0.56256
4.2	0.42046	0.55876
4.3	0.41889	0.55501
4.4	0.41957	0.55115
4.5	0.42318	0.54736
4.6	0.42833	0.54352
4.7	0.43886	0.5397
4.8	0.45445	0.53598
4.9	0.47404	0.53224
5.0	0.49965	0.52867
5.1	0.53159	0.52517

5.2	0.56523	0.52151
5.3	0.5988	0.51803
5.4	0.62983	0.51444
5.5	0.65621	0.51077
5.6	0.67424	0.50718
5.7	0.68245	0.50343
5.8	0.6805	0.49966
5.9	0.66941	0.4958
6.0	0.64936	0.49199
6.1	0.6244	0.48825
6.2	0.5933	0.48458
6.3	0.56227	0.48082
6.4	0.53352	0.47725
6.5	0.50535	0.4734
6.6	0.48045	0.46966
6.7	0.46027	0.46607
6.8	0.44383	0.4624
6.9	0.43154	0.45873
7.0	0.4204	0.45526
7.1	0.41194	0.45177
7.2	0.40291	0.44823
7.3	0.3965	0.44471
7.4	0.38953	0.44133
7.5	0.38384	0.43798
7.6	0.37898	0.4346
7.7	0.37498	0.43122
7.8	0.37306	0.42798
7.9	0.37306	0.4248
8.0	0.37543	0.4217
8.1	0.37844	0.41867
8.2	0.38455	0.41554
8.3	0.39146	0.41253
8.4	0.39887	0.40955
8.5	0.40579	0.40664
8.6	0.41011	0.40368
8.7	0.41307	0.40086
8.8	0.41289	0.39817
8.9	0.4106	0.39543
9.0	0.40611	0.39283
9.1	0.4008	0.39032
9.2	0.39447	0.38787
9.3	0.38897	0.38549
9.4	0.38337	0.38321
9.5	0.37877	0.38101
9.6	0.37484	0.37885
9.7	0.37192	0.37668

9.8	0.3708	0.37459
9.9	0.36925	0.37245
10.0	0.36759	0.37041
10.1	0.36795	0.36845
10.2	0.36894	0.36656
10.3	0.37066	0.36467
10.4	0.37219	0.36277
10.5	0.37521	0.3609
10.6	0.3784	0.35903
10.7	0.38082	0.35714
10.8	0.38198	0.35531
10.9	0.38103	0.35342
11.0	0.3788	0.35163
11.1	0.37513	0.34983
11.2	0.369	0.34813
11.3	0.3619	0.34641
11.4	0.35426	0.34475
11.5	0.34642	0.34309
11.6	0.33805	0.34149
11.7	0.33173	0.33996
11.8	0.32592	0.33843
11.9	0.32152	0.33696
12.0	0.31844	0.33551
12.1	0.31578	0.33414
12.2	0.31366	0.33279
12.3	0.31182	0.33152
12.4	0.31062	0.33025
12.5	0.30918	0.32904
12.6	0.30815	0.32787
12.7	0.30744	0.32673
12.8	0.30769	0.32566
12.9	0.3084	0.32457
13.0	0.31001	0.32349
13.1	0.31223	0.32241
13.2	0.31547	0.32137
13.3	0.31897	0.32035
13.4	0.32279	0.3193
13.5	0.32639	0.31829
13.6	0.32917	0.3173
13.7	0.33081	0.31636
13.8	0.33167	0.31545
13.9	0.33146	0.31458
14.0	0.33032	0.31373
14.1	0.32849	0.31295
14.2	0.32645	0.31224
14.3	0.32423	0.3116

14.4	0.32215	0.31102
14.5	0.32036	0.31057

b) Short nozzle-to-film distance (L = 338 mm)

s, Å^{-1}	$I(s)$	$G(s)$
3.2	2.85443	3.01377
3.3	2.64278	2.85994
3.4	2.46073	2.73339
3.5	2.29126	2.61684
3.6	2.13789	2.50694
3.7	2.00463	2.40222
3.8	1.87387	2.3015
3.9	1.76731	2.20627
4.0	1.66814	2.11623
4.1	1.58679	2.02649
4.2	1.50829	1.94539
4.3	1.44405	1.86477
4.4	1.39249	1.78911
4.5	1.36014	1.71663
4.6	1.33176	1.64622
4.7	1.31076	1.58092
4.8	1.30002	1.51892
4.9	1.30656	1.45997
5.0	1.32815	1.40575
5.1	1.36072	1.35254
5.2	1.39805	1.30466
5.3	1.43339	1.2599
5.4	1.46226	1.21859
5.5	1.47694	1.17878
5.6	1.47794	1.1428
5.7	1.45778	1.11029
5.8	1.42322	1.08029
5.9	1.37832	1.05136
6.0	1.3137	1.02453
6.1	1.24016	0.9984
6.2	1.16787	0.97286
6.3	1.08961	0.94913
6.4	1.02241	0.92613
6.5	0.95942	0.90364
6.6	0.90191	0.88233
6.7	0.85344	0.86279
6.8	0.81072	0.84263
6.9	0.77701	0.82406
7.0	0.74816	0.80592
7.1	0.72333	0.78907
7.2	0.69945	0.77227

7.3	0.67895	0.75653
7.4	0.6625	0.7418
7.5	0.64679	0.72692
7.6	0.63121	0.71351
7.7	0.61787	0.7006
7.8	0.60812	0.68821
7.9	0.60147	0.67636
8.0	0.59894	0.66522
8.1	0.59917	0.65482
8.2	0.6021	0.64472
8.3	0.6063	0.63533
8.4	0.61187	0.62617
8.5	0.61552	0.61733
8.6	0.61754	0.60883
8.7	0.61659	0.60033
8.8	0.61395	0.59302
8.9	0.60873	0.58538
9.0	0.59956	0.57817
9.1	0.58873	0.57145
9.2	0.57674	0.56489
9.3	0.56489	0.55867
9.4	0.5548	0.55253
9.5	0.54644	0.54685
9.6	0.53747	0.54104
9.7	0.53007	0.5356
9.8	0.5237	0.53013
9.9	0.5200	0.52478
10.0	0.51508	0.51953
10.1	0.51131	0.51445
10.2	0.50955	0.50977
10.3	0.51015	0.50517
10.4	0.5111	0.50075
10.5	0.51223	0.49636
10.6	0.51326	0.49188
10.7	0.51452	0.48776
10.8	0.51455	0.48345
10.9	0.51324	0.47926
11.0	0.50909	0.47521
11.1	0.50221	0.47134
11.2	0.49405	0.46735
11.3	0.48314	0.46346
11.4	0.47072	0.45959
11.5	0.45945	0.45561
11.6	0.4489	0.45191
11.7	0.43901	0.44832
11.8	0.42898	0.44491

11.9	0.42216	0.44155
12.0	0.41776	0.43823
12.1	0.41287	0.43508
12.2	0.40946	0.43218
12.3	0.4061	0.4293
12.4	0.40291	0.42649
12.5	0.4012	0.4238
12.6	0.39836	0.4214
12.7	0.39697	0.41905
12.8	0.39549	0.41671
12.9	0.39484	0.41441
13.0	0.39608	0.41234
13.1	0.39776	0.41032
13.2	0.400	0.40826
13.3	0.40328	0.40636
13.4	0.40727	0.40446
13.5	0.41029	0.40257
13.6	0.41323	0.40073
13.7	0.41507	0.39892
13.8	0.41622	0.39717
13.9	0.41569	0.3954
14.0	0.41373	0.39366
14.1	0.41067	0.39196
14.2	0.40781	0.39021
14.3	0.40373	0.38842
14.4	0.39956	0.3867
14.5	0.39565	0.38495
14.6	0.39148	0.38316
14.7	0.38787	0.38146
14.8	0.38354	0.3798
14.9	0.37947	0.37815
15.0	0.37676	0.37653
15.1	0.37291	0.37493
15.2	0.37056	0.37339
15.3	0.36719	0.37182
15.4	0.36426	0.37035
15.5	0.3622	0.36883
15.6	0.36075	0.36733
15.7	0.3591	0.36592
15.8	0.35874	0.36456
15.9	0.35813	0.36322
16.0	0.35734	0.36199
16.1	0.35727	0.36073
16.2	0.35716	0.35944
16.3	0.35674	0.35825
16.4	0.3558	0.35715

16.5	0.35506	0.35607
16.6	0.3539	0.35495
16.7	0.35216	0.35392
16.8	0.35128	0.35293
16.9	0.34866	0.35195
17.0	0.34658	0.35101
17.1	0.34528	0.35007
17.2	0.34346	0.34915
17.3	0.34124	0.34823
17.4	0.34034	0.34733
17.5	0.33909	0.34644
17.6	0.33827	0.34558
17.7	0.33865	0.3448
17.8	0.33927	0.34402
17.9	0.34048	0.34323
18.0	0.34124	0.34249
18.1	0.34262	0.34174
18.2	0.34331	0.34104
18.3	0.345	0.34037
18.4	0.34683	0.33972
18.5	0.3469	0.33907
18.6	0.34722	0.33847
18.7	0.34682	0.33785
18.8	0.34647	0.33726
18.9	0.34571	0.33666
19.0	0.34515	0.33608
19.1	0.34359	0.33551
19.2	0.34231	0.33494
19.3	0.3413	0.33437
19.4	0.34011	0.33381
19.5	0.33792	0.33326
19.6	0.33606	0.33273
19.7	0.33347	0.3322
19.8	0.3321	0.33167
19.9	0.32962	0.33117
20.0	0.32819	0.33067
20.1	0.32652	0.33016
20.2	0.32445	0.32968
20.3	0.32221	0.32924
20.4	0.32143	0.32878
20.5	0.32098	0.32835
20.6	0.31998	0.32789
20.7	0.31978	0.32748
20.8	0.32001	0.32705
20.9	0.32042	0.32662
21.0	0.32042	0.32622

21.1	0.32057	0.32583
21.2	0.32084	0.32543
21.3	0.32111	0.32503
21.4	0.32133	0.32465
21.5	0.32154	0.32428
21.6	0.32205	0.3239
21.7	0.32276	0.32352
21.8	0.32314	0.32312
21.9	0.32395	0.32275
22.0	0.32447	0.32238
22.1	0.32482	0.32201
22.2	0.3253	0.32164
22.3	0.32519	0.32127
22.4	0.32504	0.32092
22.5	0.32453	0.32055
22.6	0.32408	0.32019
22.7	0.32293	0.31985
22.8	0.32212	0.3195
22.9	0.32125	0.31915
23.0	0.32079	0.31882
23.1	0.32098	0.31849
23.2	0.32074	0.31818
23.3	0.32084	0.31786
23.4	0.32046	0.31758
23.5	0.32025	0.31729
23.6	0.32051	0.31702
23.7	0.3203	0.31675
23.8	0.31942	0.3165
23.9	0.31938	0.31625
24.0	0.31847	0.31603
24.1	0.31798	0.3158
24.2	0.31667	0.31559
24.3	0.31603	0.3154
24.4	0.31571	0.31521
24.5	0.31493	0.31504
24.6	0.31348	0.31486
24.7	0.31294	0.31471
24.8	0.31195	0.31456
24.9	0.31115	0.31442
25.0	0.31023	0.31427
25.1	0.30938	0.31415
25.2	0.3091	0.31403
25.3	0.30886	0.31391
25.4	0.30914	0.31381
25.5	0.30969	0.31372
25.6	0.30984	0.31363

25.7	0.30968	0.31356
25.8	0.30961	0.31349
25.9	0.31032	0.31343
26.0	0.31068	0.31338
26.1	0.3107	0.31333
26.2	0.311	0.31329
26.3	0.31121	0.31325
26.4	0.31125	0.31323
26.5	0.31181	0.31321
26.6	0.31268	0.3132
26.7	0.31396	0.3132
26.8	0.31435	0.31321
26.9	0.31532	0.31322
27.0	0.3158	0.31325
27.1	0.31698	0.31329
27.2	0.31755	0.31335
27.3	0.31772	0.31341
27.4	0.31782	0.31349
27.5	0.3181	0.31359
27.6	0.31849	0.3137
27.7	0.31883	0.31383
27.8	0.31871	0.31397
27.9	0.31843	0.31409
28.0	0.3184	0.31425
28.1	0.31778	0.31441
28.2	0.31731	0.31459
28.3	0.31723	0.31476
28.4	0.3169	0.31494
28.5	0.31647	0.31514
28.6	0.31651	0.31534
28.7	0.31646	0.31557
28.8	0.31602	0.31577
28.9	0.31601	0.316
29.0	0.31597	0.31622
29.1	0.31573	0.31645

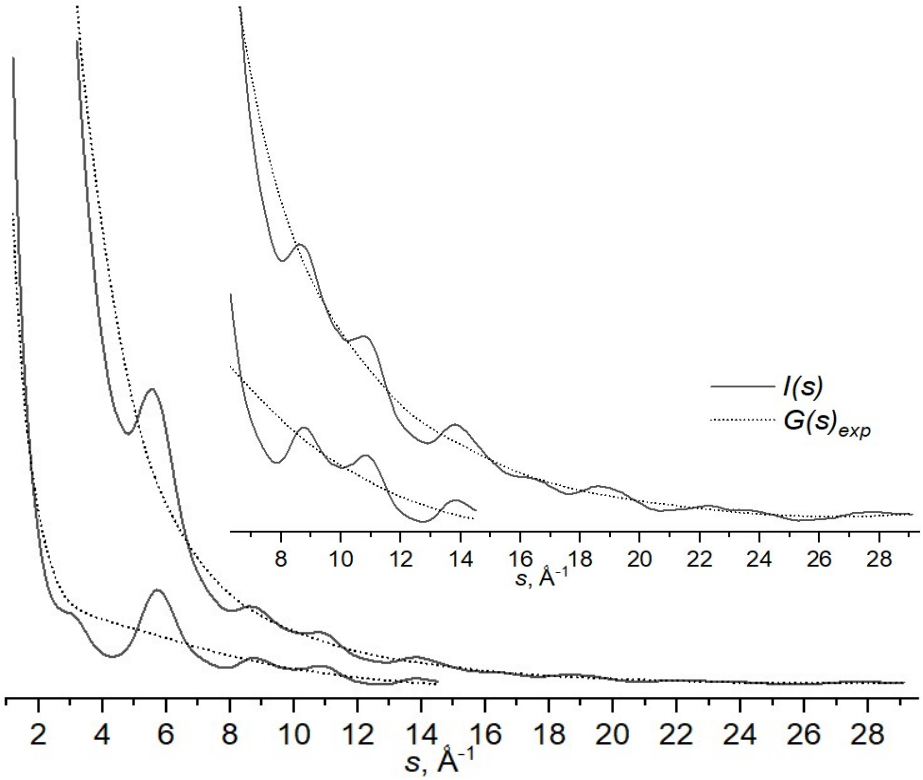

Figure S2. Experimental intensity curves $I_{tot}(s)$ (solid lines) for 3-APhI with background *G(s)* (dot lines) at the long (below) and short (above) nozzle-to film distances

Table S3. Conditions of the synchronous GED/MS experiments

Camera distance, mm	338	598
Electron beam current, μA	1.39	0.61
Effusion cell temperature, K	413(5)	414(5)
Accelerating voltage, kV	84	84
Ionizing voltage, V	50	50
Exposure time, s	90	90
Residual pressure in diffraction chamber, Torr	2.2×10^{-6}	2.5×10^{-6}
Range of scattering variables, s_{min}–s_{max}, Å^{-1}	3.2–29.1	1.2–14.5

Table S4. Geometrical parameters of 3-APhI computed at different levels of theory (bond lengths in Å, angles in degrees)

Parameters	CCSD(T)/cc-pVTZ	MP2_ae/cc-pwCVTZ	MP2/cc-pwCVTZ	MP2/cc-pVQZ	MP2/cc-pVTZ	B3LYP/cc-pVTZ	B2PLYP/cc-pVTZ
r(C4–C3a)	1.3960	1.3898	1.3926	1.3922	1.3941	1.3970	1.3956
r(C3a–C7a)	1.3971	1.3888	1.3917	1.3916	1.3932	1.3937	1.3935
r(C7a–C7)	1.3828	1.3781	1.3810	1.3805	1.3827	1.3766	1.3781
r(C7–C6)	1.4076	1.3959	1.3987	1.3983	1.4003	1.4020	1.4024
r(C6–C5)	1.3944	1.3886	1.3916	1.3910	1.3933	1.3852	1.3879
r(C3–C3a)	1.4791	1.4704	1.4736	1.4724	1.4746	1.4707	1.4711
r(C1–C7a)	1.4981	1.4846	1.4877	1.4873	1.4886	1.4955	1.4933
r(N2–C3)	1.3969	1.3888	1.3914	1.3902	1.3925	1.3969	1.3954
r(N2–H2)	1.0070	1.0062	1.0071	1.0068	1.0076	1.0070	1.0064
r(O1=C1)	1.2091	1.2084	1.2103	1.2094	1.2117	1.2057	1.2084
r(O3=C3)	1.2170	1.2154	1.2172	1.2163	1.2186	1.2150	1.2171
r(C7–H7)	1.0813	1.0788	1.0801	1.0797	1.0802	1.0798	1.0789
*r*C6–H6)	1.0832	1.0802	1.0815	1.0810	1.0816	1.0820	1.0808
r(C5–H5)	1.0842	1.0815	1.0829	1.0824	1.0830	1.0828	1.0819
r(N4–C4)	1.3787	1.3684	1.3719	1.3692	1.3731	1.3630	1.3668
r(N4–H9)	1.0062	1.0033	1.0045	1.0036	1.0050	1.0033	1.0032
r(N4–H8)	1.0101	1.0074	1.0086	1.0080	1.0091	1.0077	1.0075
∠(C4–C3a–C7a)	122.32	122.48	122.47	122.46	122.47	122.11	122.21
∠(C3a–C7a–C7)	122.18	121.97	121.96	121.97	121.95	122.15	122.13
∠(C6–C7–C7a)	116.19	116.38	116.38	116.37	116.39	116.42	116.35
∠(C5–C6–C7)	122.09	121.91	121.91	121.95	121.91	122.15	122.12
∠(C3–C3a–C4)	128.70	128.62	128.63	128.66	128.63	128.82	128.74
∠(C1–C7a–C3a)	107.78	107.96	107.96	107.89	107.96	107.80	107.75
∠(N2–C3–C3a)	105.24	105.25	105.23	105.30	105.22	105.32	105.29
∠(H2–N2–C3)	123.54	123.61	123.59	123.63	123.59	123.60	123.65
∠(O1=C1–C7a)	129.36	129.44	129.47	129.47	129.48	129.51	129.59
∠(O3=C3–C3a)	128.77	128.59	128.61	128.54	128.62	128.95	128.89

∠(H7–C7–C7a)	121.70	121.46	121.47	121.50	121.47	121.65	121.64
∠(H6–C6–C7)	119.43	119.62	119.62	119.60	119.63	119.33	119.40
∠(H5–C5–C6)	119.52	119.30	119.31	119.31	119.30	119.54	119.50
∠(N4–C4–C3a)	121.42	121.40	121.41	121.37	121.39	121.43	121.39
∠(H9–N4–C4)	116.29	117.14	116.83	117.55	116.84	119.55	118.42
∠(H8–N4–C4)	114.70	115.44	115.16	115.86	115.14	117.71	116.66
τ(C4C3aC7aC7)	-0.33	-0.29	-0.29	-0.34	-0.34	-0.28	-0.24
τ(C3aC7aC7C6)	-0.19	-0.19	-0.20	-0.15	-0.19	-0.13	-0.14
τ(C7aC7C6C5)	0.43	0.41	0.42	0.39	0.44	0.27	0.29
τ(C3C3aC4C5)	-177.84	-177.97	-177.89	-178.12	-177.97	-178.55	-178.57
τ(C1C7aC3aC4)	-179.53	-179.52	-179.48	-179.58	-179.56	-179.72	-179.80
τ(N2C3C3aC4)	179.61	179.60	179.57	179.66	179.66	179.73	179.66
τ(H2N2C3C3a)	-179.51	-179.57	-179.52	-179.58	-179.54	-179.75	-179.77
τ(O1C1C7aC3a)	-179.88	-179.89	-179.90	-179.92	-179.90	-179.93	-179.83
τ(O3C3C3aC4)	0.27	0.16	0.16	0.22	0.25	0.16	0.14
τ(H7C7C7aC3a)	-179.86	-179.88	-179.88	-179.87	-179.87	-179.89	-179.56
τ(H6C6C7C7a)	-179.75	-179.75	-179.74	-179.76	-179.74	-179.79	-179.66
τ(H5C5C6C7)	179.38	179.45	179.43	179.48	179.41	179.65	179.40
τ(N4C4C3aC7a)	-176.30	-176.52	-176.39	-176.70	-176.36	-177.72	-177.24
τ(H9N4C4C3a)	-155.43	-157.85	-157.01	-158.82	-156.94	-165.35	-164.86
τ(H8N4C4C3a)	-17.03	-15.96	-16.53	-15.14	-16.44	-10.56	-11.23

Table S5. Calculated harmonic vibrational frequencies (in cm^{-1}) of 3-APhI molecule in comparison with experimental IR spectrum measured in the range 0-3800 cm^{-1} for the solid sample.

N°	Exp. (IR)	B3LYP/ cc-pVTZ [a]	MP2/ cc-pVTZ [a]	Approximate description of vibrational modes[b]
1		111(1)	110(1)	twistL(N_2-H)
2		151(2)	175(3)	fold(C_{3a}-C_{7a})
3		180(8)	146(1)	oop(N_2), fold(C_{3a}-C_{7a})
4		215(3)	212(1)	φ($C_4C_{3a}C_3$) , φ($C_7C_{7a}C_1$), φ(HN_4H)
5		239(4)	237(5)	fold(C_5…C_{3a})
6		295(189)	402(129)	oop(C_4-N_4), φ(CN_4H), inv(NH_2)
7	349	333(21)	330(10)	φ($C_{7a}C_1O_1$), φ($N_2C_1O_1$), φ(CCN_4), r(C_{7a}-C_1)
8	409	394(1)	386(9)	φ($C_{3a}C_4N_4$), φ($C_{3a}C_3O_3$)
9		471(2)	459(1)	oop(C_{3a}-C_{7a}, C_6-C_5) twistL(N_2-H)
10	499	499(6)	493(8)	φ($C_5C_4C_{3a}$), φ($C_5C_4N_4$), def(Bz+Py),
11		532(41)	574(115)	tors(C_4-N_4)
12	550	547(92)	539(50)	oop(H_2)
13		554(10)	548(1)	ip(C_4, N-H_2), bend(Bz+Py)
14		568(1)	530(134)	oop(C_4, C_{7a}, H_2), tors(C_4-N_4)
15	643	645(9)	642(5)	φ(CN_2C), φCCN_2)
16	663	666(28)	663(17)	φ(CCO_3), φ(NCO_3)
17	682	691(4)	687(6)	φ(CCO_1), φ(NCO_1)
18	688	697(5)	673(3)	oop(C_4, C_6, C_3), bend(Bz+Py)
19	744	766(51)	754(41)	oop(C_7, C_6, C_1), bend(Bz+Py)
20	782	800(3)	804(1)	φ($C_7C_6C_5$), r(C_{3a}-C_3)
21	788	809(1)	786(2)	oop(C_6, C_5, C_3, C_1)
22	818	843(10)	808(20)	oop(C-H, C=O)
23	894	909(~0)	903(~0)	oop(C_7, C_5)
24	955	971(4)	974(1)	r(C-N_4), r(C_4-C_5), φ($C_{7a}C_7C_6$)
25	1029	996(~0)	964(~0)	oop(C-H), bend(Bz)
26		1041(70)	1048(21)	r(C-C)$_{Bz,}$ r(C-C)$_{Py}$
27	1055	1050(48)	1066(93)	r(C-N_2), r(C-C)$_{Bz}$
28		1119(13)	1137(21)	φ(CN_4H), φ(CCH_5)
29	1156	1177(23)	1192(4)	φ(CCH_6), φ(CCH_7)
30	1181	1195(7)	1184(13)	φ(CCH_7), r(C-N_2)
31		1293(5)	1298(3)	φ(CCH), def(Py+Pz)
32		1319(327)	1360(296)	def(Py+Pz)
33	1314	1340(11)	1333(32)	φ(CCH_2), r(C-N_2)
34		1362(25)	1353(49)	r(C-N_4), φ(CCH_5)
35	1422	1420(25)	1516(9)	r(C-C)$_{Py}$, r(C-C)$_{Bz}$
36	1484	1486(3)	1483(10)	r(C_{3a}-C_{7a}), φ(CCH_7)
37	1593	1520(48)	1528(54)	r(C_4-N_4), r(C_4-C_5), r(C_{7a}-C_7), φ(CCH)
38	1636	1623(58)	1633(71)	φ(HN_4H), φ(CN_4H)
39	1721	1647(23)	1658(2)	r(C_{7a}-C_7), r(C_4-C_{3a}), r(C_5-C_4), φ(HN_4H)
40	1732	1671(234)	1691(172)	r(C_4-C_{3a}), r(C_4-N_4), φ(HN_4H)
41	1748	1777(630)	1792(570)	r(C_3=O_3), r(C_1=O_1)

42		1822(252)	1818(144)	r(C_3=O_3), r(C_1=O_1)
43	2722	3164(7)	3203(5)	r(C-H_6), r(C-H_7)
44		3182(13)	3223(7)	r(C-H)
45		3209(2)	3246(2)	r(C-H_6), r(C-H_5)
46	3209	3565(66)	3572(60)	r(N_4-H_8), r(N_4-H_9)
47	3360	3635(91)	3657(113)	r(N_2-H_2)
48	3489	3701(50)	3714(50)	r(N_4-H_9), r(N_4-H_8)

[a] Calculated band intensities (in km mol^{-1}) are given in parentheses.

[b] Approximate description of vibrational modes is carried out according to potential energy distribution (PED). First coordinate has the largest contribution to the potential energy; coordinates contributed by less than 7% are omitted. Notations of coordinates: r and φ are changes of the bond lengths and angles, respectively; def (Bz) is planar deformation of the benzene ring; bend (Bz) is out-of-plane deformation of benzene ring; oop – out-of-plane coordinate of atom or bond; ip – in-plane coordinate of atom or bond; twistL - twisting around the axis indicated in parentheses; fold - folding along the bond given in parentheses; tors - torsion around the bond given in parentheses; inv(NH_2) – inversion of amino group. Previous measurements of experimental IR spectra of solid 3-APhI (Savelyev, D.S., Islyaikin, M.K., Girichev, G.V., Izv. Vys. Uch. Zav., Khim. Khim. Tekhnol. 2016, **59**(3), 35-42) were carried out with lower resolution and, therefore, they are re-investigated in the present work.

Table S6. Complete equilibrium molecular structures of 3-APhI (bond lengths in Å, bond angles and dihedral angles in degrees) derived from GED data (r_e^{se}) and coupled-cluster computations (r_e^{BO})

Parameters	r_{h1}^{se} [a,b]	r_e^{se} [a,c]	r_e^{se} [a,d]	r_e^{BO} [e]
r(C–C) [f]	1.403_2	1.393_5	1.393_5	1.393_8
r(C3a–C7a)	1.401(3) [1]	1.392(3)	1.392(3) [1]	1.392_4
r(C4–C3a)	1.400(3) [1]	1.391(3)	1.391(3) [1]	1.391_3
r(C5–C4)	1.419(3) [1]	1.410(3)	1.410(3) [1]	1.409_6
r(C6–C5)	1.398(3) [1]	1.389(3)	1.389(3) [1]	1.388_9
r(C7–C6)	1.412(3) [1]	1.403(3)	1.403(3) [1]	1.402_9
r(C7a–C7)	1.387(3) [1]	1.378(3)	1.378(3) [1]	1.377_6
r(N2–C1)	1.401(3) [2]	1.398(3) [2]	1.397(3) [2]	1.397_7
r(N2–C3)	1.395(3) [2]	1.392(3) [2]	1.391(3) [2]	1.392_1
r(N4–C4)	1.377(3) [3]	1.375(3) [3]	1.370(3) [3]	1.371_4
r(C1–C7a)	1.500(5) [4]	1.496(5) [4]	1.492(5) [4]	1.493_9
r(C3–C3a)	1.480(5) [4]	1.476(5) [4]	1.472(5) [4]	1.473_7
r(O1=C1)	1.205(3) [5]	1.203(3) [5]	1.205(3) [5]	1.204_9
r(C3=O3)	1.213(3) [5]	1.211(3) [5]	1.213(3) [5]	1.212_9
r(N2–H2)	1.005 [g]	1.005 [g]	1.005 [g]	1.005_3
r(N4–H8)	1.064(62) [6]	1.060(60) [6]	1.063(60) [6]	1.007_8

r(N4–H9)	1.060(62) [6]	1.056(60) [6]	1.059(60) [6]	1.003_{5}
r(C5–H5)	1.082 [g]	1.082 [g]	1.082 [g]	1.082_{4}
r(C6–H6)	1.081 [g]	1.081 [g]	1.081 [g]	1.081_{3}
r(C7–H7)	1.080 [g]	1.080 [g]	1.080 [g]	1.079_{5}
∠(C3–N2–C1)	113.46(21) [7]	112.80(18) [7]	112.82(17) [7]	112.9_{9}
∠(C7a–C1–N2)	105.22(22) [8]	105.51(18) [8]	105.38(19) [8]	104.9_{9}
∠(C3a–C3–N2)	104.62(22) [h]	105.14(18) [h]	105.25(21) [h]	105.3_{2}
∠(O1=C1–N2)	125.99(31) [9]	125.45(21) [9]	125.50(29) [9]	125.6_{9}
∠(O3=C3–N2)	126.29(31) [9]	125.75(21) [9]	125.80(29) [9]	125.9_{9}
∠(C4–C3a–C3)	129.21(49) [10]	128.65(33) [10]	128.62(46) [10]	128.7_{2}
∠(C7–C7a–C1)	130.38(52) [11]	130.11(40) [11]	130.16(50) [11]	130.0_{7}
∠(C4–C3a–C7a)	121.13(74) [h]	121.77(39) [h]	122.08(46) [h]	122.2_{8}
∠(C5–C4–C3a)	116.33(48) [h]	115.46(39) [h]	115.38(38) [h]	115.7_{7}
∠(C6–C5–C4)	122.37(85) [h]	122.50(75) [h]	122.29(80) [h]	121.4_{4}
∠(C7–C6–C5)	120.40(70) [h]	121.16(66) [h]	121.40(68) [h]	122.1_{2}
∠(C7a–C7–C6)	117.18(42) [12]	116.28(31) [12]	116.27(33) [12]	116.1_{7}
∠(N4–C4–C5)	122.17(49) [13]	122.64(30) [13]	122.86(29) [13]	122.7_{9}
∠(C3a–C7a–C7)	122.68(62) [h]	122.83(46) [h]	122.57(58) [h]	122.2_{2}
∠(C6–C5–H5)	119.53 [g]	119.53 [g]	119.53 [g]	119.5_{3}
∠(C7–C6–H6)	119.39 [g]	119.39 [g]	119.39 [g]	119.3_{9}
∠(C7a–C7–H7)	121.72 [g]	121.72 [g]	121.72 [g]	121.7_{2}
∠(C1–N2–H2)	123.40 [g]	123.40 [g]	123.40 [g]	123.4_{0}
∠(C4–N4–H8)	109.41(308) [14]	112.98(197) [14]	116.17(208) [14]	115.6_{9}
∠(C4–N4–H9)	111.03(308) [14]	114.60(197) [14]	117.79(208) [14]	117.3_{1}
τ(C6C5C4N4)	179.43(705) [15]	-179.24(854) [15]	179.54(648) [15]	177.2_{4}
τ(O3=C3N2C1)	178.74 [g]	178.74 [g]	178.74 [g]	178.7_{4}
τ(O1=C1N2C3)	-179.57 [g]	-179.57 [g]	-179.57 [g]	-179.57
τ(C7aC1N2C3)	-0.677 [g]	-0.677 [g]	-0.677 [g]	-0.677
τ(C3N2C1H2)	-178.94 [g]	-178.94 [g]	-178.94 [g]	-178.94
τ(C3aC3C7aC1)	179.29 [g]	179.29 [g]	179.29 [g]	179.29
τ(C7C7aC1N2)	-178.87 [g]	-178.87 [g]	-178.87 [g]	-178.87
τ(C4C3aC3N2)	179.63 [g]	179.63 [g]	179.63 [g]	179.63

τ(C6C7C7aC3a)	-0.15 [g]	-0.15 [g]	-0.15 [g]	-0.15
τ(C5C4C6C7)	0.58 [g]	0.58 [g]	0.58 [g]	0.58
τ(C3aC7aC7H7)	-179.87 [g]	-179.87 [g]	-179.87 [g]	-179.87
τ(C7aC7C6H6)	-179.78 [g]	-179.78 [g]	-179.78 [g]	-179.78
τ(C7C6C5H5)	179.47 [g]	179.47 [g]	179.47 [g]	179.47
τ(C5C4N4H8)	135.05(2291) [16]	152.44(1726) [16]	162.78(1063) [16]	167.6_8
τ(C5C4N4H9)	38.60(1666) [17]	19.12(1189) [17]	22.62(775) [17]	24.6_8
$\Sigma(-NH_2)$ [i]	309.28	341.89	347.81	351.9_7
R_f [j]	3.65	3.51	3.48	

[a] Parameters with equal superscripts were refined in one group, differences between parameters in each group were assumed at the values derived from r_e^{BO} structure. Uncertainties given in parentheses are estimated as $\sigma_{tot}=[(0.002r)^2+(2.5\sigma_{LS})^2]^{1/2}$ and $\sigma_{tot}=3\sigma_{LS}$ for the bond lengths and angles, respectively.

[b] Vibrational corrections to experimental internuclear distances were calculated from the MP2/cc-pVTZ harmonic force field.

[c] Vibrational corrections were calculated with the B3LYP/cc-pVTZ anharmonic force field.

[d] Vibrational corrections were calculated with the MP2/cc-pVTZ anharmonic force field.

[e] Composite structure of CCSD(T)_ae/cc-pwCVTZ quality (see Eq.1).

[f] Mean value in the benzene ring.

[g] Fixed at the value of the r_e^{BO} structure.

[h] Dependent parameter.

[i] Sum of the angles around the N4 atom.

[j] $R_f=\frac{\sum_i^n \omega_i(s_i)\left[s_i M_{exp}(s_i)-k_M s_i M_{theor}(s_i)\right]^2}{\sum_i^n \omega_i(s_i)\left[s_i M_{exp}(s_i)\right]^2}$ in %, ω_i is a weighting function, k_M is a scale factor.

Table S7. Energy $E^{(2)}$ of donor-acceptor interactions in 3-APhI according to NBO calculations (in kcal mol^{-1}, MP2/cc-pVTZ).

Interaction	$E^{(2)}$	Interaction	$E^{(2)}$
LP2(O3)→σ*(C3–N2)	36.8	LP2(O1)→σ*(C1–N2)	38.4
LP(N2)→π*(C3=O3)	71.6	LP(N2)→π*(C1=O1)	66.2
π(C4-C3a)→π*(C3=O3)	31.7	π(C7–C7a)→π*(C1=O1)	20.7