conversion. We anticipate that the efficiency of this step may be further improved by employing more sophisticated electrochemical equipment, in particular, through precise voltage control.

In conclusion, we have developed a novel protecting system for 5,8-dihydroxynaphthoquinones, which may be removed easily under mild conditions. This development, together with a highly enantioselective ketone reduction, has allowed us to complete concise and practical syntheses of each of the enantiomers alkannin (**1**) and shikonin (**2**). Chemical synthesis and biological investigations of a series of structural analogues of the natural products, more diverse than simple ester derivatives, are now viable. Further studies into the chemical biology of these compounds are in progress.

Received: September 18, 1998 [Z10945IE]
German version: *Angew. Chem.* **1998**, *110*, 864–866

Keywords: asymmetric synthesis · naphthoquinones · natural products · oxidations · total synthesis

---

[1] a) P. Dioscorides in *De Materia Medica, Vol. IV.23* (Ed.: Max Wellman), Berloni Apud Weidmannos, Berlin, **1958**, pp. 187–188; b) R. Gunther in *The Greek Herbal of Dioscorides, Vol. IV*, Hafner, New York, **1968**, pp. 421.
[2] R. Majima, C. Kuroda, *Acta Phytochim. (Tokyo)* **1922**, *1*, 43–65.
[3] H. Brockmann, *Justus Liebigs Ann. Chem.* **1936**, *521*, 1–47.
[4] a) R. H. Thomson, *Naturally Occurring Quinones*, 2nd ed., Academic Press, New York, **1971**, pp. 248–251; b) *Naturally Occurring Quinones III, Recent Advances*, Chapman & Hall, New York, **1987**, pp. 219–223.
[5] a) H. Fukui, M. Tsukada, H. Mizukami, M. Tabata, *Phytochemistry* **1983**, *22*, 453–456; b) Y. Ikeda, N. Ishida, C. Fukaya, K. Yokoyama, M. Tabata, H. Fukui, G. Honda, *Chem. Pharm. Bull.* **1991**, *39*, 2351–2352.
[6] V. P. Papageorgiou, *Experientia* **1978**, *34*, 1499–1501.
[7] V. P. Papageorgiou, *Planta Med.* **1980**, *38*, 193–203, and references therein.
[8] G. Honda, F. Sakakibara, K. Yazaki, *J. Nat. Prod.* **1988**, *51*, 152–154.
[9] a) M. Hayashi, *Nippon Yakurigaku Zasshi* **1977**, *73*, 193–203; b) S. Tanaka, M. Tajima, M. Tsukada, M. Tabata, *J. Nat. Prod.* **1986**, *49*, 466.
[10] B.-Z. Ahn, K.-U. Baik, G.-R. Kweon, K. Lim, B.-D. Hwang, *J. Med. Chem.* **1995**, *38*, 1044–1047, and references therein.
[11] M. Hayashi, *Nippon Yakurigaku Zasshi* **1977**, *73*, 205–214.
[12] M. Hayashi, *Nippon Yakurigaku Zasshi* **1977**, *73*, 177–191.
[13] H. Wagner, B. Kreher, K. Jurcic, *Arzneim. Forsch.* **1988**, *38*, 273–275.
[14] a) A. Terada, Y. Tanoue, A. Hatada, H. Sakamoto, *J. Chem. Soc. Chem. Commun.* **1983**, 987–988; b) *Bull. Chem. Soc. Jpn.* **1987**, *60*, 205–213; c) A. M. Moiseenkov, N. N. Balaneva, V. L. Novikov, G. B. Elyakov, *Dokl. Akad. Nauk. SSSR* **1987**, *295*, 614–617; d) Y. Tanoue, A. Terada, Y. Sugyo, *J. Org. Chem.* **1987**, *52*, 1437–1439; e) M. Braun, C. Bauer, *Liebigs Ann. Chem.* **1991**, 1157–1164; f) V. L. Novikov, N. N. Balaneva, A. M. Moiseenkov, G. B. Elyakov, *Izv. Akad. Nauk, Ser. Khim.* **1992**, 1901–1910; g) S. Torii, K. Akiyama, H. Yamashita, T. Inokuchi, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2917–2922; h) E. A. Couladouros, Z. F. Plyta, A. T. Strongilos, V. P. Papageorgiou, *Tetrahedron Lett.* **1997**, *38*, 7263–7266.
[15] Y. Shimai, T. Koga, (Pias Co., Ltd.) JP-B 63156741, **1988** [*Chem. Abstr.* **1989**, *110*, 23567u].
[16] Y. Tanoue, A. Terada, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2039–2045.
[17] A low-yielding three-step sequence to deprotect the alternate regioisomer has been reported: see Ref. [14g].
[18] Other methods for demethylation of naphthazarin ethers (e.g. $AlCl_3$)[16] are incompatible with the acid-sensitive side chain of **1** and **2**.
[19] F. A. Chen, H. W. Cheng, A.-B. Wu, H.-C. Hsu, C.-Y. Chen, *Chem. Pharm. Bull.* **1996**, *44*, 249–251.
[20] R. E. Moore, P. J. Scheuer, *J. Org. Chem.* **1966**, *31*, 3272–3283.
[21] R. Huot, P. Brassard, *Can. J. Chem.* **1974**, *52*, 838–842.
[22] D. B. Bruce, R. H. Thomson, *J. Chem Soc.* **1955**, 1089–1096.
[23] F. Dallacker, J. Jacobs, W. Coerver, *Z. Naturforsch. B* **1983**, *38*, 1000–1007. Rigorous exclusion of oxygen is required to ensure the success of this reaction.
[24] S. Nahm, S. M. Weinreb, *Tetrahedron Lett.* **1981**, *22*, 3815–3818.
[25] J. Einhorn, C. Einhorn, J.-L. Luche, *Synth. Commun.* **1990**, *20*, 1105–1112.
[26] a) H. C. Brown, J. Chandrasekharan, P. V. Ramachandran, *J. Am. Chem. Soc.* **1988**, *110*, 1539–1546; b) P. V. Ramachandran, A. V. Teodorovic, M. V. Rangaishenvi, H. C. Brown, *J. Org. Chem.* **1992**, *57*, 2379–2386; c) R. K. Dar, *Aldrichimica Acta* **1994**, *27*, 43–51.
[27] The enantiomeric excesses were determined by 500 MHz ^1H NMR spectroscopic analysis of the Mosher's esters with each enantiomer of α-methoxytrifluoromethylphenylacetic acid chloride. In each case, only a single diastereoisomer could be observed: a) J. A. Dale, D. L. Dull, H. S. Mosher, *J. Org. Chem.* **1969**, *34*, 2543–2549; b) J. A. Dale, H. S. Mosher, *J. Am. Chem. Soc.* **1973**, *95*, 512–519; c) for a very convenient experimental method, see D. E. Ward, C. K. Rhee, *Tetrahedron Lett.* **1991**, *32*, 7165–7166.
[28] K. Inoue, M. Akaji, H. Inouye, *Chem. Pharm. Bull.* **1985**, *33*, 3993–3997.
[29] D. A. Frey, N. Wu, K. D. Moeller, *Tetrahedron Lett.* **1996**, *37*, 8317–8320.

A Naphthalene-Like Si_{10}^{10-} Unit in the Novel $^{2}_{\infty}[Si_{20}^{30-}]$ Planar Anion of $Sr_{13}Mg_{2}Si_{20}$**

Antonio Currao and Reinhard Nesper*

Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

In recent years, a large number of novel silicon Zintl anions[1] in the ternary and quaternary solids $M^1M^2Si_x$ and $M^1M^2M^3Si_x$ (M^1-M^3 = alkali or alkaline earth metal) have been discovered and characterized.[2–5] Unequivocal evidence for a structure-directing influence of the metal atom on its respective Zintl anion Si_m^{n-} was observed relatively early; this effect may be exploited as a strategic aid in synthesis.[3] As was established for the oligomeric Si_m^{n-} polyanions, small, strongly polarizing cations (especially Mg^{2+}) coordinate formally highly charged terminal or isolated Si^{n-} anions, whereas larger, weakly charged cations are in the more highly networked regions of the polyanion.[2, 4] This phenomenon was used to tune the relative ratio of terminal to more highly networked atoms, the latter embedded deeper in the anion, while maintaining an identical valence electron count and mean bond order within the polyanion. In other words, the degree of disproportionation of the Si_x units is a function of the various cations and their respective stoichiometries. An unusual number of planar Si_m^{n-} polyanions have been reported

---

[*] Prof. Dr. R. Nesper, Dipl.-Chem. A. Currao
Laboratorium für Anorganische Chemie
der Eidgenössischen Technischen Hochschule
ETH-Zentrum
CH-8092 Zürich (Switzerland)
Fax: (+41)1-632-1149
E-mail: nesper@inorg.chem.ethz.ch

[**] This work was supported by the Swiss National Foundation (project no. 20-4322.958).

whose geometries are in strange contradication to the generally accepted notion that Si_m^{n-} units with multiple bonds should be more energetically stable than their isoelectronic singly bonded counterparts. For example, the doubly bound $[\mathrm{Si{=}Si}]^{4-}$ monomer is energetically less stable than a $^{1}_{\infty}[(\text{-Si-Si})^{4-}]$ linear chain.

We present here a new polymeric $^{2}_{\infty}[\mathrm{Si}_{20}^{30-}]$ anion with naphthalene-like planar ring systems that is consistent with the aforementioned unusual trends. $Sr_{13}Mg_2Si_{20}$ exists in the magnesium-poor region of the ternary phase system SrMgSi as a stable compound[6] that decomposes above 1253 K to SrSi, Sr_4Si_{6+x}, and $Sr_2Mg_{2-x}Si_3$. Long tempering below 1230 K readily provides pure-phase black products, mostly in powder form. Upon further tempering at 1240 K, beautiful, tiny, black single crystals of about 0.1 mm in diameter are obtained, which could be used for a structure determination.[4, 7]

$Sr_{13}Mg_2Si_{20}$ contains separated sheetlike silicon domains (Figures 1 a, lightly shaded area, and 1 b) that are formed from two interpenetrating $^{2}_{\infty}[\mathrm{Si}_{20}^{30-}]$ polyanions with naphthalene-like Si_{10}^{10-} building blocks (Figure 2 a). The relatively open structure of this polyanion is dictated by the large Sr^{2+} ions, which form trigonal-prismatic assemblies in the region of the rings (Figure 1 a, darkly shaded area). Consistent with their aforementioned structure-directing influence, the Mg^{2+} ions coordinate exclusively the peripheral, highly charged Si atoms of the polymers.

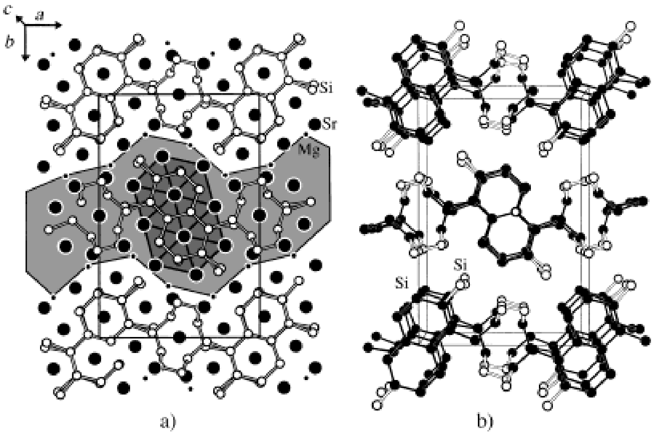

Figure 1. Structure of $Sr_{13}Mg_2Si_{20}$: a) Projection along the crystallographic *c* axis; the prismatic coordination of the Si_6 rings by the large Sr atoms is highlighted in gray (Si: large empty circles, Sr: large filled circles, Mg: small filled circles); b) perspective view of the Si_{20}^{30-} polymer anion sheets.

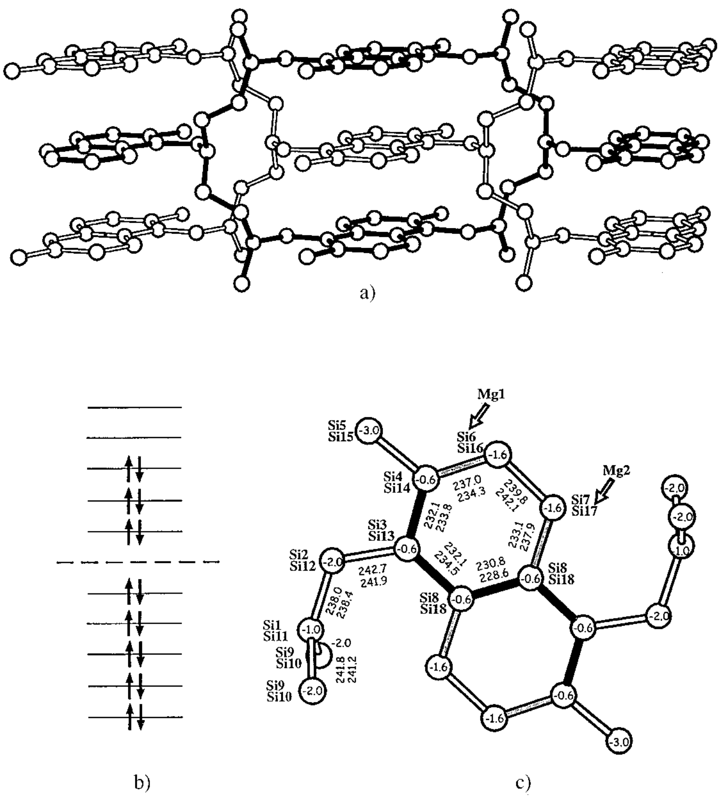

Figure 2. a) Interpenetration of the two polymeric Zintl anions in a layer of $Sr_{13}Mg_2Si_{20}$. b) Schematic MO diagram and electronic occupation of the π and π* states in the double-ring system. (below and above, respectively, the dashed line). c) Labeling scheme, formal charges (inside the circles), and bond lengths (pm) in the planar Si_{16}^{22-} fragment. Atoms Si9 and Si10 do not belong to the ring system. The relatively short Si–Si bonds are darkened. Atoms Si6 and Si17 are also coordinated by Mg and are marked with arrows; they feature the longest bond lengths to neighboring Si atoms.

The polymeric $^{2}_{\infty}[\mathrm{Si}_{20}^{30-}]$ anions contain two crystallographically independent planar Si_{10}^{10-} building blocks (Figures 1 and 2), each formed from a pair of condensed Si_6 rings. Each of these rings is bound by a terminal Si^{3-}center and a bridging, doubly branched Si_{10}^{20-} chain fragment (Figure 2 c). Each Si_{10}^{20-} unit bonds together four naphthalene-like fragments within a layer. In contrast to the other six Si atoms of the bridging piece, atoms Si9 and Si10 are not co-planar with one of the ring systems (Figure 2 a, c). Thus, a planar building block of sixteen Si atoms, $(\mathrm{Si}_{10})^{\text{ring}}(\mathrm{Si})_2^{\text{terminal}}(\mathrm{Si}_2)_2^{\text{bridging}}$, results.

On the basis of numerous new findings it has become apparent that in planar Zintl anions there is no general tendency towards the formation of aromatic systems (such as that observed for the CH arenes), even when the assembly into nearly or completely isometric rings is possible. This was corroborated by ring systems observed in Si and Ge Zintl anions.[2, 3, 8] In the title compound, there is indeed a difference between the bond lengths within the rings (230.8 to 239.8 pm); however, the distribution does not permit the assignment of localized double bonds (Figure 2 c). It is interesting that the somewhat longer bond lengths about Si6 and Si17 occur at two different Si sites in the two independent ring systems, and where the Si atoms are coordinated by Mg^{2+} ions. Even the exocyclic bonds do not show strikingly varied bond lengths, including those which one can confidently assign as Si–Si single bonds.[9] However, the mean Si–Si bond length (240.5 pm) is somewhat larger than that of the endocyclic bonds (234.6 and 235.2 pm). The double bonds are perhaps localized in the ring system.

Upon applying the (8 – N) rule and considering the planar groups, it is clear that the composition $Sr_{13}Mg_2Si_{20}$ does not contain sufficient valence electrons to achieve a completely singly bonded structure. Consequently, an incomplete occupation of the π* states in the bicyclic system results. The π MO states are depicted schematically in Figure 2 b (owing to the low C_s symmetry, there are no degenerate π levels; this is also the case in naphthalene). The observed composition leads to a degree of filling in which two of the five π* states remain unoccupied, which effectively results in two, relatively strongly delocalized double bonds in the bicyclic system. A completely singly bonded Si polymer of this type would require four additional valence electrons so that the π* levels would also be filled. The bond distances suggest that the (-Si4-Si3-Si8-Si7-)$_2$ and (-Si16-Si14-Si13-Si18-)$_2$ ring fragments carry the majority of the double-bond character (Figure 2c). We will report elsewhere on an explanation of why highly charged Zintl anions of Si are so frequently planar.[8]

The Si_{10}^{10-} units in the polyanion structure are ecliptically stacked (Figure 2a). Despite the relatively large distance of $c/2 = 4.91$ pm between neighboring rings, one-dimensional conductivity along the stacking direction could arise through π*–π* interactions. Such interactions were recently suggested for a related Group 14 compound in which bond lengths of 430 to 500 pm were observed between ecliptically stacked planar Zintl anions.[3, 4, 8] One-dimensional conductivity originates from interactions between ecliptically stacked ring systems, whereas semiconducting properties are observed in the perpendicular direction. Such semiconductors are at the border between intermetallic phases and common Zintl compounds, which strongly adhere to the valence rules. As their structural details can nevertheless be understood with electron-counting rules and a semiconducting character predominates, we call such compounds "extended Zintl phases". This description is supported by practically all of the band-structure calculations we have carried out to date on such silicides; all of the occupied electronic states are Si-centered (similar to the MO scheme in Figure 2b). In this respect, these species may be differentiated from intermetallic phases.

From a small number of examples, it can already be seen that topochemical reactions can be carried out on two-dimensional polyanions of silicon and germanium—such as those in $CaSi_2$,[10] Li_3NaSi_6,[11] and Li_7Ge_{12}[12, 13]—to afford new element modifications[11, 13] and siloxanes[14, 15]; this fosters a continued excitement in this area of research. In this respect, the Si polymer anions we recently discovered in $Ba_2Eu_3Si_7$,[15] Ca_3Si_4, $Ca_{14}Si_{19}$,[4, 2[and the title compound $Sr_{13}Mg_2Si_{20}$[4] could be of interest.

Received: March 3, 1997
Revised version: November 24, 1997 [Z 10185IE]
German version: *Angew. Chem.* **1998**, *110*, 843–845

Keywords: layered compounds • silicon • solid-state chemistry • structure elucidation • Zintl anions

---

[1] E. Zintl, *Angew. Chem.* **1939**, *52*, 1; W. Klemm, *Proc. Chem. Soc. London* **1959**, 329; H. G. von Schnering, *Angew. Chem.* **1981**, *93*, 44; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 33; H. G. von Schnering, W. Hönle, *Chem. Rev.* **1988**, *88*, 243; H. Schäfer, B. Eisenmann, *Rev. Inorg. Chem.* **1981**, *3*, 29; R. Nesper, *Prog. Solid State Chem.* **1990**, *20*, 1.

[2] R. Nesper, A. Currao, S. Wengert in *Organosilicon Chemistry II, From Molecules to Materials* (Eds.: N. Auner, J. Weis), VCH, Weinheim, **1995**.

[3] A. Currao, J. Curda, R. Nesper, *Z. Anorg. Allg. Chem.* **1996**, *622*, 85.

[4] A. Currao, Dissertation, ETH Zürich, **1995**; Diplomarbeit, ETH Zürich, **1991**.

[5] C. Häussermann, R. Nesper, *Angew. Chem.* **1995**, *107*, 1593; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1462.

[6] Differential thermal analysis (DTA) investigations on probes of Sr/Mg/Si compositions 33.3/11.7/55 and 40/10/50 demonstrate that $Sr_{13}Mg_2Si_{20}$ decomposes peritectically above 1253 K. As established by a powder diagram, pure $Sr_{13}Mg_2Si_{20}$ may be obtained by tempering a sample of the former composition at 1223 K ($t_1 = 99$ h). The crystal investigated was isolated from a synthesis at 1243 K ($t_1 = 8$ d). At this temperature, $Sr_{13}Mg_2Si_{20}$ is the main product and Sr_4Si_7 and $SrSi_2$ are side products. In the products of syntheses at 1234 K ($t_1 = 10$ h) and 1243 K ($\mathrm{t}_1 = 99$ h) for the latter composition, one finds predominantly $Si_{13}Mg_2Si_{20}$ with SrSi as a minor component. If either composition is subsequently tempered at about 1363 K ($t_1 = 30$ and 10 h, respectively) SrSi is obtained as the main component with minor Sr_4Si_7 and $Sr_2Mg_{2-x}Si_3$ impurities.

[7] Crystal structure: *Pbam* (no. 55), $a = 15.200(3)$, $b = 23.201(6)$, $c = 9.832(2)$ Å, $Z = 4$, $V = 3464.1$ Å^3, $\rho_{\text{calcd}} = 3.354$ g cm^{-3}, 2907 independent reflections ($R_{\text{int},F^2} = 0.176$), 2109 reflections with $F^2 > 2\sigma(F^2)$, $R(F^2) = 0.085$, $R_w(F^2) = 0.164$. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408183.

[8] R. Nesper, S. Wengert, unpublished results; see also S. Wengert, Dissertation, ETH Zürich, **1997**.

[9] H. Bock, *Angew. Chem.* **1993**, *105*, 413; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 414.

[10] K. Janzon, H. Schäfer, H. Weiss, *Z. Naturforsch.* ***B*1968**, *23*, 1544; J. Evers, *J. Solid State Chem.* **1978**, *24*, 199.

[11] H. G. von Schnering, M. Schwarz, R. Nesper, *J. Less-Common Met.* **1988**, *137*, 297.

[12] A. Grüttner, R. Nesper, H. G. von Schnering, *Angew. Chem.* **1982**, *94*, 933; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 912.

[13] A. Grüttner, Dissertation, Universität Stuttgart, **1982**.

[14] H. Kautsky, G. Herzberg, *Z. Anorg. Allg. Chem.* **1924**, *139*, 135.

[15] A. Weiss, G. Beil, H. Meyer, *Z. Naturforsch.* ***B*1979**, *34*, 25.

Formation of Adamantane-Like Structures by Reaction of Titanocene Fluorides with an Iminoalane**

Helge Wessel, Mavis L. Montero, Carsten Rennekamp, Herbert W. Roesky,* Peihua Yu, and Isabel Usón

Dedicated to Professor Sir John Meurig Thomas on the occasion of his 65th birthday

Imido transition metal complexes play an important role both in biological processes such as nitrogen fixation as well as in a series of industrial processes.[1] Cycloadditions, C–H activations, and ring-opening polymerizations can all be catalyzed by imido complexes.[1, 2] Numerous imidotitanium

---

[*] Prof. Dr. H. W. Roesky, Dipl.-Chem. H. Wessel, Dr. M. L. Montero, Dipl.-Chem. C. Rennekamp, Dipl.-Chem. P. Yu, Dr. I. Usón
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-37077 Göttingen (Germany)
Fax: (+49) 551-39-3373
E-mail: hroesky@gwdg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung, Forschung und Technologie and the Witco GmbH, Bergkamen. H. W. and C. R. thank the Fonds der Chemischen Industrie for Doctoral fellowships.