[5] a) N. Kobayashi, T. Fukuda, D. Lelievre, *Inorg. Chem.* **2000**, *39*, 3632–3637; b) K. Ishii, N. Kobayashi, Y. Higashi, T. Osa, D. Lelievre, J. Simon, S. Yamauchi, *Chem. Commun.* **1999**, 969–970; c) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, H. Shirai, *J. Am. Chem. Soc.* **1994**, *116*, 879–890; d) D. Lelievre, L. Bosio, J. Simon, J.-J. André, F. Bensebaa, *J. Am. Chem. Soc.* **1992**, *114*, 4475–4479; e) N. Kobayashi, M. Numao, R. Kondo, S. Nakajima, T. Osa, *Inorg. Chem.* **1991**, *30*, 2241–2244; f) E. S. Dodsworth, A. B. P. Lever, P. Seynour, C. C. Leznoff, *J. Phys. Chem.* **1985**, *89*, 5698–5705.

[6] N. Kobayashi, *J. Chem. Soc. Chem. Commun.* **1991**, 1203–1205.

[7] R. S. Nohr, J. G. MacDonald (Kimberly-Clark Worldwide, Inc., USA), PCT Int. Appl. WO 0,071,621 **2000** [*Chem. Abstr.* **2001**, *134*, 18557].

[8] These low-field proton signals at $\delta \approx 10.5$ ppm were not reported in reference [6].

[9] Few examples have been described of intramolecular interactions between phthalocyanine subunits in related binuclear phthalocyanine systems in which the two Pc moieties are connected through benzene rings.[5] In these cases, the Q band undergoes a shift to the red, which has been attributed to the enlargement of the π-conjugated system, with concomitant splitting of the Q band as a consequence of intramolecular electronic coupling between the Pc subunits. However, in these cases, both red-shifting and splitting were much smaller than observed in the present study for SubPc dimers **2** and trimers **3**.

[10] CCDC-179556 (**1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] a) R. Potz, M. Göldner, H. Hückstädt, U. Cornelissen, A. Tutaß, H. Homborg, *Z. Anorg. Allg. Chem.* **2000**, *626*, 588–596; b) J. R. Stork, R. J. Potucek, W. S. Durfee, B. C. Noll, *Tetrahedron Lett.* **1999**, *40*, 8055–8058; c) M. K. Engel, J. Yao, H. Maki, H. Takeuchi, H. Yonehara, C. Pac, *Kawamura Rikagaku Kenkyusho Hokoku* **1997**, *9*, 53–65; d) K. Kasuga., T. Idehara, M. Handa, Y. Ueda, T. Fujiwara, K. Isa, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2559–2563; e) M. Hanack, J. Rauschnabel, *Tetrahedron Lett.* **1995**, *36*, 1629–1632; f) H. Kietaibl, *Monatsh. Chem.* **1974**, *105*, 405–418.

[12] Two types of intermolecular hydrogen bonds were found in the X-ray crystal structure of SubPc **1b** : 1) C27-H2-F3a defined by $d(\mathrm{C}\cdots\mathrm{F}) = 3.265$ Å, $d(\mathrm{H}\cdots\mathrm{F}) = 2.667$ Å, $(\mathrm{C{-}H}\cdots\mathrm{F}) = 167^\circ$ and 2) C28-H3-F4b defined by $d(\mathrm{C}\cdots\mathrm{F}) = 3.432$ Å, $d(\mathrm{H}\cdots\mathrm{F}) = 2.533$ Å, $(\mathrm{C{-}H}\cdots\mathrm{F}) = 143^\circ$.

[13] The CPK models were generated on the basis of the X-ray crystal structure of compound **1b**. They do not correspond to any energy minimum.

[14] For both the *anti* and *syn* isomers, the distances were calculated after tilting the phenyl ring towards the other half of the dimer (see Figure 4).

[15] We discarded any possible intermolecular interactions or aggregation since the ^{1}H NMR chemical shifts as well as the UV bands are not sensitive to changes of concentration.

---

cis and *trans* Forms of a Binuclear Subphthalocyanine**

Takamitsu Fukuda, Jay R. Stork, Richard J. Potucek, Marilyn M. Olmstead, Bruce C. Noll, Nagao Kobayashi,* and William S. Durfee*

In 1972 Mellor and Ossko[1] reported the synthesis and spectroscopic characterization of the boron-containing subphthalocyanine (SubPc) macrocycle; the cone shape of SubPcs was confirmed by X-ray crystallography shortly thereafter.[2] After a nearly 20 year hiatus, interest in these unusual systems was renewed when one of us (N.K.) published the synthesis and spectroscopic study of a binuclear SubPc in which two SubPc units shared a central benzene ring.[3] As was subsequently pointed out, the bowl shape of the SubPc should result in *cis* and *trans* forms of the binuclear species, having C_{2v} and C_{2h} molecular symmetry, respectively.[4]

We report here on the synthesis of a variation of the original binuclear SubPc, the separation of the *cis* and *trans* binuclear forms, and their spectroscopic and structural characterization (Scheme 1). In the original procedure 4-*tert*-butylphthalonitrile and 1,2,4,5-tetracyanobenzene were allowed to react in a 20:1 ratio with BBr_3. We have replaced the 4-*tert*-butylphthalonitrile with tetrafluorophthalonitrile to prevent the formation of positional isomers that the 4-*tert*-butyl substituent engenders, and to reduce the number of benzo units that can undergo halogenation, an unavoidable side reaction when BBr_3 or BCl_3 is used in SubPc syntheses.[5] We also report the X-ray crystal structure analysis of the perfluorinated monomer,[6] derived from the cyclotrimerization of tetrafluorophthalonitrile, which is unavoidably the major product of the reaction.[7]

---

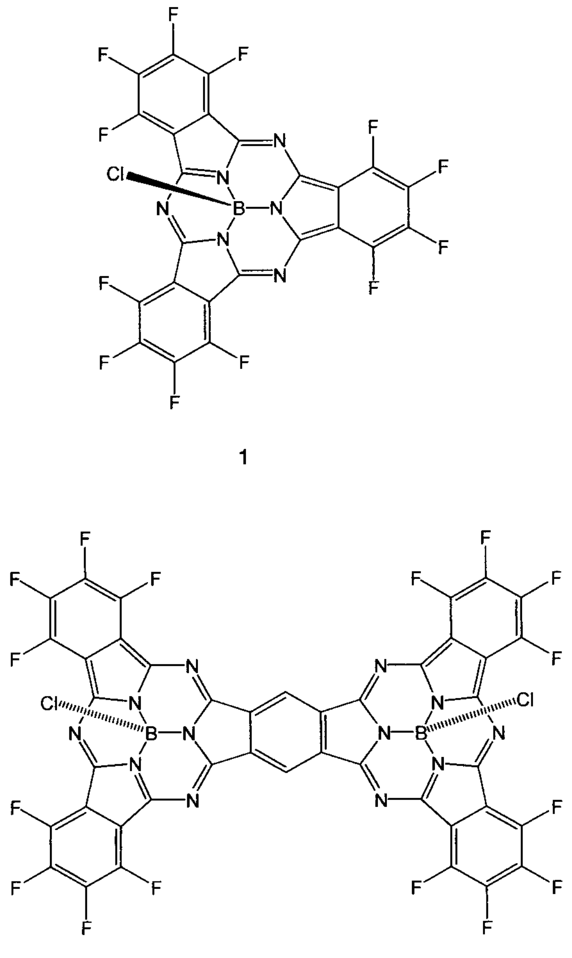
[*] Prof. Dr. Dr. N. Kobayashi, T. Fukuda
Department of Chemistry
Graduate School of Science
Tohoku University
Sendai 980-8578 (Japan)
Fax: (+81)22-217-9279
E-mail: nagaok@mail.cc.tohoku.ac.jp

Prof. W. S. Durfee, J. R. Stork, R. J. Potucek
Department of Chemistry
Buffalo State College
1300 Elmwood Avenue, Buffalo, NY 14222-1095 (USA)
Fax: (+1)716-878-4028
E-mail: durfeews@buffalostate.edu

Dr. M. M. Olmstead
Department of Chemistry
University of California
One Shields Avenue, Davis, CA 95616-5298 (USA)

Dr. B. C. Noll
Department of Chemistry and Biochemistry
University of Colorado at Boulder
Boulder, CO 80309-0215 (USA)

[**] This work was supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Foundation of the State University of New York (W.S.D.), the Daiwa Anglo-Japanese Foundation (N.K.), and a Grant-in-Aid for JSPS fellows (T.F.). Editorial Note: See also preceding communication in this issue: C. G. Claessens, T. Torres, *Angew. Chem.* **2002**, *114*, 2673; *Angew. Chem. Int. Ed.* **2002**, *41*, 2561.



Scheme 1. The structures of **1**, **2** (*cis*), and **3** (*trans*).

Figure 1 shows the X-ray structures of compounds **1**, **2** (*cis* form), and **3** (*trans* form). The structures[8] of the three compounds show how the tetrahedral boron center forces a cupped geometry on the delocalized ring system. In each molecule, the boron atom is nearly 0.6 Å out of the plane of its three bonded nitrogen atoms. In the *cis*-SubPc **2**, the combination of two cupped monomer units leads to a full hemicircular molecule large enough to encircle the hemisphere of C_{60}. In the *trans*-SubPc **3**, the molecule has crystallographic inversion symmetry and forms a novel S-shaped molecule. Highly efficient and appealing packing arrangements result from the mutual fit of projections of one molecule into the cavity of its neighbor (Figure 2). Although the near absence of hydrogen atoms (0H in **1**, 2H in **2** and **3**) plays a part, and solvated CH_2Cl_2 molecules are present in the structures of **2** and **3**, the efficiency of the packing can be appreciated from the volume/non-H atoms of 13.0 Å^3 in **1**, 14.3 Å^3 in **2**, and 14.5 Å^3 in **3**.

Figure 3 shows the electronic absorption, magnetic circular dichroism (MCD) spectra, and calculated electronic spectra (AM1 calculations using HyperChem Software[9]) for **2** and **3**. Compared with the spectra of monomeric **1**, the Q band of the dimer has more structure and is shifted to the red by about 120 nm, suggesting delocalization of electrons over the whole molecule. Both **2** and **3** show similar spectra; however, the Q band of **3** (*trans* form) appears at longer wavelength than that of **2** (*cis* form) by about 3–4 nm, and the absorbance at a shorter wavelength side of the Soret band is higher for **3**. The MCD peaks in the Q-band region correspond closely to the absorption peaks (Faraday *B* terms), characteristic of systems lacking degenerate states. Since the molecules have either C_{2v} (**2**) or C_{2h} (**3**) symmetry, the doubly degenerate bands of monomeric **1** with C_{3v} symmetry[10] split into two bands close in energy, and transitions into these orbitals give rise to pairs of intense oppositely signed *B* terms in the MCD spectra.[11] Thus, in the Q-band region, bands at about 690–695 and 600–605 nm can be safely assigned to the split Q_{00} transitions.[12] The theoretical spectra reproduce these experimental characteristics. Although not shown, the Q and Soret bands of **1** were calculated at 555 and 550 nm with an oscillator strength (*f*) value of 0.515 and 0.503, and at 336 and 332 nm with an *f* value

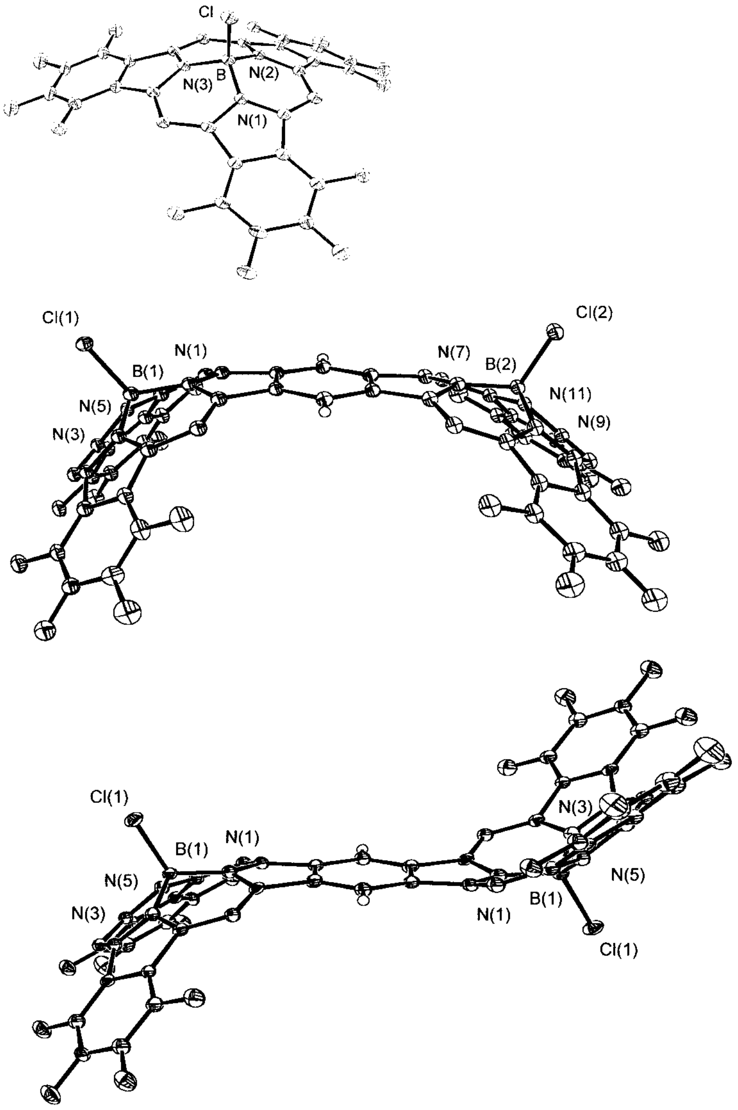


Figure 1. The X-ray crystal structures of **1** (top), **2** (middle), and **3** (bottom). Only the atoms of the boron coordination sphere are labeled.

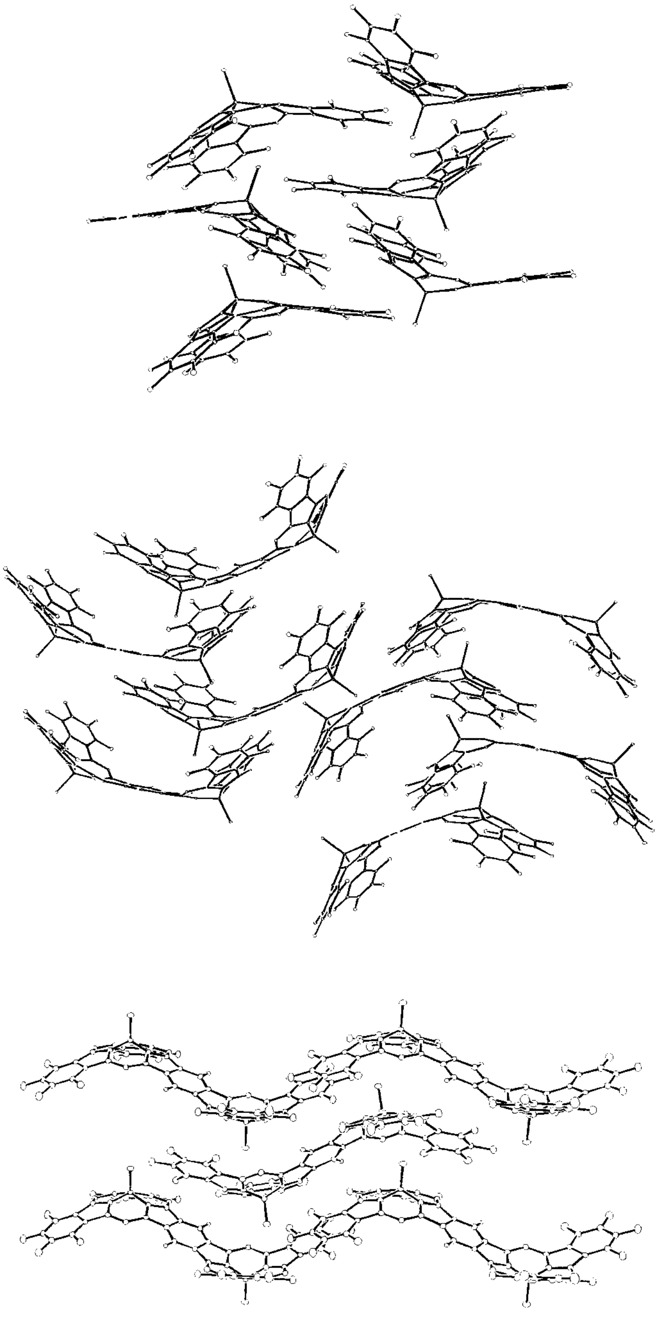


Figure 2. Crystal packing of **1** (top), **2** (middle), and **3** (bottom).

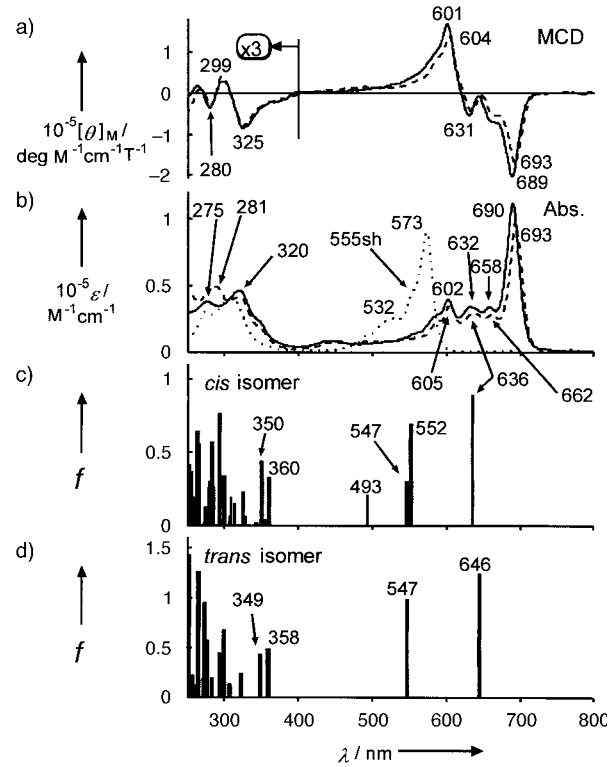


Figure 3. MCD (a) and electronic absorption spectra (b) of **2** (solid lines) and **3** (broken lines) in chloroform, and calculated electronic spectra for **2** (c) and **3** (d). Coordinates from the X-ray data of **2** and **3** were used for the calculations. The electronic absorption spectrum of monomeric **1** is shown as a dotted line in b.

of 0.350 and 0.325, respectively. As shown in Figure 3, both **2** and **3** are expected to have intense split Q bands. The Q band of longest wavelength of the *trans* isomer **3** was calculated to lie at longer wavelength than that of the *cis* isomer **2**. In addition, compared to the *cis* isomer, for the *trans* isomer many intense transitions were calculated at the shorter wavelength side of the Soret band. These results match nicely with observations.

In conclusion, we have separated the *cis* and *trans* isomers of a binuclear SubPc and characterized both isomers by various spectroscopic methods and X-ray crystallography. The electronic absorption and MCD spectra of these dimers are similar in shape, but the Q band of the *trans* isomer appeared at longer wavelength than that of the *cis* isomer by about 3–4 nm,and the shorter wavelength side of the Soret band of the *trans* isomer was stronger than that of the *cis* isomer. These characteristics were reproduced by quantum-mechanical calculations.

Experimental Section

Tetrafluorophthalonitrile (2.0 g, 10 mmol) and 1,2,4,5-benzenetetracarbonitrile (0.089 g, 0.50 mmol) were cooled in 1,2,4-trichlorobenzene (20 mL) to approximately 12 °C. Eight to ten drops of BCl_3, condensed by using a dropping cold finger, were added and the reaction mixture was heated to reflux (214 °C) for 30 min. The solvent was then removed by vacuum distillation. The crude product was adsorbed onto silica and purified by flash chromatography on silica with toluene/hexanes (1:20 v/v) as eluent. When **1** (the major product) had eluted the polarity was gradually increased with toluene and the dimer fractions were collected. To obtain pure samples of **2** and **3** it was necessary to chromatograph the dimer mixture at least two more times on silica, eluting with toluene/hexanes (1:1). By comparing X-ray data, we found that the *cis* isomer was eluted first.[7] The purity of the samples used for spectroscopy was confirmed by HPLC and TLC. Slow evaporation of a solution of **1** in toluene produced crystals suitable for X-ray diffraction. Crystals of **2** and **3** were obtained by layering solutions of the respective compound in dichloromethane with cyclohexane and allowing the slow mixing of the two phases.

Received: March 11, 2002 [Z18862]

---

[1] A. Meller, A. Ossko, *Monatsh. Chem.* **1972**, *103*, 150.
[2] H. Kietaibl, *Monatsh. Chem.* **1974**, *153*, 405.
[3] N. Kobayashi, *J. Chem. Soc. Chem. Commun.* **1991**, 1203.
[4] N. Kobayashi, *J. Porphyrins Phthalocyanines* **1999**, *3*, 453; C. G. Claessens, D. González-Rodríguez, T. Torres, *Chem. Rev.* **2002**, in press.

[5] M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, Á. Sastre, T. Torres, *Synthesis* **1996**, 1139.

[6] R. A. Kipp, J. A. Simon, M. Beggs, H. E. Ensley, R. H. Schmehl, *J. Phys. Chem. A* **1998**, *102*, 5659.

[7] Representative data. **1**: Yield: 51 %; m.p. >300 °C; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 573 (8.96), 555(sh), 532 (2.59), 309 (4.04), 275 (3.03) nm; FAB-MS (*m*-nitrobenzyl alcohol): calcd for $C_{24}BClF_{12}N_6$: *m/z*: 646 [M^+]. *cis* Isomer **2**: Yield: <1 %; m.p. >320 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.47$ ppm (s, 2H, arom); IR (KBr): $\tilde{\nu} = 2959$, 2926, 2857, 1732, 1534, 1483, 1262, 1221, 1165, 1107, 1019, 965, 801, 771, 745, 706, 660, 581, 419 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 690 (11.1), 658 (3.39), 632 (3.40), 602 (3.94), 443 (0.86), 320 (4.61), 275 (3.81) nm; HR-FAB-MS: calcd for $C_{42}H_3B_2Cl_2F_{16}N_{12}$: [$M^+$+H]: *m/z*: 1070.9911, found 1070.9927. TLC (silica), $R_f = 0.53$ (toluene/hexane, 1:1). *trans* Isomer **3**: Yield: <1 %; m.p. >320 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.49$ ppm (s, 2H, arom); IR (KBr): $\tilde{\nu} = 2924$, 2957, 2855, 1717, 1534, 1483, 1271, 1221, 1165, 1109, 1019, 992, 965, 704, 642, 592, 419 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 693 (6.43) , 662 (1.90), 636 (1.96), 605 (2.39), 448 (0.51), 320 (2.78), 281 (3.35) nm; HR-FAB-MS: calcd for $C_{42}H_3B_2Cl_2F_{16}N_{12}$: [$M^+$ + H]: *m/z*: 1070.9911, found 1070.9905. TLC (silica), $R_f = 0.43$ (toluene/hexane, 1:1).

[8] Crystal data for the SubPc **1**: 0.06 × 0.17 × 0.22 mm, monoclinic, $P2_1/c$, $a = 11.2997(11)$, $b = 10.6022(11)$, $c = 19.1563(19)$ Å, $\beta = 95.507(7)°$, $V = 2284.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.880$ Mg m^{-3}, $2\theta_{max} = 52.7°$, $\lambda = 0.71073$ Å, ω scans, 170(2) K, 20288 measured, 4664 independent reflections included in the refinement, Lorentzian but no absorption corrections performed ($\mu = 0.297$ mm^{-1}, min./max. transmission = 0.937/0.982), solved by direct methods (SHELXS-90), refined by using SHELXL-97, 397 parameters, no H atoms, $R = 0.0948$, wR = 0.1055 for all data refined against $|F^2|$, residual electron density max./min. 0.32/ – 0.31 e Å^{-3}. Crystal data for the *cis*-SubPc dimer · 2 CH_2Cl_2 **2**: 0.04 × 0.04 × 0.40 mm, monoclinic, $P2_1/c$, $a = 14.4237(13)$, $b = 31.630(3)$, $c = 10.2000(10)$ Å, $\beta = 101.354(3)°$, $V = 4562.4(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.807$ Mg m^{-3}, $2\theta_{max} = 56.6°$, $\lambda = 0.71073$ Å, ω scans, 91(2) K, 37305 measured, 6637 independent reflections included in the refinement, Lorentzian and absorption corrections (SADABS) performed ($\mu = 0.495$ mm^{-1}, min./max. transmission = 0.826/0.980), solved by direct methods (SHELXS-90), refined by using SHELXL-97, 743 parameters, H atoms constrained, $R = 0.1135$, wR = 0.1586 for all data refined against $|F^2|$, residual electron density max./min. 1.18/ – 0.85 e Å^{-3}. Crystal data for the *trans*-SubPc dimer · 3.25 CH_2Cl_2 **3**: 0.03 × 0.12 × 0.16 mm, triclinic, $P\bar{1}$, $a = 10.8638(11)$, $b = 13.4945(15)$, $c = 17.2990(18)$ Å, $\alpha = 107.608(4)$, $\beta = 91.300(5)$, $\gamma = 101.347(4)°$, $V = 2360.8(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.805$ Mg m^{-3}, $2\theta_{max} = 50.7°$, $\lambda = 0.71073$ Å, ω scans, 91(2) K, 22234 measured, 8623 independent reflections included in the refinement, Lorentzian but no absorption corrections performed ($\mu = 0.537$ mm^{-1}, min./max. transmission = 0.919/0.984), solved by direct methods (SHELXS-90), refined by using SHELXL-97, 743 parameters, H atoms constrained, $R = 0.1198$, wR = 0.1937 for all data refined against $|F^2|$, residual electron density max./min. 1.02/ – 0.95 eÅ^{-3}. CCDC-181314 (**1**), CCDC-181315 (**2**), and CCDC-181316 (**3**) contain the supplementary crystallographic data for this paper. These data can be can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

[9] HyperChem Pro software package, Hypercube, Inc. Gainesville, FL, USA, **1997**.

[10] N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, *J. Am. Chem. Soc.* **1999**, *121*, 9096.

[11] a) A. Tajiri, J. Winkler, *Z. Naturforsch.* **1983**, *38a*, 1263; b) A. Kaito, T. Nozawa, T. Yamamoto, M. Hatano, Y. Orii, *Chem. Phys. Lett.* **1977**, *52*, 154.

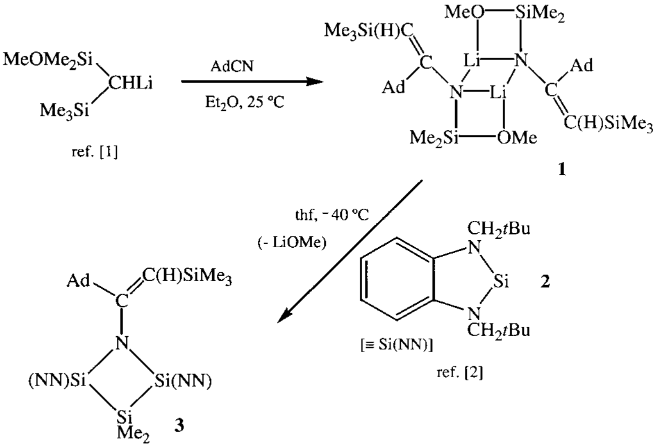
[12] Similar spectra have been reported for a planar dinuclear phthalocyanine that shares a common benzene ring (N. Kobayashi, T. Fukuda, D. Lelièvre, *Inorg. Chem.* **2000**, *39*, 3632).

Synthesis and Structure of an Azatrisilacyclobutane and Its Precursor, a Novel Lithium Enamide Having a Tricyclic $(LiNSiO)_2$ Skeleton**

Floria Antolini, Barbara Gehrhus,* Peter B. Hitchcock, and Michael F. Lappert*

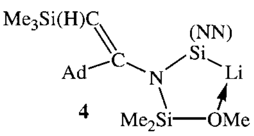
We report results that have a bearing on two diverse but related and currently topical areas of organometallic chemistry. The first concerns insertion of an α-hydrogen-free nitrile into an Li–C bond, and specifically of 1-adamantyl cyanide (AdCN) into the chiral bis(silyl)methyl compound Li[$CH(SiMe_2OMe)(SiMe_3)$][1] to yield the lithium enamide **1**. The second deals with the insertion of the thermally stable bis(amino)silylene Si[$(NCH_2t$Bu$)_2C_6H_4$-1,2] (Si(NN)) **2**[2] into an Li–N bond, and particularly of Si(NN) into **1** to afford the azatrisilacyclobutane **3**, in which a transient insertion product **4** is a plausible intermediate.

The reactions and conditions leading to the new colorless crystalline compounds **1** and **3** are summarized in Scheme 1.



Scheme 1. Synthesis of **3** via **1**.

The yields (**1**, 64 %; **3**, 50 %) of X-ray quality crystalline materials were not optimized. Each of **1** and **3** revealed the parent molecular ion in the EI mass spectra and gave satisfactory microanalyses and multinuclear NMR spectra.



The crystalline lithium enamide **1** is a centrosymmetric dimer (Figure 1).[3] It has a rhomboidal, planar $(LiN)_2$ core (the endocyclic angles at the Li atoms are wider than those at the N

---

[*] Dr. B. Gehrhus, Prof. M. F. Lappert, Dr. F. Antolini,
Dr. P. B. Hitchcock
School of Chemistry, Physics and Environmental Science
University of Sussex
Brighton, BN1 9QJ (UK)
Fax: (+44) 1273-677-196
E-mail: B.Gehrhus@sussex.ac.uk, M.F.Lappert@sussex.ac.uk

[**] We thank the EU and the University of Bologna for provision of a studentship for F.A. and the EPSRC for the award of an Advanced Fellowship for B.G. and for other support.