cyanocyclopentadienyl moiety appear as two doublets and a singlet, respectively. These results, together with the mass and ^{13}C-NMR spectroscopic data[6], suggest that 3 is an azulenofulvene derivative[7] with two *tert*-butylthio groups and two cyano groups.

A formation scheme involving 1) attack by the 2-position of 2 at the 5-position of 1, 2) opening of the three-membered ring, 3) proton transfer, 4) disrotatory 10π-electrocyclic reaction, and finally 5) dehydrogenating aromatization is shown in Scheme 2[8].

Table 1. Spectral data for **3** and **4**.

	IR (KBr) [cm⁻¹]	UV (CH₂Cl₂) λ_{max} [nm] (logε)	¹H-NMR (CDCl₃) [a] δ-values
3	2203, 2175, 1580, 1520	258 (4.58), 293 (4.62), 328 (4.37), 350 (4.35), 404 (4.31), 575 (3.96)	8.10 (s, 1H, H-4), 7.87 (s, 1H, H-3), 7.50 (d, 1H, H-8, J=5.0 Hz), 7.03 (d, 1H, H-7, J=5.0 Hz), 3.26 (s, 6H, NMe₂), 2.76 (s, 6H, NMe₂), 1.38 (s, 9H, tBu), 1.30 (s, 9H, tBu)
4	2200, 1810, 1497	247 (4.62), 266 (4.59), 335 (4.53), 408 (4.85)	7.12 (s, 2H, H-1,4), 7.05 (t, 1H, H-1', J=2.0 Hz), 6.73 (dd, 1H, H-3' or -4', J=4.5, 2.0 Hz), 6.36 (dd, 1H, H-3' or -4', J=4.5, 2.0 Hz), 3.22 (s, 12H, NMe₂), 1.71 (s, 9H, tBu)

[a] 100 MHz, 25°C.

Other calicenes, e.g., the analogue of **1** with NO₂ and H instead of 2CN[9], gave only the substitution product of type **4**[10].

CAS Registry numbers:
1, 94138-30-4; **2**, 703-24-2; **3**, 94138-31-5; **4**, 94138-32-6.

[1] A. S. Kende, P. T. Izzo, J. Am. Chem. Soc. 87 (1965) 4162.
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[3] **1**: pale pink crystals; m.p. = 205—207°C; ¹H-NMR (CDCl₃): δ = 7.05 (s, 2H), 1.70 (s, 18H).
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[5] Z. Yoshida, S. Miki, S. Yoneda, Tetrahedron Lett. 14 (1973) 4731.
[6] **3**: ¹³C-NMR (CDCl₃): δ = 168.9 (C-1'), 145.7, 143.1, 141.4, 138.5, 134.8, 131.9 (C-9b,3a,5,6,6a,9a), 137.5 (C-4), 129.1 (C-3), 122.1, 117.6 (C-7,8), 119.2, 117.2 (CN), 111.2 (C-2), 108.9 (C-1), 107.4 (C-9), 49.6, 49.2 (C(CH₃)₃), 42.7, 42.4 (N(CH₃)₂), 31.9, 31.7 (C(CH₃)₃).
[7] Very recently we synthesized an unsubstituted cyclopent[e]azulenide and some of its derivatives (diaminomethylene- and diaminocyclopropenyli-denecyclopent[e]azulenes); Z. Yoshida, M. Shibata, T. Sugimoto, Tetrahedron Lett. 24 (1983) 4585; Z. Yoshida, M. Shibata, A. Sakai, T. Sugimoto, J. Am. Chem. Soc. 106 (1984) 6383.
[8] It has been established that a carbene of the Wanzlick type, which readily accepts protons, can be easily generated under mild conditions from the cyclopropene intermediate formed in the reaction of thiocyclopropenylium ions with various nucleophiles (S. Miki, Dissertation, Kyoto University 1978; H. Hirai, Dissertation, Kyoto University 1980; S. Yoneda, H. Hirai, Z. Yoshida, Chem. Lett. 1976, 1051; Heterocycles 15 (1981) 865). However, at present other routes cannot be ruled out.
[9] **5** was synthesized in 6% yield by reaction of sodium nitrocyclopentadienide with 1,2-bis(*tert*-butylthio)-3,3-dichlorocyclopropene: yellow crystals; m.p. = 156°C; ¹H-NMR (CDCl₃): δ = 7.42 (dd, 1H), 6.89 (dd, 1H), 6.48 (dd, 1H), 1.68 (s, 18H).
[10] Analogue of **4** with NO₂ and H instead of 2CN; yield 51%, yellow oil, ¹H-NMR (CDCl₃): δ = 7.60 (t, 1H), 7.15 (t, 1H), 6.95 (dd, 1H), 6.85 (dd, 1H), 6.65 (dd, 1H), 6.40 (dd, 1H), 3.25 (s, 12H), 1.75 (s, 9H).

Probing the Structure and Crystallinity of a Lithium Silicate Glass by 29Si Magic-Angle-Spinning NMR Spectroscopy

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It is now well established that high-resolution magic-angle-spinning NMR spectroscopy (MASNMR) can monitor the nature of short-range order in both non-crystalline and crystalline solids[1, 2]. ²⁹Si-MASNMR studies of silicates have shown that the ²⁹Si chemical shift is related to the Si—O—Si angles and to interatomic distances[3]. In glasses, where a wide range of such structural parameters are simultaneously present, lineshapes provide information about the nature of the distribution functions[4]. We have found that useful information on the distribution of Si—O—Si angles may be obtained from ²⁹Si-MASNMR spectra of glasses in which the crystallinity varies from zero to 100%, as gauged by electron microscopy.

We have chosen lithium disilicate glass, thermally treated to yield a range of materials extending between the two extremes of 100% crystallinity and 100% non-crystallinity. Lithium disilicate, Li₂O·2SiO₂, is a particularly suitable material for such a study since its crystal structure is known[5], and no change of composition is observed on devitrification. Crystalline lithium disilicate consists of a double-chain arrangement of apex-shared SiO₄⁴⁻ tetrahedra in such a way that each Si atom has three equivalent silicon neighbors. Partly crystalline Li₂O·2SiO₂ contains minute microcrystals immersed in an amorphous matrix, apparent even in scanning electron micrographs, and is readily detectable by electron diffraction.

In recording the ²⁹Si-NMR spectra, we noted that the spin-lattice relaxation times T_1 of the nucleus were very different in the microcrystalline and non-crystalline regions; in the former case this was of the order of seconds while in the latter of the order of hours. This large difference in relaxation times makes it possible to distinguish between the two regions and measure the relative amounts of material in each. Whereas the spectrum of the crystalline part of the mixture can be obtained relatively easily, a spectrum comprising signals of both the amorphous and crystalline regions can be measured only if short pulses and long pulse delays are used, and we used 30° pulses separated by 90 min delays.

Even those samples which, by microscopy, appeared largely (80%) non-crystalline, contained traces of microcrystallinity, and hence the resulting spectrum (Fig. 1a) contains the characteristic, though somewhat broader signal at δ = −92 from tetramethylsilane (TMS) superimposed upon a much broader background resonance, the chemical shift of which ranges from δ = −70 to −120 and which is attributable to non-crystalline regions of the sample.

The total range of ²⁹Si-NMR chemical shifts in silicates lies between δ = −60 and −120. This is split up into five intervals[2] corresponding to Si atoms in monosilicates, i.e. to isolated SiO₄⁴⁻ groups (denoted by Q⁰), disilicates and

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chain end groups (Q^1), middle groups in chains (Q^2), chain branching sites (Q^3), and fully crosslinked framework sites (Q^4). Within each structural category the ^{29}Si chemical shift is correlated with the Si—O—Si bond angles and the interatomic distances. We conclude that, in agreement with the established structure, the sharp resonance at $\delta = -92$ is attributable to Q^3 groupings (chain branching sites), and the chemical shift corresponds to an Si—O—Si angle of ca. 135°. The single sharp resonance at $\delta = -61$ (x) is due to Q^0 (monosilicate) present as binder in the ZrO$_2$ magic-angle spinner.
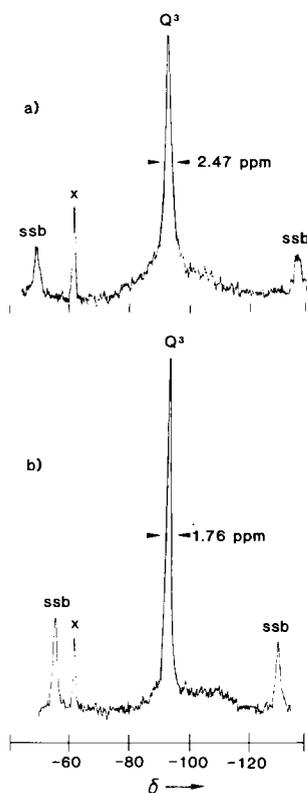

Fig. 1. ^{29}Si-MASNMR spectra (59.60 MHz, Bruker CXP-300). a) Partially crystallized lithium disilicate glass; b) almost completely crystalline Li$_2$O·2SiO$_2$. Samples spun at ca. 3.5 kHz in Andrew-Beams spinners made of Delrin. δ-values given in ppm relative to TMS branching sites.

There are also distinct spinning sidebands (ssb) equidistant from the main signal, which are due to chemical shift anisotropy. Their presence supports our assignment of the main signal as arising from Q^3 units; Q^4 (fully cross-linked framework sites) units resonate at a higher field and involve much smaller chemical shift anisotropy. Spinning sidebands from Q^4 sites in framework silicates are much less distinct than in the present Q^3 case. Finally, no Q^2 signals (corresponding to the termination of the double chain) are visible in the spectra, indicating that their concentration is low.

The range of resonances ($\delta = -70$ to -120) for the noncrystalline regions can be interpreted in several ways: 1) Q^1, Q^2 and Q^3 groups are present, 2) the Si—O—Si angles range from ca. 120 to 180° in the Q^3 groupings, and 3) the interatomic distances vary. Of these possibilities, a combination of 2) and 3) is the most likely explanation. The fact that the spectrum of the largely crystalline sample (electron diffraction studies) also contains a broad background resonance signifies the presence of some crystallographi-

cally disordered material. When the composition of a lithium silicate glass Li$_2$O·xSiO$_2$ is varied by increasing x, a broad NMR signal is observed whose chemical shift approaches that of Q^4 units.

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Photooxygenolysis of Vitamin B$_{12}$**

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Studies of the action of singlet oxygen (^{1}O$_2$) on vitamin B$_{12}$ 1 are still outstanding, but should be of interest because of the medical[1], biological[1, 2], and preparative[2, 3] role of ^{1}O$_2$. We recently found that heptamethyl-dicyano-Co^{III}-cobyrinate 2 ("cobester"[4]), the nucleotide-free methanolysis product of vitamin B$_{12}$, undergoes selective photooxygenolysis to afford the dioxosecocobyrinates 3a and 3b[5]. This degradation reaction with ^{1}O$_2$[5] opened an efficient route to 3a and 3b, the former of which Inhoffen et al.[6] had already prepared via partial ozonolysis of heptamethyl-dicyano-Co^{III}-10-bromocobyrinate. We now report on the photooxygenolytic cleavage of the corrin macrocycle of vitamin B$_{12}$ (see Scheme 1).

Upon irradiation with visible light, vitamin B$_{12}$, dissolved in oxygen-saturated CD$_3$OD, exhibited considerable inertness, even in the presence of the ^{1}O$_2$-sensitizer methylene blue (MB). Only after addition of KCN (1 mol per mol 1) to a solution of 1 (λ_{max} is shifted from 548 to 584 nm, corresponding to the conversion 1→ potassium dicyanocobalamin 4) and of MB in CD$_3$OD did the photolysis lead to degradation of the corrin within a few hours[7]. In CH$_3$OH, but otherwise under the same conditions, the photolysis proceeded approximately 7 times more slowly[8]. Irradiation[9] of an oxygen-saturated solution of 1, KCN, and MB (molar ratio 1 : 1 : 0.005) in CD$_3$OD at ca. -70°C with a 150-W tungsten lamp led after 45 min to ca. 50% degradation of the educt and to formation of products which absorb at shorter wavelengths (λ_{max} ca. 490 nm). Work-up of the reaction mixture and HPLC separation[9] allowed recovery of 31% of 1 and afforded potassium dicyano-5',6'-dimethylbenzimidazolyl-5,6-dioxo-5,6-secocobamide 5a (10%) and its regioisomer 5b (24%). The structures of the noncrystalline photooxygenolysis products 5a and 5b result from comparison of their UV/VIS, CD, IR,

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