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Synthesis and Structural Characterization of 9-Azido-9-Borafluorene: Monomer and Cyclotrimer of a Borole Azide

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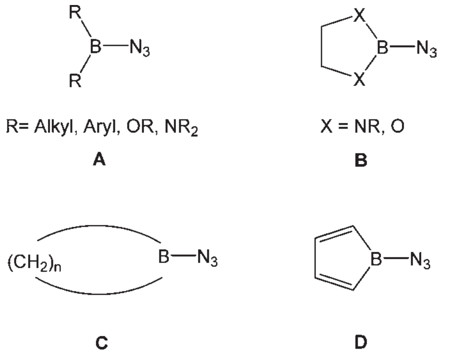
The reaction of 2,2′-dilithiobiphenyl, generated from 2,2′-dibromobiphenyl and *n*-BuLi, with BCl_3 using *n*-hexane as solvent provides a high-yielding, simple preparative route to 9-chloro-9-borafluorene **1a**. This in turn can be reacted with trimethylsilyl azide to yield 9-azido-9-borafluorene **2**. Compound **2** exists as a cyclic trimer in the solid state, but in dichloromethane solution the monomer can coexist with the trimer. Azide **2** is rather unstable both in the solid state and in solution, and it transforms with trace amounts of water and oxygen to the 1,3,5-tris(2-biphenylyl)cyclotriboroxane that was characterized by X-ray diffraction analysis. Addition of pyridine and *t*-butyl pyridine to azide **2** afford the corresponding pyridine adducts. Compound **1a** as well as the Lewis base adducts of **2** have been characterized by multinuclear NMR spectroscopy, and the structures were confirmed by X-ray diffraction analysis. The structural features of azide **2** and the strong Lewis acidity of its boron center have also been investigated by computational chemistry techniques at the MP2 level of theory.

Introduction

After the first report of an azidoborane $[B(N_3)_3]$ by Wiberg and Michaud[1] in 1954, a number of acyclic azidoboranes of type **A** (R_2BN_3; R = alkyl, aryl, oxo, amino)[2−8] (Chart 1) have been successfully synthesized. Whereas a number of heterocyclic azidoboranes of type **B** are known,[2,8−10] only two examples of stable carbocyclic azidoboranes of type **C** have been described.[11] Members of type **D** are still unknown.

Chart 1



Most of the known azidoboranes are monomeric in solution and in the solid state.[7,9,12] But the presence of a Lewis acidic boron center and a basic nitrogen center allows structural diversity by intermolecular Lewis acid−base interaction. The tendency to aggregate strongly depends on the Lewis acidity of the boron center that is controlled by electronic effects as well as by steric effects.[11,13] When R is small (Type **A**), the azide forms oligomers. A typical example is Me_2BN_3[5] that was found by Paetzold et al. to show temperature dependent oligomer formation in solution. Likewise, the small and electron withdrawing halogens of dihaloazidoboranes [BX_2N_3 (X = F, Cl, Br)] result in the formation of trimers $(BX_2N_3)_3$.[14−17] In 1971, Müller

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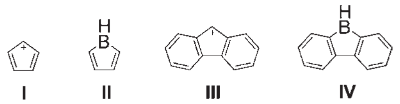
Chart 2



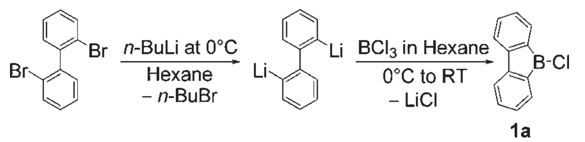
reported the crystal structure of $(BCl_2N_3)_3$,[16] wherein the six-membered $(BN)_3$ ring has a skew boat conformation and each boron atom is attached to two chlorine atoms and two nitrogen atoms in a distorted tetrahedral fashion. Later on Klapötke et al. reported the NMR data for the known $(BF_2N_3)_3$.[18] Since then only three additional aggregated azidoboranes have been structurally characterized in the solid state by Klapötke et al.: the trimer $[C_6F_5B(N_3)_2]_3$,[18] and the dimers $[(C_6F_5)_2BN_3]_2$[19] and $[(C_6H_3F_2)_2BN_3]_2$.[7] An oligomeric structure is also likely for solid $[C_6H_3F_2B(N_3)_2]$ based on vibrational spectroscopy.[7] These azides are oligomeric in the solid state and, with the exception of the insoluble $[(C_6F_5)_2BN_3]_2$, transform completely into monomers in solution.

The stability of carbocyclic azidoboranes of Type **C** appears to depend on the ring size. 1-Azido-3-methylboracyclopentane ($n = 4$) undergoes ring expansion at room temperature while carbocyclic azidoboranes with $n = 6, 7$ are found to be stable at room temperature.[11] An attempt to synthesize 9-BBN-N_3 failed as reported by Nöth et al.[9]

A carbocyclic motif that has not been explored in the context of azide formation is the borole system (Type **D**). Borole (**II**) is isoelectronic to the cyclopentadienyl cation (**I**) (Chart 2). A quantitative comparison of unsaturated five membered ring systems based on geometric, energetic, and magnetic criteria has been convincingly interpreted by Schleyer et al.[20] in terms of the aromatic and antiaromatic nature of these species. Recently Braunschweig et al.[21] observed that in the solid state structure of pentasubstituted borole $PhBC_4Ph_4$ the bond length alteration (BLA) in the BC_4 ring is significantly smaller than computed for the antiaromatic species in the gas phase. This was ascribed to result from intermolecular interactions that reduce the Lewis acidity of the boron center and induce the observed changes in bond lengths. Piers et al. could not identify the intermolecular interactions in the solid state of the highly symmetric perfluorinated pentaphenylborole and ascribed the apparently reduced BLA to crystallographic disorder.[22] Yamaguchi and co-workers also noticed π interaction as judged by intermolecular distances in less symmetric boroles [Ph_4C_4BAr, Ar = p-MeC_6H_4, p-$Me_3SiC_6H_4$, p-FC_6H_4]. However, still significant bond length alternation was present in the BC_4 unit.[23]

Dibenzoborole or 9-borafluorene, **IV**, is isostructural with the fluorenyl cation, **III**, whose antiaromaticity is still a matter of debate. Efforts to generate this fluorenyl cation as a long-lived species in strong acid were unsuccessful.[24] Numerous rate measurements[24–28] display a rate retardation in forming the fluorenyl carbocation compared to the benzhydryl system, and calculations indicate that carbocation **III** is 8–10 kcal/mol less stable.[28–30] Excitation energy calculations[31] propose antiaromatic character in **III**, that is, the longest wavelength absorption of cyclopentadienyl cation increases upon annulation going to indenyl and fluorenyl cation. Already in 1966, Armstrong and Perkins[32] have compared the calculated (using the semiempirical PPP Hamiltonian) and experimental absorption spectra of borafluorene systems with suitable models. They concluded that neutral borafluorene (**IV**) has very small π charge on boron and that the presence of the bond connecting the two phenyl rings at ortho positions "effectively cuts off π electron conjugation via boron."[32] This suggests that in borafluorenes the boron center is a strong electron acceptor. Piers et al. reported that the boron center in the perfluorinated dibenzannulated borole is more Lewis acidic than the open perfluorinated diarylborane systems.[33]

Scheme 1. Synthesis of **1a**



1a

Herein, we report the synthesis and structural characterization of the azide of dibenzoborole (Type **D**) and its cyclotrimerization. The cyclotrimer exists in the solid state and can coexist with the monomer in dichloromethane solution. The combination of the strongly Lewis acidic boron of the borole and the Lewis basic N_α atom in a single molecule limits the stability of the azide at room temperature. But pyridine adducts that are also structurally characterized enjoy enhanced stability.

Results and Discussion

9-Azido-9-borafluorene is obtained from the chloride **1a** (Scheme 1) by reaction with trimethylsilyl azide. Chloride **1a** was first prepared in 1963 by Köster and Benedikt from 9-alkyl-9-borafluorene.[34,35] Later, this compound was synthesized either by transmetalation or by salt elimination. Narula and Nöth[36] reported a high yielding (75%) transmetalation procedure using a mercury containing precursor. To avoid the highly toxic mercury compound we have improved the salt elimination procedure reported by Hong

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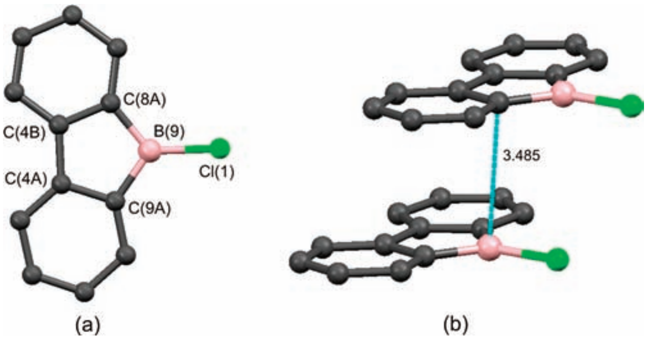

Figure 1. (a) Molecular structure of **1a**. Selected bond lengths [Å] and angles [deg] in **1a**: B(9)−Cl(1) 1.752(3), B(9)−C(9A) 1.547(4), C(8A)−B(9) 1.536(4), C(4A)−C(9A) 1.409(3), C(4A)−C(4B) 1.481(3), C(4B)−C(8A) 1.416(3); Cl(1)−B(9)−C(8A) 126.3(2), C(8A)−B(9)−C(9A) 105.9(2), B(9)−C(8A)−C(4B) 106.8(2), C(8A)−C(4B)−C(4A) 110.2(2); (b) Dimeric subunit in the crystal lattice of **1a**. The intermolecular B(9)···C(9A) distance is 3.485 Å. Hydrogen atoms are omitted for clarity.

and Chung.[37] As initially reported, this procedure suffers from a low yield (36%). But the simple modification reported here improves the yield considerably: carrying out the dilithiation of 2,2′-dibromobiphenyl in *n*-hexane[38] rather than in ether gives **1a** in 90% yield with respect to 2,2′-dibromobiphenyl.

The chloride **1a** is purified by distillation at 90 °C/10^{-3} mbar. During distillation the yellow liquid **1a** rapidly forms nice yellow needle shaped crystals upon contact with the cold trap (0 °C). These are suitable for X-ray analysis.

9-Chloro-9-borafluorene **1a** crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. Figure 1a shows the projection of the molecule. The molecule is planar having a sum of bond angles around the boron atom of 359.9(2). The B−Cl bond length [1.752(3) Å] is in the usual range.[39−41] The B−C bond lengths [B(9)−C(9A) 1.547(4) Å and C(8A)−B(9) 1.536(4) Å] are shorter than typical B−C$_{\mathrm{aryl}}$ bonds in other three-coordinated boranes [e.g., 1.589(5) and 1.571(3) in Ph$_3$B,[42] 1.579(2) and 1.580(3) in Mes$_3$B[43]] and slightly shorter than in other 9-borafluorene compounds [e.g., 1.549(3) in $F_8C_{12}B(C_6F_5)$,[33] 1.556(7) and 1.573(6) in 1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene.[44] The B−C bond lengths in **1a** are also shorter than in its pyridine adduct **1a·py** that was prepared and structurally characterized by Narula and Nöth previously.[45] Likewise, the unusually long B−Cl bond in **1a·py** [1.900(2) average] shortens significantly in free **1a** to 1.752(3) Å. The lengths of the C(4A)−C(9A) [1.409(3) Å] and C(4B)−C(8A) [1.416(3) Å] bonds are also similar to those of **1a·py** [1.404(3) and 1.408(3)] and in agreement with an aromatic ring system (1.40 Å). The distance between C(4A)−C(4B) [1.481(3) Å] bond is slightly shorter than the C−C single bond between two sp^2-hybridized carbon atoms (1.49 Å) and similar to the corresponding length in **1a·py**. To achieve the planar geometry, the bond angles inside the five membered ring also become smaller by 10−15° than the value expected for sp^2 hybridized atoms. This induces some strain that is relieved upon pyramidalization. This issue was previously discussed by Narula and Nöth in the context of the X-ray structure of the pyridine adduct of 9-chloro-9-borafluorene, **1a·py**.[45] The crystal packing of **1a** reveals the intermolecular interaction between the boron atom and the π system of a neighboring molecule. The shortest intermolecular B···C distance is 3.485 Å (Figure 1b) which is shorter than that of pentasubstituted borole compounds reported earlier.[21,23] An even shorter intramolecular distance between a boron center of a borafluorene and an aromatic ring was observed by Hoefelmeyer et al.[46]

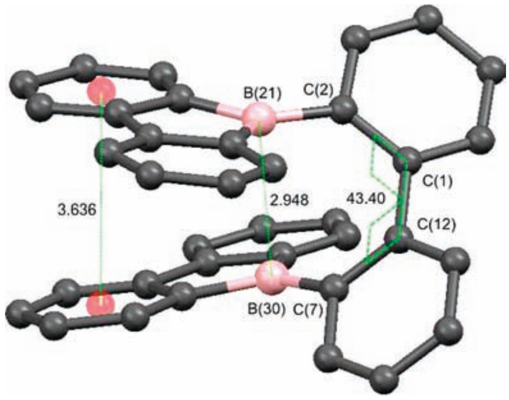

Figure 2. Molecular structure of **1b**. Hydrogen atoms are omitted for clarity. The red dots mark the center of rings. Selected bond lengths [Å] and angles [deg] (theoretical data obtained at the RI-MP2/SVP level of theory are given in parentheses): B(21)−C(2) 1.558(5) (1.557); C(2)−C(1) 1.414(4), (1.422); C(1)−C(12) 1.480(5) (1.473); C(12)−C(7) 1.415(5) (1.422); and C(7)−B(30) 1.551(5), (1.557); B···B 2.948 (2.743); Selected dihedral angle [deg]: C(2)−C(1)−C(12)−C(7) 43.40 (41.9).

Depending on the purity of **1a**, crystallization can either be retarded or not be observed at all. In one instance we were able to obtain a byproduct **1b** [2,2′-bis(9-borafluoren-9-yl)biphenyl] as deep red crystals. These grew from the yellow oil after standing for an extended period of time without interruption (Figure 2). The mechanism of formation of **1b** is not clear yet; further studies will be pursued in the future.

Compound **1b** crystallizes monoclinically in the space group $P2_1/c$ with $Z = 4$. The planar dibenzoborole units have comparable bond lengths and angles. The syn orientation of the two dibenzoborole units in **1b** is unexpected in view of their size and results in a dihedral angle C(2)−C(1)−C(12)−C(7) of 43.4°. This is rather small compared to the value of this particular dihedral angle in 1,1′-binaphthyl-2,2′-diboronic acid (96.7°).[47] In the syn conformation these two 9-borafluorene units have a short distance of 3.636 Å between the centers of six membered rings indicative of $\pi-\pi$ interaction between two dibenzoborole units. The boron−boron distance (2.948 Å) is similar to that of 1,8-bis(diphenylboryl)naphthalene (3.002 Å) indicating a significant overlap of p_z orbitals of the two boron centers as described by Hoefelmeyer and Gabbai.[48] The average

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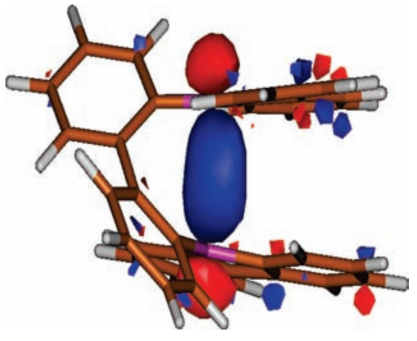

Figure 3. LUMO (*a* symmetry, $E = 0.30$ eV) of **1b** as computed at the RI-MP2/SVP level of theory.

distances between B$-$C$_{\text{biphenyl}}$ (1.555 Å) and in the borole units B$-$C (1.566 Å) are in the range of regular B$-$C(sp^2) distances. The structure observed experimentally is in good agreement with theory indicating that the syn conformation is not merely the result of packing forces.[49] The close proximity of the boron atoms allows for an overlap of the p orbitals in a σ fashion (Figure 3). This reduces the lowest unoccupied molecular orbital (LUMO) level and bathochromically shifts the longest wavelength absorption that is originating from the highest occupied to a lowest unoccupied molecular orbital (HOMO) → LUMO excitation (562 nm, B3LYP/TZVPP//RI-MP2/SVP level of theory).

9-Azido-9-borafluorene **2a** was synthesized by the reaction of **1a** with trimethylsilyl azide (TMSN$_3$) in dichloromethane solution. We found that the crude yellow reaction solution shows a ^{11}B signal at δ 50.2 which is expected for a typical three coordinated monomeric azidoborane **2a**. After removal of all volatiles from the reaction mixture followed by redissolution in CD$_2$Cl$_2$, we observe an additional signal in the ^{11}B NMR spectrum at δ 5.0 along with δ 50.3. This new signal at δ 5.0 lies in the region of tetracoordinated boron centers and is assigned to an oligomer **2b** which appears to be formed in the solid state and that persists in solution (Scheme 2).

For further understanding, we have measured the IR spectrum of the crude reaction mixture. This shows a strong absorption at 2139 cm^{-1} that is typical for the asymmetric stretching frequency of monomeric azidoboranes (2100$-$2200 cm^{-1}).[4] After removal of the solvent from the reaction mixture and redissolution in dichloromethane two absorptions in the asymmetric stretching region of azides are observed: one is at 2136 cm^{-1} and another one is blue-shifted to 2176 cm^{-1} in dichloromethane solution. This frequency shift to higher wavenumber is in agreement with an oligomer **2b** of 9-azido-9-borafluorene. IR data obtained for (BF$_2$N$_3$)$_3$ (2236 cm^{-1}),[17,18] (BCl$_2$N$_3$)$_3$ (2210 cm^{-1})[14,15] and [(C$_6$F$_5$)$_2$BN$_3$]$_2$ (2202 cm^{-1})[19] clearly show that the N$-$N stretching vibration of bridging azides are always shifted to higher wavenumber compared to that of monomeric free azides.

We have tried to explore the aggregation behavior of **2** by slightly increasing the temperature (see Supporting Information, Figures **S6** and **S7**). After keeping the temperature at 40 °C for 3 h, the intensity of the signal at δ 5.1 decreases compared to the signal at δ 50.3 as expected for a monomer$-$oligomer equilibrium. However, an additional weak signal at δ 40.0 is observed after warming which could be due to an unknown decomposition product of the azide. The azide **2** is soluble in benzene, toluene, and dichloromethane but decomposes in chloroform. Its stability in dichloromethane solution is still limited though as it slowly decomposes to a greenish compound even at -20 °C after a few days. Because of the instability of this azide, the isolation and purification is very difficult. Although the nitrogen content is below the commonly accepted critical value of 25%, sensitivity also depends on other parameters.[50] Paetzold has stated that the formation of oligomers turn the corresponding azides into labile and dangerous compounds.[11] The strongly Lewis acidic boron center could potentially catalyze the (spontaneous) decomposition of this azide. Because of this dangerous nature and the observed instability, we have not done further investigations of the monomer-trimer equilibration in solution.

The coexistence of monomer and oligomer in solution is in contrast to the behavior of [(C$_6$F$_5$B(N$_3$)$_2$]$_3$[18] or [(C$_6$F$_5$)$_2$BN$_3$]$_2$[19] and [(C$_6$H$_3$F$_2$)$_2$BN$_3$]$_2$.[7] These are trimeric or dimeric only in solid state and monomers in solution. On the other hand, spectroscopic data for (BX$_2$N$_3$)$_3$ [X = F, Cl, Br] show evidence only for trimeric azides in the solid state as well as in solution.[14−18]

The crystallization of the 9-azido-9-borafluorene **2** is difficult. We managed to get a few crystal blocks grown from dichloromethane at -20 °C but several other trials to produce high quality crystals in different solvents and under various conditions have failed. An X-ray analysis confirms that 9-azido-9-borafluorene is trimeric in nature in the solid state, but the crystal data is not of sufficiently good quality to discuss the geometry parameters (Figure 4).

We thus resort to computational chemistry techniques utilizing second-order perturbation theory (MP2) in conjunction with the resolution of the identity (RI) approximation and a polarized split-valence double-ζ basis set (RI-MP2/SVP). We first consider the monomer **2a** that is computed to be planar. The B$-$N$_\alpha$ distance of 1.436 Å and C$-$C (1.422 averaged and 1.486 Å) and B$-$C distances (1.566 Å averaged) in the central borole ring are as expected for dibenzoannulated derivatives. The LUMO is a π^* orbital of a'' symmetry and has its largest coefficient on the boron atom. The azide unit is slightly bent (N$-$N$-$N angle: 172.5°) while the B$-$N$-$N angle is 125°. This is similar to previous computational results for azidoboranes[51,52] and available experimental data.[7,9,12]

Two isomers **2b-A** and **2b-B** (Figure 5) of the trimer can be located as stationary points on the potential energy surface. The conformer **2b-A** is of C_2 symmetry and has a twist-like arrangement of the central six-membered ring. As observed in the single crystal structures of trimeric azides,[16,18] the azide units are essentially linear. One of the azide groups and a transannular boron center lie on the C_2 axis that bisects the formal C$-$C single bond between the phenyl rings in the corresponding borafluorene unit. The N$_\alpha$ atoms are in an almost trigonal planar coordination environment with sums of bond angles of 357.2 and 360.0° for the off-axis and on-axis atoms, respectively. The B$-$N bond lengths, 1.591 to 1.606 Å, are within the range expected for a dative interaction.[16,18] The

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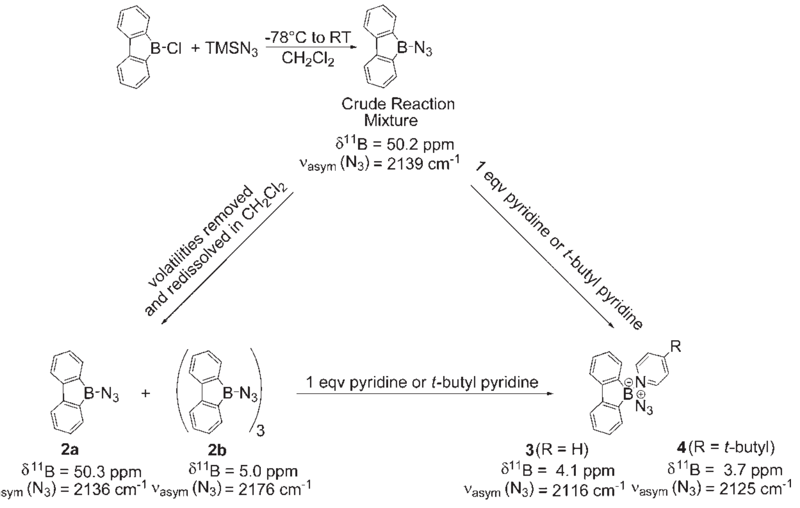
Scheme 2. Synthesis of 9-Azido-9-borafluorene **2** and Its Pyridine Adducts and Key Spectral Features of **2−4**



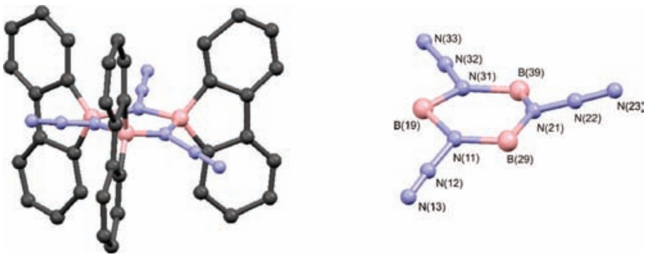


Figure 4. Molecular structure of **2b** (left) and depiction of its $B_3(N_3)_3$ core (right). Two dichloromethane solvent molecules and hydrogen atoms are omitted for clarity.

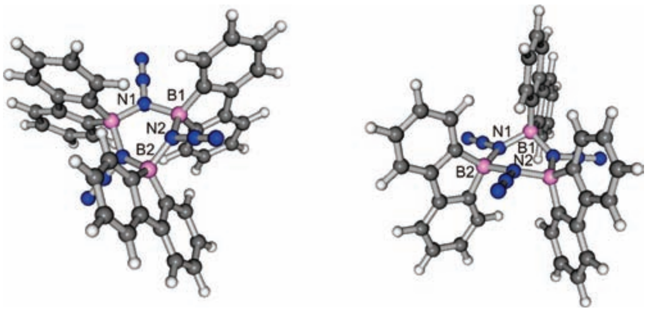


Figure 5. Structures of the two conformers of cyclotrimer **2b** as computed at the RI-MP2/SVP level of theory. Left: selected bond lengths [Å] and angles [deg] of **2b-A**: N1−B1 1.591; B1−N2 1.606; N2−B2 1.602; N1−B1−N2 102.1; B1−N2−B2 128.7; N2−B2−N2′ 98.5; B1−N1−B1′ 127.8 (symmetry equivalent atoms are labeled with primes). Right: selected bond lengths [Å] and angles [deg] of **2b-B**: B1−N1 1.597; N1−B2 1.586; B2−N2 1.619; N1′−B1−N1 102.0; B1−N1−B2 127.6; N1−B2−N2 100.6; B2−N2−B2′ 132.6 (symmetry equivalent atoms are labeled with primes).

B−C bonds are shorter for the two symmetry identical borafluorene subunits, 1.600 and 1.603 Å, but longer for the third unit, 1.613 Å.

The second isomer **2b-B** is of C_s symmetry and features a central six-membered ring in a boat conformation. Again the azide units are essentially linear. One of the borafluorene units and a transannular azide lie within the symmetry plane. The B−N bond lengths, 1.586,1.597, and 1.619 Å, differ more than in **2b-A**, while the planarity of the N_α atoms is slightly reduced (sum of bond angles: 356.7° and 358.8°). Noteworthy are two close contacts of 2.235 Å between the hydrogen atoms of the borafluorene units. Both isomers are essentially isoenergetic as they lie within 0.1 kcal mol^{-1} in energy in favor of **2b-A** at the RI-MP2/SVP level. The trimerization of azide **2a** is highly exothermic, $\Delta E(0\ K) = 57$ kcal mol^{-1}. Because of the size of the system we do not consider enthalpy or entropy corrections. It is interesting to compare the cyclotrimerization of **2a** and F_2BN_3 that was studied by Fraenk and Klapötke[51] at a similar level of theory (MP2(full)/6-31G**). Formation of a cyclotrimer of F_2BN_3 with a chairlike conformation is exothermic by 22.5 kcal mol^{-1} according to these authors.[51] At our level of theory, we find that besides the chair also a twist conformation of $(F_2BN_3)_3$ corresponds to a minimum that is 3.2 kcal mol^{-1} *lower* in energy than the chair form. The energy of trimerization, −35.7 kcal mol^{-1}, is however significantly larger at our level of theory than the previously reported value.[51] The source for the discrepancy is unclear at this time: both the RI and the frozen core approximations can be excluded as identical or very similar reaction energies are obtained in the case of conventional or full MP2 calculations. On the other hand, the basis sets SVP versus 6-31G(d,p) are of too similar quality to be responsible for such a large difference.

In any event, the computed exothermicity of the trimerization of azide **2a** to **2b** is *larger* than that for the trimerization of F_2BN_3, at least in the gas phase without any enthalpy or entropy corrections. This shows that the boron center in azide **2a** is highly Lewis acidic, and is stabilized by formation of a strong *σ* bond to the α-nitrogen atom of another molecule. The coexistence of monomeric and trimeric forms of **2** in solution indicate that the solvent appears to have a pronounced effect on the energy of cyclotrimerization, more so than for F_2BN_3 that is only known in its trimeric form.

As expected, the azide **2** is extremely sensitive toward degradation. In the presence of trace amounts of water and air it converts to 1,3,5-tris(2-biphenylyl)cyclotriboroxane **5** as depicted in Figure 6. The white compound **5** crystallizes in a triclinic space group $P\overline{1}$ (Z = 4) with two independent enantiomeric molecules in the asymmetric unit that have equal lengths of equivalent bonds. The B_3O_3 ring is nearly planar with B−O bond distances

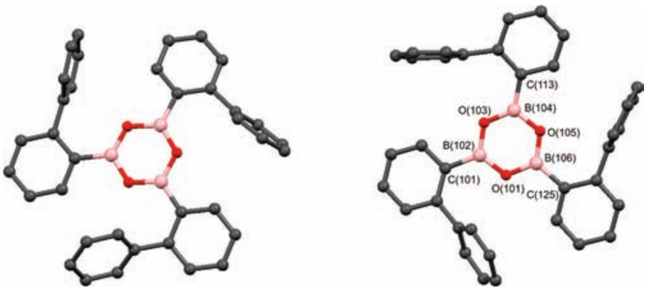


Figure 6. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond length lengths [Å] and angles [deg] in one enantiomer: O(101)−B(102) 1.376(15), O(101)−B(106) 1.381(14), O(103)−B(102) 1.377(15), O(103)−B(104) 1.378(15), O(105)−B(106) 1.364(15), O(105)−B(104) 1.385(15), B(102)−C(101) 1.562(17), B(104)−C(113) 1.557(17), B(106)−C(125) 1.563(17); B(102)−O(101)−B(106) 121.4(10), B(102)−O(103)−B(104) 120.9(9), B(106)−O(105)−B(104) 121.6(9), O(101)−B(102)−O(103) 118.9(10), O(101)−B(102)−C(101) 121.6(11), O(103)−B(102)−C(101) 119.4(10), O(103)−B(104)−O(105) 118.7(11), O(103)−B(104)−C(113) 124.3(11), O(105)−B(104)−C(113) 117.0(10), O(105)−B(106)−O(101) 118.4(10).

from 1.364(15) to 1.385(15) Å, and the boroxine ring angles are close to 120° with the B−O−B angles slightly larger [120.9(9)−121.6(9)°] than the O−B−O angles [118.4(10)−118.9(10)°]. This is similar to boroxin crystals investigated earlier.[53−56]

Note that Wehmschulte et al. have reported that the sterically encumbered borafluorene compounds 1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene and 1-(3,5-dimethylphenyl)-6,8-dimethyl-9-(bis-2,6-(3,5-dimethylphenyl)phenyl)-9-boraflorene are air and moisture stable.[44] Exposure of the pyridine adduct of 1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)-phenyl)-9-borafluorene to concentrated aqueous HCl for one week in the presence of air led to cleavage of one of the B−C bonds of the borafluorene unit. The splitting pattern is similar for the highly stable compound of Wehmschulte et al.[44] and our labile 9-azido-9-borafluorene **2**.

We also have performed the trapping reaction of **2** with pyridine and *t*-butyl pyridine as Lewis bases. Addition of pyridine to the reaction mixture as well as to the redissolved product (**2a** and **2b**) in dichloromethane, in separate experiments, yields the identical white stable pyridine adduct of 9-azido-9-borafluorene **3**. This is characterized by an ^{11}B signal at δ 4.1 and a strong absorption at 2116 cm^{-1} ($\nu_{\mathrm{asym}}\mathrm{N_3}$) in the IR vibrational spectra. This red shift of the azide asymmetric stretching vibration is very well-known for pyridine adducts of different azidoboranes as reported earlier for $\mathrm{CatBN_3}$ (2169 cm^{-1}) and $\mathrm{CatBN_3 \cdot py}$ (2132 cm^{-1});[9] $[(\mathrm{C_6F_5})_2\mathrm{BN_3}]_2$ (2202 cm^{-1}) and $(\mathrm{C_6F_5})_2\mathrm{BN_3 \cdot py}$ (2137 cm^{-1});[19] $[\mathrm{C_6F_5B(N_3)_2}]_3$ (2200/2180/2142 cm^{-1}) and $\mathrm{C_6F_5B(N_3)_2 \cdot py}$ (2146/2130 cm^{-1}).[18]

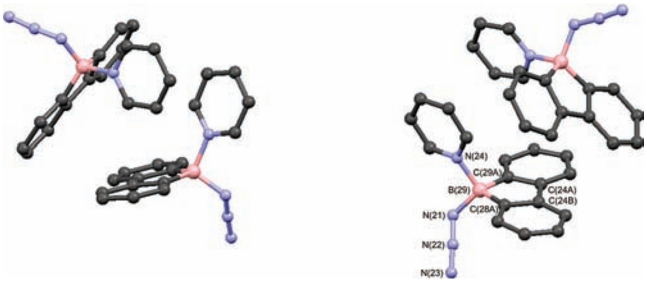


Figure 7. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond length lengths [Å] and angles [deg] in single molecule: N(21)−B(29) 1.559(3), N(21)−N(22) 1.201(2), N(22)−N(23) 1.136(2), N(24)−B(29) 1.619(2), C(28A)−B(29) 1.610(3), C(29A)−B(29) 1.598(3), C(24B)−C(28A) 1.406(2), C(24A)−C(24B) 1.485(2), C(24A)−C(29A) 1.409(2); N(21)−N(22)−N(23) 175.9(2), B(29)−N(21)−N(22) 119.99(17), C(29A)−B(29)−C(28A) 101.12(16), C(24B)−C(28A)−B(29) 108.58(17), C(24A)−C(29A)−B(29) 108.93(16), C(28A)−C(24B)−C(24A) 110.68(16), C(29A)−C(24A)−C(24B) 110.54(17).

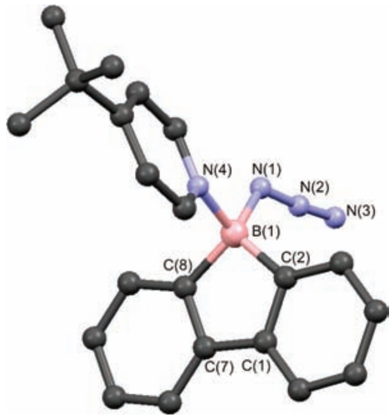


Figure 8. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond length lengths [Å] and angles [deg]:B(1)−C(2) 1.611(19), B(1)−C(8) 1.617(2), C(2)−C(1) 1.413(17), C(1)−C(7) 1.485(18), C(7)−C(8) 1.410 (17), N(1)−N(2) 1.208(14), N(2)−N(3) 1.138(15), B(1)−N(1) 1.548(16) Å, B(1)−N(4) 1.608(17) Å ; N(1)−N(2)−N(3) 174.4(13), B(1)−N(1)−N(2) 121.7(11), B(1)−C(2)−C(1) 109.1(11), C(2)−C(1)−C(7) 110.8(11), C(1)−C(7)−C(8) 110.6(11), C(7)−C(8)−B(1) 109.1(11), C(2)−B(1)−C(8) 100.5(10).

Slow evaporation of solvent from the $\mathrm{CH_2Cl_2}$ solution of compound **3** produces white needle shaped crystals. The crystal structure of compound **3** (Figure 7) confirms the existence of monomeric azide **2a** in the reaction mixture. This compound crystallizes triclinically in the $P\bar{1}$ space group with eight formula units in the unit cell and four molecules in the asymmetric unit. The boron atom is tetrahedrally arranged and bonded to pyridine with simple B−N dative bond (average length $\mathrm{B{-}N_{py}}$ 1.61 Å). Comparing this distance with earlier investigated crystal structures of pyridine adducts of azidoboranes, that is, 9-BBN-$\mathrm{N_3 \cdot py}$ [1.637(3) Å][9] or $(2\text{-}\mathrm{FC_6H_4})_2\mathrm{BN_3 \cdot py}$ [1.621(3) Å],[7] suggests that the boron center in dibenzoborole is slightly more acidic and acts as a better acceptor toward the pyridine donor. The azide group attached to boron is slightly bent [$\mathrm{N_\alpha{-}N_\beta{-}N_\gamma}$ 174−176°] in all molecules **3**. The $\mathrm{B{-}N_\alpha}$ bond length of 1.562 Å (avg.) is a little shorter than a typical B−N single bond (1.59 Å). The $\mathrm{N_\beta{-}N_\gamma}$ (avg. 1.136 Å) is shorter than $\mathrm{N_\alpha{-}N_\beta}$ (avg. 1.192 Å), and these bond distances have lengths between those of a N−N double (1.24 Å) and a triple bond (1.10 Å).[9]

The trapping reaction of **2** also has been carried out with *t*-butyl pyridine producing 9-azido-9-borafluorene·*t*-butyl py **4**. After washing with pentane, the white, crystalline, moisture sensitive clean product is obtained. Addition of *t*-butyl pyridine shifts the ^{11}B NMR signal upfield to δ 3.7 and the IR

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stretching frequency to lower frequency ($\nu_{\text{asym}}N_3$ 2125 cm^{-1}) compared to free azide **2**. The single crystal X-ray analysis confirms the structure of **4** as depicted in Figure 8.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. It shows tetrahedral coordination geometry around the boron atom. Again, the azide group is slightly bent at N(2) [N(1)−N(2)−N(3) 174.4°] and the N(2)−N(3) bond [1.138(15) Å] is shorter than N(1)−N(2) bond [1.208(14) Å]. The B(1)−N(1) [1.548(16) Å] and B(1)−N(4) [1.608(17) Å] distances are comparable to those of pyridine adduct **3**. The bond lengths in the BC_4 unit, B(1)−C(2) [1.611(19) Å], B(1)−C(8) [1.617(2) Å] are in the range that is typical for B−C(sp^3) single bonds for tetrahedral boron center 1.60−1.64 Å.[57] The bond lengths C(2)−C(1) [1.413(17) Å], C(1)−C(7) [1.485(15) Å], and C(7)−C(8) [1.410(17) Å] resemble the structural parameters found in 9-chloro-9-borafluorene. Thus, it can be concluded that these bond lengths have little dependence on the coordination number of the boron center.

Conclusions

The target compound, 9-azido-9-borafluorene **2**, is the first example of an azidoborane of the borole system (Type **D**). The azide can be prepared from 9-chloro-9-borafluorene **1a**. The boron center appears to be very Lewis acidic: Compound **2** exists as a monomer **2a** in solution just after its synthesis, but as a cyclotrimer **2b** in the solid state. Because of the pronounced instability of **2b** the structural details could not obtained from experiment. Computations indicate that two conformational isomers lie very close in energy. The computed energy of cyclotrimerzation of **2a** in the gas phase at 0 K is larger than for F_2BN_3 that only exists in trimeric form in solution. Dissolution of **2b** in dichloromethane, however, produces both **2a** and **2b**. This indicates that solvent effects are more important for **2** than for F_2BN_3. Azide **2** is easily decomposed into a boroxin that could be structurally characterized. It also can be stabilized by forming adducts with pyridines. The latter include only one azide unit as shown by X-ray crystallography.

Experimental and Computational Details

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques or in a glovebox. The solvent *n*-hexane was dried over CaH_2 just before use. The NMR spectra were recorded on a Bruker DPX 250 MHz spectrometer. Spectra were referenced to residual solvent (^{1}H, ^{13}C) and externally (^{11}B: $BF_3 \cdot OEt_2$, ^{14}N: CH_3NO_2). The NMR spectra were measured in CD_2Cl_2. It was purchased from Deutero GmbH, dried over 4 Å molecular sieve. and was Argon saturated before use. Dry solvent (CH_2Cl_2), 1,2-dibromobenzene, *n*-BuLi (1.6 M in *n*-hexane), BCl_3 (1 M in *n*-hexane), $TMSN_3$ (Aldrich), pyridine, *t*-butyl pyridine purchased from Acros or Aldrich were used as received without any modification. 2,2′-Dibromobiphenyl was prepared as described in the literature.[58,59]

Caution! *Azides described here may be explosive; appropriate safety precautions need to be taken.*

9-Chloro-9-borafluorene (1a).[37] To a cooled solution (0 °C) of 3 g (9.6 mmol) of 2,2′-dibromobiphenyl in 150 mL of *n*-hexane, 12.1 mL of *n*-BuLi (19.2 mmol) was added dropwise. After complete addition, the ice bath was removed and the white solution stirred for 3 days at ambient temperature. After removal of the solvent in vacuo, the remaining white solid was washed with *n*-hexane (3 × 100 mL). Then a white slurry was made in 150 mL of hexane by vigorous stirring, and 9.6 mL of BCl_3 (1 M in *n*-hexane, 9.6 mmol) was added slowly to it at 0 °C. After stirring overnight, the bright yellow solution was filtered from the white solid and concentrated to ~5 mL. This remaining oily liquid was distilled at 90 °C at 10^{-3} mbar to give (1.72 g, 8.6 mmol, 90% relative to 2,2′-dibromobiphenyl) pure 9-chloro-9-borafluorene as bright yellow needle shape crystals that were good enough for X-ray measurement. mp 52 °C, ^{13}C NMR (CD_2Cl_2): 153.2, 135.4, 132.6, 128.7 and 119.9, the carbon atom directly attached to boron can not be detected. ^{11}B NMR (CD_2Cl_2): 63.6. ^{1}H NMR (CD_2Cl_2): 7.53 (d, J = 7.0 Hz, 2 H), 7.39−7.35 (m, 4 H), 7.17−7.11 (m, 2 H).

9-Azido-9-borafluorene (2). A solution of 0.1 g (0.5 mmol) 9-chloro-9-borafluorene **1** in 10 mL of CH_2Cl_2 was treated with 0.067 mL of (0.5 mmol) trimethylsilyl azide at −78 °C. The reaction mixture was gradually warmed to room temperature after stirring overnight. The resulting crude bright yellow solution was monitored by boron NMR showing complete conversion into monomeric boron species **2a**. ^{11}B NMR (CD_2Cl_2): 50.2; IR (nujol + CH_2Cl_2): 2139 vs [$\nu_{\text{asym}}(N_3)$] cm^{-1}.

After complete removal of all volatile products, the remaining pale yellow solid product shows two signals for **2a** and **2b** in boron NMR. ^{11}B NMR (CD_2Cl_2): 50.3 and 5.0. IR (nujol + CH_2Cl_2): 2176 s and 2136 vs [$\nu_{\text{asym}}(N_3)$] cm^{-1}.

9-Azido-9-borafluorene·pyridine (3). Trimethylsilyl azide (0.067 mL, 0.5 mmol) was added to a solution of 0.1 g (0.5 mmol) of 9-chloro-9-borafluorene dissolved in 10 mL of CH_2Cl_2 at −78 °C. The reaction mixture is allowed to warm slowly and stirred overnight. Then 0.04 mL (0.5 mmol) of pyridine was added to the reaction mixture subsequently. After that the solvent was removed in vacuo leaving a white solid that was purified by trituration with *n*-pentane from dichloromethane solution and dried at ambient temperature under reduced pressure to produce pure product **3**. Slow evaporation of the CH_2Cl_2 solvent from the solution of the product produced colorless crystals which were found to be suitable for X-ray crystallography. Yield 0.131 g (91%), mp 176−178 °C (decomp.). ^{11}B NMR (CD_2Cl_2): 4.1. ^{13}C NMR (CD_2Cl_2): 149.0, 144.4, 141.9, 129.6, 128.4, 127.1, 126.2, 119.6. ^{1}H NMR (CD_2Cl_2): 8.68 (d, J=6.8 Hz, 2 H), 8.07 (t, J=8.1 Hz, 1 H), 7.68 (d, J = 7.4 Hz, 2 H), 7.63−7.57 (m, 2 H), 7.33−7.27 (m, 4 H), 7.18−7.12 (m, 2 H); ^{14}N NMR (CD_2Cl_2): −75.6 (N-py), −138.4 (N-2), −210.9 (N-3), N-1 not detected. IR (nujol + CH_2Cl_2): ν = 2929 w, 2854 m, 2116 vs [$\nu_{\text{asym}}(N_3)$], 1620 vs, 1457 vs, 1377 m, 1158 sw, 1058 w, 919 m, 874 s, 830 sw, 743 vs, 690 m, 690 s, 653 s, 619 s.

9-Azido-9-borafluorene·*t*-butyl Pyridine (4). Compound **4** was prepared similarly as described for compound **3** using 0.07 mL (1 equivalent) of *t*-butyl pyridine. After removal of all volatile residues by vacuum evaporation, colorless compound was obtained by a trituration process as described above for **3**. This compound is crystallized from CH_2Cl_2. Then the white needle shaped crystals were washed with *n*-pentane to give a pure product. Yield 0.152 g (88%), mp 204−206 °C (decomp.). ^{11}B NMR (CD_2Cl_2): 3.7. ^{13}C NMR (CD_2Cl_2): 167.3, 149.1, 143.9, 129.6, 128.4, 127.0, 123.3, 119.6, 35.7, 29.9. ^{1}H NMR (CD_2Cl_2): 8.53 (d, J = 6.7 Hz, 2 H), 7.66 (d, J = 7.4 Hz, 2 H), 7.54 (d, J = 6.7 Hz, 2 H), 7.33−7.25 (m, 4 H), 7.16−7.11 (m, 2 H), 1.31 (s, 9 H). ^{14}N (CD_2Cl_2): −73.0 (N-py), −135.8 (N-2), −207.6 (N-3), N-1 not detected. IR (nujol + CH_2Cl_2): ν = 3050 s, 2956 vs, 2925 vs, 2854 vs, 2125 vs [ν_{asym} (N_3)], 1632 vs, 1596 m, 1504 m, 1432 vs, 1352 s, 1221 s, 1151 sw, 1083 s, 929 s, 873 s, 851 s, 829 s, 742 vs, 707 m, 681 s.

X-ray Crystallography. The intenisity data were collected on an Oxford Diffraction Xcalibur2 diffractometer with a

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Table 1. Crystal Data and Structure Refinements

	1a	**1b**	**3**	**4**	**5**
empirical formula	$C_{12}H_8BCl$	$C_{36}H_{24}B_2$	$C_{17}H_{13}BN_4$	$C_{21}H_{21}BN_4$	$C_{36}\ H_{27}B_3O_3$
formula weight	198.44	478.17	284.12	340.23	540.01
T/K	103	108	113	110	108
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a (Å)	3.8570(5)	17.6344(17)	9.7657	10.7761(5)	13.0852(5)
b (Å)	4.0680(17)	10.2537(9)	17.5892	13.7559(7)	13.3035(6)
c (Å)	17.495(3)	14.1172(13)	18.4303	12.5533(5)	19.6082(7)
α (deg)	90°	90°	68.734(4)°	90°	70.466(4)°
β (deg)	95.237(15)°	103.205(9)°	89.620(3)°	96.300(4) °	74.187(3)°
γ (deg)	90°	90°	81.217(3)°	90°	61.449(4)°
V (Å^3)	945.3(2)	2485.1(4)	2911.5(2)	1849.60(15)	2799.41(22)
Z	4	4	8	4	4
d_{calcd} (mg/m^3)	1.394	1.278	1.296	1.222	1.281
μ (mm^{-1})	0.350	0.071	0.079	0.073	0.078
F(000)	408	1000	1184	720	1128
crystal size (mm)	0.435 × 0.063 × 0.054	0.27 × 0.24 × 0.18	0.36 × 0.32 × 0.21	0.52 × 0.43 × 0.41	0.58 × 0.55 × 0.23
2θ range (deg)	2.90 to 27.65	2.96 to 25.25	2.64 to 25.25	2.96 to 25.24	3.06 to 27.50.
index range	$-2 \leq h \leq 5$	$-21 \leq h \leq 20$	$-8 \leq h \leq 11$	$-12 \leq h \leq 12$	$-16 \leq h \leq 16$
	$-11 \leq k \leq 18$	$-12 \leq k \leq 12$	$-20 \leq k \leq 21$	$-15 \leq k \leq 16$	$-15 \leq k \leq 17$
	$-22 \leq l \leq 21$	$-16 \leq l \leq 16$	$-22 \leq l \leq 22$	$-14 \leq l \leq 15$	$-24 \leq l \leq 25$
no. of reflections collected/unique	4325/2139	27172/4498	24852/10505	9125/3300	25207/12695
	[R(int) = 0.0768]	[R(int) = 0.1124]	[R(int) = 0.0427]	[R(int) = 0.0218]	[R(int) = 0.0199]
completeness to θ = 27.50	98.0%	99.8%	99.5%	98.7%	98.6%
absorption correction	none	none	none	none	none
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	2139/0/127	4498/0/343	10505/0/793	3300/0/238	12695/0/757
goodness-of-fit, F^2	0.959	1.133	0.819	0.945	0.882
R_1, wR_2 [$I > 2\sigma(I)$]	0.0397, 0.0472	0.0797, 0.1691	0.0380, 0.0640	0.0351, 0.0855	0.0360, 0.0789
R_1, wR_2 (all data)	0.1368, 0.0573	0.1014, 0.1749	0.0906, 0.0692	0.0504, 0.0890	0.0591, 0.0821
largest diff. peak and hole (e Å^{-3})	0.221 and −0.261	0.227 and −0.229	0.256 and −0.184	0.215 and −0.176	0.305 and −0.220

Sapphire2 CCD. The crystal structures were solved by direct methods using SHELXS-97[60] and refined with SHELXL-97.[60] For refinement details see Table 1 and for further details please see Supporting Information.

Crystal structure of **2b**: the crystals were extremely air- and moisture sensitive and even covered with oil at 100 K they decomposed quite rapidly on the diffractometer. Nevertheless we were able to get a data set which was good enough to confirm the connectivity of **2b**: pale yellow crystal, 0.22 × 0.20 × 0.10 mm^3, triclinic, $P\bar{1}$, a = 11.069(4) Å, b = 11.233(3) Å, c = 16.894(5) Å, α = 90.44(2)°, β = 91.11(3)°, γ = 118.21(3)°, V = 1850(1) Å^3, Z = 2, ρ_{calc} = 1.240 g/cm^3, $\theta_{\max}$ = 23.7°, λ (Mo K$_\alpha$) = 0.71073 Å, T = 110(2) K, 5621 independent reflections, 2223 [$I > 2\sigma(I)$], 237 parameter, R = 0.216, wR = 0.537 (for all data).

Calculations. The computations were performed with the Turbomole program.[61] Geometries were fully optimized within the respective point group constraints at the second order Møller−Plesset perturbation theory level in conjunction with the resolution of the identity (RI) approximation for the fast computation of two-electron integrals (RI-MP2).[62,63] The computations used the SVP basis set (C, B, N, F: (7s4p1d)/[3s2p1d]; H: (4s1p)/[2s1p]) and the corresponding fitting bases.[61,63] The excitation energy of **1b** was computed at the B3LYP[64,65] functional as implemented in Turbomole in conjunction with the TZVP[66] basis set (C, B: (11s6p1d)/[5s3p1d]; H: (5s1p)/[3s1p]) at the RI-MP2/SVP geometry using the time-dependent DFT formalism.[67]

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Supporting Information Available: Experimental and spectroscopic details (^{11}B, ^{1}H, ^{13}C, ^{14}N NMR data) for the new compounds and CIF files of the X-ray crystal structures including tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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