Keywords: clusters · cobalt · magnetic properties · O ligands

---

[1] a) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, *383*, 145; b) D. Gatteschi, A. Caneschi, R. Sessoli, A. Cornia, *Chem. Soc. Rev.* **1996**, *25*, 101; c) A.-L. Barra, P. Debrunner, D. Gatteschi, C. E. Schulz, R. Sessoli, *Europhys. Lett.* **1996**, *25*, 101; d) H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301.

[2] a) S. Drüeke, K. Wieghardt, B. Nuber, J. Weiss, E. L. Bominaar, A. Sawaryn, H. Winkler, A. X. Trautwein, *Inorg. Chem.* **1989**, *28*, 4477; b) P. Klüfers, J. Schuhmacher, *Angew. Chem.* **1995**, *107*, 2290; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2119; c) E. Libby, K. Folting, C. J. Huffman, J. C. Huffman, G. Christou, *Inorg. Chem.* **1993**, *32*, 2549; d) A. Caneschi, A. Cornia, A. C. Fabretti, S. Foner, D. Gatteschi, R. Grandi, L. Schenetti, *Chem. Eur. J.* **1996**, *2*, 1379; e) S. Parsons, R. E. P. Winpenny, *Acc. Chem. Res.* **1997**, *30*, 89; f) J. A. Real, G. De Munno, R. Chiappetta, M. Julve, F. Lloret, Y. Journaux, J.-C. Colin, G. Blondin, *Angew. Chem.* **1994**, *106*, 1223; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1184; g) S. Teipel, K. Griesar, W. Haase, B. Krebs, *Inorg. Chem.* **1994**, *33*, 456.

[3] a) V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes, A. Terzis, *Angew. Chem.* **1997**, *109*, 1165; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1083; b) V. Tangoulis, C. P. Raptopoulou, A. Terzis, S. Paschalidou, S. P. Perlepes, E. G. Bakalbassis, *Inorg. Chem.* **1997**, *36*, 3996; c) V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, A. E. Tsohos, E. G. Bakalbassis, A. Terzis, S. P. Perlepes, *Inorg. Chem.* **1997**, *36*, 5270.

[4] E. Kefalloniti, A. E. Tsohos, C. P. Raptopoulou, A. Terzis, J. C. Huffman, S. P. Perlepes, G. Christou, unpublished results.

[5] Crystal data for **1**: $C_{60}H_{87.2}Co_9N_8O_{40.6}$, crystal dimensions $0.10 \times 0.10 \times 0.30$ mm, monoclinic, space group $C2/c$, $a = 14.37(1)$, $b = 39.28(3)$, $c = 16.62(1)$ Å, $\beta = 115.69(3)^\circ$, $V = 8451(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.651$ g cm^{-3}, $2\theta_{max} = 50^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\theta - 2\theta$ scan, $T = 298$ K, 7637 measured reflections, 7369 independent reflections ($R_{int} = 0.0384$) all included in the refinement. Lorentzian, polarization, and Ψ-scan absorption corrections were made, $\mu = 1.814$ mm^{-1}, $[\Delta/\sigma]_{max} = 0.075$, 560 parameters refined, $R1 = 0.0642$ (for 5734 reflections with $I > 2\sigma(I)$), $wR2 = 0.1712$ (on $|F^2|$). Max./min. residual peaks in the final difference map $0.840/-0.901$ e Å^{-3}. Crystal data for **2**: $C_{52}H_{50}Co_4N_8O_{17}$, crystal dimensions $0.15 \times 0.30 \times 0.50$ mm, monoclinic, space group $I2/a$, $a = 27.49(1)$, $b = 19.020(7)$, $c = 20.744(7)$ Å, $\beta = 91.31(1)^\circ$, $V = 10841.9(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.586$ g cm^{-3}, $2\theta_{max} = 50^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\theta - 2\theta$ scan, $T = 298$ K, 9833 measured reflections, 9550 independent reflections ($R_{int} = 0.0221$) all included in the refinement. Lorentzian, polarization, and Ψ-scan absorption corrections were applied, $\mu = 1.282$ mm^{-1}, $[\Delta/\sigma]_{max} = 0.025$, 923 parameters refined, $R1 = 0.0404$ (for 6908 reflections with $I > 2\sigma(I)$), $wR2 = 0.1056$ (on $|F^2|$). Max./min. residual peaks in the final difference map $0.993/-0.349$ e Å^{-3}. Crystals of **1** and **2** were mounted in capillaries filled with drops of mother liquor and in air, respectively. The structures were solved by direct methods with SHELXS-86 and refined by full-matrix least-squares techniques on F^2 by using SHELXL-93. For both structures, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the ligands in **1** were introduced at calculated positions as riding on bonded atoms; no hydrogen atoms of H_2O molecules were included in the refinement. All hydrogen atoms in **2** were located by difference maps and their positions refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-102038 and CCDC-102039. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[6] a) J. G. Bergman, F. A. Cotton, *Inorg. Chem.* **1966**, *5*, 1208; b) W. O. Koch, J. T. Kaiser, H.-J. Krüger, *Chem. Commun.* **1997**, 2237.

[7] E. K. Brechin, A. Graham, S. G. Harris, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* **1997**, 3405, and references therein.

[8] a) E. K. Brechin, S. G. Harris, S. Parsons, R. E. P. Winpenny, *Angew. Chem.* **1997**, *109*, 2055; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1967; b) T. J. R. Weakley, *J. Chem. Soc. Chem. Commun.* **1984**, 1406.

[9] a) K. S. Murray, *Adv. Inorg. Chem.* **1995**, *43*, 261; b) E. K. Brechin, S. G. Harris, S. Parsons, R. E. P. Winpenny, *Chem. Commun.* **1996**, 1439.

[10] J. J. Smit, G. M. Nap, L. J. De Jongh, J. A. C. van Ooijen, J. Reedijk, *Physica B* **1979**, *97*, 365.

Isomerism and Blue Electroluminescence of a Novel Organoboron Compound: $B_2^{III}(O)(7\text{-azain})_2Ph_2$**

Qingguo Wu, Mohammad Esteghamatian,
Nan-Xing Hu, Zoran Popovic, Gary Enright,
Steven R. Breeze, and Suning Wang*

Organic electroluminescent (EL) devices based on organic or organometallic materials have attracted much attention because of their high luminance, low driving voltage, and easy fabrication.[1–4] To achieve a full color display, the three basic color components red, green, and blue are required. Red and green emitters for organic EL devices have become readily available. Useful and efficient organic or organometallic blue emitters are however still very rare. Previously reported blue emitters of organometallic or coordination compounds in organic EL devices employed either derivatives of 8-hydroxyquinoline or azomethine as the emitting ligands.[3, 4] The common feature of those previously reported blue emitting ligands is that they are all chelating ligands and bind to the central atom through both nitrogen and oxygen donor atoms. We have been interested in the application of organometallic and coordination compounds in EL devices because the properties of this class of compounds such as volatility and stability can be modified readily by manipulating the coordination environment around the central atom.[5] We have discovered recently that 7-azaindole and di-2-pyridylamine ligands yield a strong blue luminescence when bound to an aluminum or boron center.[6] The 7-azaindole or di-2-pyridyl amine ligands contain nitrogen donor atoms only and can bind to the central atom by either a bridging mode or a chelating mode. They are therefore very different from the previously

---

[*] Prof. Dr. S. Wang, Q. Wu
Department of Chemistry
Queen's University
Kingston, Ontario, K7L 3N6 (Canada)
Fax: (+1) 613-533-6669
E-mail: wangs@chem.queensu.ca

M. Esteghamatian, N.-X. Hu, Z. Popovic
Xerox Research Center of Canada, Mississauga
Ontario (Canada)

G. Enight, S. R. Breeze
Steacie Institute for Molecular Science, National Research Council, Ottawa (Canada)

[**] This work was supported by the Natural Sciences and Engineering Research Council of Canada and Xerox Research Foundation. 7-azain = 7-azaindole anion.

reported blue emitting ligands. Furthermore, the commonly used central ions in previously known organometallic or coordination blue emitters[3, 4] are Al^{III}, Zn^{II}, and Be^{II}. Blue emitters using boron as the central atom are previously unknown, although a few blue photoluminescent boron-containing polymers and small molecules and electron-transporting organoboron compounds have been reported recently.[7] The main advantage of boron over aluminum is that boron–ligand bonds are in general much more covalent than the corresponding aluminum–ligand bonds.[8] As a consequence, boron compounds, in general, are much more stable than the corresponding aluminum compounds,[8] making them an attractive and potentially useful class of compounds for electroluminescence. Recently, we reported the synthesis and structure of $B_2^{III}(O)(7\text{-azain})_2(C_2H_5)_2$.[6a] Although this compound has a bright blue photoluminescence, it is however not stable enough for EL applications. To improve the stability of the boron compound so that electroluminescence can be achieved, we investigated the syntheses of new 7-azaindole boron compounds, $B_2^{III}(O)(7\text{-azain})_2R_2$, where R is an aryl group. We have successfully synthesized the new boron compound, $B_2^{III}(O)(7\text{-azain})_2Ph_2$ (**1**) which is not only stable and emits blue electroluminescence, but also displays an unusual structural isomerism. We report herein the synthesis, structures, and blue electroluminescence of **1**.

Compound **1** can be obtained by several synthetic routes, of which the best (50 % yield) is to react $PhBCl_2$ with 7-azaindole and H_2O in a 2:2:1 ratio in the presence of a base such as triethylamine. Compound **1** was found to exist in two isomeric forms, one with an approximate twofold rotation symmetry (**A**) and the other with an approximate mirror plane symmetry (**B**) (Figure 1), as established by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.[9] These two isomers can be separated by repeated crystallization from CH_2Cl_2/hexane (**A** is less soluble than **B**). Both isomers have an oxo ligand bridging two boron atoms. A similar oxo bridge has been observed in the compound $B_4^{III}(2,2'\text{-biimidazole})_2(O)(C_2H_5)_6$ reported by Niedenzu et al.[10a] The B–O, B–N, and B–C bond lengths in **A** and **B** are similar and typical.[10, 11] The structure of **A** is similar to that of $B_2^{III}(O)(7\text{-azain})_2(C_2H_5)_2$ where the environment around both boron centers is identical. In ^1H and ^{13}C NMR spectra of **A**, only one set of resonances due to the phenyl group are observed, while one resonance is present in ^{11}B NMR spectrum of **A**, indicating that the structure of **A** in solution is the same as that in the solid state. The structure of **B** is very unusual—one of the boron centers is bound by two nitrogen atoms of the six-membered rings, while the other boron center is bound by two negatively charged nitrogen atoms of the five-membered rings. Thus, the two boron centers and the two phenyl groups in **B** are chemically inequivalent. Indeed, two distinct boron chemical shifts are present in the ^{11}B NMR spectrum of **B**. There are also two sets of distinct chemical shifts for the protons and carbon atoms at 2,6 positions of the two phenyl rings in ^1H NMR and ^{13}C NMR spectra of **B**, respectively, again indicating that **B** retains its structure in solution. There is no interconversion between **A** and **B** in solution as established by NMR studies. The unusual geometric structural isomerism exhibited by $B_2^{III}(O)(7\text{-azain})_2Ph_2$ has not been observed previously in either boron or aluminum 7-azaindole complexes.

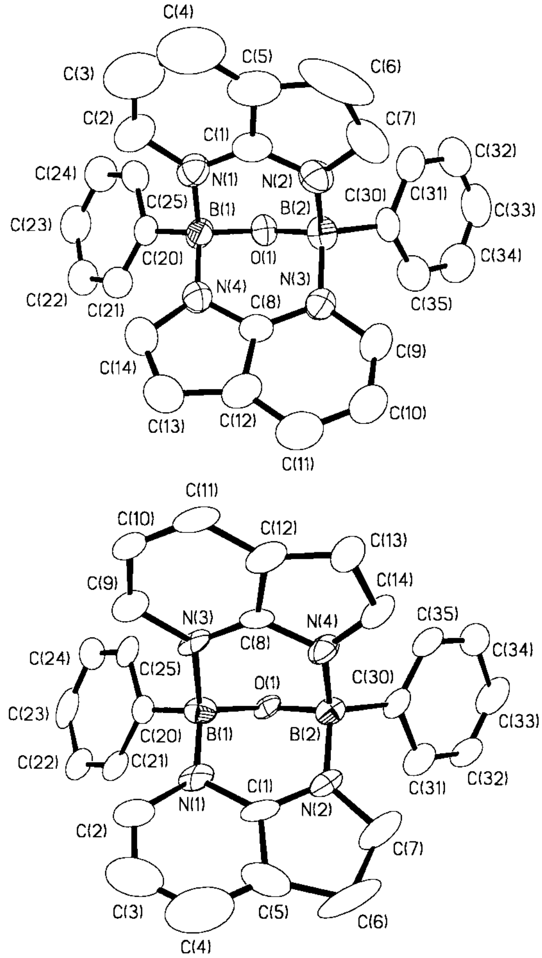

Figure 1. Molecular structures of **A** (top) and **B** (bottom) in the crystal (50 % thermal ellipsoids). Hydrogen atoms are omitted for clarity. Important bond lengths [Å] and angles [°]: **A**: B(1)–O(1) 1.429(6), B(2)–O(1) 1.414(6), B(1)–N(1) 1.619(6), B(1)–N(4) 1.582(7), B(2)–N(2) 1.591(7), B(2)–N(3) 1.628(7), B(1)–C(20) 1.584(7), B(2)–C(30) 1.625(7); B(1)-O(1)-B(2) 120.4(4). **B** (There are two similar and independent molecules of **B** in the asymmetric unit. The structure for one of them is shown here.): B(1)–O(1) 1.399(12), B(2)–O(1) 1.422(12), B(1)–N(1) 1.611(11), B(1)–N(3) 1.648(12), B(2)–N(2) 1.578(12), B(2)–N(4) 1.613(12), B(1)–C(20) 1.591(14), B(2)–C(30) 1.589(14); B(1)-O(1)-B(2) 120.4(7).

Isomers **A** and **B** are stable in the solid state upon exposure to air, which can be attributed to the oxo bridge and the covalent B–N and B–C bonds. The thermal stability of these two isomers is however very different. Compound **A** has a melting point of 274 °C and can be sublimed readily. In contrast, compound **B** decomposes at temperature greater than 150 °C in the solid state, as established by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Compound **A** and[12] $B_3^{III}O_3Ph_3(7\text{-azainH})$ were found among the decomposition products. The details of the thermal decomposition mechanism of **B** are not yet fully understood.

The other exciting property of compounds **A** and **B** is that they produce an intense photoluminescence (PL) when irradiated by UV light in solution and the solid state. The PL spectra of both isomers are very similar with an emission maximum at $\lambda = 450$ nm, attributable to a $\pi^* \rightarrow \pi$ transition of the 7-azaindole anion. The role of the boron atoms in **1** is believed to stabilize the 7-azaindole anion, as the aluminum ion does in related 7-azaindole compounds reported previously.[6b,c] The high air and thermal stability of compound **A** along with its intense blue photoluminescence makes it an ideal candidate as a blue emitter in EL devices.

To investigate the electroluminescent properties of compound **A**, an EL device using **A** as the light-emitting layer and indium-tin-oxide (ITO) as the substrate was constructed by using vacuum deposition methods. Tris(8-hydroxyquinolino)aluminum (Alq_3) and *N,N'*-di-1-naphthyl-*N,N'*-diphenylbenzidine (NPB) doped with 1 % of 9,10-diphenylanthracence were used as the electron-transporting and hole-transporting layer, respectively. A magnesium silver alloy ($Mg_{0.9}Ag_{0.1}$) was used as the cathode. When a positive bias was applied to the ITO electrode, the EL device produced a bright blue emission with a peak at 450 nm. The EL spectrum shown in Figure 2 is very similar to the PL spectrum of **A**, indicating that the light emission originates from compound **A**. As shown in Figure 2, the device has a turn-on voltage of approximately 7 V and provides a luminance of 1024 cd m^{-2} at 14 V. These preliminary results indicate that compound **A** is very promising for EL applications. Further investigation on the chemistry and EL device optimization of new organboron compounds is also in progress.

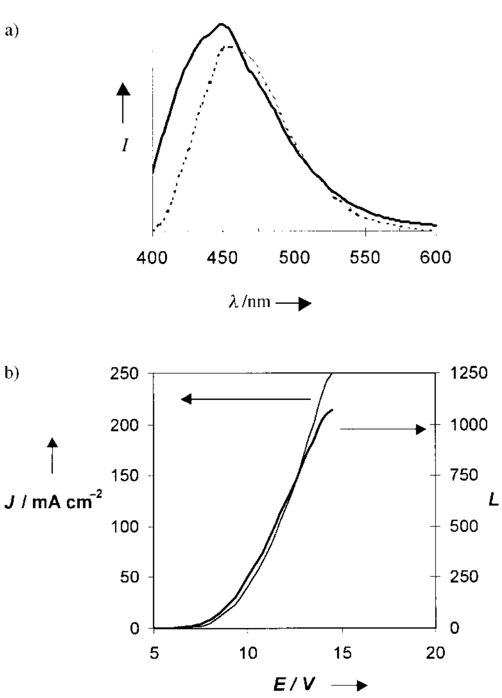

Figure 2. a) The PL (solid line) and EL (dashed line) spectra of **A**. I = intensity. b) The current density (J), voltage (E), and luminance (L) characteristics of the EL device.

Experimental Section

1: 7-Azaindole (0.474 g, 4 mmol) was added to phenylboron dichloride (0.635 g, 4 mmol) in THF (20 mL) at 23 °C under N_2. After the mixture was stirred for 10 min, water (0.036 g, 2 mmol) was added, and the mixture was stirred for another 10 min. Finally, triethylamine (0.8096 g, 8 mmol) was added to the mixture slowly and the solution was heated at 60 °C for 5 h. After the solution was allowed to cool to room temperature, THF (40 mL) was added to the solution and then the mixture was filtered. The filtrate was collected and evaporated to dryness in vacuum. Recrystallization of the resulting white powder from CH_2Cl_2/hexane yielded colorless crystalline **1** in 50 % yield (isomer **A** dominant). Pure isomer **A** can be obtained by repeated recrystallization from CH_2Cl_2/hexane. Pure isomer **B** can be obtained from the concentrated mother liquor after the removal of **A**. Single crystals suitable for X-ray diffraction analyses were obtained from THF/hexane for **A** and CH_2Cl_2/hexane for **B**. **A**: ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 8.13$ (d, $^3J = 6.0$ Hz, 2 H, 7-azain), 8.05 (d, $^3J = 7.8$ Hz, 2 H, 7-azain), 7.78 (d, $^3J = 6.8$ Hz, 4H at 2,6 positions of Ph), 7.69 (d, $^3J = 3.3$ Hz, 2 H, 7-azain), 7.44 – 7.35 (m, 6H at 3,4,5 positions of Ph), 7.03 (dd, $^3J = 6.0$ Hz, $^3J' = 7.8$ Hz, 2 H, 7-azain), 6.51 (d, $^3J = 3.3$ Hz, 2 H, 7-azain); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 134.28$ (7-azain), 134.19 (3,5-Ph (the prefix indicates the positions of the carbon atoms)), 133.54 (7-azain), 132.33 (4-Ph), 127.71 (2,6-Ph), 127.31 (7-azain), 113.64 (7-azain), 100.88 (7-azain); ^{11}B NMR ($CDCl_3$, relative to BCl_3, 25 °C): $\delta = -42.75$; m.p. 274 °C. **B**: ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 8.17$ (d, $^3J = 6.0$ Hz, 2 H, 7-azain), 8.08 (d, $^3J = 7.8$ Hz, 2 H, 7-azain), 7.83 (d, $^3J = 6.9$ Hz, 2H at 2,6 positions of Ph), 7.67 (d, $^3J = 3.3$ Hz, 2 H, 7-azain), 7.60 (d, $^3J = 6.0$ Hz, 2H at 2,6 positions of Ph'), 7.40 – 7.33 (m, 6H at 3,4,5 positions of Ph and Ph'), 7.05 (dd, $^3J = 6.0$, $^3J' = 7.8$ Hz, 2 H, 7-azain), 6.49 (d, $^3J = 3.3$ Hz, 2 H, 7-azain); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 134.33$ (7-azain), 133.82 (3,5-Ph, Ph'), 133.53 (7-azain), 132.66 (4-Ph, Ph'), 127.77 (2,6-Ph), 127.58 (2,6-Ph'), 126.96 (7-azain), 113.08 (7-azain), 100.10 (7-azain); ^{11}B NMR ($CDCl_3$, relative to BCl_3, 25 °C): $\delta = -40.70$, -45.15; m.p. ≈ 150 °C, decompose. Elemental analysis calcd. for the mixture of **A** (60 %) and **B** (40 %), $C_{26}H_{20}N_4OB_2 \cdot 0.4\,CH_2Cl_2$ (%): C 66.60, H 4.40, N 11.77; found: C 60.71, H 4.57, N 11.82.

EL device: The device was fabricated on an indium-tin-oxide (ITO) substrate which was cleaned by an ultraviolet ozone cleaner immediately before use. Organic layers and a metal cathode composed of magnesium silver alloy ($Mg_{0.9}Ag_{0.1}$) were deposited on the substrate by conventional vapor vacuum deposition. Prior to the deposition, all the organic materials were purified by a train sublimation method.[13] The device structure used in this experiment is as follows: ITO /hole transport layer/light-emitting layer/electron-transport layer/MgAg, in which NPB-doped with 1 % of 9,10-diphenylanthracence was employed as the hole-transport layer and Alq_3 as the electron transport layer. To obtain the photoluminescence spectrum of **A**, a thin film (100 nm) deposited on a quartz substrate was measured with a fluorescence spectrophotometer. The current-voltage characteristics were measured by using a Keithley 238 current/voltage unit. The light intensity was measured by a Minolta Chroma Meter CS100. The EL spectrum was obtained by an in-house setup made up of a series of electronic components including a monochromator (Instruments SA Inc), a photomultiplier tube, and a photon counter.

Received: August 24, 1998 [Z 12322 IE]
German version: *Angew. Chem.* **1999**, *111*, 1039 – 1041

Keywords: boron · electroluminescence · isomerism

---

[1] a) Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, K. Imai, *Appl. Phys. Lett.* **1994**, *65*, 80; b) Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Jpn. J. Appl. Phys.* **1993**, *32*, L514; c) V. Bulovic, G. Gu, P. E. Burrows, S. R. Forrest, *Nature* **1996**, *380*, 29; d) C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913; e) C. W. Tang, S. A. VanSlyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*, 3611; f) C. Adachi, S. Tokito, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys.* **1988**, *27*, L713; g) C. Adachi, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* **1990**, *56*, 799; h) Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Chem. Lett.* **1993**, 905; i) Z. Shen, P. E. Burrows, V. Bulovic, S. R. Borrest, M. E. Thompson, *Science* **1997**, *276*, 2009.

[2] a) T. Tsutsui, *MRS Bull.* **1997**, *22*, 39; b) H. J. Brouwer, V. V. Krasnikov, A. Hilberer, G. Hadziioannou, *Adv. Mater.* **1996**, *8*, 935; c) A. Edwards, S. Blumstengel, I. Sokolik, R. Dorsinville, H. Yun, K. Kwei, Y. Okamoto, *Appl. Phys. Lett.* **1997**, *70*, 298; d) Y. Ohmori, M. Uchida, K. Muro, K. Yoshino, *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.

[3] Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Jpn. J. Appl. Phys.* **1993**, *32*, L511.

[4] a) C. P. Moore, S. A. VanSlyke, H. J. Gysling (Eastman Kodak Co., Rochester, NY), US-A, No. 5484922, **1996**; b) T. Sano, M. Fujita, T. Fujii, Y. Nishio, Y. Hamada, K. Shibata, K. Kuroki (Sanyo Electric Co., Osaka, Japan), US-A, No. 5432014, **1995**; c) Y. Hironaka, H. Nakamura, T. Kusumoto (Idemitsu Kosan Co., Tokyo, Japan), US-A, No. 5466392, **1995**; d) S. A. VanSlyke, P. S. Bryan, F. V. Lovecchio (Eastman Kodak Co., Rochester, NY), US-A, No. 5150006, **1992**; e) P. Bryan, F. V. Lovecchio, S. A. VanSlyke (Eastman Kodak Co., Rochester, NY), US-A, No. 5141671, **1992**.

[5] a) *Inorganic Materials* (Ed.: D. W. Bruce, D. O'Hare), Wiley, New York, **1992**; b) *The Chemistry of Metal CVD* (Ed.: T. T. Kodas, M. J. Hampden-Smith), VCH, Weinheim, **1994**.

[6] a) A. Hassan, S. Wang, *Chem. Commun.* **1998**, 211; b) W. Liu, A. Hassan, S. Wang, *Organometallics* **1997**, *16*, 4257; c) J. Ashenhurst, L. Brancaleon, A. Hassan, W. Liu, H. Schmider, S. Wang, Q. Wu, *Organometallics* **1998**, *17*, 3186.

[7] a) N. Matsumi, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **1998**, *120*, 5112; b) Z. Yuan, N. J. Taylor, R. Ramachandran, T. B. Marder, *Appl. Organomet. Chem.* **1996**, *10*, 305; b) T. Noda, Y. Shirota, Y. Chujo, *J. Am. Chem. Soc.* **1998**, *120*, 9714.

[8] a) F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, **1988**; b) N. N. Greenwood, A. Earnshaw, *Chemistry of The Elements*, Pergamon Press, Oxford, **1984**; c) E. L. Muettertues, *The Chemistry of Boron and Its Compounds*, Wiley, New York, **1967**.

[9] Crystal data for **A**: $C_{26}H_{20}N_4OB_2 \cdot 0.5\,THF$, monoclinic, space group $P2_1/n$, $a = 11.184(6)$, $b = 13.891(8)$, $c = 16.281(8)$ Å, $\beta = 108.72(3)^\circ$, $V = 2395(2)$ Å^3, $Z = 4$, GOF on $F^2 = 1.048$, R_1 $(I > 2\sigma(I)) = 0.0693$, $wR_2 = 0.1540$. Crystal data for **B**: $C_{26}H_{20}N_4OB \cdot CH_2Cl_2$, triclinic, space group $P\bar{1}$, $a = 12.5473(13)$, $b = 13.4960(13)$, $c = 16.7659(17)$ Å, $\alpha = 90.345(10)$, $\beta = 102.211(10)$, $\gamma = 116.055(10)^\circ$, $V = 2476.5(4)$ Å^3, $Z = 4$, GOF on $F = 3.67$, R_1 $(I > 2.5\sigma(I)) = 0.093$, $wR_2 = 0.076$. For **A**, data were collected on a Siemens P4 X-ray diffractometer operated at 50 kV and 40 mA at ambient temperature. Data for **B** were collected on a Siemens SMART CCD diffractometer operated at 50 kV and 35 mA at −100 °C. The structural solution and refinement of **A** were performed on a PC using Siemens SHELXTL software package while the structural solution and refinement of **B** were performed on a workstation using NRCVAX software package. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-113985 and CCDC-113986. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] a) K. Niedenzu, H. Deng, D. Knoeppel, J. Krause, S. G. Shore, *Inorg. Chem.* **1992**, *31*, 3162; b) L. Y. Hsu, J. F. Mariategui, K. Niedenzu, S. G. Shore, *Inorg. Chem.* **1987**, *26*, 143; c) W. Kiegel, G. Lubkowitz, S. J. Rettig, J. Trotter, *Can. J. Chem.* **1991**, *69*, 234; 1217; 1227.

[11] a) G. Heller, *Top. Curr. Chem.* **1986**, *131*, 39; b) A. Dal Negro, L. Ungaretti, A. Perotti, *J. Chem. Soc. Dalton Trans.* **1972**, 1639; c) H. Binder, W. Matheis, H.-J. Deiseroth, F. S. Han., *Z. Naturforsch. B* **1984**, *39*, 1717; d) W. Clegg, N. Noltemeyer, G. M. Shelderick, W. Maringgele, A. Meller, *Z. Naturforsch. B* **1980**, *35*, 1499.

[12] Q. Wu, S. Wang, unpublished results.

[13] H. J. Wagner, R. O. Loutfy, C. K. Hsiao, *J. Mater. Sci.* **1982**, *17*, 2781.

The Melting Point Alternation in the Short-Chain *n*-Alkanes: Single-Crystal X-Ray Analyses of Propane at 30 K and of *n*-Butane to *n*-Nonane at 90 K[**]

Roland Boese,[*] Hans-Christoph Weiss, and Dieter Bläser

Dedicated to Professor Reiner Sustmann on the occasion of his 60th birthday

It was probably A. Baeyer who first stated in 1877 that the melting points of the fatty acids do not show a monotonic increase with increasing chain length as do their boiling points. Instead the melting points of the members with even numbers of C atoms are relatively higher than those of the members with odd numbers.[1] The longer the chain length, the smaller are the relative differences. This is true for the *n*-alkanes as well as for most[2] of the α-substituted and α,ω-disubstituted *n*-alkane derivatives; a fact that is mentioned in almost all standard text books of organic chemistry. Mostly, "packing effects" are given as an explanation for such an alternation in melting points. This is justified insofar as physical properties, such as sublimation enthalpy and solubility, that are related to the solid state display a similar alternation whereas the properties of the liquid phase have a monotonic dependency on increasing chain length.[3]

For the *n*-alkanes with $n = 6-24$ (n = number of C atoms) the even numbered members crystallize at low temperatures in a triclinic space group, while for $n = 26$ monoclinic packing is observed. It is possible to define an orthorhombic sub-cell for the latter,[3a] which is also found as the real cell for polyethylene[4] and mixed paraffins.[5] When $n = 7$ the odd-numbered *n*-alkanes also crystallize in a triclinic, ordered modification with an orthorhombic sub-cell. Glassy crystalline "rotator phases" with hexagonal symmetry are found below the melting points for the odd-numbered *n*-alkanes with $n \geq 9$, and the difference between the phase transition and melting point increases with an increase in the chain length. From $n = 22$ hexagonal modifications are also observed for the even-numbered *n*-alkanes.

Although the phenomenon of the even/odd alternation has been known for a very long time, there does not exist a plausible explanation pattern, not even for the short chain ($n < 10$) *n*-alkanes with a triclinic crystal system. Kitaigorodski[6a] analyzed the arrangements of sections through the long axes of the aliphatic chains, and distinguished between triclinic, monoclinic, and hexagonal subcells. At longer chain lengths these represent the real cells. Further considerations referred to parallel arrangements of cylinderlike units, in

---

[*] Prof. Dr. R. Boese, Dipl.-Chem. H.-C. Weiss, D. Bläser
Institut für Anorganische Chemie der Universität-GH
Universitätsstrasse 5–7, D-45117 Essen (Germany)
Fax: (+49) 201-1832535
E-mail: boese@structchem.uni-essen.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The authors wish to express their gratitude to Mr. Bonk from the in-house glass blowing workshop, his engagement and abilities enabled us to perform the experiments especially with the liquid helium in order to crystallize propane.