Solid State Studies of Phthalazinylhydrazones and Triazolophthalazines The Role of Nitro Group

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Synthesis and spectral analysis

2-(2-nitrobenzylidene)-1-(phthalazin-1(2*H*)-ylidene)hydrazinium chloride hemihydrate (**1**): orange rectangular prism crystals; mp 213°C; IR (KBr, cm^{-1}): 3395 (νNH, νOH), 3130-2700 (νCH), 1612 (νC=N, δNH, νCC_{ring}, δOH), 1590 ($\nu C{=}N_{ring}$), 1562 (νCC_{ring}), 1520 (νNO_2, δNH, νC=N, νCC_{ring}), 1505 (νCC_{ring}), 1470 (δNH, δOH), 1440 (νCC_{ring}), 1360 (νNO_2, δNH, δCH), 1280 (νCN_{ring}), 1100 (νCN), 1050 (νNN), 875 (δCH), 745 (δNO_2, δCH), 590 (δNO_2, δCH).

2-(3-nitrobenzylidene)-1-(phthalazin-1(2*H*)-ylidene)hydrazinium chloride (**2**): yellow hexagonal plate crystals; mp 280°C; IR (KBr, cm^{-1}): 3435 (νNH), 3100-2700 (νCH), 1610 (νC=N, δNH, νCC_{ring}), 1590 ($\nu C{=}N_{ring}$, νCC_{ring}), 1530 (νNO_2, δNH, νC=N), 1504 (νCC_{ring}), 1475 (δNH), 1350 (νNO_2, δNH, δCH), 1275 (νCN_{ring}), 1090 (νCN), 1050 (νNN), 890 (δCH), 800 (δCH), 760 (δNO_2, δCH), 730 (δCH), 590 (δNO_2, δCH).

2-(3-nitrobenzylidene)-1-(phthalazin-1(*2H*)-ylidene)hydrazine (**2A**): orange needle crystals; mp 236°C; IR (KBr, cm^{-1}): 3338 (νNH), 3100-2830 (νCH), 1617 (νC=N, δNH, νCC_{ring}), 1600 (νCC_{ring}), 1580 ($\nu C{=}N_{ring}$), 1565 (νCC_{ring}), 1520 (νNO_2, δNH, νC=N), 1480 (δNH), 1435 (νCC_{ring}), 1378 (δCH, δNH), 1355 (νNO_2, δNH, δCH), 1260 (νCN_{ring}), 1082 (νCN), 1007 (νNN), 890 (δCH), 778 (δCH), 735 (δNO_2, δCH), 673 (δCH, δCC), 590 (δNO_2, δCH).

2-(4-nitrobenzylidene)-1-(phthalazin-1(2*H*)-ylidene)hydrazinium chloride methanol solvate (**3**): yellow needle crystals; mp 288°C; IR (KBr, cm^{-1}): 3420 (νNH), 3110-2740 (νCH), 1613 (νC=N, δNH, νCC_{ring}, δOH), 1590 ($\nu C{=}N_{ring}$, νCC_{ring}), 1515 (νNO_2, δNH, CC_{ring}, νC=N), 1475 (δNH, δOH), 1340 (νNO_2, δNH, δCH), 1275 (νCN_{ring}), 1090 (νCN), 1045 (νNN), 1025 (νCO), 840 (δCH), 760 (δNO_2, δCH), 590 (δNO_2, δCH).

2-(4-nitrobenzylidene)-1-(phthalazin-1(*2H*)-ylidene)hydrazine (**3A**): orange prism crystals; mp 260°C; IR (KBr, cm-1): 3290 (νNH), 3085-2880 (νCH), 1613 (νC=N, δNH, νCC_{ring}), 1590 ($\nu C{=}N_{ring}$, νCC_{ring}), 1567 (νCC_{ring}), 1515 (νNO_2, δNH, νCC_{ring}, νC=N), 1475 (δNH), 1385 (δCH, δNH), 1345 (νNO_2), 1260 (νCN_{ring}), 1105 (νCN, νNN_{ring}), 1014 (νNN), 850 (δCH), 750 (δNO_2, δCH), 590 (δNO_2, δCH).

2-[3-(4-nitrophenyl)prop-2-en-1-ylidene]-1-(phthalazin-1(2H)-ylidene)hydrazinium chloride methanol solvate (**4**): yellow prism crystals; mp 150°C; IR (KBr, cm-1): 3470 (νNH, νOH), 3100-2800 (νCH), 1630 (νCC), 1610 (νC=N, δNH, νCC_{ring}), 1590 ($\nu C{=}N_{ring}$), 1560 (νCC_{ring}), 1510 (νNO_2, δNH, νCC_{ring}, νC=N), 1475 (δNH, δOH), 1380 (δNH, δCH), 1340 (νNO_2), 1280 (νCN_{ring}), 1100 (νCN), 1040 (νNN), 1000 (νCO, δCH), 830 (δCH), 750 (δNO_2, δCH), 600 (δNO_2, δCH).

2-(3-phenylprop-2-en-1-ylidene)-1-(phthalazin-1(2H)-ylidene)hydrazinium chloride methanol solvate (**5**): yellow prism crystals; mp 190°C; IR (KBr, cm-1): 3235 (νNH, νOH), 3120-2700 (νCH), 1625 (νCC), 1612 (νC=N, δNH, νCC_{ring}), 1595 ($\nu C{=}N_{ring}$, νCC_{ring}), 1500 (νCC_{ring}, νC=N), 1470 (δNH, δOH), 1445 (νCC_{ring}), 1375 (δNH, δCH), 1275 (νCN_{ring}), 1090 (νCN), 1045 (νNN), 1030 (νCO), 980 (δCH), 750 (δCH), 690 (δCH), 590 (δCC, δCH).

1-[(3-phenylprop-2-en-1-ylidene)hydrazinylidene]-1,2-dihydrophthalazine (**5A1**): yellow plate crystals; mp 138°C; IR (KBr, cm-1): 3235 (νNH), 3080-2880 (νCH), 1624 (νCC), 1615 (νC=N, δNH), 1602 (νCC_{ring}), 1592 ($\nu C{=}N_{ring}$), 1575 (νCC_{ring}), 1526 (νCC_{ring}, δNH, νC=N), 1475 (δNH, δCH), 1448 (νCC_{ring}), 1380 (δCH, δNH), 1354 (δCH, δNH), 1245 (νCN_{ring}), 1145 (νCN, νNN_{ring}), 1000 (νNN), 970 (δCH), 745 (δCH), 690 (δCH), 660 (δCC), 590 (δCC, δCH).

1-[(3-phenylprop-2-en-1-ylidene)hydrazinylidene]-1,2-dihydrophthalazine (**5A2**): yellow needle crystals; mp 128°C; IR (KBr, cm-1): 3235 (νNH), 3080-2835 (νCH), 1623 (νCC), 1615 (νC=N, δNH), 1602 (νCC_{ring}), 1590 ($\nu C{=}N_{ring}$), 1574 (νCC_{ring}), 1521 (νCC_{ring}, δNH, νC=N), 1498 (νCC_{ring}), 1473 (δNH, δCH), 1446 (νCC_{ring}), 1377 (δCH, δNH,), 1355 (δCH, δNH), 1243 (νCN_{ring}), 1143 (νCN, νNN_{ring}), 1012 (νNN), 968 (δCH), 742 (δCH), 687 (δCH), 662 (δCC), 585 (δCC, δCH).

3-(2-nitrophenyl)[1,2,4]triazolo[3,4-*a*]phthalazine (**1B**): yellow rectangular prism crystals (recrystallized by slow evaporation from MeOH/MeCN); mp 279°C; IR (KBr, cm-1): 3090-2870 (νCH), 1625 (νCC, νC=N), 1600 (νCC), 1574 (νCC), 1525 (νCC, νC=N, νNO_2), 1460 (νCC, νCN), 1382 (δCH), 1355 (νNO_2, νCN), 1220 (νNN, δCH), 1100 (νNN), 960 (δCC, δCH, δCN), 850 (δNCN), 750 (δCH), 710 (δNO_2), 695 (δCNN), 590 (δCC, δCH, δNO_2).

3-(3-nitrophenyl)[1,2,4]triazolo[3,4-*a*]phthalazine (**2B**): yellow needle crystals (recrystallized by slow evaporation from MeOH/DMF); mp 287°C; IR (KBr, cm-1): 3130-2830 (νCH), 1628

(νCC, νC=N), 1600 (νCC), 1578 (νCC), 1560 (νCC), 1540 (νNO_2), 1526 (νCC), 1510 (νC=N), 1460 (νCC, νCN), 1370 (δCH), 1355 (νNO_2, νCN), 1267 (δCH), 1220 (νNN, δCH), 1087 (νNN), 974 (δCC, δCH, δCN), 873 (δNCN), 830 (δNO_2, δCC), 780 (δCH), 765 (δCH), 745 (δCH), 726 (δCH), 700 (δNO_2, δCNN), 595 (δCC, δCH, δNO_2).

3-(4-nitrophenyl)[1,2,4]triazolo[3,4-*a*]phthalazine (**3B**): orange rectangular plate crystals (recrystallized by slow evaporation from MeOH/MeCN); mp 308°C; IR (KBr, cm-1): 3120-2820 (νCH), 1623 (νCC, νC=N), 1600 (νCC), 1560 (νCC), 1512 (νCC, νC=N, νNO_2), 1470 (νCC, νCN), 1450 (νCC), 1382 (δCH), 1345 (νNO_2, νCN), 1220 (νNN, δCH), 1100 (νNN), 964 (δCC, δCH, δCN), 855 (δNCN, δCH), 756 (δCH), 704 (δNO_2), 695 (δCNN), 590 (δCC, δCH, δNO_2).

3-[2-(4-nitrophenyl)ethenyl][1,2,4]triazolo[3,4-*a*]phthalazine (**4B**): orange plate crystals (recrystallized by slow evaporation from MeOH/MeCN and MeOH/DMF); mp 324°C; IR (KBr, cm-1): 3140-2800 (νCH), 1622 (νCC, νC=N), 1593 (νCC, νNO_2), 1510 (νCC, νC=N, νNO_2), 1470 (νCC, νCN), 1450 (νCC), 1390 (δCH), 1340 (νNO_2, νCN), 1225 (νNN, δCH), 1103 (νNN), 974 (δCC, δCH, δCN), 840 (δNCN, δCH), 746 (δCH), 705 (δNO_2), 694 (δCNN), 590 (δCC, δCH, δNO_2).

3-[2-phenylethenyl][1,2,4]triazolo[3,4-a]phthalazine (**5B**): pale yellow prism crystals (recrystallized by slow evaporation from MeOH/DMF); mp 197°C; IR (KBr, cm-1): 3100-2820 (νCH), 1638 (νCC), 1626 (νCC, νC=N), 1596 (νCC), 1576 (νCC), 1558 (νCC), 1523 (νCC, νC=N), 1505 (νCC), 1470 (νCC, νCN), 1450 (νCC), 1385 (δCH), 1350 (νCN), 1205 (νNN, δCH), 1115 (νNN), 963 (δCC, δCH, δCN), 845 (δNCN, δCH), 760 (δCH), 754 (δCH), 696 (δCNN), 590 (δCC, δCH).

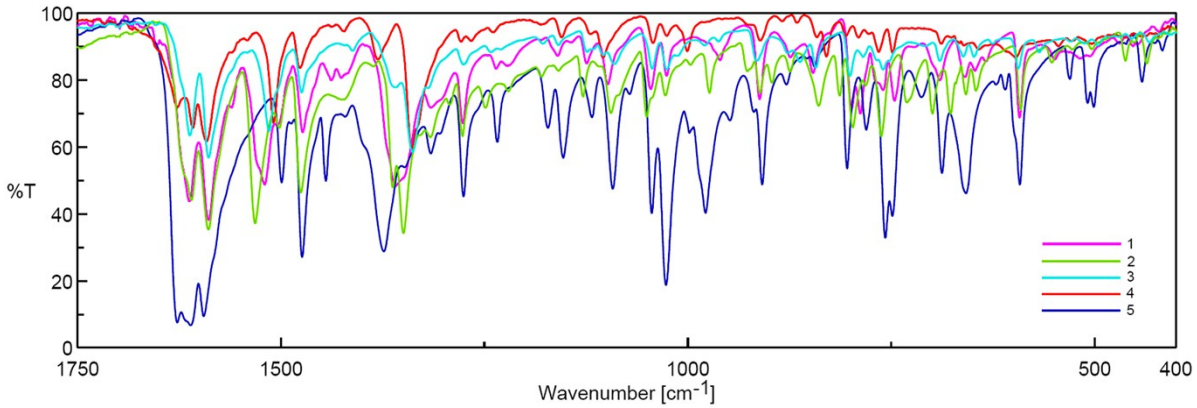

Fig. S1. The partial IR spectra of hydrazonium chlorides (**1**-**5**).

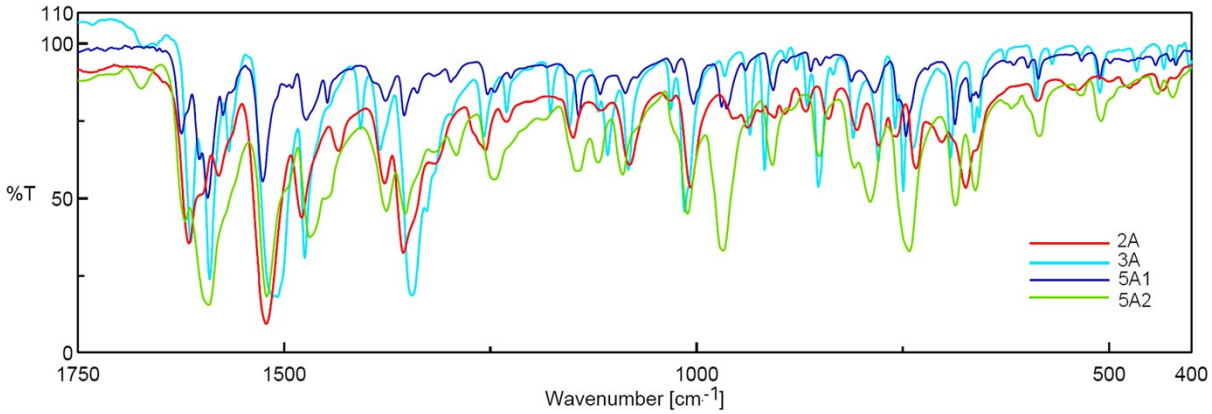

Fig. S2. The partial IR spectra of phthalazinylhydrazones (**2A**, **3A**, **5A1**, **5A2**).

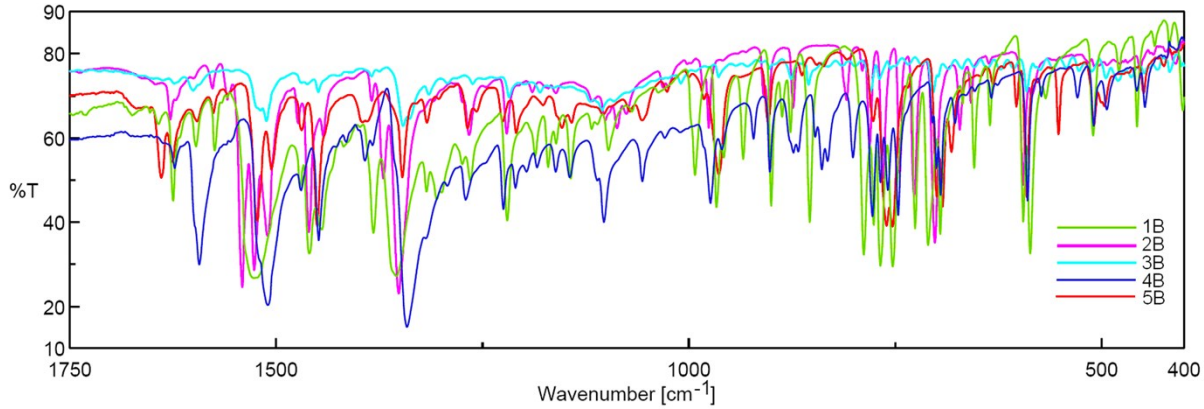

Fig. S3. The partial IR spectra of triazolophthalazines (**1B-5B**).

Table S1. Some characteristic vibration frequencies of phthalazinylhydrazones.

Assignment	**1**	**2**	**2A**	**3**	**3A**	**4**	**5**	**5A1**	**5A2**
νNH, νOH	3395	3435	3338	3420	3290	3470	3235	3235	3235
νCH	3090, 3020, 2765	3086, 3020, 2968, 2920, 2872, 2723	3082, 2954, 2854	3084, 3020, 2922, 2856, 2767	3074, 3024, 2925, 2850	3100, 3043, 2924, 2831	3106, 3039, 2928, 2822, 2757	3077, 3055, 3028, 2950	3078, 3025, 2993, 2950, 2855
νCC						1630	1625	1624	1623
νC=N, δNH	1612	1610	1617	1613	1613	1610	1612	1615	1615
νCC_{ring}			1600					1602	1602
$\nu C{=}N_{ring}$	1590	1590	1580	1590	1590	1590	1595	1592	1590
νCC_{ring}	1562		1565		1567	1560		1575	1574
$\nu C{=}N_{ring}$, νCC_{ring}	1520	1530	1520	1515	1515	1510	1500	1526	1521
νCC_{ring}	1505	1504							1498
δNH	1470	1475	1480	1475	1475	1475	1470	1475	1473
νCC_{ring}	1440		1435				1445	1448	1446
δNH, δCH			1378		1385	1380	1375	1380	1377
νNO_2, δNH, δCH	1360	1350	1355	1340	1345	1340		1354	1355
νCN_{ring}	1280	1275	1260	1275	1260	1280	1275	1245	1243
νCN	1100	1090	1082	1090	1105	1100	1090	1145	1143
νNN	1050	1050	1007	1045	1014	1040	1045	1000	1012
δNO_2	745	760	735	760	750	750			

Table S2. Some characteristic vibration frequencies of triazolophthalazines.

Assignment	**1B**	**2B**	**3B**	**4B**	**5B**
νCH	3085, 3048, 3030, 2874	3104, 3057, 3018, 2960, 2886	3098, 3076, 2925, 2850	3107, 3062, 2929, 2836	3057, 2036, 3000, 2920, 2848
νCC					1638
νCC, νC=N	1625	1628	1623	1622	1626
νCC	1600, 1574	1600, 1578, 1560	1600, 1560	1593	1596, 1576, 1558
νNO_2	1525	1540	1512	1510	
νC=N	1525	1510	1512	1510	1523
νCC, νCN	1460	1460	1470	1470	1470
νNO_2, νCN	1355	1355	1345	1340	1350
νNN, δCH	1220	1220	1220	1225	1205
νNN	1100	1087	1100	1103	1115
δNCN, δCH	850	873	855	840	845

Structural studies

The description of X-ray measurement of 5B

The crystals of the compound **5B** were well shaped and gave discrete diffraction. All reflections were in the places of the frames, in which they should appear, i.e. the placement of the reflections was in agreement with those calculated from the orientation matrix. There were no observable reflections beyond the places calculated from the orientation matrix. The reflections were well shaped, i.e. shapes of the reflections fit well the Gaussian curve with a 2-dimensional domain. Solution of the structure in the statistically best space group ($P2_1/c$, a = 9.6808(12) Å, b = 5.1248(7) Å, c = 13.8869(18) Å, $\alpha = 90°$, $\beta = 100.306(11)°$, $\gamma = 90°$, 100.0(1) K) leads to the model (Fig. S4 (a)) with overlapped 2-phenylethenyl and triazolophthalazine moieties by symmetry (the symmetry center located at the gravity center of the molecule). The domains can be separated in the initial model (Fig. S4 (b)) but the refinement leads to the abnormal interatomic distances, impossible isotropic displacement parameters, unacceptable goodness of fit and R1 = 0.7288. Because the wrongly interpreted statistic may lead to introduction of the non-existing symmetry centre (the internal molecular symmetry may cause the false statistics, because the molecularly equivalent groups of atoms may not be connected by crystallographic symmetry), as well as, because the symmetry centre forces the occupation factors of both domains to be equal 0.5, the structure was solved and refined in the maximal non-isomorphic subgroup, which does not posses this ambiguous symmetry element (space group *Pc*). Solution of the structure in the *Pc* space group leads to the model (Fig. S4 (c)) still possessing the overlapped 2-phenylethenyl and triazolophthalazine moieties. The domains can be separated in the initial model (Fig. S4 (d)) but the refinement leads to the abnormal interatomic distances, impossible isotropic displacement parameters, unacceptable goodness of fit and R1 = 0.6528. The slight increase of the structure quality originates mainly from the unequal occupation of both domain (0.63843:0.36157), what proves that the $P2_1/c$ space group was incorrect (the internal molecular symmetry leads to false statistics, because the molecularly equivalent groups of atoms were not connected by crystallographic symmetry). The introduction of the anisotropy to the displacement parameters of the *Pc* space group refinement leads to the enormous prolation of the anisotropic displacement ellipsoids. The two-domain disorder model (with overlapped 2-phenylethenyl and triazolophthalazine moieties of the opposite domains) was modified and two further domains were introduce to the refinement (each domain was

separated into the two domains slightly relocated along the major axis of spheroid). The refinement of four-domain model was stable only with the isotropic displacement parameters. The close inspection of the atoms positions of this model shows some deviation from the *Pc* space group symmetry. Thus the measurement data were reduced in the triclinic crystal system. The unit cell parameters (a = 5.1248(7) Å, b = 9.6808(12) Å, c = 13.8869(18) Å, α = 100.306(11)°, β = 90.030(9)°, γ = 90.033(8)°, 100.0(1) K) show some deviations from the values required for monoclinic crystal system symmetry. The refinement of the structural model of two molecules, of which each was disordered unequally over two positions (with the anisotropy introduced to the displacement parameters of all non-hydrogen atoms), in the *P*1 space group, leads to the stable convergence with the R1 = 0.2579. The quality of the model is unsatisfactory for the full structural description and analysis of the structural parameters, but it allows to confirm that the *P*1 space group is the correct one and that studied compound is the solvent-free 3-[2-phenylethenyl][1,2,4]triazolo[3,4-a]phthalazine.

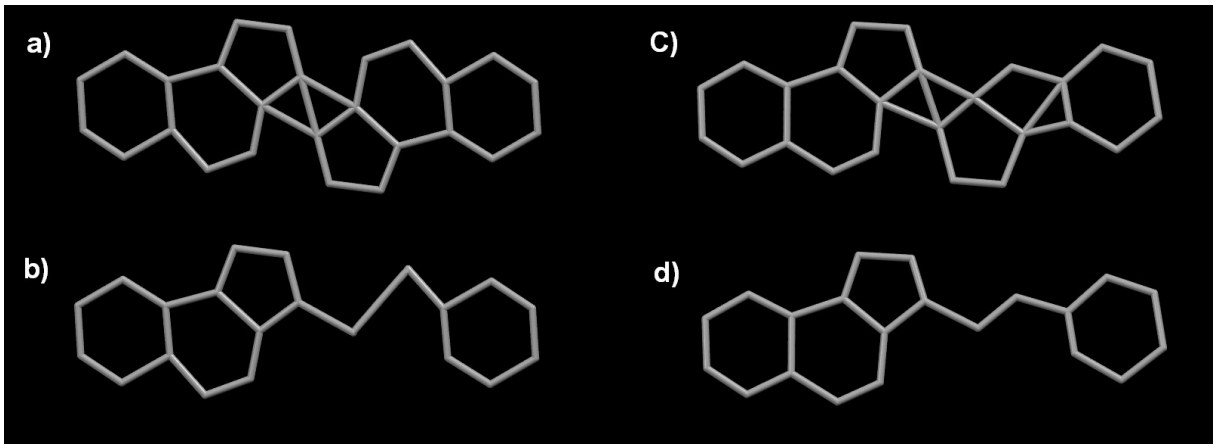

Fig. S4. The initial model of the **5B** after the solution in a) the $P2_1/c$ space group, c) the *Pc* space group; the separated domain of the **5B** in b) the $P2_1/c$ space group, d) the *Pc* space group.

Table S3. Selected structural data for compounds **1-5** and **2A**, **3A**, **5A1**, **5A2** [Å].

	N2-C2	N1-N2	C1-N1	C1-C4	C1-N3	N3-N4	N4-C9	N5-O1	N5-O2
1	**1.287(3)** **1.289(3)**	**1.370(2)** **1.370(2)**	**1.333(2)** **1.337(2)**	**1.446(2)** **1.445(3)**	**1.335(2)** **1.337(2)**	**1.380(2)** **1.383(2)**	**1.274(3)** **1.283(2)**	**1.190(3)/ 1.300(9)** **1.224(2)**	**1.243(5)/ 1.145(9)** **1.213(2)**
2	**1.2946(15)**	**1.3742(13)**	**1.3371(15)**	**1.4471(15)**	**1.3360(15)**	**1.3778(13)**	**1.2815(15)**	**1.2289(14)**	**1.2273(14)**
2A	**1.2927(14)**	**1.3670(13)**	**1.3685(14)**	**1.4601(15)**	**1.3080(14)**	**1.3925(13)**	**1.2839(15)**	**1.2264(13)**	**1.2257(12)**
3	**1.2962(16)**	**1.3735(14)**	**1.3337(15)**	**1.4468(16)**	**1.3375(15)**	**1.3827(13)**	**1.2821(16)**	**1.2239(16)**	**1.2293(15)**
3A	**1.2928(13)**	**1.3685(11)**	**1.3660(12)**	**1.4582(13)**	**1.3125(13)**	**1.3889(11)**	**1.2845(13)**	**1.2206(12)**	**1.2272(12)**
4	**1.2972(16)**	**1.3745(15)**	**1.3362(15)**	**1.4447(16)**	**1.3406(16)**	**1.3801(13)**	**1.2874(16)**	**1.2269(14)**	**1.2286(14)**
5	**1.2944(16)**	**1.3734(13)**	**1.3354(14)**	**1.4396(17)**	**1.3386(14)**	**1.3813(14)**	**1.2889(15)**	-	-
5A1	**1.2914(14)**	**1.3639(12)**	**1.3744(13)**	**1.4597(14)**	**1.3060(13)**	**1.3985(12)**	**1.2853(14)**	-	-
5A2	**1.2936(13)**	**1.3578(11)**	**1.3724(12)**	**1.4610(13)**	**1.3092(13)**	**1.3960(11)**	**1.2855(13)**	-	-

Table S4. Hydrogen bonds in studied compounds [Å, °].

	D-H	H•••A	D•••A	D-H•••A
Compound **1**				
N1—H1N•••O99	0.94	1.83	2.684(2)	149.6
N3—H3N•••Cl1^{i}	0.87	2.25	3.1000(16)	163.9
N21—H21N•••Cl1^{ii}	0.94	2.21	3.0415(16)	146.1
N23—H23N•••Cl21	0.98	2.15	3.0988(15)	160.6
O99—H99O•••Cl1	0.91	2.21	3.1149(17)	172.2
O99—H99P•••Cl21	0.94	2.16	3.0897(16)	171.3
C8—H8•••Cl1^{i}	0.95	2.71	3.633(2)	163.9
C9—H9•••O1	0.95	2.25	2.828(3)	118.6
C9—H9•••Cl1^{i}	0.95	2.67	3.4814(19)	143.4
C15—H15•••O99	0.95	2.53	3.461(3)	167.0
C22—H22•••O99^{iii}	0.95	2.51	3.448(2)	171.6
C29—H29•••O21	0.95	2.43	2.883(2)	109.2
C29—H29•••Cl21	0.95	2.64	3.4260(18)	140.7
C35—H35•••Cl1^{ii}	0.95	2.75	3.6937(19)	175.0

Compound **1B**				
C6—H6•••O1i[v]	0.95	2.54	3.4677(14)	164.9
C8—H8•••O1[v]	0.95	2.60	3.5221(14)	164.1
Compound **2**				
N1—H1N•••Cl1[vi]	0.88	2.39	3.1825(10)	150.9
N3—H3N•••Cl1	0.89	2.26	3.1322(10)	164.1
C2—H2•••O1[vi]	0.95	2.44	3.3101(14)	152.1
C6—H6•••O1[vii]	0.95	2.58	3.4432(14)	151.0
C7—H7•••O2[vii]	0.95	2.54	3.2801(15)	134.8
C8—H8•••Cl1	0.95	2.63	3.5567(12)	164.4
C9—H9•••Cl1	0.95	2.81	3.6026(12)	142.0
C15—H15•••Cl1[vi]	0.95	2.63	3.5599(12)	166.8
Compound **2A**				
N1—H1N•••N2[viii]	0.89	2.25	2.9500(13)	135.1
C2—H2•••O1[viii]	0.95	2.59	3.4019(14)	143.6
C7—H7•••O2[ix]	0.95	2.57	3.4869(14)	162.4
Compound **2B**				
C2—H2•••N4[x]	0.93	2.57	3.481(4)	165.7
C5—H5•••N3[x]	0.93	2.55	3.459(4)	166.8
C6—H6•••O22[ii]	0.93	2.52	3.223(4)	132.7
C15—H15•••O1[x]	0.93	2.55	3.178(4)	125.1
C15—H15•••N2	0.93	2.36	2.998(4)	125.8
C22—H22•••N24[xi]	0.93	2.48	3.406(3)	171.1
C25—H25•••N23[xi]	0.93	2.57	3.466(4)	162.3
C35—H35•••N22	0.93	2.36	2.996(4)	125.8
Compound **3**				
N1—H1N•••Cl1[xii]	0.89	2.25	3.0893(10)	158.5
N3—H3N•••Cl1	0.90	2.20	3.0831(11)	166.8
O91—H91O•••Cl1	0.91	2.20	3.114(2)	175.0
C2—H2•••O91[xiii]	0.95	2.41	3.336(2)	166.5
C8—H8•••Cl1	0.95	2.67	3.5818(12)	161.8
C9—H9•••Cl1	0.95	2.66	3.4885(12)	146.4
C11—H11•••Cl1[xii]	0.95	2.79	3.5859(12)	141.8
C14—H14•••O91[xiv]	0.95	2.41	3.299(3)	156.3
C6—H6•••O1[xv]	0.95	2.93	3.8593(16)	166.7
C6—H6•••O2[xv]	0.95	2.62	3.2684(15)	125.7
C5—H5•••O2[xv]	0.95	2.69	3.3016(15)	122.4

Compound **3A**				
N1—H1N•••N2^{xvi}	0.92	2.20	2.9391(12)	137.7
C6—H6•••O2^{xvii}	0.95	2.48	3.1139(13)	124.2
Compound **3B**				
C7—H7•••O2^{xviii}	0.95	2.48	3.3266(18)	148.2
C11—H11•••N2	0.95	2.48	3.0735(19)	120.8
C12—H12•••N4^{xix}	0.95	2.39	3.2515(18)	151.2
C15—H15•••O1^{x}	0.95	2.50	3.3808(17)	154.7
Compound **4**				
N1—H1N•••O91	0.90	1.87	2.7311(13)	159.5
N3—H3N•••Cl1	0.92	2.27	3.1638(11)	164.4
O91—H91O•••Cl1^{xx}	0.88	2.18	3.0540(9)	174.4
C5—H5•••O1^{xxi}	0.95	2.53	3.0812(16)	117.4
C8—H8•••Cl1	0.95	2.70	3.6136(13)	160.5
C9—H9•••Cl1	0.95	2.83	3.6079(12)	139.9
C13—H13•••O91^{x}	0.95	2.49	3.3820(15)	157.2
C14—H14•••O1^{xxii}	0.95	2.52	3.3199(14)	142.0
C16—H16•••O2^{xxiii}	0.95	2.51	3.1019(16)	120.2
Compound **4B**				
C13—H13•••N3^{x}	0.95	2.56	3.4247(16)	151.0
C17—H17•••O1^{xxiv}	0.95	2.34	3.2151(16)	153.1
C7—H7•••O2^{xxv}	0.95	2.61	3.3737(17)	137.7
Compound **5**				
N1—H1N•••O91^{xxvi}	0.99	1.80	2.7396(13)	155.9
N3—H3N•••Cl1	0.89	2.22	3.1072(10)	169.1
O91—H91O•••Cl1	0.93	2.12	3.0431(8)	169.6
C2—H2•••O91^{xxvii}	0.95	2.52	3.3548(14)	146.8
C5—H5•••O91^{xxvii}	0.95	2.57	3.3912(14)	144.3
C8—H8•••Cl1	0.95	2.82	3.6470(12)	146.4
C9—H9•••Cl1	0.95	2.81	3.5471(12)	134.6
Compound **5A1**				
N1—H1N•••N2^{xxviii}	0.93	2.14	2.9258(13)	140.3

Compound **5A2**

N1—H1N•••N2^{xxix}	0.93	2.15	2.9561(12)	143.8
C13—H13•••N3^{xxx}	0.95	2.62	3.5655(13)	172.8

Symmetry transformations used to generate equivalent atoms: (i) -*x*+1, -*y*+2, -*z*; (ii) -*x*+2, -*y*+2, -*z*; (iii) -*x*+2, -*y*+1, -*z*; (iv) -*x*, -*y*+1, -*z*+1; (v) *x*+1/2, -*y*+3/2, *z*+1/2; (vi) -*x*+1/2, *y*-1/2, -*z*+3/2; (vii) *x*-3/2, -*y*+1/2, *z*+1/2; (viii) -*x*+2, -*y*, -*z*+1; (ix) *x*+1, *y*+1, *z*; (x) *x*, *y*+1, *z*; (xi) *x*-1, *y*, *z*; (xii) -*x*+1, *y*+1/2, -*z*+1/2; (xiii) -*x*, *y*+1/2, -*z*+1/2; (xiv) *x*+1, *y*, *z*; (xv) *x*-2, -*y*+3/2, *z*+1/2; (xvi) -*x*, -*y*+3, -*z*+1; (xvii) *x*+1, -*y*+3/2, *z*+1/2; (xviii) *x*-1, *y*+1, *z*+1; (xix) *x*, *y*-1, *z*; (xx) -*x*, -*y*, -*z*+1; (xxi) *x*, *y*-1, *z*+1; (xxii) -*x*+1, -*y*+1, -*z*; (xxiii) -*x*+1, -*y*, -*z*; (xxiv) *x*, *y*-1, *z*; (xxv) *x*, *y*-2, *z*+1; (xxvi) *x*+1/2, -*y*+1/2, -*z*+1; (xxvii) *x*, -*y*+1/2, *z*+1/2; (xxviii) -*x*+2, -*y*+2, -*z*+1; (xxix) -*x*+1,-*y*+2,-*z*+1; (xxx) -*x*+1,*y*-1/2,-*z*+3/2.

Table S5. Stacking interactions [Å, °]. Cg(1)-C(8) indicate the centroids of the aromatic rings containing N2, C8, C12, N22, C28, C32, N4, N24 atoms respectively, α is a dihedral angle between planes I and J, β is an angle between Cg(I)-Cg(J) vector and normal to plane I and d_p is a perpendicular distance of Cg(I) on ring J plane.

Cg(I)•••Cg(J)	Cg•••Cg	α	β	d_p
Compound **1**				
Cg(1)•••Cg(2)^{i}	3.6941(11)	1.84(9)	24.16	-3.3643(7)
Cg(1)•••Cg(3)^{ii}	3.6531(11)	6.54(9)	16.34	3.3663(7)
Cg(2)•••Cg(1)^{i}	3.6942(11)	1.84(9)	24.40	-3.3706(8)
Cg(2)•••Cg(3)^{ii}	3.8295(11)	8.34(9)	23.96	3.6532(8)
Cg(3)•••Cg(1)^{ii}	3.6530(11)	6.53(9)	22.86	3.5055(8)
Cg(3)•••Cg(2)^{ii}	3.8296(11)	8.34(9)	17.44	3.4997(8)
Cg(4)•••Cg(5)^{iii}	3.5033(11)	0.63(9)	16.44	-3.3521(7)
Cg(4)•••Cg(6)^{iv}	3.6701(10)	8.09(8)	25.27	-3.3167(7)
Cg(5)•••Cg(4)^{iii}	3.5033(11)	0.63(9)	16.90	-3.3601(8)
Cg(5)•••Cg(5)^{iii}	3.9875(11)	0.0	32.47	-3.3643(8)
Cg(5)•••Cg(6)^{iv}	3.8212(11)	8.64(9)	29.90	-3.5595(8)
Cg(6)•••Cg(4)^{v}	3.6701(10)	8.09(8)	25.35	3.3188(7)
Cg(6)•••Cg(5)^{v}	3.8212(11)	8.64(9)	21.33	3.3125(7)
Compound **1B**				
Cg(7)•••Cg(2)^{vi}	3.5194(7)	2.54(6)	17.72	-3.3779(4)
Cg(1)•••Cg(2)^{vi}	3.7267(7)	1.57(5)	25.23	-3.3823(4)
Cg(2)•••Cg(7)^{vi}	3.5194(7)	2.54(6)	16.30	-3.3525(4)
Cg(2)•••Cg(1)^{vi}	3.7267(7)	1.57(5)	24.82	-3.3712(4)
Cg(2)•••Cg(2)^{vii}	3.8849(7)	0.0	31.50	3.3124(4)
Cg(3)•••Cg(3)^{i}	3.7635(7)	0.0	18.72	-3.5644(4)
Compound **2**				
Cg(1)•••Cg(2)^{viii}	3.7368(8)	1.38(5)	23.26	3.4126(5)
Cg(1)•••Cg(3)^{ix}	3.6548(7)	9.77(5)	22.94	3.0970(5)
Cg(2)•••Cg(1)^{viii}	3.7367(8)	1.38(5)	24.04	3.4330(5)
Cg(2)•••Cg(3)^{ix}	3.7006(8)	9.09(6)	24.97	3.3303(5)
Cg(3)•••Cg(1)^{x}	3.6549(7)	9.77(5)	32.07	-3.3658(5)
Cg(3)•••Cg(2)^{x}	3.7006(8)	9.09(6)	25.85	-3.3548(5)
Cg(3)•••Cg(3)^{x}	3.4806(7)	0.0	22.21	-3.2223(5)

Compound **2A**				
Cg(1)•••Cg(1)^{xi}	3.7858(7)	0.0	27.67	3.3529(5)
Cg(1)•••Cg(2)^{xi}	3.6101(7)	0.87(5)	20.85	3.3605(5)
Cg(2)•••Cg(2)^{xi}	3.7858(7)	0.0	26.88	3.3766(5)
Cg(3)•••Cg(3)^{xi}	3.7859(7)	0.0	27.00	3.3732(5)
Compound **2B**				
Cg(7)•••Cg(7)^{xii}	3.2961(18)	0.0	9.04	3.2552(13)
Cg(2)•••Cg(3)^{ii}	3.9032(19)	4.75(16)	29.21	-3.5252(14)
Cg(8)•••Cg(8)^{xiii}	3.2788(14)	0.0	4.40	-3.2691(10)
Cg(8)•••Cg(4)^{xiii}	3.9873(15)	2.07(12)	35.75	-3.3142(10)
Cg(4)•••Cg(6)^{i}	3.9295(16)	9.43(12)	31.78	3.5646(9)
Cg(5)•••Cg(6)^{i}	3.8906(16)	7.99(13)	29.69	3.5664(11)
Compound **3**				
Cg(1)•••Cg(3)^{ix}	3.9534(8)	16.36(5)	27.51	-3.8176(4)
Cg(3)•••Cg(1)^{xiv}	3.9533(8)	16.36(5)	15.05	3.5063(5)
Compound **3A**				
Cg(1)•••Cg(2)^{v}	3.6624(6)	1.46(5)	21.63	-3.3875(4)
Cg(2)•••Cg(1)^{iv}	3.6624(6)	1.46(5)	22.34	3.4045(5)
Compound **3B**				
Cg(7)•••Cg(1)^{xv}	3.6686(9)	1.24(7)	22.29	-3.4148(5)
Cg(7)•••Cg(2)^{xv}	3.6641(9)	2.63(7)	18.69	-3.4330(5)
Cg(7)•••Cg(2)^{xvi}	3.5938(9)	2.63(7)	19.32	3.3513(5)
Cg(1)•••Cg(7)^{xv}	3.6687(9)	1.24(7)	21.44	-3.3945(5)
Cg(1)•••Cg(1)^{xv}	3.6798(9)	0.0	22.14	-3.4086(5)
Cg(1)•••Cg(1)^{xvi}	3.8772(9)	0.0	27.63	3.4348(5)
Cg(1)•••Cg(2)^{xvi}	3.5554(9)	2.27(6)	16.74	3.4406(5)
Cg(2)•••Cg(7)^{xv}	3.6641(9)	2.63(7)	20.46	-3.4708(6)
Cg(2)•••Cg(7)^{xvi}	3.5938(9)	2.63(7)	21.17	3.3915(6)
Cg(2)•••Cg(1)^{xvi}	3.5554(9)	2.27(6)	14.60	3.4046(6)
Compound **4**				
Cg(1)•••Cg(3)^{x}	3.7167(8)	1.64(6)	11.60	-3.6352(5)
Cg(2)•••Cg(3)^{xvii}	3.6951(8)	1.93(6)	20.13	3.4516(5)
Cg(3)•••Cg(1)^{x}	3.7167(8)	1.64(6)	12.02	-3.6409(5)
Cg(3)•••Cg(2)^{xvii}	3.6951(8)	1.93(6)	20.91	3.4694(5)
Compound **4B**				
Cg(7)•••Cg(1)^{xviii}	3.5522(10)	1.13(6)	23.65	3.2782(5)
Cg(7)•••Cg(2)^{xix}	3.6142(11)	1.52(7)	23.40	-3.2787(5)
Cg(7)•••Cg(2)^{xviii}	3.5361(11)	1.52(7)	21.55	3.2843(5)
Cg(1)•••Cg(7)^{xviii}	3.5522(10)	1.13(6)	22.65	3.2538(5)
Cg(1)•••Cg(1)^{xviii}	3.5064(10)	0.0	21.68	3.2583(5)
Cg(1)•••Cg(2)^{xix}	3.3839(10)	0.0.45(6)	12.15	-3.3137(5)
Cg(2)•••Cg(7)^{xix}	3.6141(11)	1.52(7)	24.88	-3.3170(5)
Cg(2)•••Cg(7)^{xviii}	3.5362(11)	1.52(7)	21.76	3.2890(5)
Cg(2)•••Cg(1)^{xix}	3.3839(10)	0.45(6)	11.70	-3.3081(5)
Cg(3)•••Cg(3)^{vi}	3.6014(11)	0.0	19.41	-3.3967(5)

Compound **5**

Cg(1)•••Cg(3)^{xix}	3.5386(7)	3.45(6)	16.20	3.4251(4)
Cg(2)•••Cg(3)^{x}	3.9811(7)	5.85(6)	26.49	-3.5037(5)
Cg(3)•••Cg(1)^{xx}	3.5386(7)	3.45(6)	14.55	3.3981(5)
Cg(3)•••Cg(2)^{x}	3.9811(7)	5.85(6)	28.35	-3.5633(5)

Compound **5A2**

Cg(1)•••Cg(1)xi	3.9130(6)	0	30.49	3.3719(4)
Cg(1)•••Cg(2)v	3.8076(7)	2.18(5)	26.05	-3.3909(4)
Cg(2)•••Cg(2)xi	3.9130(7)	0	28.67	3.4331(4)
Cg(3)•••Cg(3)xi	3.9130(7)	0	26.19	3.5112(5)

Symmetry transformations used to generate rings: (i) -*x*+1, -*y*+1, -*z*; (ii) -*x*+1, -*y*+2, -*z*; (iii) -*x*+2, -*y*+1, -*z*; (iv) *x*, *y*-1, *z*; (v) *x*, *y*+1, *z*; (vi) -*x*+1, -*y*+1, -*z*+1; (vii) -*x*, -*y*+1, -*z*+1; (viii) -*x*, -*y*, -*z*+2; (ix) *x*-1, *y*, *z*; (x) -*x*+1, -*y*, -*z*+1; (xi) *x*, -*y*-1/2, *z*+1/2; (xii) -*x*+2, -*y*+1, -*z*+1; (xiii) -*x*+2, -*y*, -*z*; (xiv) *x*+1, *y*, *z*; (xv) -*x*, -*y*+2, -*z*+2; (xvi) -*x*-1, -*y*+2, -*z*+2; (xvii) -*x*, -*y*, -*z*+1; (xviii) -*x*+2, -*y*-1, -*z*+2; (xix) -*x*+1, -*y*-1, -*z*+2; (xx) *x*+1/2, -*y*+1/2, -*z*+1.

Table S6. Selected structural data for **1B-4B** [Å]

	N2-C2	N1-N2	C1-N1	C1-C4	C1-N3	N3-N4	N4-C9	N5-O1	N5-O2
1B	1.2951(14)	1.3786(12)	1.3739(13)	1.4433(15)	1.3171(14)	1.3954(12)	1.3135(14)	1.2363(12)	1.2201(12)
2B	1.280(4) 1.287(4)	1.374(3) 1.385(3)	1.370(3) 1.359(3)	1.422(4) 1.421(4)	1.306(4) 1.319(3)	1.375(4) 1.372(3)	1.317(4) 1.318(3)	1.205(4) 1.203(3)	1.209(4) 1.212(4)
3B	1.2991(18)	1.3847(15)	1.3732(18)	1.4374(19)	1.3187(18)	1.3781(16)	1.3217(18)	1.2340(16)	1.2313(15)
4B	1.3311(16)	1.3811(14)	1.3814(15)	1.4755(16)	1.3318(15)	1.4126(14)	1.3195(15)	1.2199(14)	1.2171(14)

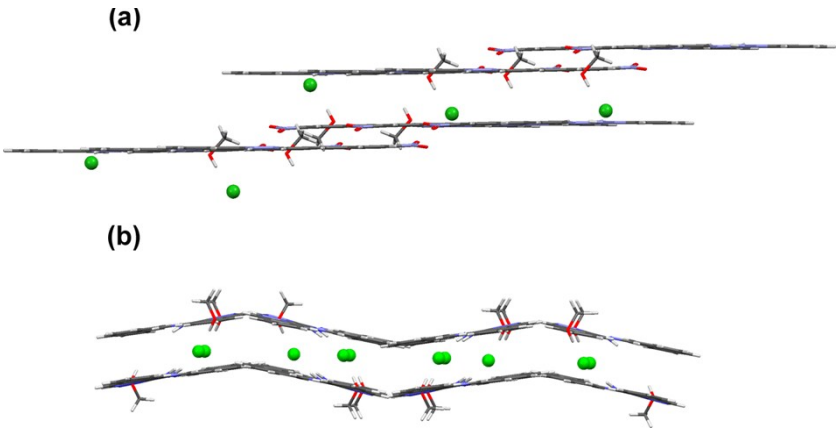

Fig. S5. The comparison of crystal packing of **4** (a) and **5** (b).

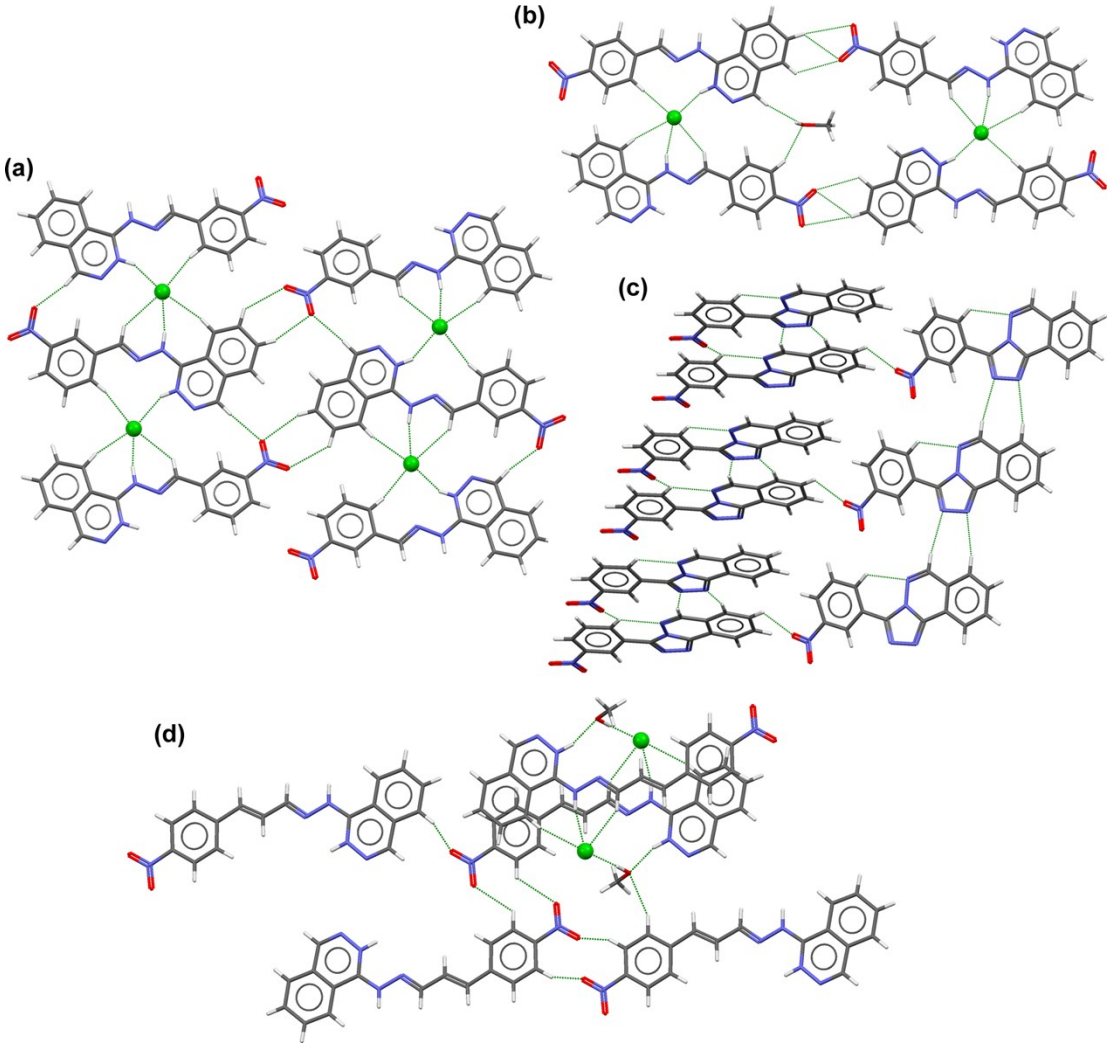

Fig. S6. The part of crystal packing including the C-H···O hydrogen bonds formed by the nitro group for **2** (a), **3** (b), **2B** (c) and **4** (d). For **3** the disordered methanol atoms were omitted.

Computational studies on O···O contacts

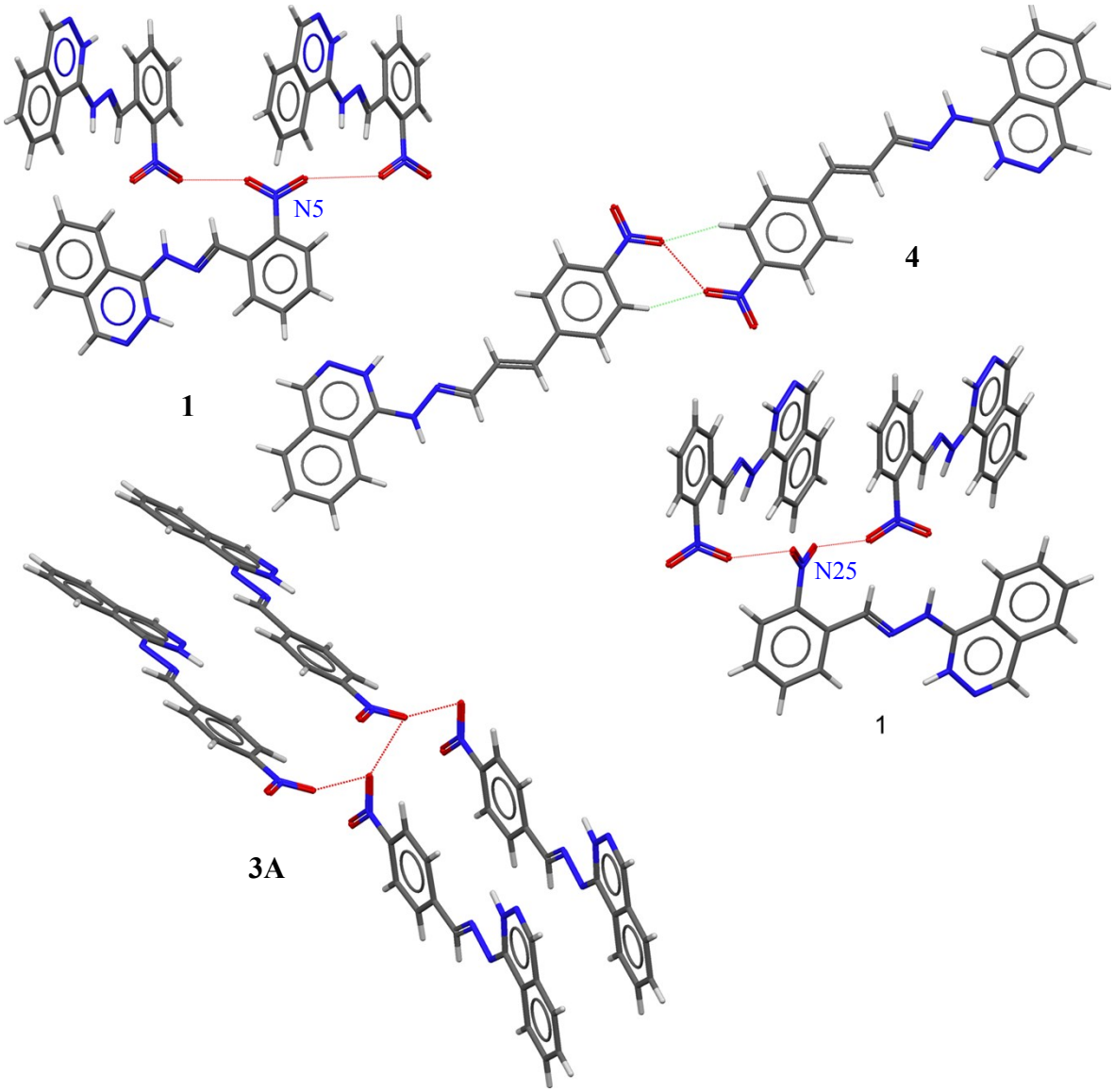

Fig. S7. The part of crystal packing showing the O···O contacts.

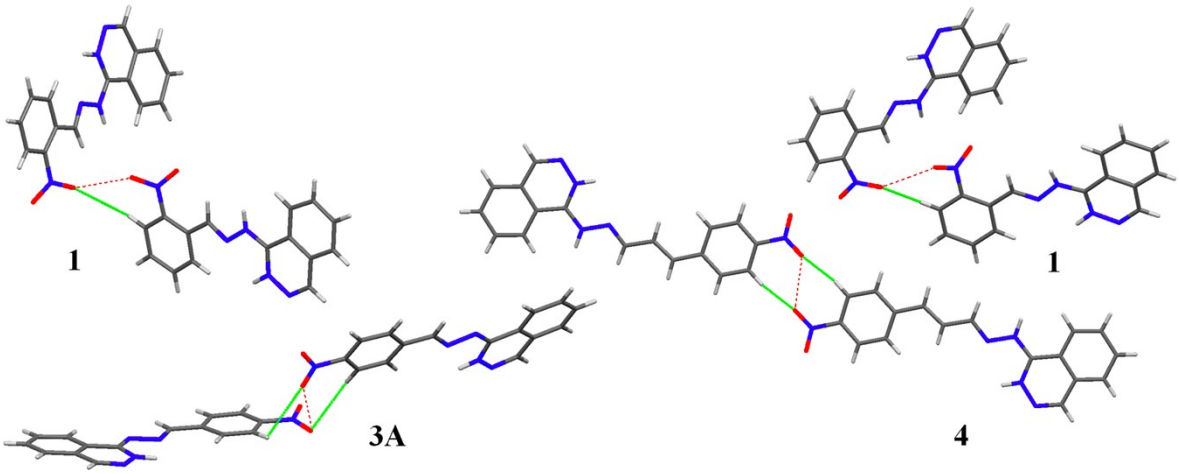

Fig. S8. The part of crystal packing showing the O···O contacts (marked in red) and the weak C-H···O hydrogen bonds (possessing the H···O distance longer than the sum of van der Waals radii, except for **4** (marked in green)).

Table S7. Hydrogen bonds that were included in the calculations of energy of the O···O interactions [Å, °].

D-H•••A	d(D-H)	d(H•••A)	d(D•••A)	<(DHA)
Compound **1**				
C12—H12•••O1^{i}	0.95	3.13	3.871	136.0
C32—H32•••O21^{ii}	0.95	2.71	3.514	142.3
Compound **3A**				
C12—H12•••O1^{iii}	0.95	2.82	3.684	152.1
C12—H12•••O1^{iii}	0.95	2.89	3.303	107.3
Compound **4**				
C14—H14—O1^{iv}	0.95	2.52	3.320	142.0

Symmetry transformations used to generate equivalent atoms: (i) -*x*+1, *y*+1/2, -*z*+1/2; (ii) -*x*+2, *y*+1/2, -*z*+1/2; (iii) -*x*-1, *y*-1/2, -*z*+1/2; (iv) -*x*+1, -*y*+1, -*z*.

Table S8. The hydrogen bonds with the shortest H···A distances that were considered in the calculations of the O···O interaction energies [Å, °].

D-H•••A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
Compound **1**				
C10-H···O2^{i}	0.95	3.72	4.132	109.0
C12-H12···O1^{i}	0.95	3.13	3.871	136.0
Compound **1**				
C32-H32···O21^{ii}	0.95	2.71	3.514	142.3
C30-H···O22^{ii}	0.95	3.45	4.092	127.2
Compound **3A**				
C12-H12···O1^{iii}	0.95	2.82	3.684	152.1
C12-H12···O1^{iii}	0.95	2.89	3.303	107.3
Compound **4**				
C14-H14···O1^{iv}	0.95	2.52	3.320	142.0

Symmetry transformations used to generate equivalent atoms: (i) -*x*+1, y+1/2, -*z*+1/2; (ii) -*x*+2, *y*+1/2, -*z*+1/2; (iii) -*x*-1, *y*-1/2, -*z*+1/2; (iv) -*x*+1, -*y*+1, -*z*.

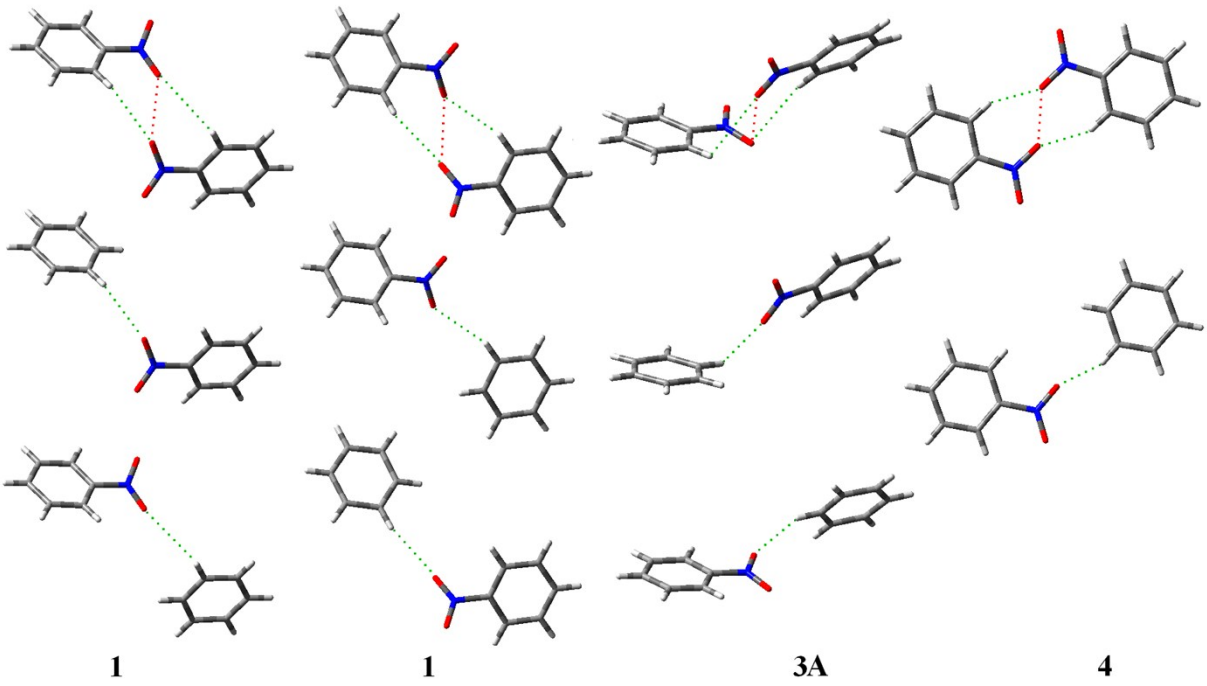

Fig. S9. The molecular moieties used for the theoretical calculations of the O···O interaction energies (All computed moieties were visualized by GaussView. GaussView, Version 5, Roy Dennington, Todd Keith, and John Millam, Semichem Inc., Shawnee Mission, KS, 2009.)

Table S9. The geometrical parameters of the O···O contacts [Å, °].

N-O···O	D(O···O)	<(N-O···O)
Compound **1**		
N5-O1···O2^{i}	2.729(8)	137.0(3)
N5-O2···O1^{i}	2.729(8)	151.1(3)
N25-O21···O22^{ii}	2.742(2)	148.74(14)
N25-O22···O21^{ii}	2.742(2)	134.38(14)
Compound **3A**		
N5-O1···O1^{iii}	2.8629(14)	92.90(8)
N5-O1···O1^{iii}	2.8629(14)	145.28(8)
Compound **4**		
N5-O1···O1^{iv}	2.8619(13)	122.58(8)

Symmetry transformations used to generate equivalent atoms: (i) -*x*+1, *y*+1/2, -*z*+1/2; (ii) -*x*+2, *y*+1/2, -*z*+1/2; (iii) -*x*-1, *y*-1/2, -*z*+1/2; (iv) -*x*+1, -*y*+1, -*z*.