Heterocyclic Compounds

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Synthesis of 1-Phospha-2-boraacenaphthenes: Reductive 1,2-Aryl Migration of 1-Diarylboryl-8-dichlorophosphinonaphthalenes**

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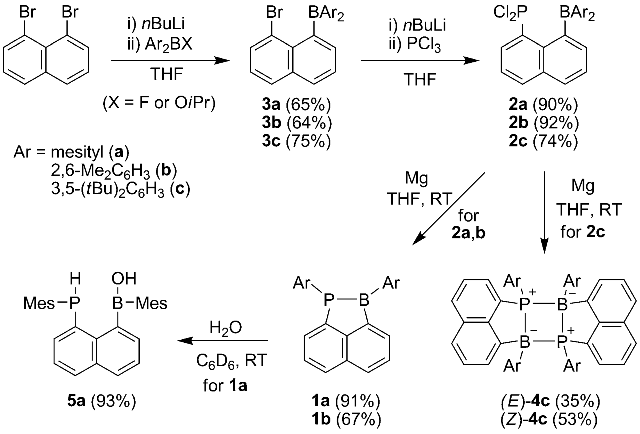
The chemistry of organic π-electron conjugated systems has attracted much attention in recent years from the viewpoint of material science, such as organic light-emitting diodes, photovoltaic cells, and liquid crystals. It is well known that the incorporation of main group elements into a π-electron conjugated backbone can effectively modify the electronic properties of a π-electron conjugated molecule.[1,2] In particular, main group elements from groups 13 and 15 are employed in these systems because they can drastically change the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the π-conjugated systems as a result of the characteristic interactions of their vacant p orbital (group 13) and lone pair (group 15). With regard to this type of compound, azaborine,[3] phosphaborine,[4] boryl-substituted azobenzene,[5] diborin,[6] and ladder-type π-electron conjugated systems[7] have been synthesized and revealed unique photophysical and electrochemical properties.

Phosphinoborane ($R_2P{-}BR'_2$)[8] is a heavier analogue of aminoborane ($R_2N{-}BR'_2$), which exhibits an isoelectronic structure to an alkene ($R_2C{=}CR'_2$). Theoretical calculations showed that the ground state of $H_2P{-}BH_2$ has a C_s symmetric structure with a pyramidal phosphorus atom; this structure is in contrast to the planar structure of the ground state of $H_2N{-}BH_2$, which has C_{2v} symmetry.[9] Although $H_2P{-}BH_2$ and $H_2N{-}BH_2$ have different conformations in their ground states, their $H_2E{=}BH_2$ (E = N, P) π-bond energies are estimated to be almost the same (34 kcal mol^{-1} for E = N, 36 kcal mol^{-1} for E = P).[9d,f] Thus, a P–B bond is a candidate to be a π-electron unit in π-electron conjugated systems. However, kinetic or thermodynamic stabilization would be necessary to isolate monomeric phosphinoborane as a stable compound, because phosphinoborane undergoes facile oligomerization in a head-to-tail manner by the formation of intermolecular P–B dative bonds.[8a,10] A series of kinetically stabilized phosphinoboranes bearing mesityl, phenyl, trimethylsilyl, and 1-adamantyl groups have been reported by Power and co-workers,[11] and phosphinoboranes ($(LA)H_2P{-}BH_2(LB)$; LA = Lewis acid, LB = Lewis base) that are thermodynamically stabilized by the coordination of a Lewis acid and base have been reported by Scheer and co-workers.[12] We report herein the synthesis and properties of 1-phospha-2-boraacenaphthene **1**, which is a unique heterocyclic compound bearing a P–B bond attached to a naphthyl unit at the 1- and 8-positions.[13] Compound **1** was synthesized by the reduction of 1-diarylboryl-8-dichlorophosphinonaphthalenes **2** by a unique intramolecular aryl migration from the boron atom to the phosphorus atom (Scheme 1).



Scheme 1. Synthesis of **1**. THF = tetrahydrofuran.

1-Diarylboryl-8-dichlorophosphinonaphthalenes **2** were synthesized from 1,8-dibromonaphthalene in two steps (Scheme 1). The reaction of 1,8-dibromonaphthalene with *n*BuLi and Ar_2BX (X = F or O*i*Pr; Ar = mesityl (**a**), 2,6-dimethylphenyl (**b**), and 3,5-di-*tert*-butylphenyl (**c**)) in THF gave 1-bromo-8-diarylborylnaphthalenes **3** in moderate yields. Then, treatment of **3** with *n*BuLi at low temperature (−40 °C for **3a** and **3b**, and −78 °C for **3c**) followed by the addition of PCl_3 gave **2** in relatively high yields.[14] It should be noted that the ^{11}B NMR spectra of **2a** and **2b** ($\delta = 63.9$ ppm for **2a**, $\delta = 64.3$ ppm for **2b**), and **2c** ($\delta = 10.1$ ppm) revealed the tri- (**2a** and **2b**) and tetra-coordination states (**2c**) of the boron atom. The steric repulsion resulting from the methyl

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groups on the aryl group of **2a** and **2b** is believed to prevent the formation of an intramolecular P–B dative bond.

The reduction of **2c** with magnesium metal in THF at room temperature gave a mixture of two isomers, (*E*)-**4c** and (*Z*)-**4c**, which can be considered as dimers of the corresponding 1-phospha-2-boraacenaphthene **1c**, in 35 and 53 % yields, respectively, upon isolation (Scheme 1).[15,16] Therefore, the introduction of 3,5-$t\text{Bu}_2\text{C}_6\text{H}_3$ groups would not be suitable for the synthesis and isolation of a 1-phospha-2-boraacenaphthene in the monomeric form. On the other hand, the reduction of **2a** and **2b** with magnesium metal afforded **1a** and **1b** as orange crystals in 91 and 67 % yields, respectively, upon isolation.[14] These results suggest it is necessary to have a substituent at the *ortho* positions of the aryl groups on the boron atom to isolate **1** as a stable compound. The monomeric molecular structure of **1a** was unambiguously determined by X-ray crystallographic analysis (Figure 1).[17] The deviation of the phosphorus atom from the naphthalene plane is 0.36 Å, while the boron atom is located on the same plane as naphthalene (Figure 1 b). The sum of the bond angles around the phosphorus and boron atoms are 328.4(3)° and 359.5(6)°, respectively, thus confirming the pyramidal (phosphorus) and trigonal planar (boron) geometries. The P–B bond length in **1a** is 1.889(3) Å, which is slightly longer than those in $\text{Mes}_2\text{PBMes}_2$ (**6**; 1.839(8) Å) and $\text{Ph}_2\text{PBMes}_2$ (**7**; 1.859(3) Å).[11] The ^{11}B NMR spectra of **1a** and **1b** in C_6D_6 showed broad signals at $\delta_\text{B} = 77.9$ ppm ($\Delta\nu_{1/2} = 1400$ Hz) for **1a** and $\delta_\text{B} = 77.8$ ppm ($\Delta\nu_{1/2} = 930$ Hz) for **1b**, thus suggesting a trigonal planar geometry around the boron atom in solution. These values are similar to those of **6** ($\delta_\text{B} = 82.4$ ppm) and **7** ($\delta_\text{B} = 70.9$ ppm).[11] On the other hand, the ^{31}P NMR signals, observed at $\delta_\text{P} = -28.2$ ppm (**1a**) and $\delta_\text{P} = -27.7$ ppm (**1b**), were shifted relatively upfield compared to the signals of **6** ($\delta_\text{P} = 27.4$ ppm) and **7** ($\delta_\text{P} = 26.7$ ppm),[11] probably due to the different geometries of the phosphorus atoms. That is, **1a** exhibits the pyramidal geometry, and **6** exhibits almost planar geometry.[8a] 1-Phospha-2-boraacenaphthenes **1a** and **1b** were stable under an inert atmosphere even on heating at 100 °C (C_6D_6 solution, sealed tube) for 24 h, but they underwent decomposition within three hours in dilute C_6D_6 solution at room temperature on exposure to air. The addition of degassed water into the C_6D_6 solution of **1a** afforded 1-hydroxy(mesityl)boryl-8-mesitylphosphinonaphthalene (**5a**) in 93 % yield.[14]

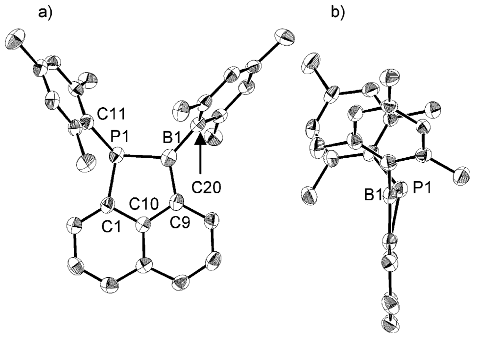
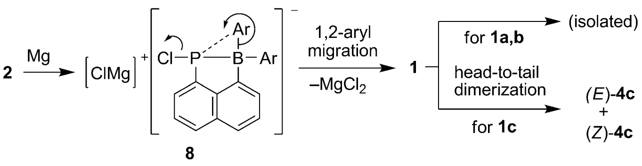


Figure 1. Molecular structure of **1a** with thermal ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and dihedral angles [deg]: P(1)–B(1) 1.889(3), P(1)–C(1) 1.817(3), B(1)–C(9) 1.582(4); P(1)-C(1)-C(10) 108.59(17), B(1)-C(9)-C(10) 113.6(2), P(1)-C(1)···C(9)-B(1) 10.24(14).

A plausible mechanism for the formation of **1a**, **1b**, and **4c** is shown in Scheme 2. At first, the P–Cl bond of dichlorophosphine **2** could be reduced with magnesium metal to give borate **8**. Then, one of the two aryl groups on the boron atom in **8** migrates to the phosphorus atom to afford 1-phospha-2-boraacenaphthenes **1**, together with the elimination of MgCl_2. Compounds **1a** and **1b** bearing mesityl or 2,6-dimethylphenyl were isolated as monomers, while **1c** bearing 3,5-di-*tert*-butylphenyl groups is believed to undergo ready head-to-tail dimerization, thus leading to the formation of (*E*)-**4c** or (*Z*)-**4c**. When a 1:1 mixture of **2a** and **2b** was reduced under the same reaction conditions as used for the synthesis of **1**, compounds **1a** and **1b** were obtained in a 1:1 ratio without the formation of any crossover product, as determined by the ^{1}H and ^{31}P NMR spectra, thus suggesting the intramolecular migration of the aryl group in these reactions.[14]



Scheme 2. Plausible mechanism for the formation of **1** and **4** from **2** by aryl migration from the boron atom to the phosphorus atom.

It is worth noting that compound **1a** was found to be orange in color, both in the crystalline form and in solution, in contrast to the previously reported phosphinoboranes, which were colorless or yellow crystals. Furthermore, **1a** exhibited weak but apparent orange emission in solution. Thus, we measured the cyclic voltammetry, UV/Vis, and emission spectra of **1a** to clarify the influence of the rigid geometry of the structure comprising of the P–B bond and the naphthyl moiety, to the electrochemical and photophysical properties of **1a**.[18]

While **1a** showed an irreversible oxidation wave at $E_\text{pa} = +0.65$ V (versus Fc/Fc$^+$; Fc = ferrocene; Figure S1 in the Supporting Information), a reversible one-electron reduction couple was observed at $E_{1/2} = -2.22$ V together with an irreversible reduction wave at $E_\text{pc} = -3.28$ V (versus Fc/Fc$^+$; Figure S2 in the Supporting Information).[14] The first reduction occurred at a less-negative region than that of dimesityl(1-naphthyl)borane (**9**; $E_{1/2} = -2.51$ V and $E_\text{pc} = -3.30$ V) under the same reaction conditions.[19] The less-negative reduction potential of **1a** compared to that of **9** is probably due to the very effective pπ–π* conjugation between the naphthyl unit and the vacant p orbital of the boron atom; this conjugation could be a result of the rigid conformation, caused by the P–B bond attached to the naphthyl unit.

The UV/Vis spectra of **1a** in hexane, THF, and CH_2Cl_2 solutions were similar to each other (Figure 2). In all cases,

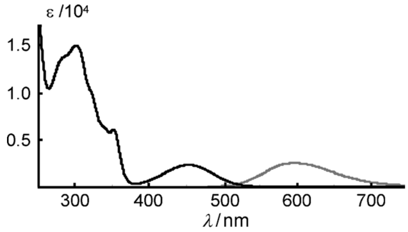


Figure 2. UV/Vis (black) and fluorescence (gray) spectra of **1a** in hexanes.

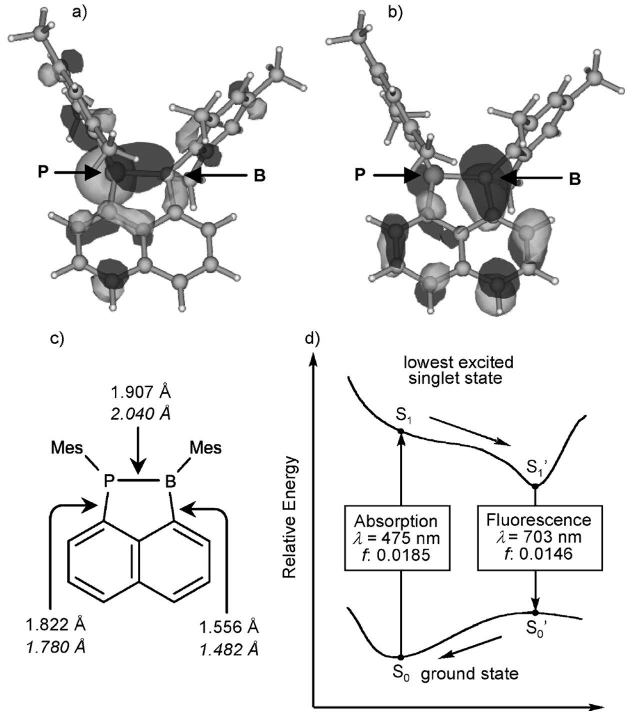


Figure 3. a) HOMO of **1a**(S_0) and b) LUMO of **1a**(S_0) (isosurface at 0.04 a.u). c) Selected bond lengths of the optimized structures of **1a**(S_0) (normal font) and **1a**(S_1) (*italic font*). d) Schematic energy diagram for the ground (S_0) and excited (S_1) states of **1a**. Mes = mesityl.

three characteristic absorption maxima were observed at 452 (ε, 0.23–0.25×10^4), 353 (ε, 0.61–0.63×10^4), 302 (ε, 1.4–1.5×10^4) together with 280 nm (sh, ε, 1.2–1.3×10^4) as a shoulder.[14,20] The longest absorption of **1a** is red-shifted in comparision with that of acenaphthene ($\lambda_{max} = 320$ nm).[21] Compound **1a** showed a broad fluorescence spectrum in the range of ca. 510–750 nm.[22] It should be noted that a subtle solvent effect [$\lambda_{max} = 595$ nm (hexane), 609 nm (THF), and 612 nm (CH_2Cl_2)] with the large Stokes shift ($\Delta = 5300$–$5700\ cm^{-1}$) suggested a large structural change between ground and excited states with the similar polarity. The observed lifetimes were 5.2, 1.5, and 3.6 ns, and the quantum yields were 0.032, 0.020, and 0.017 in hexane, THF, and CH_2Cl_2, respectively. The calculated radiative (k_r) and non-radiative (k_{nr}) rate constants from the singlet excited state were $k_r = 6.1\times10^6$, $k_{nr} = 1.8\times10^8\ s^{-1}$ (hexane); $k_r = 1.3\times10^7$, $k_{nr} = 6.5\times10^8\ s^{-1}$ (THF); and $k_r = 4.7\times10^6$, $k_{nr} = 2.7\times10^8\ s^{-1}$ (CH_2Cl_2).[23] The significantly small values of k_r compared to those of k_{nr} may retard the effective emission of **1a**.

Theoretical calculations of the ground (S_0) and excited (S_1) states of **1a** (denoted as **1a**(S_0) and **1a**(S_1) hereafter) were performed at the B3LYP/def2-TZVPP level of theory with the TURBOMOLE program.[24] The optimized structural parameters of **1a**(S_0) are in good agreement with the experimentally observed parameters (**1a**(S_0): P–B, 1.907 Å; P–C(Naph), 1.822 Å; B–C(Naph), 1.556 Å). The HOMO and LUMO of **1a**(S_0) are shown in Figures 3a and b, respectively. The HOMO of **1a**(S_0), which is similar to that seen in H_2P–BH_2 with C_s symmetric structure,[9a] exhibited a dominant contribution from the lone pair n orbital of the phosphorus atom (Figure 3a). On the other hand, the LUMO was the result of the vacant p orbital of the boron atom delocalized with the π* orbital of the naphthalene unit, thus indicating an effective pπ–π* conjugation (Figure 3b). TDDFT calculations for **1a**(S_0) ($\lambda = 475$ nm ($f = 0.0185$)) indicate that the longest absorption observed in the UV/Vis spectra ($\lambda = 452$ nm) should be principally assignable to the intramolecular charge transfer from the phosphorus atom to the boron atom (HOMO–LUMO transition). It should be noted that the P–B, P–C(Naph), and B–C(Naph) bond lengths of **1a**(S_1) were significantly different to those of **1a**(S_0) (Figure 3c).[14] The P–B bond length of **1a**(S_1) (2.040 Å) is significantly longer than that of **1a**(S_0) (1.907 Å), while the P–C(Naph) (1.780 Å) and B–C(Naph) (1.482 Å) bond lengths of **1a**(S_1) are shorter than those of **1a**(S_0) (P–C(Naph), 1.822 Å; B–C(Naph) 1.556 Å). Therefore, the phosphorus and boron atoms strongly interact with the naphthalene unit accompanied by a weakening of the P–B bond. Despite of the large structural changes, the HOMO and LUMO of **1a**(S_1) are similar to those of **1a**(S_0) (Figure S4 in the Supporting Information). TDDFT calculations for **1a**(S_1) predicted the wavelength and oscillation strength (f) of the HOMO–LUMO transitions in the excited state are 703 nm and 0.0146, respectively, thus supporting the large Stokes shift (calculated as $\Delta = 6800\ cm^{-1}$) and slow radiative process of **1** (Figure 3d).[25] While the theoretical results are somewhat red-shifted in comparison to the experimental transition energies, a result that is typical for DFT calculations in the case of charge-transfer (CT) excited states.

In summary, 1,2-diaryl-1-phospha-2-boraacenaphthenes **1a** and **1b** have been synthesized by the reduction of 1-diarylboryl-8-dichlorophosphinonaphthalenes **2a** and **2b** by a unique intramolecular aryl migration from the boron atom to the phosphorus atom. Attractive electrochemical and photochemical properties of **1a** are provided by not only the intrinsic nature of the P–B bond but also the rigid conformation of the structure owing to the P–B bond being attached to the naphthyl unit at the 1- and 8-positions. This work provides insight into the intrinsic potential of a P–B bond in π-electron conjugated systems. Further investigations on the synthesis of such molecules are currently underway.

Experimental Section

Synthesis of **1a**: In a glovebox filled with argon, a solution of 1-dichlorophophino-8-dimesitylborylnaphthalene (**2a**, 239 mg, 0.501 mmol) and magnesium metal (12.3 mg, 0.506 mmol) in THF (5 mL) was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, *n*-hexane was added to the residue, and then the mixture was filtered through Celite with hexanes. The filtrate was concentrated under reduced pressure, and the residue was washed with cooled hexanes to afford 1,2-dimesityl-1-phospha-2-boraacenaphthene (**1a**, 185 mg, 0.455 mmol, 91 %). **1a**: orange crystals, m.p. 127 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, RT): $\delta =$ 2.02 (s, 3 H), 2.18 (s, 3 H), 2.280–2.282 (m, 6 H), 2.30 (s, 6 H), 6.67–6.68 (m, 2 H), 6.798–6.800 (m, 2 H), 7.28 (ddd, $^3J_{HH} = 8.2$ Hz, 7.0 Hz, $^4J_{HP} =$ 2.7 Hz, 1 H), 7.30 (dd, $^3J_{HH} = 8.2$, 6.8 Hz 1 H), 7.47 (ddd, $^3J_{HP} = 7.3$ Hz, $^3J_{HH} = 7.0$ Hz, $J = 1.0$ Hz, 1 H), 7.55 (d, $^3J_{HH} = 8.2$ Hz, 1 H), 7.75 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.0$ Hz, 1 H), 7.89 ppm (ddd, $^3J_{HH} = 6.8$ Hz, $^4J_{HH} = 1.0$ Hz, $^4J_{HP} = 1.0$ Hz, 1 H); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, RT): $\delta = 20.96$ (CH_3), 21.23 (CH_3), 23.72 (d, $^4J_{CP} = 4.6$ Hz, CH_3), 24.51 (d, $^3J_{CP} = 14.2$ Hz, CH_3), 126.26 (CH), 126.74, 127.17 (CH), 127.37 (d, $^3J_{CP} = 7.7$ Hz, CH), 128.00 (CH), 128.76 (d, $^2J_{CP} = 10.9$ Hz, CH), 129.44 (d, $^3J_{CP} = 5.7$ Hz, CH), 132.09 (d, $^3J_{CP} = 1.9$ Hz), 133.81 (d, $^4J_{CP} = 1.8$ Hz, CH), 134.87 (d, $^3J_{CP} = 8.6$ Hz, CH), 137.52 (br), 137.57, 138.31 (d, $^3J_{CP} = 5.7$ Hz), 139.01, 141.77 (d, $^1J_{CP} = 8.3$ Hz), 142.66 (d, $^2J_{CP} = 17.6$ Hz), 143.07 (br d, $^2J_{CP} = 12.0$ Hz), 144.09 ppm (d, $^2J_{CP} =$ 12.9 Hz); ^{11}B NMR (95 MHz, C_6D_6, RT): $\delta = 77.6$ ($\Delta\nu_{1/2} = 1390$ Hz); ^{31}P NMR (121 MHz, C_6D_6, RT): $\delta = -28.2$ ppm. HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{29}BP$ ($[M{+}H]^+$): 407.2100; found: 407.2098 ($[M + H]^+$). Elemental analysis calcd (%) for $C_{28}H_{28}BP$: C 82.77, H 6.95 %; found: C 82.80, H 6.96 %. Assignment of the signals in ^{1}H and ^{13}C NMR spectra is shown in the Supporting Information.

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[14] See the Supporting Information for details.

[15] The ^{1}H NMR spectra of the crude mixture showed the signals of (*E*)-**4c** and (*Z*)-**4c** in the ratio of 7:10.

[16] Bertrand and co-workers have reported P_2B_2 four-membered-ring systems with B–B bonds. For examples, see; a) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880; b) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem.* **2004**, *116*, 595; *Angew. Chem. Int. Ed.* **2004**, *43*, 585.

[17] CCDC 832939 (**1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] To the best of our knowledge, there has been no report on the electrochemical and photophysical properties of phosphinoboranes.

[19] The reduction potentials of $NaphBMes_2$ were previously reported as $E_{1/2} = -2.41$ V and $E_{pc} = -3.36$ V, see: J. D. Hoefelmeyer, S. Solé, F. P. Gabbaï, *Dalton Trans.* **2004**, 1254.

[20] The broad absorption was observed around 280–400 nm ($\lambda_{max} =$ 334 nm; ε, 1.4×10^3) in the UV/Vis spectrum of **2a** in hexanes.

[21] T. A. Smith, D. J. Haines, K. P. Ghiggino, *J. Fluoresc.* **2000**, *10*, 365, and references therein.

[22] No emission was observed using the excitation wavelengths at every 10 nm from 280 to 370 nm.

[23] Both k_r and k_{nr} values of acenaphthene are calculated as 1.2×10^7 s^{-1} (quantum yield, 0.50; lifetime, 46 ns in cyclohexane), see: M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi in *Handbook of Photochemistry*, 3rd. ed., CRC, Boca Raton, **2006**, p. 86.

[24] a) R. Ahlrichs, M. Bar, M. Haser, H. Horn, C. Kolmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) *TURBOMOLE User's Manual, Version* 6.2; R. Ahlrichs, F. Furche, C. Hättig, W. Klopper, M. Sierka, F. Weigend, TURBOMOLE *ver.* 6.2, **2010**.

[25] The emission is most likely interpreted in terms of the intramolecular charge transfer (HOMO–LUMO) with a small change of the polarity at the excited state.