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A mild and efficient synthesis of 3-hetarylamino-*s*-tetrazines

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Table S1 Screening[a] of bases and solvents for the preparation of compound **3a**.

Entry	Base	Solvent	Time,[b] h	Isolated yield[c] of **3a**, %
1	Pyridine	MeCN	6	0[e]
2	NEt_3	MeCN	6	11[d]
3	Li_2CO_3	MeCN	6	0[e]
4	Na_2CO_3	MeCN	6	0[e]
5	$Na_2CO_3\times10H_2O$	MeCN	3.5	40[f]
6	NaF	MeCN	6	0[e]
7	Na_3PO_4	MeCN	7.5	70
8	K_2CO_3	MeCN	1	85
9	KF	MeCN	11	84
10	K_3PO_4	MeCN	3.5	81
11	Cs_2CO_3	MeCN	0.3	86
12	CsF	MeCN	1.5	78
13	K_2CO_3	DME	1	85
14	K_2CO_3	THF[g]	1	73
15	K_2CO_3	Diglyme	0.5	70
16	K_2CO_3	Dioxane	1	60
17	K_2CO_3	DMSO	0.5	60
18	K_2CO_3	DMF	1	42[h]

[a] *Reaction conditions*: Diaminofurazan **2a** (1.1 mmol), tetrazine **1** (1 mmol), base (1 mmol), solvent (10 ml), 80 °C. [b] It is time at which TLC (CCl_4/MeCN 3/1) indicated complete consumption of starting materials. [c] The yields reflect only the amounts of product **3a** that separated at dilution of the reaction mixture with water and acidification to pH 1. [d] Big amounts of reactants **1** and **2a** remain. [e] Starting reactants were fully recovered. [f] 3-Hyrdoxy-6-(3,5-dimethylpyrazol-1yl)-1,2,4,5-tetrazine[12] (mp 205 °C) was isolated as byproduct (53%). [g] Reaction temperature was 66 °C. [h] 3-Dimethylamino-6-(3,5-dimethylpyrazol-1yl)-1,2,4,5-tetrazine[11c] (mp 141-142 °C) was isolated as byproduct (51%).

General Information.

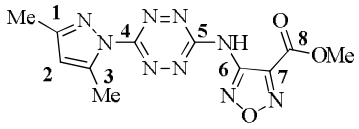
Infrared spectra were determined in KBr pellets on a Perkin-Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311A instrument. The ^{1}H, ^{13}C, ^{15}N and ^{14}N NMR (external standard: CH_3NO_2) spectra were recorded at 300.13, 75.47, 50.7 and 21.68 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the solvent-*d* or to external standard without correction nitromethane (^{14}N and ^{15}N). Analytical TLC was performed using commercially precoated silica gel plates (Silufol UV_{254}), and visualization was effected with short wavelength UV light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected.

All the reagents were analytical reagents purchased from commercial sources and used as received. 3,6-Bis(3,5-dimethylpyrazol-1yl)-*s*-tetrazine **1** [15], 3,4-diaminofurazan **2a** [16], 3-amino-4-methylfurazan **2b** [17], 3-amino-4-methoxyfurazan **2c** [18 -], 3-amino-4-phenylfurazan **2d** [19], 3-amino-4-azidofurazan **2e** [20], 3-amino-4-carbmethoxyfurazan **2f** [21], 4,4'-diaminoazofurazan **2g** [22], 4,4'-diaminoazoxyfurazan **2h** [22], 3-amino-4-nitrofurazan **2i** [23], 4,4'-diaminotrifurazan **2j** [24], 3,4-di(3-aminofurazan-4-yl)furoxan **2k** [25], 1-amino-4-nitroimidazole **5a** [26], 3-amino-5-nitrotriazole **5b** [27], 1-amino-3-nitrotriazole **5c** [26], and 3-amino-6-(3,5-dimethylpyrazol-1yl)-*s*-tetrazine **5f** [13] were prepared according to literature procedures.

Synthesis of secondary amines **3** *and* **6** *(general procedure)*.

A mixture of the corresponding amine (**2** or **4**, 1.0 mmol), tetrazine **1** (0.27 g, 1.0 mmol), K_2CO_3 (0.138 g, 1.0 mmol), and MeCN (10 ml) was heated to reflux (~80 °C), checking the efficiency of the reaction by TLC, until the starting material **1** had totally disappeared (R_f = 0.81 in CCl_4:MeCN 3:1). After the time indicated (see, Table 1 and 2), the reaction mixtures were cooled and diluted with ice water (10 ml). The mixture was acidified to a pH of 1 by dropwise addition of 5% HCl to generate a fine precipitate that was collected by vacuum filtration. This red precipitate was washed with cold water (3 × 5 ml) and dried overnight (16 h) under high vacuum to provide pure product. If impurities were evident, products were purified by crystallization from an organic solvent.

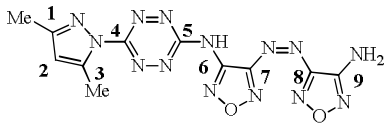
Methyl 4-{[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]amino}furazan-3-carboxylate 3f:



Red solid, mp 189 °C. ^{1}H NMR ([D_6]DMSO): δ = 2.25 (s, 3H, C1-Me), 2.50 (s, 3H C3-Me), 3.87 (s, 3H, R), 6.26 (s, 1H, C2-H), 11.95 (br.s, 1H, NH). ^{13}C NMR ([D_6]DMSO): δ = 13.1, 13.4 (C3-Me, C1-Me), 151.7 (C1), 110.1 (C2), 142.4 (C3), 158.1 (C4), 159.5 (C5), 149.9 (C6), 143.5 (C7), 158.3

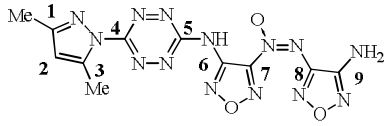
(C8), 53.7 (OMe); ^{15}N NMR ([D$_6$]DMSO): δ = 46.69, 13.24, -9.21 (×2), -26.87 (×2), -78,07, -174.18, -296.69; IR (KBr): ν = 3556, 3406, 3270, 3126, 2967, 1757, 1587, 1485, 1428, 1291, 1262, 1199, 1149, 1073, 1047, 1027, 974, 944, 841, 820, 785. C,H,N analysis (%): calcd for $C_{11}H_{11}N_9O_3$ (317.26): C 41.64, H 3.49, N 39.73. found C 41.68, H 3.54, N 41.64.

4-[(4-Aminofurazan-3-yl)diazenyl]-*N*-[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]furazan-3-amine 3g:



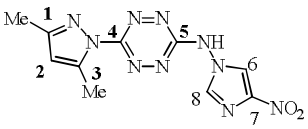
Red solid, mp 212-214 °C; ^{1}H NMR ([D$_6$]DMSO): δ = 2.25 (s, 3H, C1-Me), 2.48 (s, 3H C3-Me), 6.28 (s, 1H, C2-H), 6.6 (s, 2H, NH$_2$), 12.75 (br. s, 1H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 13.0, 13.3 (C3-Me, C1-Me), 110.1 (C2), 142.3 (C3), 146.7 (C6), 151.7 (C1), 150.6 (C9), 155.7 (C8), 157.4 (C7), 158.0 (C4), 159.6 (C5); IR (KBr): ν = 3442, 3334, 1621, 1599, 1560, 1487, 1421, 1274, 1076, 1038, 974, 948, 798, 778, 727, 683, 666, 584, 564; C,H,N analysis (%): calcd for $C_{11}H_{10}N_{14}O_2$ (370.29): C 35.68, H 2.72, N 52.96. found C 35.73, H 2.75, N 52.89.

2-(4-Aminofurazan-3-yl)-1-{4-[(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl)-amino]furazan-3-yl}diazene oxide 3h:



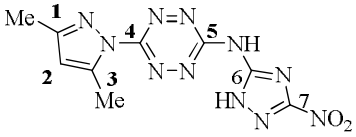
Red solid, mp 221-224 °C (decomp.); ^{1}H NMR ([D$_6$]DMSO): δ = 2.25 (s, 3H, C1-Me), 2.47 (s, 3H C3-Me), 6.28 (s, 1H, C2-H), 6.59 (s, 2H, NH$_2$), 12.2 (br. s, 1H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 13.1, 13.4 (C3-Me, C1-Me), 110.2 (C2), 142.4 (C3), 145.3 (C6), 147.7 (C8), 151.8 (C1), 153.6 (C7), 153.6 (C9), 158.2 (C4), 159.3 (C5); IR (KBr): ν = 3624, 3432, 3334, 3247, 1607, 1585, 1486, 1456, 1074, 1022, 972, 945, 801, 681, 553. C,H,N analysis (%): calcd for $C_{11}H_{10}N_{14}O_3$ (386.29): C 34.26, H 2.61, N 50.76. found C 34.30, H 2.64, N 50.68.

6-(3,5-Dimethyl-1*H*-pyrazol-1-*yl*)-*N*-(4-nitro-1*H*-imidazol-1-yl)-1,2,4,5-tetrazin-3-amine 6a:



Red solid, mp 261-262 °C (decomp.); ^{1}H NMR ([D$_6$]DMSO): δ = 2.24 (s, 3H, C1-Me), 2.48 (s, 3H C3-Me), 6.26 (s, 1H, C2-H), 8. 20 (s, 1H, C6-H), 8.74 (s, 1H, C8-H), 12.65 (br. s, 1H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 13.0, 13.4 (C3-Me, C1-Me), 110.0 (C2), 122.8 (C8), 138.1 (C6), 142.2 (C3), 145.4 (C7), 151.6 (C1), 158.8 (C4), 162.2 (C5); ^{15}N NMR ([D$_6$]DMSO): δ = -269.18, -197.58, -174.30, -126.89, -78.06, -32.64 (×2), -17.44, -8.96 (×2); IR (KBr): ν = 3179, 3137, 1579, 1550, 1485, 1410, 1362, 1293, 1267, 1079, 1035, 988, 971, 956, 834, 821, 749, 660; C,H,N analysis (%): calcd for $C_{10}H_{10}N_{10}O_2$ (302.25): C 39.74, H 3.33, N 46.34. found C 39.80, H 3.30, N 46.26.

6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-*N*-(5-nitro-4*H*-1,2,4-triazol-3-yl)-1,2,4,5-tetrazin-3-amine 6b*:



Orange solid, mp 241 °C (decomp.); ^{1}H NMR ([D$_6$]DMSO): δ = 2.26 (s, 3H, C1-Me), 2.54 (s, 3H C3-Me), 6.26 (s, 1H, C2-H), 13.26 (br. s, 2H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 12.9, 13.2 (C3-Me, C1-Me), 109.9 (C2), 142.3 (C3), 149.2 (C6), 151.6 (C1), 158.1 (C7), 159.0 (C4) 161.0 (C5); IR (KBr): ν = 3315, 3116, 2935, 1618, 1582, 1556, 1524, 1491, 1442, 1404, 1313, 1277, 1251, 1127, 1088, 1043, 1008, 965, 890, 839, 816, 759, 693, 557; C,H,N analysis (%): calcd for $C_9H_9N_{11}O_2$ (303.24): C 35.65, H 2.99, N 50.81. found C 35.71, H 3.04, N 50.76.

Compound **6c** is an acid and well soluble in aqueous solution of NaOH with formation of dark red solution; from the solution starting compound **6c** can be quality precipitated by acidification with conc. HCl.

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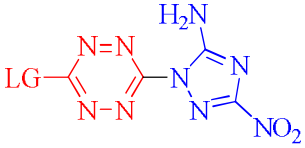
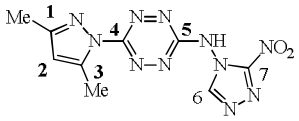
* - At preparation of the compound could be supposed the formation of its isomer **6b'**. Such, a few literature reports indicated that hetarylation of 3-amino-5-nitro-1,2,4-triazole **5b** with hetaryl halides should favor reaction at the triazole nitrogen instead of at the amino group.[2d,28-33] At using of such mild leaving group as -*SMe*, on the other hand, hetarylation of the amino group of the compound **5d** was observed.[34] For the current protocol, hetarylation regioselectivity was confirmed by NMR (these data agree with those reported for isomeric substituted 1,2,4-triazoles[35-38]) and acidic properties of the product **6b**; an isomer **6b'** not include acidic protons and will not dissolve in alkaline solution.

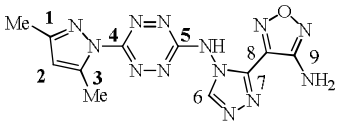


6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-*N*-(3-nitro-4*H*-1,2,4-triazol-4-yl)-1,2,4,5-tetrazin-3-amine 6c:



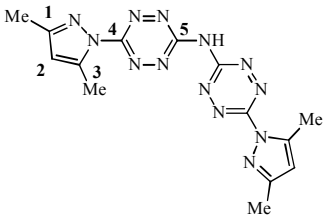
Red solid, mp 251 °C (decomp.); ^{1}H NMR ([D$_6$]DMSO): δ = 2.24 (s, 3H, C1-Me), 2.48 (s, 3H C3-Me), 6.26 (s, 1H, C2-H), 9.26 (s, 1H, C6-H), 12.57 (br. s, 1H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 13.0, 13.3 (C3-Me, C1-Me), 110.1 (C2), 142.4 (C3), 148.2 (C6), 151.7 (C1), 159.1 (C4), 159.9 (C7), 161.8 (C5); ^{14}N NMR ([D$_6$]DMSO): δ = - 24.02; ^{15}N NMR ([D$_6$]DMSO): δ = -260.06, -174.20, -159.86, -132.65, -81.30, -78.18, -31.79 (×2), -25.57, -8.73 (×2); IR (KBr): ν = 3436, 3132, 2851, 1548, 1506, 1482, 1421, 1306, 1279, 1083, 1025, 959, 892, 832, 663; C,H,N analysis (%): calcd for $C_9H_9N_{11}O_2$ (303.24): C 35.65, H 2.99, N 50.81. found C 35.70, H 3.02, N 50.73.

3-Amino-4-{4-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-ylamino]-4*H*-1,2,4-triazol-3-yl}furazan 6d:



Red solid, mp 190-193°C; ^{1}H NMR ([D$_6$]DMSO): δ = 2.22 (s, 3H, C1-Me), 2.45 (s, 3H, C3-Me), 6.25 (s, 1H, C2-H), 6.71 (br. s, 2H, NH$_2$), 9.21 (s, 1H, C6-H), 11.89 (br. s, 1H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 13.1, 13.4 (C3-Me, C1-Me), 110.2 (C2), 138.7 (C6), 142.5 (C3), 146.7 (C8), 150.0 (C7), 151.8 (C1), 155.5 (C9), 158.2 (C4), 161.8 (C5); IR (KBr): ν = 3441-2930, 1631, 1580, 1484, 1423, 1275, 1196, 1075, 1048, 1026, 973, 948, 883, 799, 642, 570; C,H,N analysis (%): calcd for $C_{11}H_{11}N_{13}O$ (341.29): C 38.71, H 3.25, N 53.35. found C 35.75, H 3.19, N 53.27.

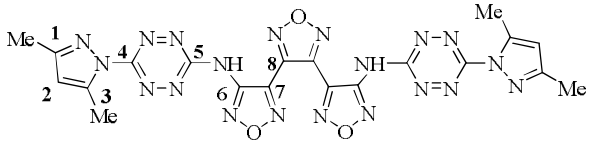
Bis[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]amine 6f:



Red solid, mp 239-240 °C; ^{1}H NMR ([D$_6$]DMSO): δ = 2.27 (s, 6H, C1-Me), 2.56 (s, 6H C3-Me), 6.30 (s, 2H, C2-H), 13.08 (br., 1H, NH); ^{13}C NMR ([D$_6$]DMSO): δ = 13.3, 13.4 (C3-Me, C1-Me), 110.3 (C2), 142.6 (C3), 151.8 (C1), 158.1 (C4), 159.8 (C5); IR (KBr): ν = 3443, 3224, 1578, 1493, 1457, 1402, 1298, 1081, 1044, 1027, 970, 857, 791, 560; C,H,N analysis (%): calcd for $C_{14}H_{15}N_{13}$ (365.36): C 46.02, H 4.14, N 49.84. found C 46.10, H 4.21, N 49.77.

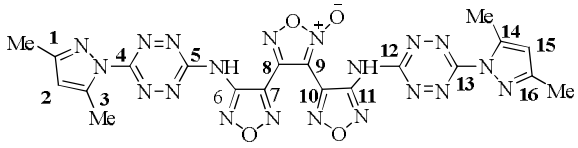
Synthesis compounds with two NH bridges (general procedure).
Using the procedure described above, diamine (**2a**, **2g**, **2h** or **2j**, 1.0 mmol), tetrazine **1** (0.135 g, 0.5 mmol), Cs_2CO_3 (0.33 g, 1.0 mmol), and MeCN (15 ml) gave corresponding product **4** as a red solid.

{Bis[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]amino}trifurazan 4d:



Red solid, mp 253-256 °C; ^{1}H NMR ([D_6]DMSO): δ = 2.26 (s, 6H, C1-Me), 2.47 (s, 6H, C3-Me), 6.27 (s, 2H, C2-H), 12.44 (br. s, 2H, NH); ^{13}C NMR ([D_6]DMSO): δ = 13.0, 13.4 (C3-Me, C1-Me), 110.1 (C2), 139.2 (C8), 142.4 (C3), 143.4 (C7), 150.4 (C6), 151.7 (C1), 158.1 (C4), 159.6 (C5); IR (KBr): ν = 3425, 2932, 1622, 1575, 1487, 1470, 1423, 1272, 1161, 1079, 1053, 1029, 998, 983, 950, 916, 897, 880, 806, 749, 701, 656, 592, 568; C,H,N analysis (%): calcd for $C_{20}H_{16}N_{20}O_3$ (584.47): C 41.10, H 2.76, N 47.93. found C 41.15, H 2.82, N 47.88.

{Bis[6-(3,5-dimethyl-*1H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]aminofurazan-3-yl}furoxan 4e:



Red solid, mp 173-174 °C (decomp.); ^{1}H NMR ([D_6]DMSO): δ = 2.28, 2.33 (s, 3H, C1-Me, 3H, C16-Me), 2.52, 2.66 (s, 3H C3-Me, 3H C14-Me), 6.30, 6.43 (s, 1H, C2-H, 1H, C15-H), 12.2, 15.3 (br. s, 1H + 1H, NH); ^{13}C NMR ([D_6]DMSO): δ = 13.1, 13.4, 13.5, 13.7 (C3-Me, C1-Me, C14-Me, C16-Me), 152.9, 153.3 (C1, C16), 108.7, 111.5 (C2, C15), 110.1 (C9), 124.2, 142.4 (C7, C10), 143.7 (C3, C14), 151.2, 151.7 (C6, C11), 157.9 (C4, C13), 159.1 (C8), 159.4 (C5, C12); IR (KBr): ν = 3392, 2972, 1614, 1570, 1471, 1431, 1375, 1300, 1161, 1068, 1029, 998, 950, 916, 881, 784, 749, 656, 592; C,H,N analysis (%): calcd for $C_{20}H_{16}N_{20}O_4$ (600.47): C 41.00, H 2.69, N 46.65. found C 41.07, H 2.78, N 47.59.

Crystal data for compound **6c**.

In the crystal structure of compound **6c**, in addition to ordinary Van der Waals interactions, molecules interact to each other by H-bonds and close contacts. The most significant interactions are the N7-H7…N1(-*x*+1, *y*-0.5, -*z*+0.5) H-bond (N…N, 2.853(2), H…N, 1.96Å, <NHN, 171°) and O2…N3(*x*, 0.5-*y*, -0.5+*z*) close contact (2.8505(13)Å) which links molecules into corrugated layers

perpendicular to crystallographic axis *a* (Figure S1). The structure of the layer is additionally stabilized by slightly shortened N9…N3(1-*x*, 1-*y*, -*z*) (3.0728(14)Å), N9…N4(1-*x*, 1-*y*, -*z*) (3.1397(14)Å), O1…N3(1-*x*, 1-*y*, -*z*) (3.080(2)Å), O1…N4(*x*, 0.5-*y*, -0.5+*z*) (3.068(2)Å) contacts (Figure S2).

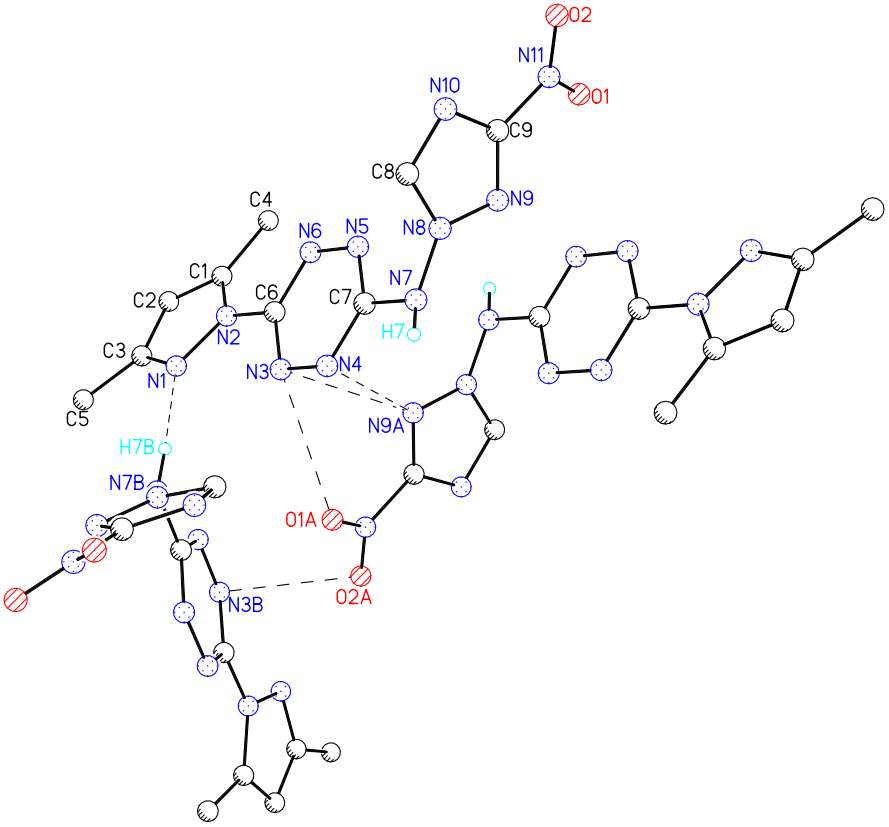


Figure S1 The strongest intermolecular interactions in the crystal structure of compound **6c**.

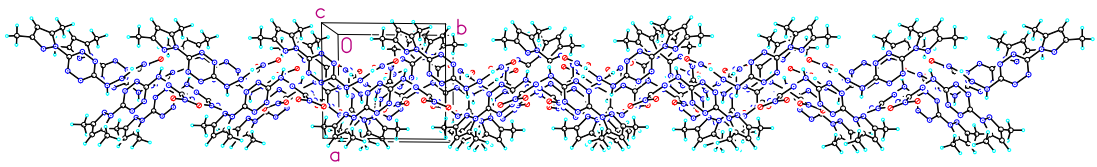


Figure S2 The structure of layer perpendicular to crystallographic axis *a*.

References

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