# Structure of 8-(diethylborylmethylamino)-3-phenyl-1-azaazulene: characteristics of the non-alternant ligand

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Letter

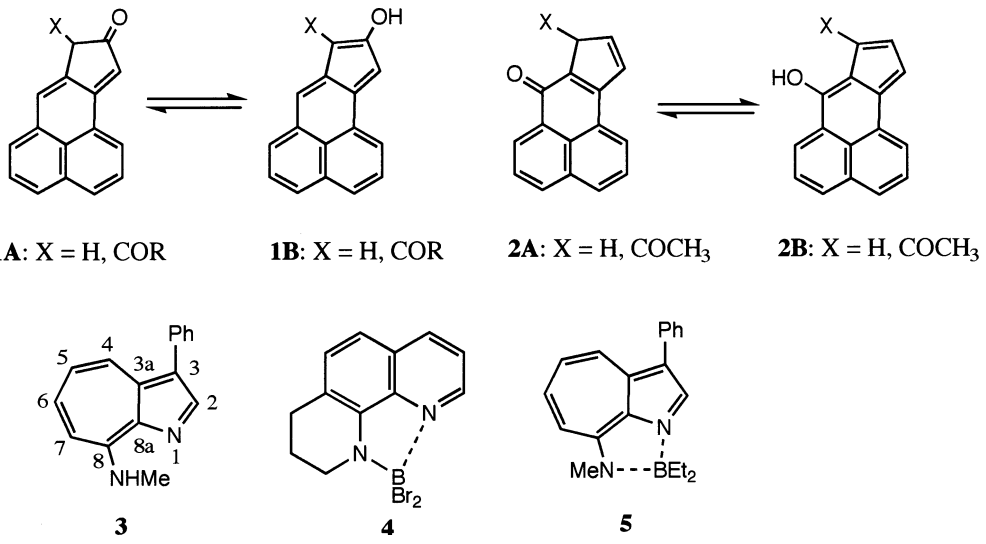
8-(Diethylborylmethylamino)-3-phenyl-1-azaazulene (**5**) has been synthesized, in which the 8-methylamino-azaazulene moiety is found to act as a bidentate ligand whose two boron–nitrogen bond lengths are almost equivalent.

Non-alternant conjugation is known to endow molecules with a variety of properties that are markedly different from those given by alternant conjugation. In contrast to alternant conjugation, the resonance stabilization energy in non-alternant conjugation has been indicated to be small.[1] Hence, a slight modification of the structure causes a loss of this conjugation, resulting in a significant change of the properties. For example, bathochromic shifts of *ca.* 200 nm were observed in the UV/VIS spectra by the introduction of the acyl group to the adjacent position of the oxy function in the alternant extended phenalenones (**1A**, **2A**),[2] exhibiting the pronounced contribution of the non-alternant hydroxycyclopenta[*a*]-phenalenes (**1B**, **2B**) in the tautomerism.

Despite extensive studies on alternant bidentate ligands such as phenanthroline, the non-alternant ones have rarely been examined.[3] Their high electron-donating and -accepting characters[4] allow production of coordination molecules showing the new interaction between the ligand and the central metal or between the ligands. In line with our work on conjugated boron heterocycles,[5] we have examined a coordination molecule composed of a boron atom and the conjugate base of 8-methylamino-3-phenyl-1-azaazulene (**3**),[6]† and compared it with the structures of both **3** and dibromoboryl-1,2,3,4-tetrahydro-1,10-phenanthroline (**4**).[7]

A solution of **3** (234 mg, 1.00 mmol) in tetrahydrofuran (11 ml) was treated with BuLi (1.20 mmol) at −78 °C. After 15 min, a tetrahydrofuran solution (1.0 M) of diethylmethoxyborane (1.20 mmol) was added dropwise and the mixture was stirred at −78 °C for 2 h. Then the solution was allowed to stand at room temperature overnight, and was refluxed for 1 d. After extraction with chloroform, the mixture was chromatographed over silica gel with a mixture of chloroform and ethyl acetate (1 : 1 v/v) to give 8-(diethylborylmethylamino)-3-phenyl-1-azaazulene (**5**) as orange prisms (270 mg, 89.3%, mp 93–94 °C). (All the compounds here are identified spectro-

† Synthesis of **3**: A mixture of 8-chloro-3-phenyl-1-azaazulene[6] (4.00 g, 16.8 mmol) and 40% aq. methylamine (20 ml) in ethanol (20 ml) was stirred for 1 d at room temperature. Filtration gave 8-methylamino-3-phenyl-1-azaazulene (3.10 g, 79%), which was recrystallized from chloroform–hexane to give reddish orange prisms, mp 159–161 °C.




**Scheme 1**

scopically, and by means of combustion analysis.) Though the coordination compound **5** is stable under the ambient conditions, it decomposes gradually in a protic solvent such as methanol.‡

UV/VIS spectra of **5** in acetonitrile are similar to those of **1**, the long-wavelength end up to 600 nm suggesting the high-lying HOMO and low-lying LUMO.§

Though each corresponding vicinal coupling constant in **3** and **5** is not markedly changed, all the proton signals of **5** display upfield shifts in the range 0.49–0.86 ppm, indicating the decrease of the diamagnetic ring current. The distinct downfield shifts of C6, C7, C8 and C8a by 1.1, 2.6, 3.2 and 1.6 ppm, respectively, together with the slight upfield shifts of C3 and C3a by 1.6 and 1.8 ppm, respectively, exhibit the electron donation from the seven-membered ring to the five-membered ring. The marked upfield shift of C2 by 16.5 ppm suggests the formation of the coordinate bond between the boron and N1 nitrogen atom.[8] The signal of the boron atom at 6.8 ppm, which is similar to the value of 8.5 ppm of **4**, indicates this atom to be tetracoordinate.

Single-crystal X-ray crystallography of **3** (Fig. 1),¶ showed that the amino-hydrogen atom in **3** is located more closely to the amino-nitrogen atom (N2) than the skeletal nitrogen (N1)

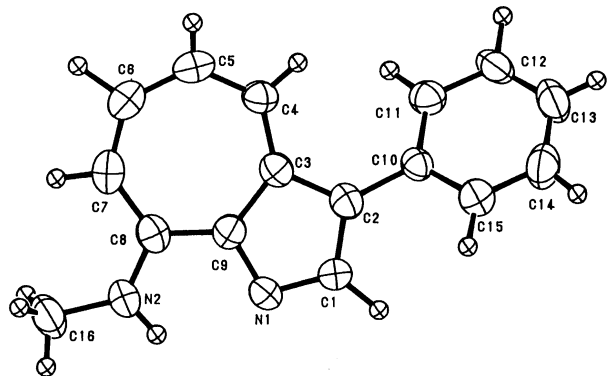



**Fig. 1** Computer-generated thermal ellipsoid of **3**. Some important bond distances (Å) and angles (°) not given in the text are as follows: N1—C1 = 1.359(5), C1—C2 = 1.379(6), C2—C3 = 1.443(6), C3—C9 = 1.450(5), C3—C4 = 1.400(6), C4—C5 = 1.372(7), C5—C6 = 1.402(6), C6—C7 = 1.376(6), C7—C8 = 1.428(7), C8—C9 = 1.426(6), C9–N1 = 1.345(6), C9—N1—C1 = 105.4(4), N1—C1—C2 = 113.8(4), C1—C2—C3 = 105.4(4), C2—C3—C9 = 103.6(4), C3—C9—N1 = 111.8(4), C4—C3—C9 = 129.1(4), C3—C4—C5 = 127.8(4), C4—C5—C6 = 128.3(5), C5—C6—C7 = 131.1(5), C6—C7—C8 = 130.0(5), C7—C8—C9 = 124.1(4), C8—C9—C3 = 129.4(4), C8—C9—N1 = 118.8(4)

‡ The attempted synthesis using 8-(dimethylamino)-3-phenyl-1-aza-azulene as a ligand resulted in failure.

§ UV/VIS of **5** (acetonitrile): $\lambda_{max}$/nm (log $\varepsilon$) 244(4.45), 260(4.34, sh), 324(4.27), 446(3.63), 464(3.64), 494(3.39, sh).

¶ Data were collected at 293 K on a Rigaku AFC5S diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å) and a 2 kW stationary anode generator. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Crystal data for **3**: $C_{16}H_{14}N_2$, $M$ = 234.30, brown, prismatic crystal (0.24 × 0.46 × 0.54 mm), orthorhombic $P2_12_12$ (#18), $a$ = 18.313(3), $b$ = 7.320(6), $c$ = 9.242(6) Å, $V$ = 1239(2) Å$^3$, $Z$ = 4, $D_C$ = 1.256 g cm$^{-3}$, $\mu$ = 0.70 cm$^{-1}$, $F(000)$ = 496. The final cycle of full-matrix least-squares refinement was based on 967 observed reflections [$I > 2.00\ \sigma(I)$] and 220 variable parameters and converged with unweighted and weighted agreement factors of $R$ = 0.050 and $R_w$ = 0.052. Crystal data for **5**: $C_{20}H_{23}BN_2$, $M$ = 302.23, orange, prismatic crystal (0.24 × 0.48 × 0.64 mm), triclinic $P\bar{1}$ (#2), $a$ = 9.040(8), $b$ = 12.214(4), $c$ = 8.039(5) Å, $\alpha$ = 102.98(4), $\beta$ = 92.23(7), $\gamma$ = 93.28(5)°, $V$ = 862(1) Å$^3$, $Z$ = 2, $D_c$ = 1.164 g cm$^{-3}$, $\mu$ = 0.63 cm$^{-1}$, $F(000)$ = 324. The final cycle of full-matrix least-squares refinement was based on 2162 observed reflections [$I > 2.00\ \sigma(I)$] and 301 variable parameters and converged with unweighted and weighted agreement factors of $R$ = 0.057 and $R_w$ = 0.063. CCDC reference number 440/052.

[0.90(4) and 2.79(5) Å, respectively], and that the bond distance of N2—C8 is 1.340(5) Å, which is shortened compared with the correspondng bond distance of the amino-substituted alternant aromatic compound (1.375 Å).[9] These imply that the resonance energy of the 1-azaazulene skeleton is moderate, though being smaller than that in alternant conjugation.

Study of **5** (Fig. 2) showed the dihedral angle constituted by C1—N2 and B1—N1 bonds through N2—B1 is 175.5(3)°, and furthermore that of B1—N1 and C8—C7 bonds through N1—C8 is 176.4(3)°. That is, the boron atom is almost co-planar with the skeletal atoms of the ligand. In contrast to the amino-hydrogen atom (N2) of **3**, the distances between the boron atom and two nitrogen atoms in **5** (N1, N2) are 1.605(4) (B1—N1) and 1.591(4) Å (B1—N2), respectively. The tetrahedral character of the boron atom is estimated to be 73%.[10] The marked structural change of the aromatic ring is evident from comparison of bond distances in **3** and **5**. The shortened distance between N1 nitrogen and C8 carbon atoms [1.326(3) Å] would be due to the higher double bond character between these atoms. The small dihedral angle [1.8(5)°] of C10—N1 and C8—C7 bonds through N1—C8 proves this conjugation as well. Furthermore, upon coordination of the boron atom, the three carbon–carbon bonds (C3—C9, C4—C5, C6—C7) are shortened (0.047, 0.010, and 0.013 Å, respectively) and two bonds (C3—C4, C5—C6) are elongated (0.024 and 0.016 Å, respectively), the 8-azaheptafulvenyl character being pronounced in the seven-membered ring. The equivalent boron–nitrogen bonds and the marked structural change of the skeleton of **5** are attributable to the easy destruction of non-alternant conjugation in the 1-azaazulene skeleton with low aromatic resonance energy. The corresponding bond distances of **4** differ by 5.9% (1.584 and 1.490 Å, respectively); furthermore, the nitrogen atom incorporated into the aromatic ring forms the longer coordinate bond.[8]

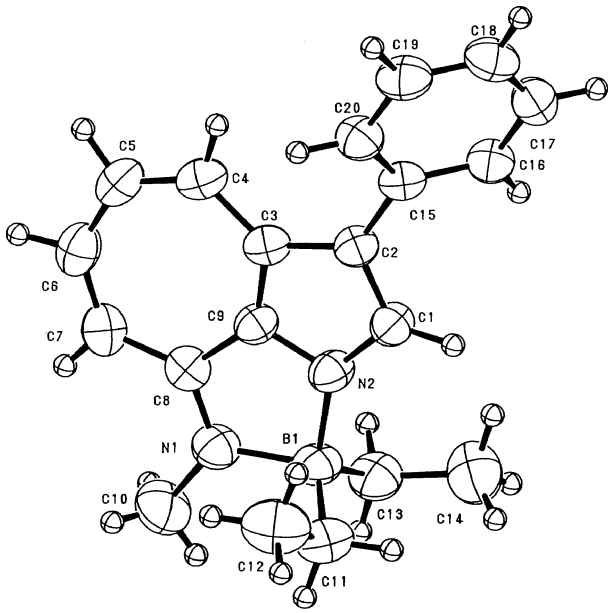



**Fig. 2** Computer-generated thermal ellipsoid of **5**. Some important bond distances (Å) and angles (°) not given in the text are as follows: N2—C1 = 1.361(3), C1—C2 = 1.385(4), C2—C3 = 1.434(4), C3—C9 = 1.403(3), C3—C4 = 1.424(4), C4—C5 = 1.362(4), C5—C6 = 1.418(4), C6—C7 = 1.363(4), C7—C8 = 1.426(4), C8—C9 = 1.417(4), C9—N2 = 1.351(3), C9—N2—C1 = 107.2(2), N2—C1—C2 = 110.8(2), C1—C2—C3 = 106.1(2), C2—C3—C9 = 105.1(2), C3—C9—N2 = 110.8(2), C4—C3—C9 = 124.3(3), C3—C4—C5 = 126.0(3), C4—C5—C6 = 130.2(3), C5—C6—C7 = 133.4(3), C6—C7—C8 = 125.7(3), C7—C8—C9 = 122.6(3), C8—C9—C3 = 137.5(3), C8—C9—N2 = 111.7(2), N1—B1—C13 = 109.5(2), N1—B1—C11 = 111.4(3), C11—B1—C13 = 116.2(3), N1—B1—N2 = 94.7(2)

In conclusion, this work shows potential utility of non-alternant ligands in sophisticated systems, such as three-dimensionally interacting organometallics using both the σ and π type coordinations with the metals.

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