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Theoretical Study of Donor–Acceptor Ability of Borazine, Alumazine, and Boraphosphinine

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Abstract—Donor–acceptor complexes of borazine, alumazine, and boraphosphinine were studied by a quantum-chemical method. Structural and thermodynamic characteristics of complexes with Lewis acids (BCl_3 and $AlCl_3$) and bases (NH_3 and pyridine Py) were calculated by the B3LYP method with the TZVP basis set. Energies of donor–acceptor bonds and energies of reorganization of donors, acceptors, and heterocycles upon the complex formation were found. Analysis of the energy variations occurring at the complex formation has shown that the reorganization energies of acceptors (BCl_3 and $AlCl_3$) and heterocycles play a key role in the complex stabilizations, whereas the reorganization energies of donors (NH_3 and Py) are small and do not bring essential contribution to the complex-formation energy. The stability of donor–acceptor complexes decreases in the sequence alumazine > boraphosphinine > borazine. High alumazine reactivity toward chlorine atoms of the acceptor molecules BCl_3 and $AlCl_3$ was noted.

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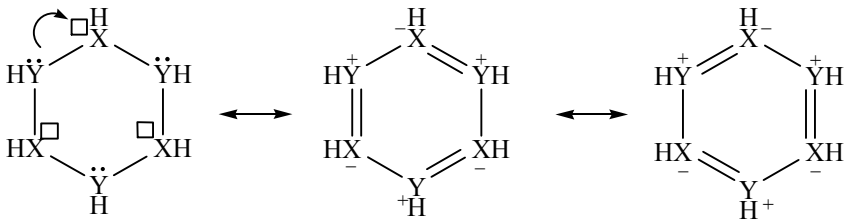
Borazine ($B_3N_3H_6$), alumazine ($Al_3N_3H_6$), and boraphosphinine ($B_3P_3H_6$) are valence isoelectronic to benzene and represent hexatomic heterocycles with alternating atoms of III and V groups. Aromatic stabilization of inorganic heterocycles is reached by the formation of a π-system owing to delocalization of six valence electrons (one electronic pair on each atom of the V group) over six *p*-orbitals (Scheme 1).

Scheme 1.

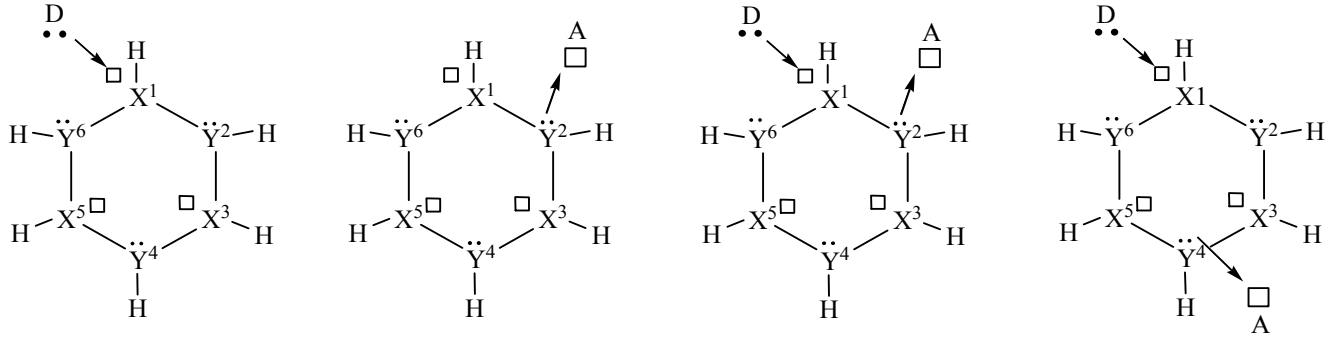


Similarly to benzene, borazine and its derivatives form complex compounds owing to conjugated heterocycle π-systems. For example, hexamethylborazine forms π-complexes with tetracyanoethylene, *n*-benzoquinone, iodine, picric acid [1-4], and chromium tricarbonyl $Cr(CO)_3$ [5, 6].

In the present work we studied the possibility of the destruction of the heterocycle π-system by introducing donor and acceptor molecules with the formation of *nv*-complexes [7]. When a complex involving a heterocycle and a donor (acceptor) is formed, one atom of the heterocycle is involved in the formation of a donor–acceptor bond, which results in the partial destruction of the heterocycle π-system (Scheme 2).

Thus, the complex formation process competes with aromatic stabilization of a heterocycle. At present only two neutral nv-complexes of hexamethylborazine with Lewis acids, $AlBr_3$ and $GaCl_3$, are known, which were prepared and characterized in the 1980s [8, 9]. A substituted alumazine [$R_3Al_3N_3R'_3$] (R = Me, R' = 2,6-

Scheme 2.



a *b* *c* *d*

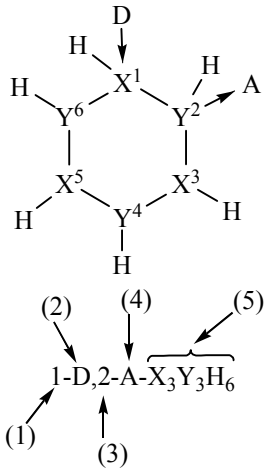
X = B, Al; Y = N, P; donor D = NH_3, Py, acceptor A = BCl_3, $AlCl_3$.

i-$Pr_2C_6H_3$) [10] forms a series of *n*v-complexes with donor molecules, such as pyridine and nitriles [11, 12]. We have fulfilled the detailed quantum-chemical study of the complex formation of borazine and its derivatives with Lewis acids and bases [13]. The effect of the nature and number of substituents in a heterocycle on the stability of borazine nv-complexes containing simultaneously donor and acceptor molecules was studied (Scheme 2, *c* and *d* structures). In the present work acceptor and donor abilities of borazine (BZ) and its analogs, alumazine (AZ) and boraphosphinine (BP), were compared on the basis of the analysis of the energies of formation of donor–acceptor complexes of these heterocycles.

Quantum-chemical calculations were carried out on a high-performance calculation cluster of St. Petersburg State University using the standard software package Gaussian03 [14]. The functional density method B3LYP with Becke's exchange three-parametric functional B3 [15] and Lee, Young, and Parr correlation functional (LYP) [16] was applied in combination with the TZVP basis set [17], which has provided reliable data on the complex formation energy [18] and has been used in our work at tudying donor–acceptor borazine complexes [13]. Structures of all complexes completely optimized with the subsequent vibrational analysis, corresponded to a minimum on a potential energy surface (PES). The notation system for donor–acceptor complexes of inorganic heterocycles accepted in the present work is presented in Scheme 3.

We have studied donor–acceptor complexes of borazine in detail [13]. It has been shown that the existence of borazine donor–acceptor complexes with one donor molecule (NH_3) (Scheme 2) is unprofitable

Scheme 3.



(1) Number of atom X, with which donor D forms a donor-acceptor bond; (2) donor D; (3) number of atom Y, with which acceptor A forms a donor–acceptor bond; (4) acceptor A; (5) heterocycle: borazine (BZ; X = B, Y = N), alumazine (AZ; X = Al, Y = N), and boraphosphabenzene (BP; X = B, Y = P).

in energy, whereas borazine complexes with acceptor molecules (BCl_3 and $AlCl_3$) (Scheme 2) correspond to minima on PES, which points to the predominance of borazine donor ability above acceptor ability. Simultaneous introduction of donor and acceptor molecules in a cyclic system (Scheme 2, structures *c* and *d*) results in the energy stabilization of a complex. It has been found that 1-D, 2-A-BZ isomers (Scheme 2, structure *c*) are more stable than 1-D, 4-A-BZ-isomers (Scheme 2, structure *d*) by approximately 16–25 kJ mol^{-1} [13].

Let us consider in more detail the energy changes corresponding to the formation of borazine donor–

acceptor complexes. The formation of the 1-NH_3,2-$AlCl_3$-BZ complex can be presented as the sum of the following processes (Fig. 1):

(1) donor (*a*) and acceptor (*b*) reorganization;

(2) heterocycle reorganization (*c*);

(3) formation of donor–acceptor bonds (*d*).

The energy of the complex dissociation is described by expression (1).

$$\Delta E_{dis} = nE_b - \Delta E_D^{reo}\,\Delta E_A^{reo}\,\Delta E_{cycl}^{reo}. \quad (1)$$

Here nE_b is the total energy of dissociation of donor–acceptor bonds B^1-N and N^2-Al; ΔE_D^{reo}, ΔE_A^{reo}, and ΔE_{cycl}^{reo} are energies of reorganization of a donor, an acceptor, and a heterocycle, respectively. The values appearing in Eq. (1) calculated by the B3LYP/TZVP method are given in Table 1.

The instability of the 2-BCl_3-BZ complex attracts our attention (the process of dissociation into components is exothermic, ΔE_{dis} –43 kJ mol^{-1}), whereas the 2-$AlCl_3$-BZ complex is stable (ΔE_{dis} 50 kJ mol^{-1}). Both complexes correspond to true minima on the potential energy surface (Fig. 2).

It is seen from Table 1 that the main factor destabilizing the 2-BCl_3-BZ complex is a very high energy of BCl_3 reorganization (ΔE_A^{reo} ~119 kJ mol^{-1}), which results in the exothermic dissociation of the borazine complex with the acceptor BCl_3 molecule. The energy expenditures for the $AlCl_3$ reorganized are much lower (ΔE_A^{reo} ~ 36 kJ mol^{-1}). The energy of the B-N donor–acceptor bond in the 2-BCl_3-BZ complex (134 kJ mol^{-1}) exceeds the energy of the Al-N bond in the 2-$AlCl_3$-BZ complex (119 kJ mol^{-1}) by 15 kJ mol^{-1}. Thus, the energy of the acceptor reorganization essentially affects stability of the complex and is responsible for the metastability of the borazine complexes with BCl_3. Reorganization energies of the donors are small (0.3 and 2.7 kJ mol^{-1} for Py and NH_3, respectively) and do not bring essential contribution to the complex-formation energy. According to our quantum-chemical calculations, borazine complexes with $AlCl_3$ as an acceptor are more stable than borazine complexes with the BCl_3 acceptor molecule though the donor–acceptor bond B–N is stronger than the Al–N bond.

Replacement of boron and nitrogen atoms in a heterocycle by their analogs in the group will affect

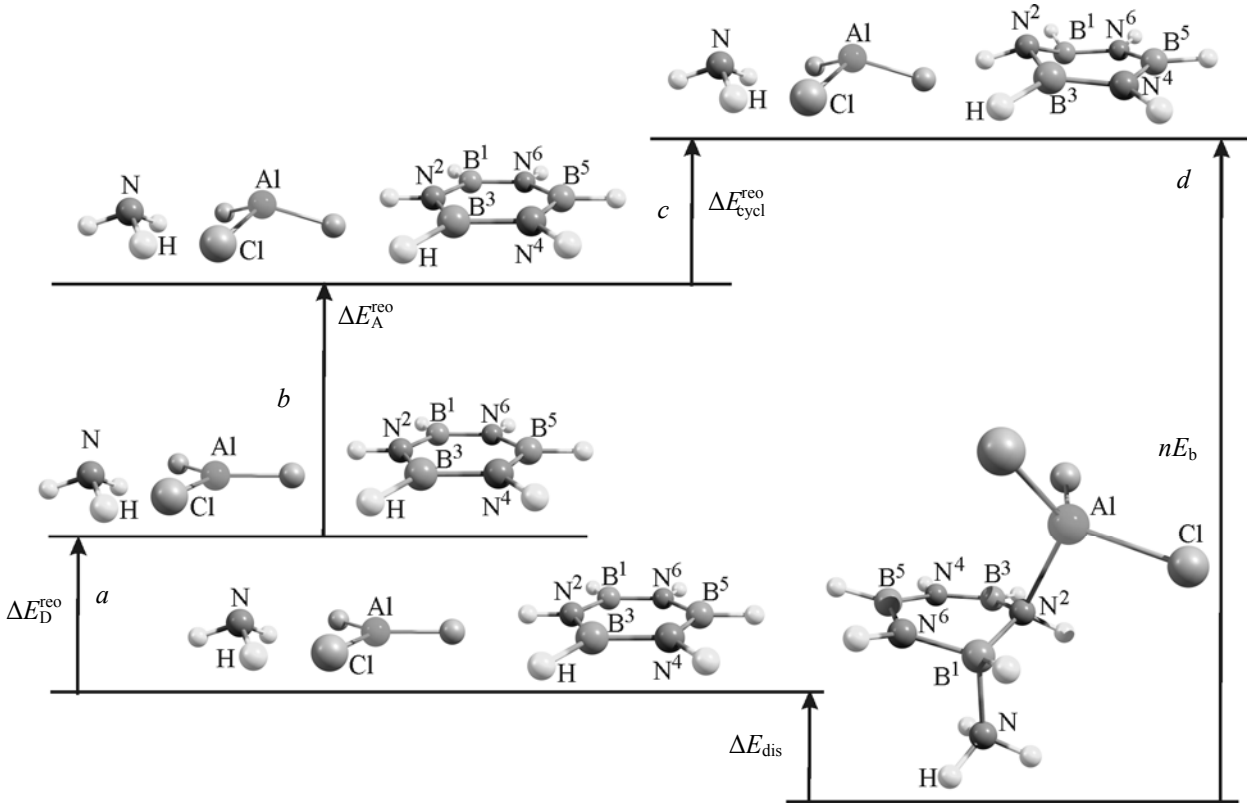


Fig. 1. Thermochemical cycle of the 1-NH_3, 2-$AlCl_3$-BZ complex formation.

Table 1. Energy (kJ mol^{-1}) of formation of complexes with borazine (B3LYP/TZVP method)

Complex	ΔE_{dis}	ΔE^{reo}_{cycl}	ΔE^{reo}_{D}	ΔE^{reo}_{A}	nE_b
2-BCl_3-BZ	–43	58	–	119	134
2-$AlCl_3$-BZ	50	34	–	36	119
1-NH_3,4-BCl_3-BZ	–26	159	0.2	127	261
1-NH_3,4-$AlCl_3$-BZ	62	134	0.3	45	242
1-NH_3,2-BCl_3-BZ	-6	148	0.3	133	276
1-NH_3,2-$AlCl_3$-BZ	80	125	0.3	50	255
1-Py,4-BCl_3-BZ	–18	180	2.4	129	294
1-Py,4-$AlCl_3$-BZ	70	155	2.4	47	275
1-Py,2-BCl_3-BZ	8	170	3.0	140	321
1-Py,2-$AlCl_3$-BZ	92	147	2.9	54	296

donor–acceptor ability of heterocycles. We shall consider two versions.

(1) Replacement of nitrogen atoms by phosphorus atoms results in the formation of boraphosphinine (BP) $B_3P_3H_6$.

(2) Replacement of boron atoms by aluminum atoms results in the formation of alumazine (AZ) $Al_3N_3H_6$.

Difference in the electronegativities (Δ_{EN}) of atoms forming the heterocyclic ring essentially affects the stability of the aromatic π-system. If the difference of the electronegativities is high, electronic density will be preferentially concentrated on a more electronegative atom, which will lead to weakening the π-system. Therefore, the less is Δ_{EN}, the more stable is the π-system of a heterocyclic molecule. For example, in benzene possessing the greatest aromaticity degree all atoms in the cycle are equal and Δ_{EN} is equal to zero. The electronegativities of B, N, P, and Al atoms according to Pauling are 2.04, 3.04, 2.19, and 1.61, respectively [19]. In the case of boraphosphinine the difference of the electronegativities of boron and phosphorus atoms [Δ_{EN}(P–B) = 0.15] decreases as compared to the difference of the electronegativities of boron and nitrogen atoms in borazine [Δ_{EN}(N–B) = 1.0], which should result in a rise of aromatic stabilization of boraphosphinine as compared to borazine. On the contrary, in the case of alumazine the difference of electronegativities of atoms increases [Δ_{EN}(N–Al) = 1.43], and it is necessary to expect that the aromatic stabilization will be essentially reduced. These qualitative suppositions are quantitatively supported by the values of nuclear-independent chemical shifts (NICS) [20]. The calculated NICS values [21] for benzene (–11.5), borazine (–2.1), boraphosphinine (–7.9), and alumazine (–2.2) show that the degree of aromatic stabilization of the π-system of a planar heterocycle molecule decreases in the sequence C_6H_6 > BP > BZ ≈ AZ.

The weakening aromatic stabilization should lead to the formation of more stable *n*ν-complexes. To check this assumption, we have optimized for the first time the structures of boraphosphinine and alumazine donor–acceptor complexes with Lewis acids and bases.

Free boraphosphinine (Fig. 3a) has the C_{3v} symmetry and is not a planar structure because of pyramidal surrounding of phosphorus atoms [22]. The

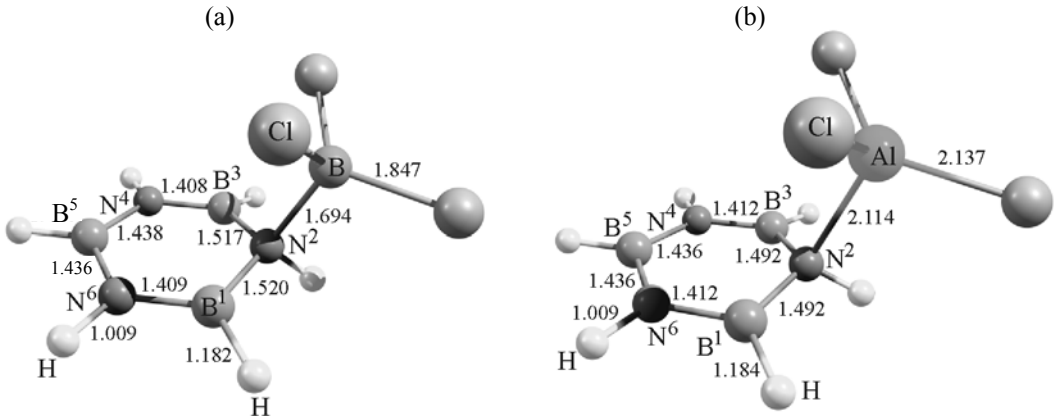


Fig. 2. Optimized structures of complexes: (a) 2-BCl_3-BZ and (b) 2-$AlCl_3$-BZ.

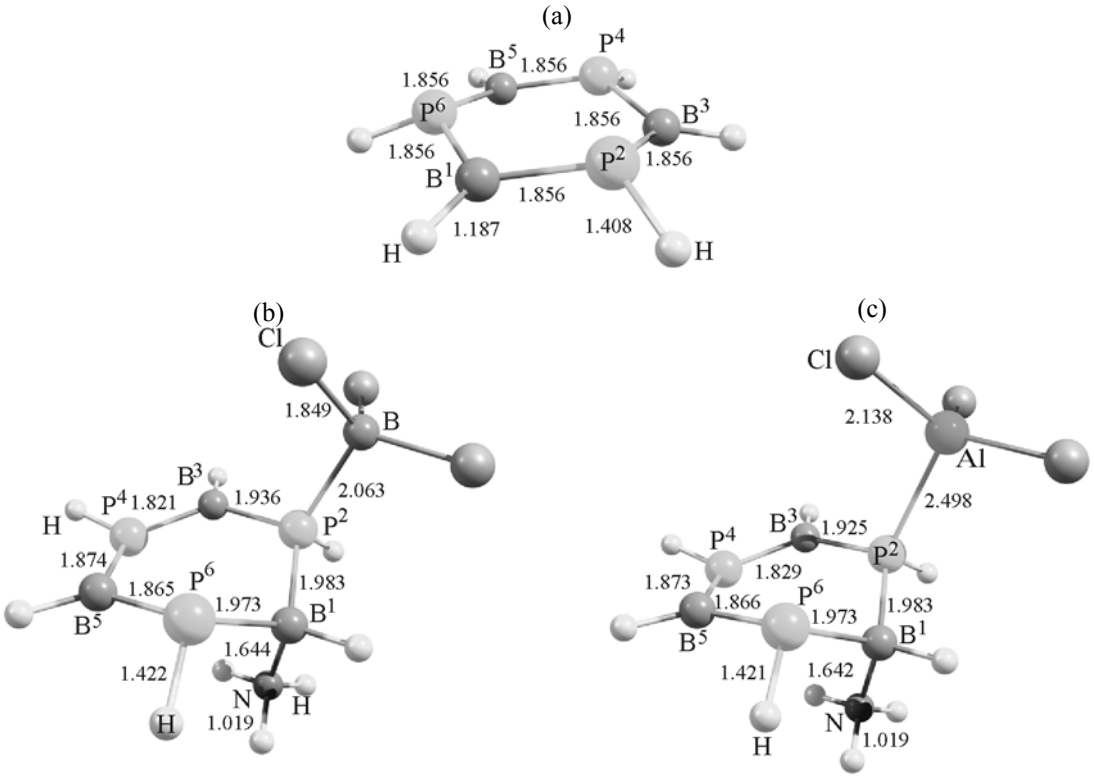


Fig. 3. Optimized structures: (a) $(HBPH)_3$ (point group C_{3v}), (b) 1-NH_3,2-BCl_3-BP; and (c) 1-NH_3,2-$AlCl_3$-BP.

structures of boraphosphinine complexes optimized in the present work are illustrated in Figs. 3b and 3c by the examples of 1-NH_3,2-BCl_3-BP and 1-NH_3, 2-$AlCl_3$-BP complexes. The energy of formation of donor–acceptor boraphosphinine complexes are given in Table 2. Observed trends are similar to those described above for borazine complexes (Table 1). 1,2-Isomers are more stable than 1,4-isomers approximately by 20 kJ mol^{-1}; the value of ΔE_D^{reo} remains practically unchanged on replacing NH_3 by Py; on passing from BCl_3 to $AlCl_3$ the dissociation energy of complexes increases due to the fact that the energy of $AlCl_3$ reorganization (30–44 kJ mol^{-1}) is less than the energy of BCl_3 reorganization (88–117 kJ mol^{-1}).

We note some essential distinctions between complexes of borazine and boraphosphinine. First, boraphosphinine complexes with donors (NH_3 and Py) correspond to local minima on PES, which points to greater acceptor ability of boraphosphinine compared to borazine. Second, boraphosphinine complexes as a whole are more stable (have greater values of dissociation energy, Table 2) than borazine complexes (Table 1), contrary to the trend expected on the basis of noticeably negative NICS value (–7.9) and a small difference in electronegativities of the atoms [Δ_{EN}(P–B) = 0.15]. We note that the value of boraphosphinine NICS in [21] was calculated for the planar structure of the D_{3h} symmetry, which does not correspond to a minimum on PES [22]. Therefore the NICS value does not reflect properties of a real boraphosphinine molecule. As phosphorus atoms in free boraphosphinine form a pronounced pyramidal

Table 2. Energy (kJ mol^{-1}) of formation of complexes with boraphosphabenzene (B3LYP/TZVP method)

Complex	ΔE_{dis}	ΔE_{cycl}^{reo}	ΔE_D^{reo}	ΔE_A^{reo}	nE_b
2-BCl_3-BP	–21	7	–	88	74
2-$AlCl_3$-BP	54	6	–	30	90
1-NH_3-BP	62	81	0.4	–	143
1-Py-BP	57	87	2.6	–	147
1-NH_3,4-BCl_3-BP	57	80	0.3	101	238
1-NH_3,4-$AlCl_3$-BP	130	76	0.3	36	243
1-NH_3,2-BCl_3-BP	80	77	0.4	107	265
1-NH_3,2-$AlCl_3$-BP	152	78	0.4	39	270
1-Py,2-BCl_3-BP	90	123	3.3	117	333
1-Py,2-$AlCl_3$-BP	160	96	3.1	44	303

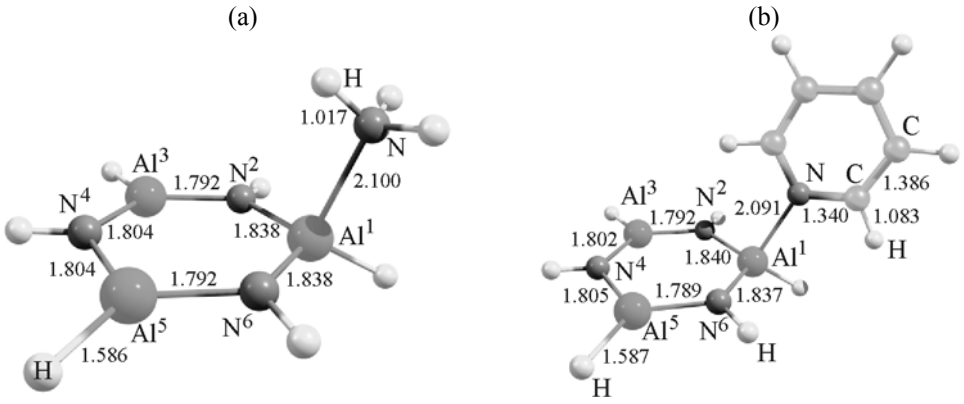


Fig. 4. Optimized structures of complexes: (a) NH_3-AZ and (b) 1-Py-AZ.

structure (Fig. 3a), the energy of the heterocycle reorganization on transition from BZ to BP decreases by approximately 50 kJ mol^{-1}, and therefore the addition of donors and acceptors to boraphosphinine occurs easier. Thus, despite a smaller difference in the electronegativities of the atoms, boraphosphinine forms stronger complexes than borazine.

Free alumazine, as well as borazine, has a planar structure (D_{3h} point group). Unlike borazine and by analogy with boraphosphinine, alumazine forms stable complexes with donor molecules (NH_3 and Py). Structures of such complexes are presented in Fig. 4, the energies of formation of these complexes are given in Table 3. The energy of alumazine reorganization at the formation of complexes with donor molecules is less than the energy of boraphosphinine reorganization at the formation of analogous complexes by approximately 50 kJ mol^{-1}. Thus, the energies of heterocycle reorganization decrease in the sequence BZ > BP > AZ.

In the optimized structures of alumazine complexes with acceptors ($AlCl_3$ and BCl_3) Cl^1 and Cl^3 atoms of an acceptor molecule (Figs. 5a and 5b) are arranged directly above Al^1 and Al^3 atoms of the heterocycle, respectively. In this case an additional intramolecular interaction with the formation of two bridging fragments M–Cl^1–Al^1 and M–Cl^3–Al^3 appears (here donor atom M = Al, B). It points to the essential weakening of the π-system in alumazines as compared to borazines. In fact, a greater difference in the electronegativities [Δ_{EN}(N–Al) = 1.43] results in the preferential localization of electronic density on nitrogen atoms of a heterocycle, which opens up a possibility for Al atoms in the ring to additional interactions with lone electronic pairs of chlorine atoms of an acceptor molecule. As boron atoms in the borazine ring are involved in the π-system to a greater degree, they are not inclined to participate in the additional interaction with chlorine atoms of an acceptor molecule. Thus, at the formation of borazine complexes with $AlCl_3$ and BCl_3 chloride bridges are not formed (Figs. 2a and 2b), whereas structures with chloride bridges exist in the case of the alumazine complexes (Figs. 5a and 5b).

Table 3. Energy (kJ mol^{-1}) of formation of alumazine complexes with donors (B3LYP/TZVP method)

Complex	ΔE_{dis}	ΔE_{cycl}^{reo}	ΔE_{D}^{reo}	nE_b
1-NH_3-AZ	78	25	0.1	103
1-Py-AZ	75	31	1.5	108

We have considered isomers of alumazine complexes with $AlCl_3$ and BCl_3, in which a hydrogen atom occupies a bridging position. In the case of $AlCl_3$ optimization results in the structure shown in Fig. 5c, which is higher in energy than the 2-$AlCl_3$-AZ complex only by 7.2 kJ mol^{-1}. In the course of the BCl_3 optimization the complete transfer of the chlorine atom to aluminum atoms of the heterocycle takes place (Fig. 5e), and the resulting structure corresponds to the true minimum on PES and is more stable by 40 kJ mol^{-1} than the initial donor–acceptor complex 2-BCl_3-AZ (Fig. 5b). The complete transfer of the chlorine atom in the 2-$AlCl_3$ results in the formation of the cluster structure shown in Fig. 5d, which is more stable by 41 kJ mol^{-1} than the initial complex. In this structure all aluminum atoms have the coordination number 4. Thus, alumazine possesses a high reactivity toward chlorine-containing acceptors and is capable to react with them to form structures with Al–Cl–Al bridging fragments.

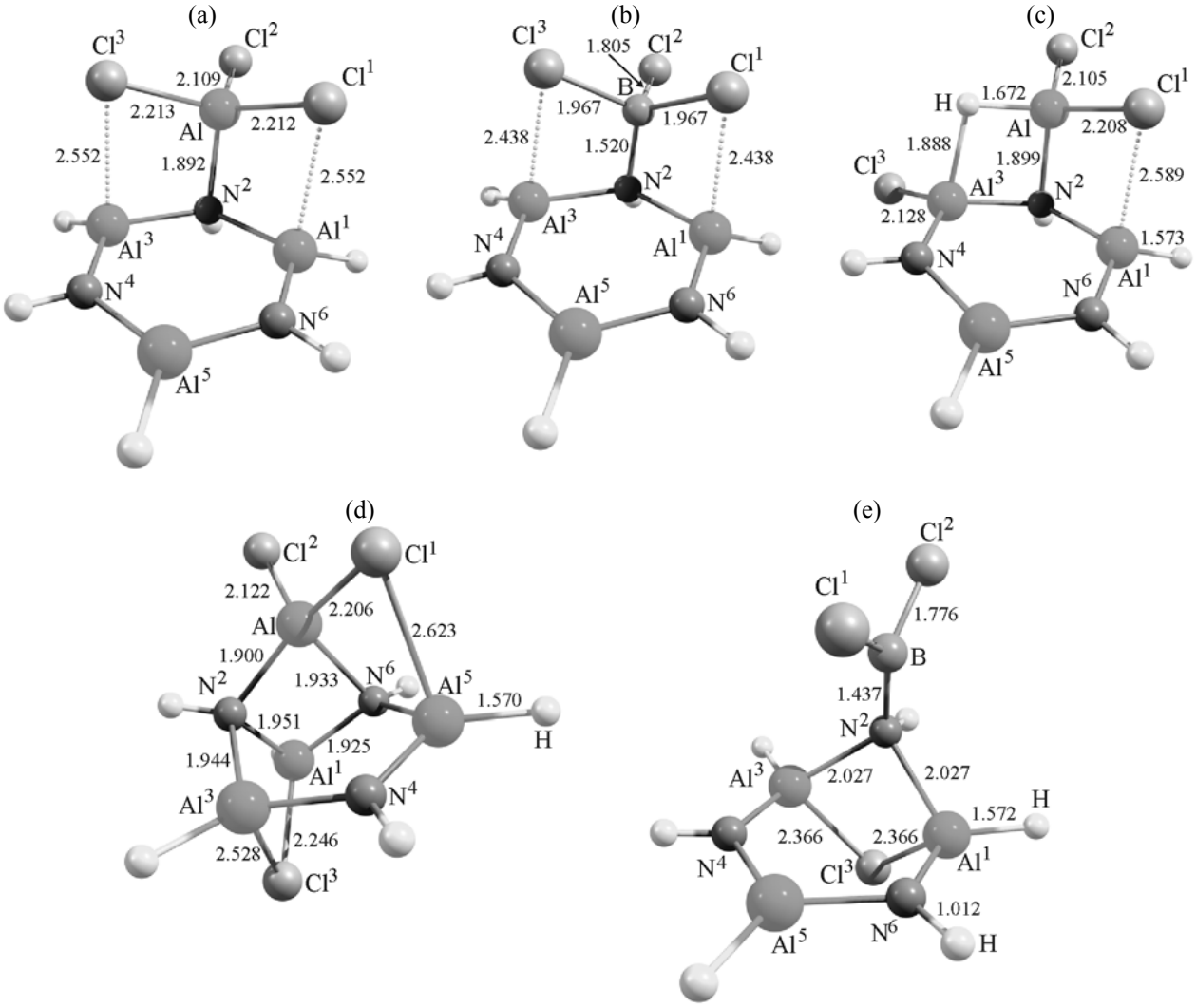


Fig. 5. Optimized structures of compounds: (a) 2-$AlCl_3$-AZ; (b) 2-BCl_3-AZ; (c) 2-$AlCl_2$,3-(H,Cl)-AZ; (d) 2-$AlCl_2$,1,3-(Cl)-AZ; and (e) 2-BCl_2,1,3-(Cl)-AZ.

A similar situation is also observed in the complexes with donor and acceptor molecules. No chloride bridges are formed in borazine complexes [13]. In the alumazine complex with ammonia and aluminum trichloride (Fig. 6a) only one bridging fragment Al–Cl_3–Al_3 is formed, as Al^1 has already reached the coordination number 4 due to a donor–acceptor bond with the donor molecule NH_3. The isomer of this complex with the hydride bridge Al–H–Al_3 (Fig. 6b) is less stable only by 2.2 kJ mol^{-1}. During optimization of the isomer of the alumazine complex with ammonia and boron trichloride (Fig. 6c) the B–Cl^3 bond is broken and the Al^3–Cl^3 covalent bond is formed. Comparison of structural characteristics of bridging fragments M–Cl^3–Al^3 (M = Al, B) in the 2-$AlCl_3$-AZ (Fig. 5a), 2-BCl_3-AZ (Fig. 5b), and 1-NH_3, 2-$AlCl_3$-AZ (Fig. 6a) complexes with those of the analogous fragment in the Al_2Cl_6 dimeric molecule is presented in Table 4. Relative energies of all considered isomers are presented in Table 5. We note that Al^3-Cl^3 bridging bonds in the complexes are longer by 4–11% than in the Al_2Cl_6 dimeric molecule and M···Al^3 distance in complexes (~2.8 E) is somewhat longer than in Al_2Cl_6 (3.24 E). The $AlCl^3Al^3$ bond angle, close to right angle for Al_2Cl_6 (89.7°), in complexes is an acute angle (75°–78°).

Thus, alumazine forms stable complexes both with donor and acceptor molecules. Acceptor ability of aluminum atoms in the alumazine cycle is so great that

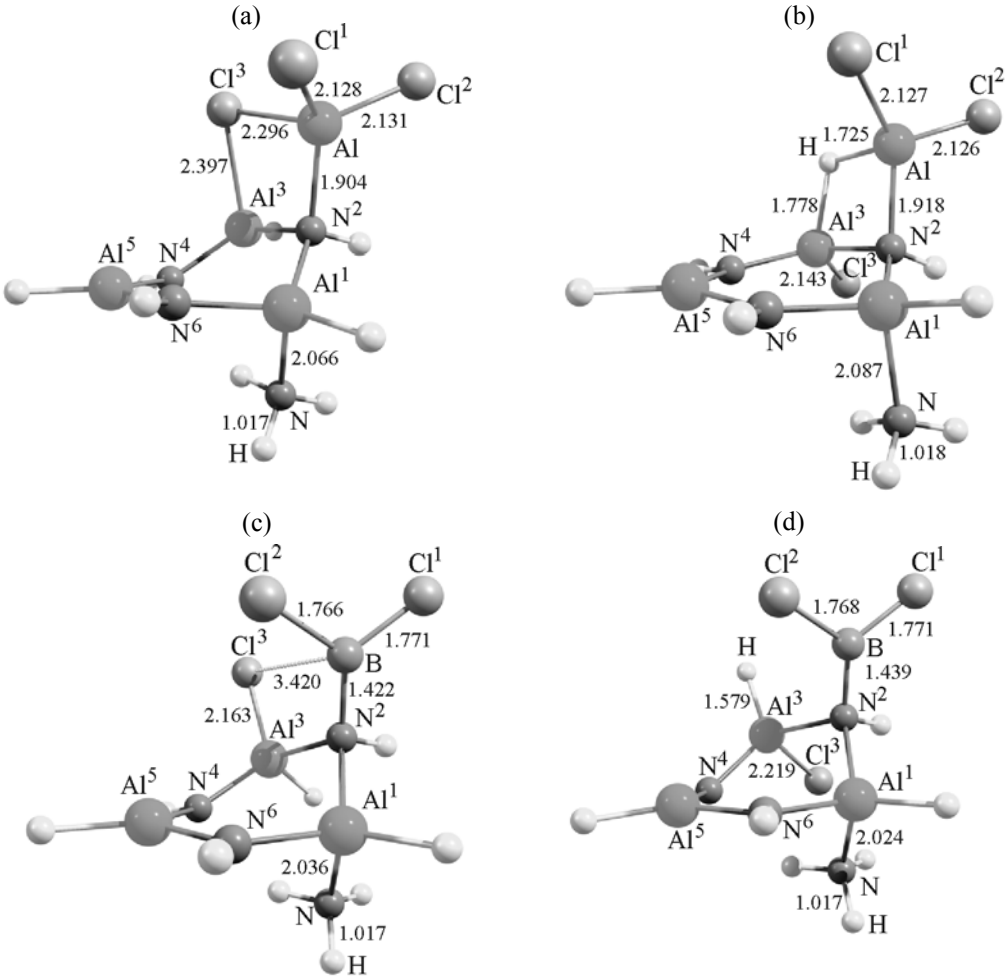


Fig. 6. Optimized structures of compounds: (a) 1-NH_3,2-$AlCl_3$-AZ; (b) 1-NH_3,2-$AlCl_2$,3-(H,Cl)-AZ; (c) 1-NH_3,2-BCl_3-AZ; and (d) 1-NH_3,2-BCl_2,3-(H,Cl)-AZ.

Table 4. Structural characteristics of bridging fragments MCl^3Al^3 (M = Al, B) in the Al_2Cl_6 molecule and in alumazine complexes[a]

Compound	$r_{(M–Cl^3)}$, Å	$r_{(Al^3–Cl^3)}$, Å	$r_{(M–Cl^2)}$, Å	$r_{(M–Al^3)}$, Å	$\angle MCl^3Al^3$, deg
Al_2Cl_6	2.298	2.298	2.096	3.240	89.7
2-$AlCl_3$-AZ	2.212 (–3.7%)	2.553 (11.1%)	2.109 (0.6%)	2.976	76.9
2-BCl_3-AZ	1.967	2.438 (6.1%)	1.805	2.710	75.1
1-NH_3, 2-$AlCl_3$-AZ	2.296 (–0.1%)	2.397 (4.3%)	2.131 (1.7%)	2.969	78.4
1-NH_3, 2-BCl_3-AZ	3.420	2.163 (–0.1%)	1.771	2.977	59.5

[a] The differences of the specified values and similar values for the Al_2Cl_6 molecule are given in brackets.

Table 5. Relative energies (E^{rel}, kJ mol^{-1}) of isomers of alumazine donor–acceptor complexes (B3LYP/TZVP method)

Compound	E^{rel}
2-$AlCl_3$-AZ	41.4
2-$AlCl_2$,3-(H,Cl)-AZ	48.6
2-$AlCl_2$,1,3-(Cl)-AZ	0.0
2-BCl_3-AZ	39.9
2-BCl_2,1,3-(Cl)-AZ	0.0
1-NH_3,2-$AlCl_3$-AZ	0.0
1-NH_3,2-$AlCl_2$,3-(H,Cl)-AZ	2.2
1-NH_3,2-BCl_3-AZ	15.5
1-NH_3,2-BCl_2,3-(H,Cl)-AZ	0.0

they are prone to additional intramolecular interactions with chlorine atoms of acceptor molecules. The final result of this additional interaction is the complete transfer of the chlorine atom from the acceptor to the aluminum atoms of the heterocycle with the formation of a stable cluster structure (Fig. 5d).

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