Supplementary Materials

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Molecular Structure and Vibrational Spectra of 4-(4-Hydroxyphenylazo)phthalonitrile: DFT Study

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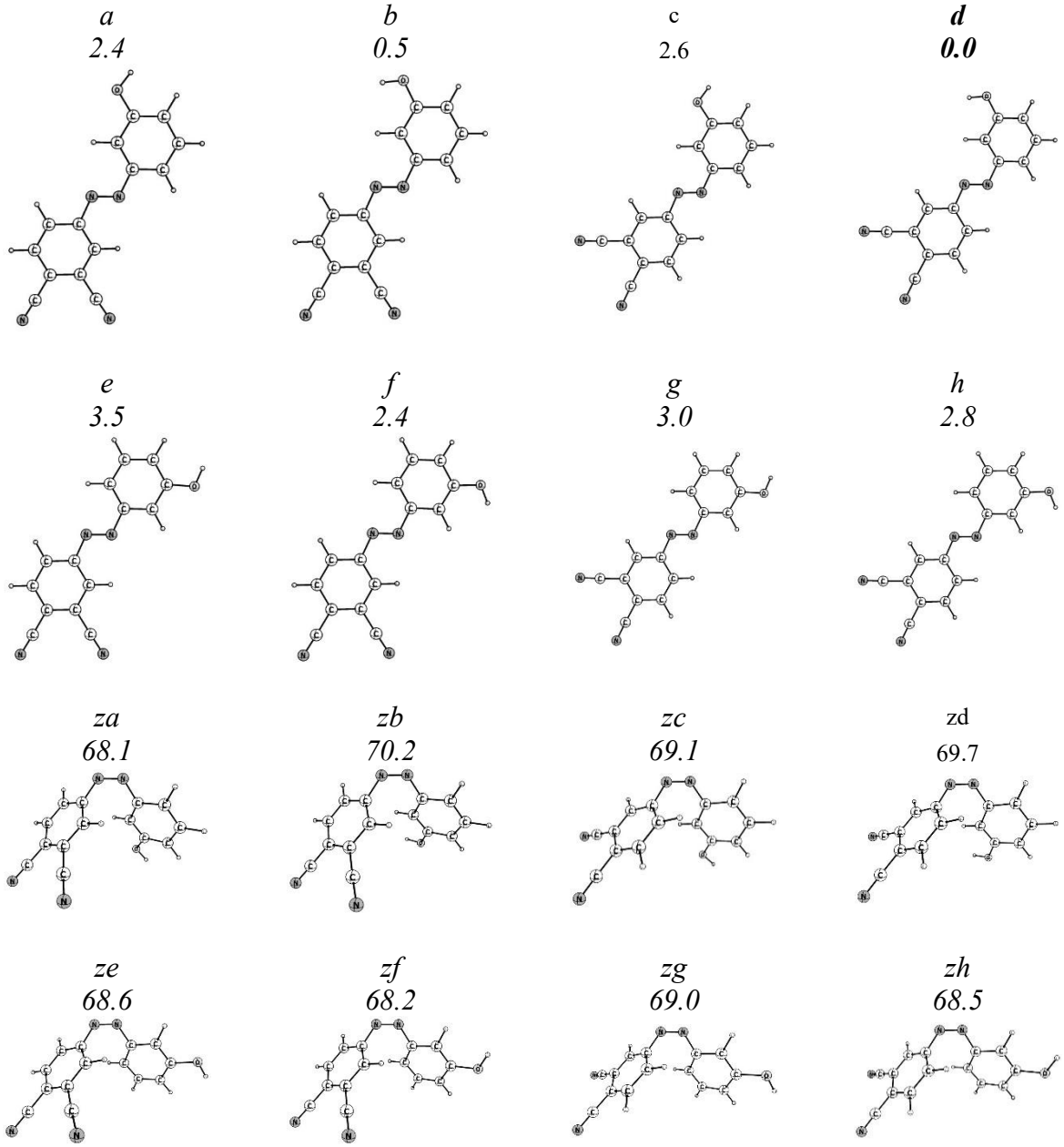

Figure S1. Conformer and isomer models of **m-HPhAPN** and appropriate relative energies (kJ·mol^{-1}).

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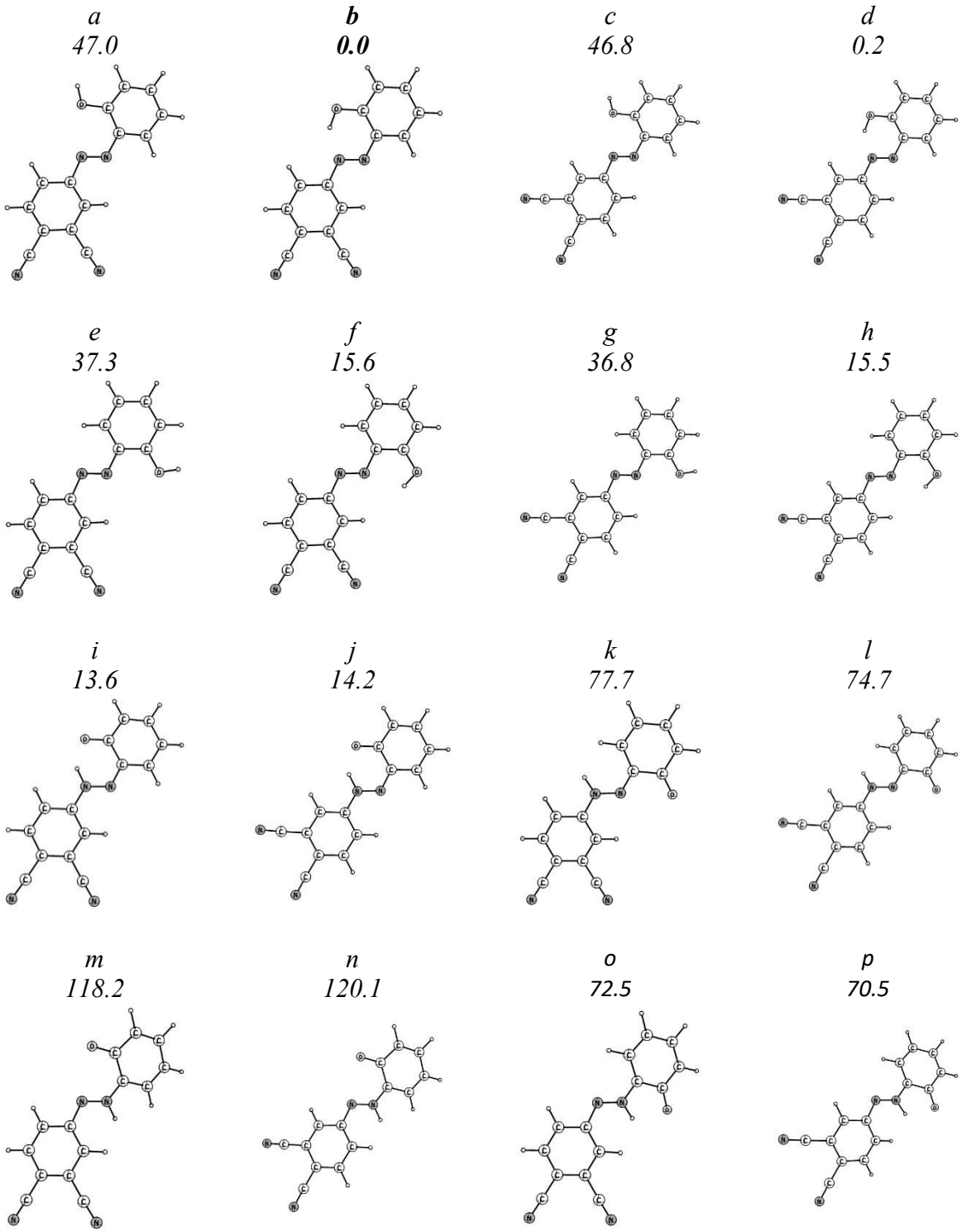

Figure S2. Conformer and isomer models of **E-o-HPhAPN** and appropriate relative energies (kJ·mol^{-1}).

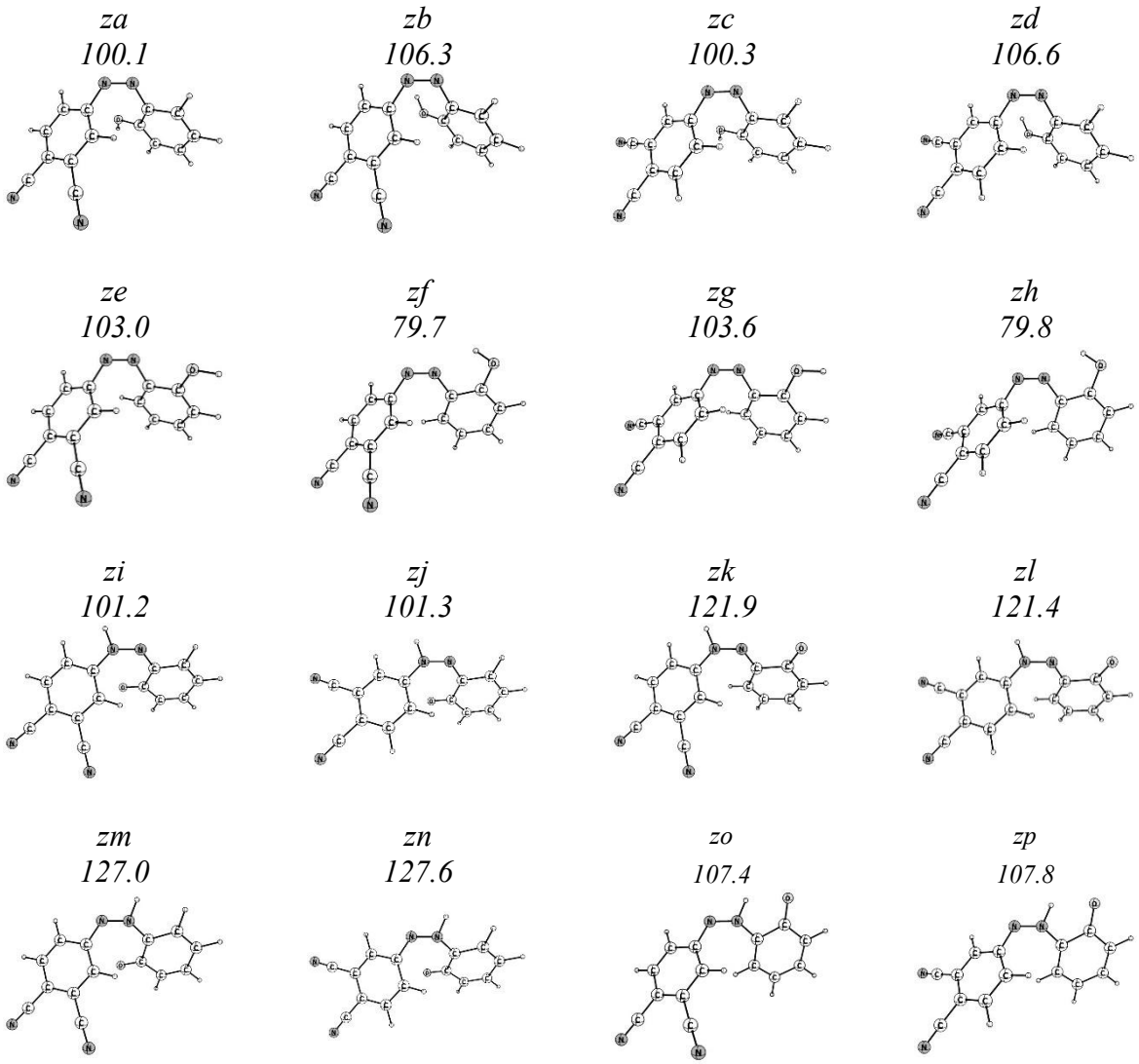

Figure S3. Conformer and isomer models of **Z-o-HPhAPN** and appropriate relative energies (kJ·mol^{-1}).

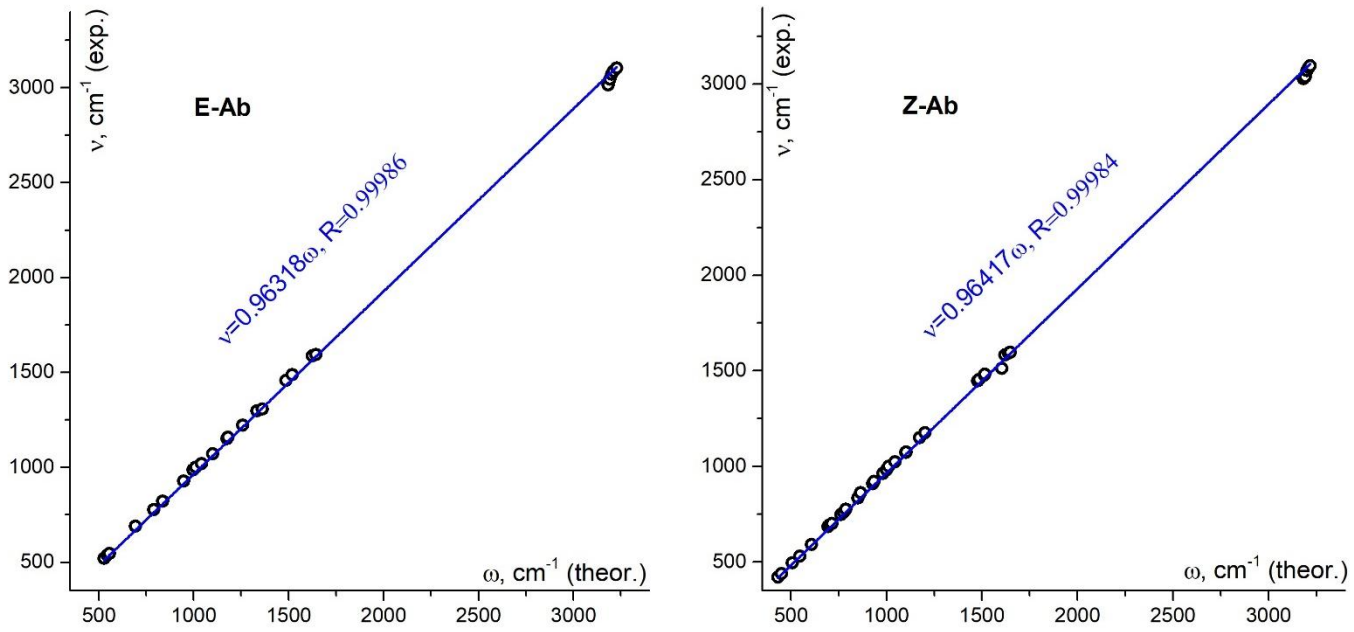

Figure S4. Correlation dependences ν = f(ω): ν – the experimental wavenumbers (cm^{-1}) of the absorption bands in the IR spectra of **Ab** (**E-Ab** and **Z-Ab**) isolated in an Ar matrix at 15 K [1]; ω – the theoretical wavenumbers (cm^{-1}) at the B3LYP/6-31++G** level. R – adjusted R squared.

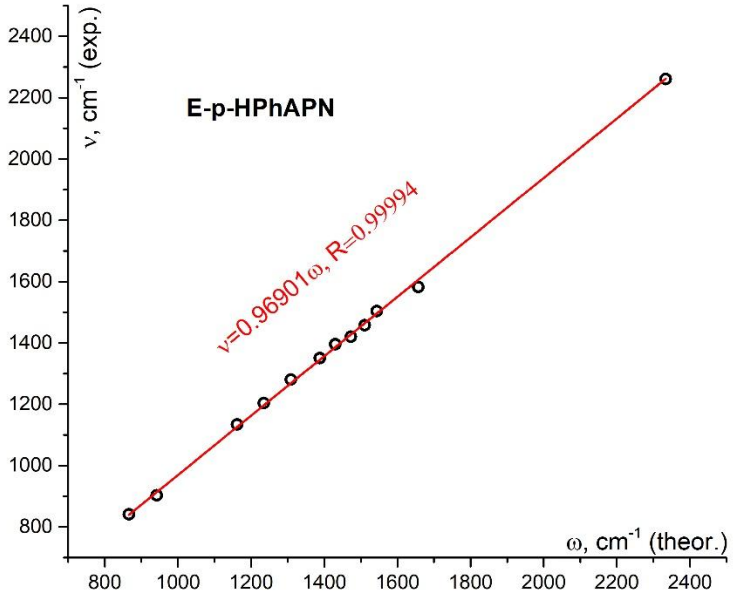

Figure S5. Correlation dependences ν = f(ω): ν and ω – the positions of the band maxima in the experimental and B3LYP/6-31++G** model spectra (Figure 2) for **E-p-HPhAPN**, respectively. R – adjusted R squared.

Table S1. Nucleus-independent chemical shifts (NICS) indexes, Wiberg bond indexes (WI) and electron delocalization indexes (DI) calculated for **Ab, Ab-2OH, Ab-4CN, p-HPhAPN**, **m-HPhAPN**, **o-HPhAPN.**

Index	**Ab**		**Ab-2OH**		**Ab-4CN**		**p-HPhAPN**		**o-HPhAPN**				**m-HPhAPN**	
	E-	Z-	E-	Z-	E-	Z-	a	za	b	i	zf	zb	b	zb
NICS(0)	-6.9	-8.2	-	-	-8.0	-9.1	-6.9	-8.7	-7.9	-8.2	-8.6	-9.2	-8.0	-8.9
NICS(1)	-9.0	-9.4	-	-	-9.1	-9.4	-8.1	-8.9	-8.9	-8.8	-8.9	-9.4	-9.1	-9.2
NICS(0) '	-	-	-7.5	-8.7	-	-	-8.0	-8.3	-6.9	0.1	-6.7	-8.9	-7.6	-9.0
NICS(1) '	-	-	-8.4	-8.8	-	-	-9.0	-8.8	-7.9	-3.3	-7.9	-9.0	-8.5	-9.0
$r_e(N_1\text{-}N'_1)$, Å	1.258	1.249	1.261	1.253	1.257	1.246	1.262	1.251	1.274	1.310	1.254	1.253	1.259	1.248
$r_e(N_1\text{-}C_2)$, Å	1.420	1.436	1.413	1.433	1.418	1.434	1.418	1.428	1.414	1.395	1.425	1.433	1.420	1.432
$r_e(N'_1\text{-}C'_2)$, Å	1.420	1.436	1.413	1.433	1.418	1.434	1.404	1.424	1.386	1.333	1.410	1.434	1.413	1.432
r_e(O-C), Å	-	-	1.367	1.368	-	-	1.361	1.361	1.339	1.653	1.347	1.367	1.367	1.366
$WI(N_1\text{-}N'_1)$	1.76	1.90	1.73	1.87	1.76	1.92	1.72	1.86	1.64	1.32	1.82	1.88	1.74	1.90
$WI(N_1\text{-}C_2)$	1.11	1.06	1.12	1.07	1.11	1.06	1.11	1.07	1.10	1.09	1.07	1.07	1.10	1.06
$WI(N'_1\text{-}C'_2)$	1.11	1.06	1.12	1.07	1.11	1.06	1.14	1.09	1.21	1.47	1.13	1.06	1.12	1.06
WI(O-C)	-	-	1.03	1.03	-	-	1.05	1.05	1.12	0.10	1.09	1.03	1.03	1.03
$DI(N_1\text{-}N'_1)$	1.88	1.95	1.86	1.93	1.88	1.96	1.85	1.92	1.77	1.48	1.88	1.93	1.87	1.01
$DI(N_1\text{-}C_2)$	1.03	1.01	1.05	1.02	1.03	1.01	1.05	1.02	1.03	0.98	1.02	1.02	1.04	1.02
$DI(N'_1\text{-}C'_2)$	1.03	1.00	1.05	1.02	1.03	1.01	1.05	1.03	1.10	1.26	1.06	1.00	1.03	1.95
DI(O-C)	-	-	0.92	0.92	-	-	0.93	0.93	0.98	0.14	0.95	0.92	0.92	0.92

Table S2. Calculated frequencies (ω_i), IR-intensities ($I_{IR\,i}$) and vibrational modes descriptions [a] for **E-Ab** and **Z-Ab**.

i	E-Ab								Z-Ab				
	sym	ω_i, cm^{-1}	$I_{IR\,i}$, $km \cdot mol^{-1}$	Assignment [a]	[b]	[c]	Benzene modes parentage [d]	ν_{exp}, cm^{-1} [e]	sym	ω_i, cm^{-1}	$I_{IR\,i}$, $km \cdot mol^{-1}$	Assignment [a]	ν_{exp}, cm^{-1} [e]
1	A_u	21.4	0.1	rot(Ph);	44	44			A	45.2	0.0	rot(Ph); $\delta(N'_1N_1C_2)$; $\delta(N_1C_2C)$;	
2	A_u	62.8	1.5	π scissoring;	43	43			A	69.3	0.4	π scissoring	
3	B_u	85.1	2.1	δ scissoring;	66	66			B	287.1	5.8	$\delta(N_1C_2C)$; $\delta(N'_1N_1C_2)$; τ(CCCN)	
4	B_g	111.0	0.0	π shearing;	33	33			B	44.3	1.4	rot(Ph); $\delta(N_1C_2C)$;	
5	A_g	223.5	0.0	δ shearing;	23	23			A	272.6	0.4	$\delta(N'_1N_1C_2)$; $\delta(N_1C_2C)$; τ(Ph);	
6	B_g	260.9	0.0	π shearing;	32	32			B	155.9	2.8	τ(CCCN); $\delta(N'_1N_1C_2)$;	
7	A_g	306.8	0.0	δ shearing;	22	22			A	172.6	0.2	τ(CNNC); $\delta(N_1C_2C)$;	
8	A_u	307.5	0.9	π(Ph); τ(CNNC);	42	42	16		A	432.3	3.5	τ(CNNC); π(Ph); $\nu(N_1\text{-}C_2)$; δ(CCC);	420
9	A_u	415.9	0.0	π(Ph);	41	41	16		A	413.2	0.0	π(Ph);	
10	B_g	422.2	0.0	π(Ph);	31	31	16		B	409.9	3.9	π(Ph);	
11	B_g	485.9	0.0	π(Ph);	30	29	16		B	452.1	2.4	π(Ph); $\delta(N_1C_2C)$;	439
12	B_u	529.0	26.2	$\delta(N'_1N_1C_2)$; $\delta(N_1C_2C)$; δ(CCC);	65	65		521	B	715.0	93.0	π(C-H): $\pi(C_5\text{-}H_5)$, $\pi(C_4\text{-}H_4)$, $\pi(C_6\text{-}H_6)$; $\delta(N'_1N_1C_2)$;	701
13	B_u	545.6	5.6	δ(CCC): $\delta(C_3C_2C_7)$, $\delta(C_4C_5C_6)$, $\delta(C_2C_3C_4)$; $\delta(N_1C_2C)$;	64	64	6	536	B	506.4	4.9	δ(CCC): $\delta(C_3C_2C_7)$; π(Ph); $\nu(N_1\text{-}C_2)$; $\delta(N_1C_2C)$;	495
14	A_u	556.6	13.1	τ(CNNC), τ(Ph)	40	39		546	A	607.5	4.8	τ(CNNC); δ(CCC);	592
15	A_g	624.0	0.0	δ(CCC): $\delta(C_5C_6C_7)$, $\delta(C_3C_4C_5)$, $\delta(C_2C_3C_4)$, $\delta(C_2C_7C_6)$;	21	21	6		A	630.9	0.3	δ(CCC): $\delta(C_5C_6C_7)$, $\delta(C_2C_3C_4)$, $\delta(C_3C_4C_5)$; τ(CNNC);	
16	B_u	630.0	0.6	δ(CCC): $\delta(C_3C_4C_5)$, $\delta(C_5C_6C_7)$, $\delta(C_2C_7C_6)$, $\delta(C_2C_3C_4)$;	63	63	6		B	627.1	0.0	δ(CCC): $\delta(C_3C_4C_5)$, $\delta(C_2C_7C_6)$, $\delta(C_5C_6C_7)$, $\delta(C_2C_3C_4)$;	
17	A_g	681.9	0.0	δ(CCC): $\delta(C_4C_5C_6)$, $\delta(C_3C_2C_7)$; $\delta(N'_1N_1C_2)$;	20	20	6		A	763.1	0.7	$\nu(N_1\text{-}C_2)$; δ(CCC): $\delta(C_4C_5C_6)$; π(C-H); ν(C-C);	749
18	A_u	693.4	75.6	τ(Ph); π(C-H);	39	40	4	689	A	703.0	21.9	τ(Ph); π(C-H): $\pi(C_6\text{-}H_6)$, $\pi(C_4\text{-}H_4)$; $\nu(N_1\text{-}C_2)$; δ(CCC); ν(C-C);	694
19	B_g	693.8	0.0	τ(Ph); π(C-H);	29	29	4		B	693.3	6.9	τ(Ph); $\delta(N'_1N_1C_2)$;	686

20	B_g	772.8	0.0	π(C-H); π(N_1-C_2);	28	28	11		B	776.0	52.8	π(C-H): π(C_5-H_5); ν(N_1-C_2); δ(CCC); π(N_1-C_2); ν(C-C);	760
21	A_u	789.7	86.9	π(C-H); π(N_1-C_2);	38	38	11	778	A	787.5	15.7	π(C-H): π(C_5-H_5); π(N_1-C_2); ν(N_1-C_2);	777
22	B_u	837.1	0.5	δ(CCC): δ($C_4C_5C_6$); ν(C-C): ν(C_2-C_7), ν(C_2-C_3); ν(N_1-C_2);	62	62		821	B	866.1	5.5	δ($N'_1N_1C_2$); ν(N_1-C_2);	863
23	A_u	854.8	0.1	π(C-H): π(C_7-H_7), π(C_4-H_4), π(C_3-H_3), π(C_6-H_6);	37	37	10		A	851.5	1.0	π(C-H): π(C_3-H_3), π(C_7-H_7), π(C_6-H_6), π(C_4-H_4);	
24	B_g	856.8	0.0	π(C-H): π(C_4-H_4), π(C_7-H_7), π(C_3-H_3), π(C_6-H_6);	27	27	10		B	850.0	2.4	π(C-H): π(C_3-H_3), π(C_7-H_7), π(C_6-H_6), π(C_4-H_4);	834
25	A_g	936.0	0.0	δ($N'_1N_1C_2$); ν(C-C): ν(C_2-C_3); δ(C-C-C); ν(N_1-C_2);	19	19			A	547.1	0.5	δ($N'_1N_1C_2$); δ(CCC): δ($C_3C_2C_7$);	531
26	B_g	942.8	0.0	π(C-H): π(C_7-H_7), π(C_5-H_5), π(C_3-H_3); τ(Ph)	26	26	17		B	934.2	21.0	π(C-H): π(C_3-H_3), π(C_3-H_7), π(C_5-H_5); π(N_1-C_2); δ($N'_1N_1C_2$);	921
27	A_u	946.9	9.2	π(C-H): π(C_7-H_7), π(C_5-H_5), π(C_3-H_3); π(Ph);	36	36	17	927	A	929.4	0.3	π(C-H): π(C_3-H_3), π(C_7-H_7), π(C_5-H_5); π(Ph);	910
28	A_u	987.3	0.0	π(C-H): π(C_6-H_6), π(C_7-H_7), π(C_3-H_3); π(Ph);	35	35	17		A	981.5	0.1	π(C-H): π(C_4-H_4), π(C_6-H_6), π(C_7-H_7), π(C_3-H_3); π(Ph);	
29	B_g	989.6	0.0	π(C-H): π(C_6-H_6), π(C_7-H_7), π(C_3-H_3), π(C_4-H_4); π(Ph);	25	25	17		B	981.5	0.4	π(C-H): π(C_4-H_4), π(C_6-H_6), π(C_7-H_7), π(C_3-H_3); π(Ph);	963
30	A_u	998.5	0.0	π(C-H): π(C_4-H_4), π(C_5-H_5); π(Ph);	34	34	5	986	A	1000.2	0.0	π(C-H): π(C_5-H_5), π(C_6-H_6), π(C_4-H_4); π(Ph);	
31	B_g	1002.9	0.0	π(C-H): π(C_4-H_4), π(C_5-H_5), π(C_3-H_3), π(C_7-H_7); π(Ph);	24	24	5		B	1000.0	0.4	π(C-H): π(C_5-H_5), π(C_6-H_6), π(C_4-H_4), π(C_5-H_5); π(Ph);	981
32	B_u	1012.6	2.3	δ(CCC); ν(C-C); δ(C-H);	61	61	12	1001	B	1012.6	1.1	δ(C-C-C); ν(C-C): ν(C_2-C_3); δ(C-H);	1001
33	A_g	1012.8	0.0	δ(CCC); ν(C-C); δ(C-H);	18	18	12		A	1012.4	0.2	δ(C-C-C); ν(C-C); δ(C-H);	
34	A_g	1041.2	0.0	ν(C-C): ν(C_4-C_5), ν(C_5-C_6); δ(C-H);	17	17	19		A	1045.9	2.9	ν(C-C): ν(C_5-C_6), ν(C_4-C_5); δ(C-H);	
35	B_u	1041.4	15.0	ν(C-C): ν(C_4-C_5), ν(C_5-C_6); δ(C-H);	60	60	19	1019	B	1045.8	5.3	ν(C-C): ν(C_5-C_6), ν(C_4-C_5); δ(C-H);	1024
36	A_g	1097.8	0.0	δ(C-H): δ(C_3-H_3), δ(C_7-H_7), δ(C_5-H_5); ν(C-C): ν(C_6-C_7), ν(C_3-C_4);	16	16	19		A	1103.3	0.8	δ(C-H): δ(C_3-H_3), δ(C_7-H_7), δ(C_5-H_5); ν(C-C): ν(C_6-C_7), ν(C_3-C_4);	1075
37	B_u	1101.3	13.5	δ(C-H): δ(C_7-H_7), δ(C_3-H_3), δ(C_5-H_5); ν(C-C): ν(C_6-C_7), ν(C_3-C_4);	59	59	19	1072	B	1102.2	13.2	δ(C-H): δ(C_7-H_7), δ(C_5-H_5); ν(C-C): ν(C_3-C_4), ν(C_6-C_7);	1072
38	A_g	1165.5	0.0	δ(C-H): δ(C_7-H_7); ν(N_1-C_2); ν(C-C);	15	15	8		A	1151.0	0.2	ν(N_1-C_2); ν(C-C): ν(C_2-C_7); δ(C-H): δ(C_7-H_7);	
39	B_u	1176.9	29.6	δ(C-H): δ(C_3-H_3), δ(C_4-H_4), δ(C_7-H_7); ν(C-C); ν(N_1-C_2);	58	58	8	1152	B	1173.5	1.9	ν(N_1-C_2); δ(C-H): δ(C_3-H_3); ν(C-C);	1151
40	B_u	1181.9	0.3	δ(C-H): δ(C_6-H_6), δ(C_5-H_5); ν(C-C);	57	57	14	1158	B	1183.1	0.0	δ(C-H): δ(C_5-H_5), δ(C_4-H_4), δ(C_6-H_6); ν(C-C);	
41	A_g	1182.0	0.0	δ(C-H): δ(C_5-H_5), δ(C_6-H_6), δ(C_4-H_4); ν(C-C);	14	14	14		A	1183.0	0.1	δ(C-H): δ(C_5-H_5), δ(C_6-H_6), δ(C_4-H_4); ν(C-C);	
42	A_g	1209.7	0.0	δ(C-H): δ(C_4-H_4), δ(C_6-H_6); ν(N_1-C_2); ν(C-C);	13	13	8		A	1202.0	0.5	δ(C-H): δ(C_4-H_4), δ(C_6-H_6), δ(C_3-H_3), δ(C_7-H_7); ν(C-C): ν(C_3-C_4);	1176

43	B_u	1258.8	23.9	$\nu(N_1\text{-}C_2)$; ν(C-C); δ(C-H): $\delta(C_4\text{-}H)$;	56	56	8	1221	B	1202.4	0.2	δ(C-H): $\delta(C_4\text{-}H_4)$, $\delta(C_6\text{-}H_6)$; ν(C-C): $\nu(C_3\text{-}C_4)$; $\nu(N_1\text{-}C_2)$;	
44	B_u	1333.6	2.0	δ(C-H): $\delta(C_7\text{-}H_7)$, $\delta(C_3\text{-}H_3)$, $\delta(C_6\text{-}H_6)$, $\delta(C_4\text{-}H_4)$; ν(C-C);	55	55	3	1298	B	1329.3	1.5	ν(C-C): $\nu(C_2\text{-}C_3)$, $\nu(C_2\text{-}C_7)$; δ(C-H): $\delta(C_6\text{-}H_6)$, $\delta(C_4\text{-}H_4)$;	
45	A_g	1340.3	0.0	δ(C-H): $\delta(C_7\text{-}H_7)$, $\delta(C_3\text{-}H_3)$, $\delta(C_4\text{-}H_4)$, $\delta(C_6\text{-}H_6)$;	12	12	3		A	1337.2	0.1	δ(C-H): $\delta(C_6\text{-}H_6)$, $\delta(C_4\text{-}H_4)$, $\delta(C_7\text{-}H_7)$, $\delta(C_3\text{-}H_3)$; ν(C-C): $\nu(C_2\text{-}C_3)$, $\nu(C_2\text{-}C_7)$;	
46	B_u	1363.0	8.8	$\nu(C_3\text{-}C_4)$, $\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_7)$, $\nu(C_4\text{-}C_5)$, $\nu(C_2\text{-}C_3)$, $\nu(C_6\text{-}C_7)$; δ(C-H);	54	54	15	1307	B	1354.4	0.7	$\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$, $\nu(C_4\text{-}C_5)$; δ(C-H): $\delta(C_3\text{-}H_3)$, $\delta(C_7\text{-}H_7)$, $\delta(C_5\text{-}H_5)$;	
47	A_g	1365.9	0.0	$\nu(C_3\text{-}C_4)$, $\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_3)$, $\nu(C_4\text{-}C_5)$, $\nu(C_2\text{-}C_7)$, $\nu(C_6\text{-}C_7)$; δ(C-H);	11	11	15		A	1358.2	0.0	$\nu(C_3\text{-}C_4)$, $\nu(C_6\text{-}C_7)$, $\nu(C_5\text{-}C_6)$, $\nu(C_4\text{-}C_5)$; δ(C-H): $\delta(C_3\text{-}H_3)$, $\delta(C_7\text{-}H_7)$;	
48	A_g	1482.0	0.0	δ(C-H): $\delta(C_5\text{-}H_5)$, $\delta(C_4\text{-}H_4)$; ν(C-C): $\nu(C_6\text{-}C_7)$; $\nu(N_1\text{-}N'_1)$;	10	10	18		A	1484.3	2.8	δ(C-H): $\delta(C_5\text{-}H_5)$, $\delta(C_4\text{-}H_4)$, $\delta(C_6\text{-}H_6)$; ν(C-C): $\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$;	1453
49	B_u	1486.0	10.1	δ(C-H): $\delta(C_5\text{-}H_5)$, $\delta(C_4\text{-}H_4)$, $\delta(C_6\text{-}H_6)$; ν(C-C): $\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$;	53	53	18	1457	B	1478.1	5.5	δ(C-H): $\delta(C_5\text{-}H_5)$, $\delta(C_4\text{-}H_4)$, $\delta(C_6\text{-}H_6)$; ν(C-C): $\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$;	1448
50	A_g	1507.1	0.0	δ(C-H): $\delta(C_3\text{-}H_3)$, $\delta(C_6\text{-}H_6)$; ν(C-C): $\nu(C_2\text{-}C_7)$;	9	9	18		A	1512.6	6.6	δ(C-H): $\delta(C_3\text{-}H_3)$, $\delta(C_7\text{-}H_7)$, $\delta(C_4\text{-}H_4)$, $\delta(C_6\text{-}H_6)$; ν(C-C);	1478
51	B_u	1520.6	8.6	δ(C-H): $\delta(C_4\text{-}H_4)$, $\delta(C_3\text{-}H_3)$, $\delta(C_6\text{-}H_6)$, $\delta(C_7\text{-}H_7)$; ν(C-C): $\nu(C_4\text{-}C_5)$;	52	52	18	1487	B	1515.1	6.3	δ(C-H): $\delta(C_3\text{-}H_3)$, $\delta(C_6\text{-}H_6)$, $\delta(C_4\text{-}H_4)$, $\delta(C_7\text{-}H_7)$; ν(C-C);	1482
52	A_g	1557.2	0.0	$\nu(N_1\text{-}N'_1)$; ν(C-C); δ(C-H);	8	8			A	1605.0	25.3	$\nu(N_1\text{-}N'_1)$; ν(C-C);	1513
53	B_u	1626.8	3.5	$\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_3)$, $\nu(C_2\text{-}C_7)$; δ(C-H);	51	51	9	1588	B	1620.2	4.6	$\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_3)$, $\nu(C_4\text{-}C_5)$; δ(C-H);	1582
54	A_g	1632.7	0.0	$\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_7)$, $\nu(C_2\text{-}C_3)$, $\nu(C_4\text{-}C_5)$; δ(C-H);	7	7	9		A	1627.5	0.8	$\nu(C_4\text{-}C_5)$, $\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_7)$, $\nu(C_2\text{-}C_3)$; δ(C-H);	
55	B_u	1643.8	3.4	$\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$, $\nu(C_2\text{-}C_7)$, $\nu(C_4\text{-}C_5)$; δ(C-H);	50	50	9	1593	B	1638.2	4.0	$\nu(C_4\text{-}C_5)$, $\nu(C_5\text{-}C_6)$, $\nu(C_2\text{-}C_7)$, $\nu(C_2\text{-}C_3)$; δ(C-H);	1593
56	A_g	1649.0	0.0	$\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$; δ(C-H); $\nu(N_1\text{-}N'_1)$;	6	6	9		A	1648.6	12.9	$\nu(C_6\text{-}C_7)$, $\nu(C_3\text{-}C_4)$; $\nu(N_1\text{-}N'_1)$; δ(C-H);	1596
57	B_u	3182.1	2.9	ν(C-H): $\nu(C_4\text{-}H_4)$, $\nu(C_5\text{-}H_5)$, $\nu(C_6\text{-}H_6)$;	49			3015	B	3184.1	1.4	ν(C-H): $\nu(C_5\text{-}H_5)$, $\nu(C_4\text{-}H_4)$, $\nu(C_6\text{-}H)$;	3028
58	A_g	3182.1	0.0	ν(C-H): $\nu(C_5\text{-}H_5)$, $\nu(C_4\text{-}H_4)$, $\nu(C_6\text{-}H_6)$;	5				A	3184.2	0.2	ν(C-H): $\nu(C_5\text{-}H_5)$, $\nu(C_4\text{-}H_4)$, $\nu(C_6\text{-}H_6)$;	
59	A_g	3192.3	0.0	ν(C-H): $\nu(C_6\text{-}H_6)$, $\nu(C_4\text{-}H_4)$, $\nu(C_7\text{-}H_7)$;	4				A	3192.3	1.1	ν(C-H): $\nu(C_4\text{-}H_4)$, $\nu(C_6\text{-}H_6)$, $\nu(C_7\text{-}H_7)$;	
60	B_u	3192.3	21.8	ν(C-H): $\nu(C_6\text{-}H_6)$, $\nu(C_4\text{-}H_4)$, $\nu(C_7\text{-}H_7)$;	48			3046	B	3192.2	12.3	ν(C-H): $\nu(C_4\text{-}H_4)$, $\nu(C_6\text{-}H_6)$, $\nu(C_7\text{-}H_7)$;	3038
61	B_u	3202.9	43.2	ν(C-H): $\nu(C_5\text{-}H_5)$, $\nu(C_7\text{-}H_7)$, $\nu(C_4\text{-}H_4)$;	47			3070	B	3203.0	7.2	ν(C-H): $\nu(C_7\text{-}H_7)$, $\nu(C_5\text{-}H_5)$, $\nu(C_4\text{-}H_4)$;	
62	A_g	3203.0	0.0	ν(C-H): $\nu(C_5\text{-}H_5)$, $\nu(C_7\text{-}H_7)$, $\nu(C_4\text{-}H_4)$;	3				A	3202.9	18.1	ν(C-H): $\nu(C_7\text{-}H_7)$, $\nu(C_5\text{-}H_5)$, $\nu(C_4\text{-}H_4)$;	3070
63	B_u	3212.4	32.7	ν(C-H): $\nu(C_7\text{-}H_7)$, $\nu(C_6\text{-}H_6)$, $\nu(C_5\text{-}H_5)$;	46			3087	B	3210.3	35.6	ν(C-H): $\nu(C_7\text{-}H_7)$, $\nu(C_6\text{-}H_6)$, $\nu(C_5\text{-}H_5)$;	3085
64	A_g	3212.6	0.0	ν(C-H): $\nu(C_7\text{-}H_7)$, $\nu(C_6\text{-}H_6)$, $\nu(C_5\text{-}H_5)$;	2				A	3210.6	1.8	ν(C-H): $\nu(C_7\text{-}H_7)$, $\nu(C_6\text{-}H_6)$, $\nu(C_5\text{-}H_5)$;	
65	A_g	3228.5	0.0	$\nu(C_3\text{-}H_3)$;	1				A	3217.6	2.1	ν(C-H): $\nu(C_3\text{-}H)$, $\nu(C_4\text{-}H_4)$;	
66	B_u	3228.6	8.4	$\nu(C_3\text{-}H_3)$;	45			3104	B	3217.7	3.8	ν(C-H): $\nu(C_3\text{-}H)$, $\nu(C_4\text{-}H_4)$;	3095

[a] Based on PED. Coordinates are listed if their contributions are greater than ~10%. Coordinates are presented in descending order of their contributions. The designation "*Coord-1*: *Coord-2*, *Coord-3*;" means that the displacement along coordinates *Coord-2* and *Coord-3* are a part of the general displacement *Coord-1*. Given that the molecules have the symmetries C_{2h} and C_2, the following pairs of atoms are symmetrically equivalent: N'_1 and N_1, C_2 and C'_2, C_3 and C'_3, C_4 and C'_4, C_5 and C'_5, C_6 and C'_6, C_7 and C'_7, etc, therefore it is assumed in assignment that, for example, vibration $\nu(C_2\text{-}C_3)$ includes both vibration $\nu(C_2\text{-}C_3)$ and $\nu(C'_2\text{-}C'_3)$, etc. The following designations are used: ν(X-Y) – stretching of the X–Y bond; δ – in-plane bending; π – out-of-plane bending; τ – torsion; rot(Ph) – rotation of the phenyl fragment around an axis N-C; π scissoring - ring-ring out-of-plane scissoring (with analogy at [2]); δ scissoring – ring-ring in-plane scissoring (with analogy at [2]); π shearing – out-of-plane shearing (with analogy at [2]); δ shearing – in-plane shearing (with analogy at [2]);

[b] Gagliardi [3] numbering of modes;

[c] Armstrong [4] numbering of modes;

[d] Gardner labels [5] for the vibrational modes of benzene (the labeling is based on Varsányi labeling [6] with renumbering of modes 8 and 9, 14 and 15, 18 and 19);

[e] experimental wavenumbers (cm^{-1}) of the absorption bands in the IR spectra of **Ab** (**E-Ab** and **Z-Ab**) isolated in an Ar matrix at 15 K [1].

Table S3. Calculated frequencies (ω_i), IR-intensities ($I_{IR\,i}$) and vibrational modes descriptions [a] for **E-p-HPhAPN**.

i	ω_i, cm^{-1}	$I_{IR\,i}$, $km \cdot mol^{-1}$	Assignment [a]	ν_{exp}, cm^{-1}
1	19.3	1.2	rot(Ph): rot(Ph), rot(Ph');	
2	35.8	0.4	π scissoring;	
3	53.4	0.5	δ scissoring;	
4	78.0	2.6	π shearing;	
5	114.3	0.9	$\delta(C_{4,5}\text{-}CN^{(4,5)})$;	
6	130.3	0.1	$\pi(C_4\text{-}CN^{(4)})$; τ(Ph, Ph');	
7	148.5	4.0	$\delta(C_{5,4}\text{-}CN^{(5,4)})$; $\delta(N_1N'_1C'_2)$; $\delta(N'_1C'_2C')$;	
8	164.3	7.0	$\pi(C_{4,5}\text{-}CN^{(4,5)})$; $\tau(N_1N'_1C'_2C')$;	
9	205.6	6.8	$\delta(C_{4,5}\text{-}CN^{(4,5)})$; ν(N-C); δ(CCC); $\delta(N'_1N_1C_2)$;	
10	208.3	0.1	$\tau(N_1N'_1C'_2C')$; τ(Ph'); $\tau(C'C'C'_5O)$	
11	282.8	2.2	δ(NCC): $\delta(N_1C_2C)$, $\delta(N'_1C'_2C')$; $\delta(C_{4,5}\text{-}CN^{(4,5)})$;	
12	296.5	0.0	$\pi(C_{4,5}\text{-}CN^{(4,5)})$; $\tau(N_1N'_1C'_2C')$;	
13	381.4	38.2	$\tau(C'C'_5OH)$; τ(Ph');	
14	390.7	24.2	π(Ph); $\pi(C_4\text{-}CN^{(4)})$; $\tau(C'C'_5OH)$;	
15	397.5	58.1	$\tau(C'C'_5OH)$; τ(Ph');	
16	405.0	11.4	$\delta(C'_5\text{-}OH)$; δ(CCC);	
17	424.4	29.0	δ(CCC); $\nu(C_{4,5}\text{-}C^{CN(4,5)})$; $\delta(C'_5\text{-}OH)$;	
18	434.8	0.1	π(Ph');	
19	461.9	9.5	$\delta(C_{5,4}\text{-}CN^{(5,4)})$; δ(CCC); ν(C-C);	
20	470.3	0.3	τ(Ph); $\pi(C\text{-}CN^{(4,5)})$	
21	508.8	8.1	$\delta(C_4\text{-}CN^{(4)})$; δ(NNC); δ(NCC): $\delta(N_1C_2C)$; δ(CCC);	
22	534.2	7.8	τ(Ph');	
23	535.2	0.8	$\delta(N'_1N_1C_2)$; δ(NNC); δ(CCC);	
24	549.5	19.7	$\pi(C_{4,5}\text{-}CN^{(4,5)})$;	
25	606.9	4.5	ν(C-C): $\nu(C_5\text{-}C^{CN(5)})$; δ(NNC); δ(CCC);	
26	634.9	1.2	$\delta(C_{4,5}\text{-}CN^{(4,5)})$; $\delta(C_{4,5}\text{-}CN^{(4,5)})$; δ(Ph');	
27	649.1	5.1	π(Ph; $C^{CN(4)}$);	
28	653.2	2.1	δ(Ph'): $\delta(C'_5C'_6C'_7)$, $\delta(C'_2C'_7C'_6)$, $\delta(C'_2C'_3C'_4)$, $\delta(C'_3C'_4C'_5)$; ν(C-C); δ(C-H);	
29	722.8	1.4	τ(Ph');	
30	733.3	1.3	ν(C-C): $\nu(C_4\text{-}C_5)$, $\nu(C_5\text{-}C^{CN(5)})$, $\nu(C_4\text{-}C^{CN(4)})$; δ(CCC);	
31	751.2	1.3	τ(Ph);	
32	755.8	3.8	δ(Ph): $\delta(C_2C_7C_6)$; ν(C-C): $\nu(C_5\text{-}C^{CN(5)})$; ν(N-C);	
33	818.7	10.3	π(C-H): $\pi(C'_6\text{-}H'_6)$, $\pi(C'_7\text{-}H'_7)$, $\pi(C'_4\text{-}H'_4)$;	
34	833.9	14.0	ν(C-C): $\nu(C'_5\text{-}C'_6)$; δ(CCC): $\delta(C'_3\text{-}C'_2\text{-}C'_7)$; $\nu(O\text{-}C'_5)$; δ(NNC);	
35	855.5	19.9	π(C-H): $\pi(C'_4\text{-}H'_4)$, $\pi(C'_3\text{-}H'_3)$, $\pi(C'_6\text{-}H'_6)$;	
36	866.8	56.6	π(C-H): $\pi(C_6\text{-}H_6)$, $\pi(C_7\text{-}H_7)$;	841
37	899.5	2.5	ν(C-C): $\nu(C'_2\text{-}C'_3)$; δ(NNC): $\delta(N'_1N_1C_2)$, $\delta(N_1N'_1C'_2)$; δ(CCC);	
38	941.7	13.9	π(C-H): $\pi(C_3\text{-}H_3)$;	903

39	960.6	2.5	π(C-H): π(C'$_7$-H'$_7$), π(C'$_6$-H'$_6$);	
40	987.4	0.2	π(C-H): π(C'$_3$-H'$_3$), π(C'$_4$-H'$_4$);	
41	989.1	0.1	π(C-H): π(C$_7$-H$_7$), π(C$_6$-H$_6$);	
42	989.9	0.9	ν(C-C): ν(C$_2$-C$_3$); δ(NNC): δ(N'$_1$N$_1$C$_2$), δ(N$_1$N'$_1$C'$_2$); ν(N$_1$-C$_2$);	
43	1018.1	1.9	ν(C'-C'): ν(C'$_2$-C'$_3$); δ(Ph'); δ(C'-H');	
44	1107.1	10.7	ν(C-C): ν(C$_4$-C$^{CN(4)}$); δ(C-H): δ(C$_7$-H$_7$); δ(CCC); ν(N$_1$-C$_2$);	
45	1123.8	18.8	δ(C'-H'): δ(C'$_3$-H'$_3$), δ(C'$_7$-H'$_7$), δ(C'$_4$-H'$_4$); ν(C'-C');	
46	1162.0	301.3	δ(C-H): δ(C'$_7$-H'$_7$); ν(N-C): ν(N'$_1$-C'$_2$), ν(N$_1$-C$_2$); ν(C-C);	1134
47	1174.2	95.2	δ(C-H): δ(C$_6$-H$_6$), δ(C$_3$-H$_3$); ν(C-C); ν(N-C);	
48	1185.7	180.7	δ(O-H); ν(C-C); δ(C-H): δ(C'$_6$-H'$_6$);	
49	1208.3	4.0	ν(C-C): ν(C$_5$-C$^{CN(5)}$); δ(C-H): δ(C$_7$-H$_7$); δ(CCC); ν(N-C);	
50	1235.5	45.7	ν(C-C): ν(C$_5$-C$^{CN(5)}$); ν(N-C): ν(N'$_1$-C'$_2$); δ(C-H);	1204
51	1268.8	0.4	δ(C-H): δ(C$_6$-H$_6$); ν(C-C); ν(N-C): ν(N'$_1$-C'$_2$);	
52	1299.2	60.9	δ(C-H): δ(C$_3$-H$_3$); ν(O-C); ν(N-C); ν(C-C);	1281
53	1309.2	280.3	ν(O-C); ν(C-C); δ(C-H); ν(N-C): ν(N'$_1$-C'$_2$);	
54	1331.5	7.9	δ(C-H): δ(C'$_3$-H'$_3$), δ(C'$_7$-H'$_7$), δ(C'$_4$-H'$_4$), δ(C'$_6$-H'$_6$); ν(C-C);	
55	1344.2	23.3	ν(C-C): ν(C$_4$-C$_5$), ν(C$_5$-C$_6$),ν(C$_2$-C$_3$),ν(C$_3$-C$_4$),ν(C$_2$-C$_7$);	
56	1387.9	32.9	ν(C-C): ν(C'$_5$-C'$_6$), ν(C'$_2$-C'$_7$),ν(C'$_2$-C'$_3$),ν(C'$_3$-C'$_4$),ν(C'$_4$-C'$_5$); δ(O-H);	1350
57	1430.5	43.0	ν(C-C): ν(C$_3$-C$_4$), ν(C$_6$-C$_7$); δ(C-H): δ(C$_7$-H$_7$);	1396
58	1472.7	37.7	ν(C-C): ν(C'$_6$-C'$_7$), ν(C'$_3$-C'$_4$); δ(C-H): δ(C'$_4$-H'$_4$), δ(C'$_6$-H'$_6$); ν(N$_1$-N'$_1$);	1420
59	1509.6	88.1	ν(C-C): ν(C$_4$-C$_5$); δ(C-H);	1458
60	1523.5	104.6	ν(N$_1$-N'$_1$); ν(C-C); δ(C-H);	1504
61	1544.3	296.9	δ(C-H); ν(C-C); ν(N$_1$-N'$_1$);	
62	1603.5	9.8	ν(C-C): ν(C$_2$-C$_7$), ν(C$_5$-C$_6$), ν(C$_2$-C$_3$), ν(C$_4$-C$_5$); δ(C-H);	
63	1624.0	49.7	ν(C-C): ν(C'$_5$-C'$_6$), ν(C'$_2$-C'$_3$), ν(C'$_2$-C'$_7$); δ(C-H);	1582
64	1638.2	6.4	ν(C-C): ν(C$_6$-C$_7$), ν(C$_3$-C$_4$); δ(C-H);	
65	1657.3	259.7	ν(C-C): ν(C'$_6$-C'$_7$), ν(C'$_3$-C'$_4$), ν(C'$_4$-C'$_5$), ν(C'$_2$-C'$_7$); δ(C-H);	
66	2333.9	42.9	ν(N-C): ν(N$_5$-C$^{CN(5)}$); ν(C$_5$-C$^{CN(5)}$);	2261
67	2340.2	10.4	ν(N-C): ν(N$_4$-C$^{CN(4)}$); ν(C$_4$-C$^{CN(4)}$)	
68	3180.3	19.6	ν(C-H): ν(C'$_6$-H'$_6$);	
69	3211.7	3.7	ν(C-H): ν(C'$_4$-H'$_4$);	
70	3213.1	0.5	ν(C-H): ν(C$_7$-H$_7$), ν(C$_6$-H$_6$);	
71	3215.0	3.3	ν(C-H): ν(C'$_7$-H'$_7$);	
72	3226.3	1.3	ν(C-H): ν(C$_6$-H$_6$), ν(C$_7$-H$_7$);	
73	3232.7	3.4	ν(C-H): ν(C'$_3$-H'$_3$), ν(C'$_4$-H'$_4$);	
74	3241.8	3.1	ν(C$_3$-H$_3$);	
75	3819.5	158.7	ν(O-H);	

[a] Based on PED. Coordinates are listed if their contributions are greater than ~10%. Coordinates are presented in descending order of their contributions. The designation "*Coord-1*: *Coord-2*, *Coord-3*;" means that the displacement along coordinates *Coord-2* and *Coord-3* are a part of the general displacement *Coord-1*. The following designations are used: ν(X-Y) – stretching of the X–Y bond; δ – in-plane bending; π – out-of-plane bending; τ – torsion; rot(Ph) – rotation of the phenyl fragment around an axis N-C; π scissoring - ring-ring out-of-plane scissoring; δ scissoring – ring-ring in-plane scissoring; π shearing – out-of-plane shearing.

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