[4+2] Cycloaddition reactions of 1,2,4,5-tetrazines with allylcarboranes

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The [4+2] cycloaddition reactions of 3,6-disubstituted 1,2,4,5-tetrazines with 9-allyl-1,7-, 9-allyl-1,2-dicarba-*closo*-dodecaboranes and 1-allyl-2-isopropyl-1,2-dicarba-*closo*-dodecaborane have been studied. The pyridazines containing carborane cage have been synthesized for the first time.

Key words: 3,6-disubstituted 1,2,4,5-tetrazines, allylcarboranes, pyridazines, [4+2] cycloaddition.

One of the promising ways of the search for compounds for the boron neutron capture therapy of cancer is modification of carboranes with functionalized nitrogen-containing heterocycles.[1—3] Such modification is needed for targeted delivery of carborane-containing molecules to the cancer cells and specific binding to them.

For this purpose, we studied the Diels—Alder reaction (inverted electronic demand) of symmetrically 3,6-disubstituted tetrazines **1a—f** with 9-allyl-*m*- and 9-allyl-*o*-carboranes (**2**, **3**), as well as with 1-allyl-2-isopropyl-*o*-carborane (**4**) (Scheme 1).

The reaction was carried out under reflux in toluene, *o*-xylene or mesitylene (Table 1). The [4+2] cycloaddition of allylcarborane to the tetrazine ring and subsequent elimination of molecular nitrogen results in dihydropyridazines **5a—f**, **6a**, **7a**. In the reactions with tetrazines **1a,b** having 3,5-dimethylpyrazolyl or indazolyl substituents, the expected dihydropyridazines **5a,b** and **6a** form. In the other cases, dihydropyridazines **5c—e**, **7a** produced in the reaction are oxidized by the starting tetrazines to aromatic compounds **8c—e** and **10a** (see Scheme 1). 1,2,4,5-Tetrazines can act as oxidants due to their high electrophilicity. For example, initial tetrazine **1a** has the electrochemical reduction potential (φ) in acetonitrile equal to −1.040 V and the energy of its LUMO is 3.841 eV (see Ref. 4).

The reaction of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**1f**) with 9-allyl-*m*-carborane (**2**) affords a mixture of dihydropyridazine **5f** and aromatic pyridazine **8f** (^{1}H NMR data).

It is known that 4,5-dihydropyridazines formed upon [4+2] cycloaddition of ethylene derivatives to 1,2,4,5-tetrazines are generally isomerized to more stable 1,4-dihydropyridazines.[5—8] Carborane-containing 4,5-dihydro de-

Схема 1

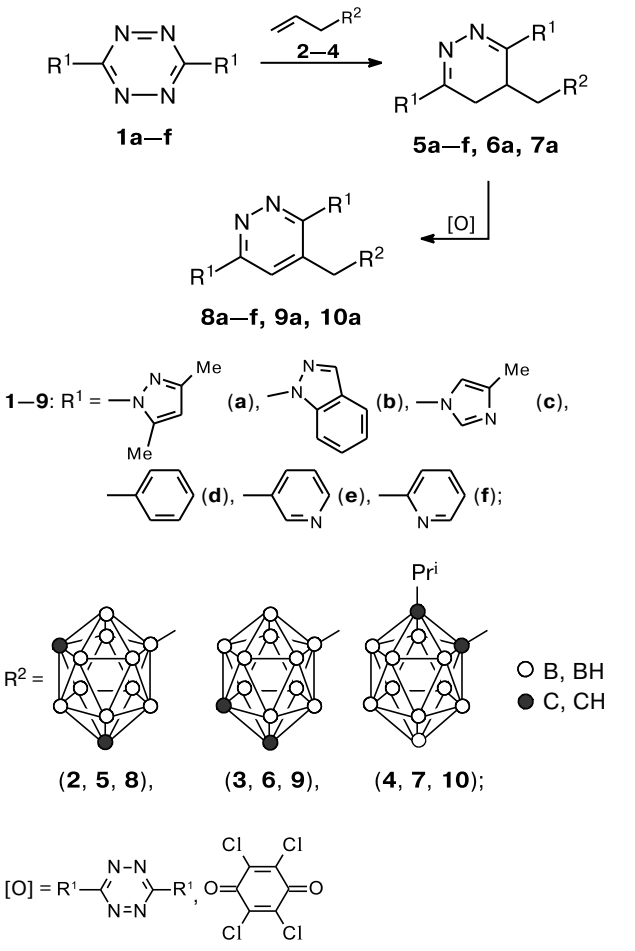

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Table 1. Yields and conditions for the synthesis of compounds **5a,b**, **6a**, **8a—f**, **9a**, **10a**

Starting compound	Solvent	τ/h[a]	Product	Yield (%)
1a	Toluene	5	**5a**	52
1b	*o*-Xylene	7	**5b**	35
1a	Toluene	2	**6a**	41
1a[b]	*o*-Xylene	2.5	**8a**	44
5a	*o*-Xylene	3	**8a**	64
1b[b]	*o*-Xylene	6	**8b**	39
5b	*o*-Xylene	5	**8b**	58
1c	*o*-Xylene	8	**8c**	26
1d	Mesitylene	3.5	**8d**	34
1e	*o*-Xylene	0.5	**8e**	44
1f[b]	Toluene	0.5	**8f**	42
6a	Toluene	1.5	**9a**	47
1a	Toluene	10	**10a**	33
1a	Toluene[c]	4	**10a**	34
1a	*o*-Xylene	4	**10a**	46

[a] τ is reaction time.
[b] 1 equivalent of chloranil was added to the reaction mixture.
[c] The reaction was carried out in an autoclave at 200 °C.

rivatives **5a,b** and **6a** are stable and, according to the ^{1}H NMR data, do not transform to 1,4-dihydropyridazines even upon prolonged heating in *o*-xylene at 143 °C.

The structures of aromatic pyridazines and dihydropyridazines containing the carborane fragments were confirmed by elemental analysis, ^{1}H NMR spectroscopy, chromato-mass spectrometry, and X-ray diffraction analysis (Figs 1—3). The ^{1}H NMR spectra of compounds **5a,b**, **6a**, **8a—f**, **9a**, **10a** (Table 2) contain the BH signals as weakly-resolved multiplets in the region of δ 0.8—3.7.

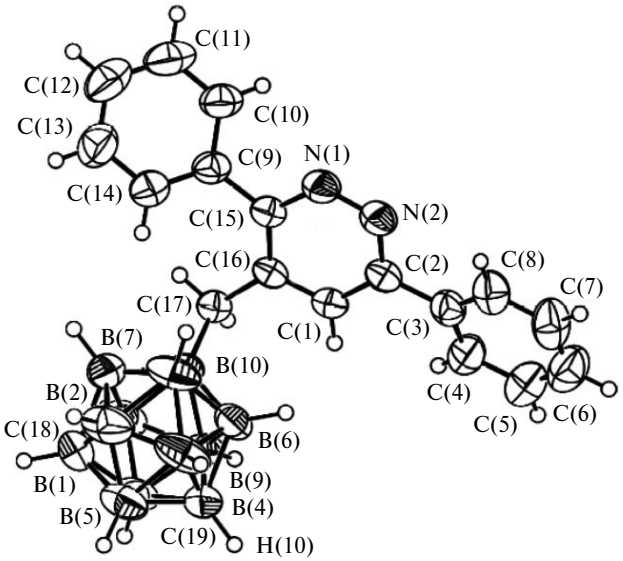

Fig. 1. Crystal structure of **8d** (the thermal ellipsoids are shown with 50% probability).

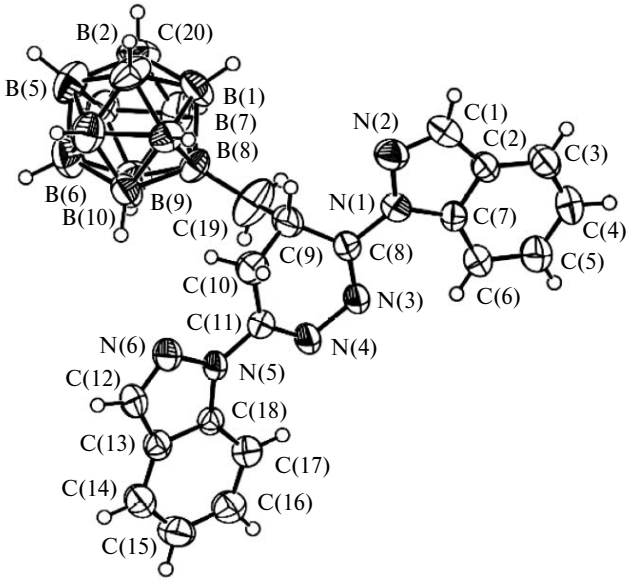

Fig. 2. Crystal sturcture of **5b** (the thermal ellipsoids are shown with 50% probability).

The signals for the proton H(5) of the aromatic pyridazine ring of compounds **8a—f**, **9a**, **10a** are present in the region of δ 7.39—8.39. The ^{1}H NMR spectra of dihydropyrazines **5a,b**, **6a** are characterized by the presence of multiplets at δ 3.46—4.31 and 2.67—2.98. The signals for the protons of the methylene bridges are present at δ 0.89—1.25 in the case of dihydropyridazines and are shifted to the region of δ 2.57—4.13 on passing to the aromatic systems.

Product **8d** crystallizes as colorless triclinic crystals. The pyridazine ring is planar, the deviations of atoms from the mean-square plane is no more than 0.03 Å. Both phenyl substituents have planar geometry (to within 0.01 Å) and are turned relative the plane of the heterocycle: the dihedral angles are 23.70° and 42.51°. The increase in one

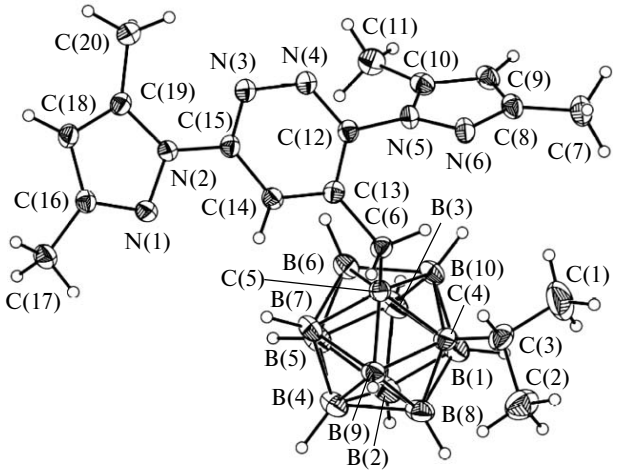

Fig. 3. Crystal structure of **10a** (the thermal ellipsoids are shown with 50% probability).

Table 2. The ^{1}H NMR spectra ($CDCl_3$) of compounds **5a,b**, **6a**, **8a—f**, **9a**, **10a**

Compound	δ (*J*/Hz)
5a	0.98—3.46 (m, 9 H, 9 BH); 1.05 (m, 2 H, CH_2); 2.26 (s, 6 H, 2 Me_{Pz}*); 2.65, 2.69 (both s, 3 H each, 2 Me_{Pz}); 2.73 (m, 1 H, H(4) pyridazine); 2.91 (br.s, 2 H, H(1), H(7) carborane); 3.94, 4.00 (both m, 1 H each, 2 H(5) pyridazine); 5.99 (s, 2 H, 2 H(4) pyrazole)
5b	1.36—4.02 (m, 9 H, 9 BH); 1.25 (m, 2 H, CH_2); 2.94 (br.s, 2 H, H(1), H(7) carborane); 2.98 (m, 1 H, H(4) pyridazine); 4.16, 4.31 (both m, 1 H each, 2 H(5) pyridazine); 7.34, 7.58, 7.78, 8.21 (all m, 2 H each, 8 CH indazole); 8.89, 8.95 (both m, 1 H each, 2 CH indazole)
6a	0.90—3.28 (m, 9 H, 9 BH); 0.89 (m, 2 H, CH_2); 2.26, 2.27, 2.62, 2.66 (all s, 3 H each, 4 Me_{Pz}); 2.67 (m, 1 H, H(4) pyridazine); 3.46, 3.53 (both br.s, 1 H each, H(1), H(2) carborane); 3.83, 3.89 (both m, 1 H each, 2 H(5) pyridazine); 5.97 (s, 2 H, 2 H(4) pyrazole)
8a · 0.5 DHB**	0.53—3.30 (m, 9 H, 9 BH); 2.31, 2.32, 2.39, 2.74 (all s, 3 H each, 4 Me_{Pz}); 2.84 (br.s, 4 H, CH_2, H(1), H(7) carborane); 5.99 (br.s, 1 H, OH 2,3,5,6-tetrachloro-1,4-dihydroxybenzene); 6.03, 6.05 (both s, 1 H each, 2 H(4) pyrazole); 8.04 (s, 1 H, H(5) pyridazine)
8b · 0.5 DHB	0.82—3.03 (m, 9 H, 9 BH); 2.69 (br.s, 2 H, H(1), H(7) carborane); 3.08 (s, 2 H, CH_2); 5.74 (br.s, 1 H, OH 2,3,5,6-tetrachloro-1,4-dihydroxybenzene); 7.27, 7.35, 7.48, 7.59, 7.99, 9.01 (all m, 1 H each, 6 CH indazole); 7.81, 8.29 (both m, 2 H each, 4 CH indazole); 8.28 (s, 1 H, H(5) pyridazine)
8c	0.78—3.62 (m, 9 H, 9 BH); 2.34, 2.35 (both s, 3 H each, 2 Me imidazole); 2.57 (s, 2 H, CH_2); 2.93 (br.s, 2 H, H(1), H(7) carborane); 7.10, 7.45, 7.87, 8.35 (all s, 1 H each, 2 H(2), 2 H(5) imidazole); 7.39 (s, 1 H, H(5) pyridazine)
8d	0.88—3.70 (m, 9 H, 9 BH); 2.60 (s, 2 H, CH_2); 2.83 (br.s, 2 H, H(1), H(7) carborane); 7.43—7.56 (m, 6 H, 6 CH, Ph); 7.65, 8.14 (both m, 2 H each, 4 CH, Ph); 7.69 (s, 1 H, H(5) pyridazine)
8e	1.10—3.05 (m, 9 H, 9 BH); 2.62 (s, 2 H, CH_2); 2.87 (br.s, 2 H, H(1), H(7) carborane); 7.49—7.55, 8.74—8.77 (both m, 2 H each, 4 CH pyridyl); 8.05, 8.59, 8.93, 9.29 (all m, 1 H each, 4 CH pyridyl); 7.75 (s, 1 H, H(5) pyridazine)
8f · DHB	0.95—2.69 (m, 9 H, 9 BH); 2.75 (br.s, 2 H, H(1), H(7) carborane); 3.13 (s, 2 H, CH_2); 6.00 (br.s, 2 H, OH 2,3,5,6-tetrachloro-1,4-dihydroxybenzene); 7.36—7.41, 7.85—7.91, 8.75 (all m, 2 H each, 6 CH pyridyl); 8.07, 8.72 (both m, 1 H each, 2 CH pyridyl); 8.39 (s, 1 H, H(5) pyridazine)
9a	0.89—3.35 (m, 9 H, 9 BH); 2.30, 2.32, 2.38, 2.73 (all s, 3 H each, 4 Me_{Pz}); 2.68 (s, 2 H, CH_2); 3.41, 3.46 (both br.s, 1 H each, H(1), H(7) carborane); 6.01, 6.04 (both s, 1 H each, 2 H(4) pyrazole); 7.95 (s, 1 H, H(5) pyridazine)
10a	1.02—2.94 (m, 10 H, 10 BH); 1.19 (д, 6 H, 2 Me, Pr^i, *J* = 7.4); 2.26 (m, 1 H, CH, Pr^i); 2.27, 2.33, 2.51, 2.79 (all s, 3 H each, 4 Me_{Pz}); 4.13 (s, 2 H, CH_2); 6.09, 6.13 (both s, 1 H each, 2 H(4) pyrazole); 8.22 (s, 1 H, H(5) pyridazine)

* Pz is pyrazol-1-yl.

** DHB is 2,3,5,6-tetrachloro-1,4-dihydroxybenzene.

of the dihedral angles by ~20° and in the bond angle C(16)—C(15)—C(9) up to 125.9° is associated with the steric interference of the carborane polyhedron on the closest phenyl substituent. The values of other geometric parameters are close to the standard ones. It is noteworthy that shortened intermolecular contact (IMC) is present between the proton H(10) of the carborane polyhedra and the atoms N(1), N(2) of the pyridazine ring (N(1)···H(10) 2.16 Å, [1 + *x*,*y*,*z*], N(2)···H(10) 2.30 Å, [1 + *x*,*y*,*z*]). Taking into account the specific character of the C—H bond in the carborane polyhedra, one can speak on the formation of intermolecular hydrogen bond (IMHB) having triangular geometry with virtually equal distances H···N for both donor atoms.

Product **5b** crystallizes as colorless monoclinic crystals. Dihydropyridazine ring is nonplanar and has pseudo-twist conformation, the deviations of the atoms C(9) and C(10) from the mean-square plane passing through the atoms C(8)—N(3)—N(4)—C(11) are 0.367 and 0.189 Å, respectively. The carborane substituent occupies the pseudo-axial position. The indazolyl substituents do not virtually exit from the plane of conjugation. No equalization of conjugated double bond lengths in the pyridazine ring was observed (N(3)—N(4) 1.424(2) Å, N(4)=C(11) 1.268(2) Å, N(3)=C(8) 1.275(2) Å). The values of the other geometric parameters are close to the standard ones.

Product **10a** crystallizes as colorless triclinic crystals. The pyridazine ring has a planar geometry. One of the pyrazolyl rings lies in the plane of conjugation with pyridazine, the deviations of atoms from the mean-square plane passing through both heterocycles are no more than 0.07 Å. The second pyrazolyl substituent is turned relative

to the plane of the azine (dihedral angle is ~47°) due to the steric interaction with the carborane polyhedron. The values of the other geometric parameters are close to the standard ones.

The carbon-substituted 1-allyl-2-isopropyl-*o*-carborane (**4**) undergoes the [4+2] cycloaddition reaction with 1,2,4,5-tetrazines considerably more slowly than boron-substituted allylcarboranes **2** and **3**, which apparently is associated with the influence of the carborane cage, as well as with the steric hindrance caused by the isopropyl substituent. By the example of reaction of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**1a**) with carborane **4**, it was shown that the increase in the reaction temperature to 200 °C reduces the process time from 10 h to 4 h (see Table 1).

Dihydropyridazines **5a,b,f** and **6a** can be oxidized to the corresponding aromatic derivatives **8a,b,f** and **9a** by chloranil. It was established that pyridazines **8a,b,f**, having the *m*-carborane fragment, contrary to pyridazine **9a** having the *o*-carborane cage, form 1 : 1 and 1 : 2 molecular complexes with the reduction product of chloranil, *viz.*, 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (DHB). Oxidation can be carried out both after isolation and purification of dihydropyridazines and under their synthesis conditions. *In situ* oxidation allows reduction of the losses of the target products in the intermediate steps.

Thus, it was shown that [4+2] cycloaddition reaction (inverted electronic demand) of allylcarboranes with 1,2,4,5-tetrazines is very a convenient method for the preparation of carborane-containing dihydropyridazines and aromatic pyridazines. The process is influenced by the substituents in positions 3 and 6 of the tetrazine ring, as well as by the structure of allylcarborane.

Experimental

Tetrazines **1a**,[9] **1b,c**,[10] **1d—f**[11] and allylcarboranes **2** and **3**[12] were synthesized according to the known procedures.

The NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer (400 MHz) using $SiMe_4$ as the internal standard. The chemical shifts are presented in the δ scale. The mass spectra were measured on a Shimadzu LCMS-2010 liquid chromatomass spectrometer after chromatographic separation (Supelcosil LC-18 (250×4.6 mm, 5 μm) column, a MeCN—H_2O (85 : 15) mixture as a mobile phase, the flow rate 1 mL min^{-1}, the column temperature 60 °C, the APCI ionization mode, the source temperature 400 °C; the gas flow rate was 2.5 L min^{-1}, the other parameters of mass-spectrometer were established according to the autotuning procedure). The melting points were measured on a Boetius heating table. The elemental analysis was carried out on a Perkin Elmer PE-2400 autoanalyzer. The course of the reaction was monitored, and the purity of the products was checked, by TLC on plates with a Sorbfil fixed layer in a benzene—acetonitrile (1 : 1) solvent system.

3,6-Di(indazol-1-yl)-1,2,4,5-tetrazine (1b). The yield was 81%. M.p. 274—275 °C. Found (%): C, 61.23; H, 3.14; N, 36.02. $C_{16}H_{10}N_8$. Calculated (%): C, 61.14; H, 3.21; N, 35.65. ^{1}H NMR ($CDCl_3$, δ): 7.45, 7.68, 7.89, 8.72 and 8.52 (all m, 2 H each, 2 indazolyls).

3,6-Di-(4-methylimidazol-1-yl)-1,2,4,5-tetrazine (1c). The yield was 48%. M.p. 208—209 °C. Found (%): C, 49.66; H, 4.00; N, 46.54. $C_{10}H_{10}N_8$. Calculated (%): C, 49.58; H, 4.16; N, 46.26. ^{1}H NMR ($CDCl_3$, δ): 2.37 (s, 6 H, 2 C(4)Me); 7.71 (s, 2 H, 2 H(5)); 8.65 (s, 2 H, 2 H(2)).

1-Allyl-2-isopropyl-1,2-dicarba-*closo*-dodecaborane (4). To a solution of 1-isopropyl-*o*-carborane (3.72 g, 20 mmol) in anhydrous diethyl ether (30 mL), a 1.62 *M* solution of BuLi (13.0 mL, 21 mmol) in hexane was added with stirring in an argon atmosphere at 10 °C and the reaction mixture was stirred at 20 °C for 30 min. Allyl bromide (2.54 g, 21 mmol) was added to the obtained lithium derivative at 0 °C. The reaction mixture was stirred at 25 °C for 4 h, then poured into water and extracted with hexane (2×15 mL). The extract was dried with Na_2SO_4. After evaporation of the solvent *in vacuo* and distillation, 1-allyl-2-isopropyl-*o*-carborane was obtained in a yield of 3.8 g (84%). B.p. 91—92 °C (1 Torr). Found (%): C, 42.21; H, 9.82; B, 47.90. $C_8H_{22}B_{10}$. Calculated (%): C, 42.48; H, 9.73; B, 47.79. ^{1}H NMR ($CDCl_3$, δ): 1.22 (d, 6 H, 2 Me, Pr^i, J = 6.9 Hz); 2.33 (hept, 1 H, CH, Pr^i, J = 6.9 Hz); 1.53—2.90 (m, 10 H, 10 BH); 2.94 (d, 2 H, $C\underline{H}_2$—CH=CH_2, J = 7.2 Hz); 5.13 (m, 2 H, CH_2—CH=$C\underline{H}_2$); 5.76 (m, 1 H, CH_2—$C\underline{H}$=CH_2).

Preparation of pyridazines 5a,b, 6a, 8a—f, 10a (general procedure). A solution of 3,6-disubstituted 1,2,4,5-tetrazine (1 mmol) and allylcarborane (1.1 mmol) in a solvent (15 mL) was refluxed for 0.5—10 h. For the synthesis of **8a,b,f**, chloranil (270 mg, 1.1 mmol) was added. The course of the reaction was monitored by TLC. The solvent was removed and the obtained crystalline residue was purified by recrystallization from methanol, ethyl acetate, benzene or acetonitrile. The ^{1}H NMR spectra of the obtained compounds are presented in Table 2.

3,6-Bis(3,5-dimethylpyrazol-1-yl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]-4,5-dihydropyridazine (5a). M.p. 180—182 °C (from methanol). Found (%): C, 47.87; H, 7.18; N, 19.57. $C_{17}H_{30}B_{10}N_6$. Calculated (%): C, 47.86; H, 7.09; N, 19.70. MS, m/z (I_{rel} (%)): 428 $[MH]^+$ (100).

3,6-Di(indazol-1-yl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]-4,5-dihydropyridazine (5b). M.p. 234 °C (from ethyl acetate). Found (%): C, 53.28; H, 5.45; N, 17.82. $C_{21}H_{26}B_{10}N_6$. Calculated (%): C, 53.60; H, 5.57; N, 17.86. MS, m/z (I_{rel} (%)): 471 $[MH]^+$ (100).

3,6-Bis(3,5-dimethylpyrazol-1-yl)-4-[(1,2-dicarba-*closo*-dodecaboran-9-yl)methyl]-4,5-dihydropyridazine (6a). M.p. 202—205 °C (from methanol). Found (%): C, 47.46; H, 7.19; N, 19.74. $C_{17}H_{30}B_{10}N_6$. Calculated (%): C, 47.86; H, 7.09; N, 19.70. MS, m/z (I_{rel} (%)): 427 $[M]^+$ (100).

Molecular complex of 3,6-bis(3,5-dimethylpyrazol-1-yl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]pyridazine with 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (8a·0.5 DHB). M.p. 181—183 °C (from acetonitrile). Found (%): C, 44.05; H, 5.37; N, 15.62. $C_{17}H_{28}B_{10}N_6 \cdot 0.5\ C_6H_2Cl_4O_2$. Calculated (%): C, 43.79; H, 5.33; N, 15.32.

Molecular complex of 3,6-di(indazol-1-yl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]pyridazine with 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (8b·0.5 DHB). M.p. 213 °C (from benzene). Found (%): C, 48.44; H, 4.31; N, 14.03. $C_{21}H_{24}B_{10}N_6 \cdot 0.5\ C_6H_2Cl_4O_2$. Calculated (%): C, 48.65; H, 4.25; N, 14.18.

Table 3. Crystallographic data and main details of structure refinement

Parameter	**5b**	**8d**	**10a**
Molecular weight	470.58	388.50	466.63
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P*2(1)/*n*	*P*1	*P*1
a/Å	13.0829(17)	10.5095(4)	12.2628(2)
b/Å	10.6332(12)	11.3783(11)	13.5304(3)
c/Å	17.753(2)	11.5337(16)	23.4623(4)
α/deg	90	62.008(12)	84.092(2)
β/deg	92.218(10)	81.750(9)	86.567(2)
γ/deg	90	65.167(8)	88.114(2)
V/Å^3	2467.8(5)	1102.77(19)	3863.85(13)
Z	4	2	6
d_{calc}	1.267	1.170	1.203
μ/mm^{-1}	0.072	0.061	0.068
Scan interval	26.38 ≥ θ ≥ 2.75	26.37 ≥ θ ≥ 2.83	26.37 ≥ θ ≥ 2.62
Number of reflections measured (R_{int})	13345 (0.0584)	7584 (0.0182)	32665 (0.0412)
Number of independent reflections	4955	4342	15662
with $I > 2\sigma(I)$	1997	2358	9706
Number of parameters in refinement	378	282	1378
R_1 (with $I > 2\sigma(I)$)	0.0563	0.0535	0.0427
wR_2 (with $I > 2\sigma(I)$)	0.0813	0.1421	0.0891
R_1 (for all reflections)	0.1581	0.0969	0.0787
wR_2 (for all reflections)	0.0916	0.1562	0.0963

3,6-Bis(4-methylimidazol-1-yl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]pyridazine (8c). M.p. 194 °C (from methanol). Found (%): C, 45.43; H, 6.23; N, 21.17. $C_{15}H_{24}B_{10}N_6$. Calculated (%): C, 45.44; H, 6.10; N, 21.20.

3,6-Diphenyl-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]pyridazine (8d). M.p. 140—141 °C (from acetonitrile). Found (%): C, 58.60; H, 6.26; N, 7.41. $C_{19}H_{24}B_{10}N_2$. Calculated (%): C, 58.73; H, 6.23; N, 7.21.

3,6-Bis(3-pyridyl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]pyridazine (8e). M.p. 159—161 °C (from methanol). Found (%): C, 52.22; H, 6.37; N, 14.27. $C_{17}H_{22}B_{10}N_4$. Calculated (%): C, 52.02; H, 6.16; N, 14.28. MS, *m*/*z* (I_{rel} (%)): 391 $[MH]^+$ (100).

Molecular complex of 3,6-bis(2-pyridyl)-4-[(1,7-dicarba-*closo*-dodecaboran-9-yl)methyl]pyridazine with 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (8f·DHB). M.p. 170—172 °C (from acetonitrile). Found (%): C, 43.29; H, 3.59; N, 8.73. $C_{17}H_{22}B_{10}N_4 \cdot C_6H_2Cl_4O_2$. Calculated (%): C, 43.27; H, 3.79; N, 8.78. MS, *m*/*z* (I_{rel} (%)): 391 $[MH]^+$ (100).

3,6-Bis(3,5-dimethylpyrazol-1-yl)-4-[(2-isopropyl-1,2-dicarba-*closo*-dodecaboran-1-yl)methyl]pyridazine (10a). M.p. 207—208 °C (from methanol). Found (%): C, 51.57; H, 7.20; N, 17.97. $C_{20}H_{34}B_{10}N_6$. Calculated (%): C, 51.48; H, 7.35; N, 18.01. MS, *m*/*z* (I_{rel} (%)): 467 $[MH]^+$ (100).

Preparation of pyridazines 8a,b, 9a (general procedure). Chloranil (1 mmol) was added to a solution of dihydropyridazine (0.5 mmol) in *o*-xylene (5 mL) (in the case of **5a,b**) or toluene (5 mL) (in the case of **6a**). The reaction mixutre was kept under reflux for 1.5—5 h. The solvent was removed and the obtained crystalline residue was recrystallized from acetonitrile or benzene.

The characteristics of compounds **8a,b** are presented above, the ^{1}H NMR spectra of **8a,b**, **9a** are presented in Table 2.

3,6-Bis(3,5-dimethylpyrazol-1-yl)-4-[(1,2-dicarba-*closo*-dodecaboran-9-yl)]methylpyridazine (9a). M.p. 218—220 °C (from acetonitrile). Found (%): C, 47.92; H, 6.93; N, 19.82. $C_{17}H_{28}B_{10}N_6$. Calculated (%): C, 48.09; H, 6.65; N, 19.80. MS, *m*/*z* (I_{rel} (%)): 426 $[MH]^+$ (100).

X-ray diffraction study. The single crystals of compounds **5b**, **8d**, **10a** were prepared by crystallization from MeCN. X-ray diffraction analysis was performed on an Xcalibur-3 X-ray diffractometer equipped with a CCD-detector (λ(Mo-Kα) = = 0.71073 Å, graphite monochromator, ω scan mode, scanning step 1°). The temperature of experiment was 295(2) K for **5b**, **8d** and 100(2) K for **10a**. The structures were solved by the direct method using the SHELXS-97 program and refined using the SHELXL-97 program. The positional and temperature parameters for the nonhydrogen atoms were refined using the full-matrix least-squares method, first, in the isotropic approximation and, then, in the anisotropic approximation. The hydrogen atoms were localized at the maxima of the electron density and included in the refinement within a riding model. The main crystallographic data and parameters of the structure solution and refinement are presented in Table 3.

The results of X-ray diffraction studies were deposited with the Cambridge Structural Database (CCDC Nos. 735714-735716 for compounds **5b**, **8d**, **10a**, respectively)*.

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* This data can be obtained free of charge on application to the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

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