

This study shows that (I) is a centrosymmetric dimer linked by the C(1)–C(1') bond. Since this bond must be cleaved upon dissociation of (I) to pyrrolyl radicals, the inconspicuous nature of the valencies of C(1) is surprising. Bond distances in the pyrrole ring are consistent with azabutadiene bonding in the C(2)–C(3)–C(4)–N fragment. This view is in line with the ring being essentially planar (r.m.s. deviation 0.013 Å) as well as the minor deviations [0.002 (4) – 0.061 (4) Å] of S(2), S(3) and S(4) from this plane.

The average S–C(*sp*²) bond length, 1.76 (2) Å, agrees with that found in Hg[N(CSCF₃)₄]₂, 1.756 (9) Å (Brauer, 1979) and is 0.10 (2) Å shorter than the S–C(*sp*³) bond formed by C(1). Compensation for the latter bond being long is indicated by S(1)–C(5) being somewhat, 0.04 (2) Å, shorter than the average of the other three S–C(CF₃) bond lengths, 1.79 (1) Å. The latter value is essentially the same as that in Hg[N(CSCF₃)₄]₂, 1.79 (2) Å.

While the structural parameters of the CF₃ groups suffer from the large thermal displacements of the F atoms and should be treated with caution, the 10 (1)° variation in the S–C–F bond angles is noteworthy. As in Hg[N(CSCF₃)₄]₂, these angles are large when the moduli of the C–S–C–F torsion angles are small and *vice versa*.

The structure of the analogous 1,1'-bipyrrole is known (Gerstenberger, Haas, Kirste, Krüger & Kurreck, 1982). Although rotational disorder of the CF₃ groups precludes a discussion of the finer details of that structure, the planes of the C–S–C fragments were

found to be nearly perpendicular to their respective rings. Planes through corresponding fragments of the Hg[N(CSCF₃)₄]₂ structure are also nearly orthogonal. The importance of the conformation of these groups may be gauged by the normals to the C(2)–S(2)–C(6), C(3)–S(3)–C(7), and C(4)–S(4)–C(8) planes in (I) forming dihedral angles of 44 (2), 90 (2) and 4 (2)°, respectively, with the normal to the ring, and inspection of Fig. 1. The SCF₃ groups are oriented so as to fill the hollow regions of the molecule and thus provide a molecular shape which can be packed efficiently. Intermolecular contacts in (I) are normal, the shortest being F(11)–F(11)(–1–*x*, 1–*y*, –*z*), 2.94 (1) Å.

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(1SR, 2SR, 6SR)-2-[(*tert*-Butyldiphenylsiloxy)methyl]-1-methyl-6-(2-methylenebutyl)-5-oxocyclohexanecarbonitrile, C₃₀H₃₉NO₂Si

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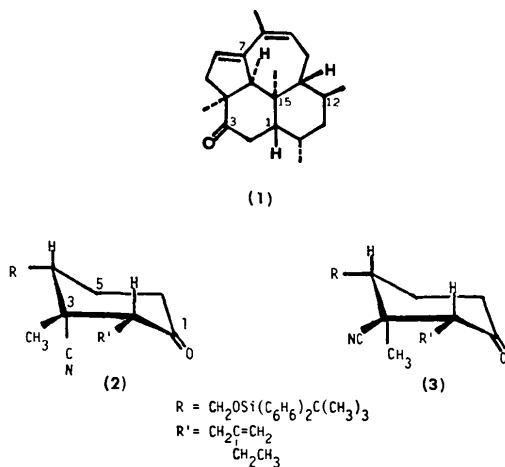
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Abstract. *M_r* = 473.7, triclinic, *P* $\bar{1}$, *a* = 9.7630 (8), *b* = 10.1483 (8), *c* = 14.3484 (11) Å, α = 105.935 (6), β = 92.003 (6), γ = 93.096 (7)°, *V* = 1363.2 (4) Å³, *Z* = 2, *D_m* = 1.136 (4), *D_x* = 1.154 g cm^{–3}, Mo *K* α , λ = 0.71073 Å, μ = 1.069 cm^{–1}, *F*(000) = 512.0, *T* = 298 K. *R* = 0.0351 for 2717 independent reflections with *F*² > 3 σ (*F*²). The cyclohexanone ring is in a chair conformation with the nitrile moiety in an axial position. Bond lengths and angles are normal.

Introduction. Kempene-2 (1) is one of two diterpenes isolated from *Nasutitermes kempae* termite soldiers which possess a novel tetracyclic cembrene-derived carbon skeleton verified by ¹³C NMR spectroscopy and single-crystal X-ray structural analysis (Prestwich, Solheim, Clardy, Pilkiewicz, Miura, Tanis & Nakanishi, 1977). The title compound was an intermediate in the attempted total synthesis of kempene-2 (1) by Professor William Dauben and Mr Kevin Henegar. The synthetic

sequence could have afforded either isomer (2) or (3). The structure determined the relative stereochemistry at C(3) to be that in (2). C(3) corresponds to C(15) in kempene-2 (1).



Experimental. Colorless transparent rhombohedra, crystallized from an oil obtained from MPLC separation of reaction products, kindly provided by Mr Kevin Henegar and Professor William Dauben. D_m by flotation in salt (KI, NaCl) water. Crystal 0.15 × 0.27 × 0.23 mm. Precession photographs, triclinic symmetry. Enraf-Nonius CAD-4 diffractometer. Unit cell: least squares on 24 reflections, $25 < 2\theta < 32^\circ$, graphite-monochromatized Mo $K\alpha$, θ - 2θ scans. 3754 intensities in hemisphere $\pm h, +k, \pm l$ ($h = -10$ to 10 , $k = 0$ to 10 , $l = -15$ to 15), $2 < 2\theta < 45^\circ$, $0.75 < \text{scan speed} < 6.7^\circ \text{ min}^{-1}$, no decrease in intensity in three intensity standards nor was crystal reorientation required during data collection. Data correction for background, scan speed, Lorentz and polarization factors (Frenz, 1982); negligible absorption. 3754 reflections collected with 2717 reflections having $F^2 > 3\sigma(F^2)$. Structure solved by direct methods (MULTAN 11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) giving a solution which determined the positions of the Si, O and N atoms and 29 of 30 C atoms. Subsequent full-matrix least-squares refinements and Fourier synthesis yielded the position of the remaining C atom. The majority of the H atoms were located following full anisotropic refinement of non-hydrogen atoms. All H atoms were assigned idealized coordinates with C-H = 0.95 Å. H atoms were assigned isotropic thermal factors ($B = 5.0$ to 9.0 \AA^2) based on the magnitudes of the thermal parameters of their parent C atoms. Examination of the most intense low-angle reflections indicated some secondary extinction: extinction coefficient refined to 6.4×10^{-7} (Darwin, 1922). $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]$, $p = 0.03$. $\sum w(\Delta F)^2$ minimized. Final least-squares cycle $R = 3.51\%$, $wR = 4.73\%$,

Table 1. Positional parameters and their estimated standard deviations

$$B_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$$

	x	y	z	B _{eq} (Å ²)
Si	0.29899 (6)	0.01271 (5)	0.23308 (4)	2.99 (1)
O(1)	0.0539 (2)	0.5471 (2)	0.6219 (1)	5.97 (5)
O(2)	0.2469 (1)	0.1044 (1)	0.33747 (9)	3.36 (3)
N	0.3342 (2)	0.4446 (2)	0.4267 (1)	5.76 (6)
C(1)	0.0850 (2)	0.4304 (2)	0.6100 (2)	3.95 (5)
C(2)	-0.0137 (2)	0.3091 (3)	0.5657 (2)	4.58 (6)
C(3)	0.0488 (2)	0.2109 (2)	0.4799 (2)	3.81 (5)
C(4)	0.1900 (2)	0.1718 (2)	0.5060 (1)	3.19 (5)
C(5)	0.2913 (2)	0.2990 (2)	0.5473 (1)	3.08 (5)
C(6)	0.2280 (2)	0.3972 (2)	0.6377 (1)	3.32 (5)
C(7)	0.3179 (2)	0.5271 (2)	0.6893 (2)	4.09 (5)
C(8)	0.2941 (2)	0.5784 (2)	0.7959 (2)	3.93 (5)
C(9)	0.3578 (3)	0.5007 (3)	0.8585 (2)	5.49 (7)
C(10)	0.3299 (3)	0.5452 (4)	0.9650 (2)	8.4 (1)
C(11)	0.2220 (3)	0.6848 (3)	0.8299 (2)	5.88 (7)
C(12)	0.4310 (3)	0.2550 (2)	0.5775 (2)	4.54 (6)
C(13)	0.3138 (2)	0.3781 (2)	0.4761 (2)	3.58 (5)
C(14)	0.2398 (2)	0.0595 (2)	0.4227 (2)	3.57 (5)
C(15)	0.4890 (2)	-0.0003 (2)	0.2484 (1)	3.26 (5)
C(16)	0.5660 (2)	0.0989 (2)	0.3205 (2)	4.01 (5)
C(17)	0.7055 (2)	0.0963 (2)	0.3340 (2)	4.86 (6)
C(18)	0.7745 (2)	-0.0063 (3)	0.2744 (2)	4.95 (6)
C(19)	0.7027 (2)	-0.1050 (2)	0.2019 (2)	4.60 (6)
C(20)	0.5615 (2)	-0.1029 (2)	0.1894 (2)	3.97 (5)
C(21)	0.2129 (2)	-0.1648 (2)	0.2026 (2)	3.36 (5)
C(22)	0.2669 (2)	-0.2638 (2)	0.2407 (2)	4.24 (5)
C(23)	0.2040 (3)	-0.3933 (2)	0.2251 (2)	5.43 (6)
C(24)	0.0842 (3)	-0.4281 (2)	0.1701 (2)	6.18 (7)
C(25)	0.0267 (3)	-0.3347 (3)	0.1313 (2)	6.40 (8)
C(26)	0.0900 (2)	-0.2037 (2)	0.1468 (2)	5.06 (6)
C(27)	0.2598 (2)	0.1130 (2)	0.1442 (2)	3.73 (5)
C(28)	0.3582 (3)	0.2416 (3)	0.1667 (2)	6.08 (7)
C(29)	0.1137 (3)	0.1607 (3)	0.1519 (2)	5.84 (7)
C(30)	0.2792 (3)	0.0261 (3)	0.0408 (2)	6.61 (8)

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°)

C(1)-O(1)	1.207 (2)	C(8)-C(9)	1.489 (2)
C(1)-C(2)	1.498 (2)	C(8)-C(11)	1.311 (2)
C(1)-C(6)	1.519 (2)	C(9)-C(10)	1.509 (3)
C(2)-C(3)	1.526 (2)	C(13)-N	1.120 (2)
C(3)-C(4)	1.517 (2)	C(14)-O(2)	1.420 (2)
C(4)-C(5)	1.549 (2)	Si-O(2)	1.645 (1)
C(4)-C(14)	1.522 (2)	Si-C(15)	1.877 (2)
C(5)-C(6)	1.571 (2)	Si-C(21)	1.876 (2)
C(5)-C(12)	1.542 (2)	Si-C(27)	1.879 (2)
C(5)-C(13)	1.478 (2)	C(27)-C(28)	1.531 (2)
C(6)-C(7)	1.533 (2)	C(27)-C(29)	1.529 (2)
C(7)-C(8)	1.505 (2)	C(27)-C(30)	1.527 (2)
O(2)-Si-C(15)	107.50 (6)	C(11)-C(6)-C(5)	109.91 (12)
O(2)-Si-C(21)	109.36 (6)	C(11)-C(6)-C(7)	111.92 (13)
O(2)-Si-C(27)	105.32 (6)	C(5)-C(6)-C(7)	115.38 (13)
C(15)-Si-C(21)	108.45 (7)	C(6)-C(7)-C(8)	113.14 (13)
C(15)-Si-C(27)	110.81 (7)	C(7)-C(8)-C(9)	115.61 (15)
C(21)-Si-C(27)	115.11 (7)	C(7)-C(8)-C(11)	121.27 (17)
Si-O(2)-C(14)	124.79 (9)	C(9)-C(8)-C(11)	123.12 (17)
O(1)-C(1)-C(2)	122.40 (16)	C(8)-C(9)-C(10)	116.86 (18)
O(1)-C(1)-C(6)	121.85 (15)	N-C(13)-C(5)	175.75 (17)
C(2)-C(1)-C(6)	115.75 (14)	O(2)-C(14)-C(4)	110.55 (11)
C(1)-C(2)-C(3)	110.29 (13)	Si-C(15)-C(16)	119.72 (12)
C(2)-C(3)-C(4)	112.40 (13)	Si-C(15)-C(20)	123.85 (12)
C(3)-C(4)-C(5)	112.19 (12)	Si-C(21)-C(22)	120.18 (12)
C(3)-C(4)-C(14)	110.51 (12)	Si-C(21)-C(26)	123.65 (13)
C(5)-C(4)-C(14)	115.95 (12)	C(27)-C(28)	109.00 (11)
C(4)-C(5)-C(6)	108.72 (11)	Si-C(27)-C(29)	111.74 (11)
C(4)-C(5)-C(12)	110.43 (12)	Si-C(27)-C(30)	110.14 (12)
C(4)-C(5)-C(13)	111.88 (12)	C(28)-C(27)-C(29)	107.34 (14)
C(6)-C(5)-C(12)	109.95 (12)	C(28)-C(27)-C(30)	108.91 (15)
C(6)-C(5)-C(13)	107.15 (12)	C(29)-C(27)-C(30)	109.64 (15)
C(12)-C(5)-C(13)	108.65 (12)		
C(1)-C(2)-C(3)-C(4)	52.3	C(4)-C(5)-C(6)-C(11)	-54.0
C(2)-C(3)-C(4)-C(5)	-56.6	C(5)-C(6)-C(1)-C(2)	54.7
C(3)-C(4)-C(5)-C(6)	56.5	C(6)-C(1)-C(2)-C(3)	-52.9

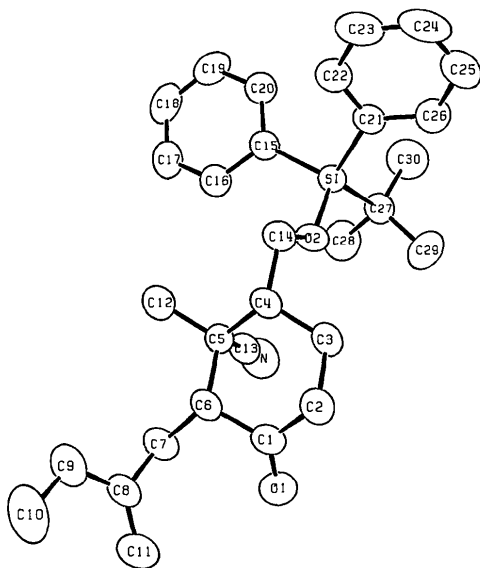


Fig. 1. Molecular structure of (2) with crystallographic numbering scheme.

GOF = 2.0638, $(\Delta/\sigma)_{\max} = 0.02$. Highest peak in final difference Fourier map = $0.34 \text{ e } \text{Å}^{-3}$. Atomic scattering factors of C, N, O, Si and H atoms and f' and f'' values taken from *International Tables for X-ray Crystallography* (1974).*

* Lists of structure factors, r.m.s. amplitudes, anisotropic thermal parameters, H-atom coordinates, and phenyl-ring intramolecular bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39915 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The final atomic parameters are listed in Table 1. Representative bond distances, angles, and torsional angles are listed in Table 2.

The molecular structure of the title compound is shown in Fig. 1 along with the crystallographic numbering scheme. Thus the structure of the compound is unambiguously shown to be isomer (2). All bond lengths and bond angles are fully consistent with literature values. The shortest intermolecular contact was $3.416(2) \text{ Å}$ between O(1) and C(2). There were no others shorter than 3.5 Å .

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erythro-2-Methoxymethyl-2,4-dimethylglutaric Anhydride,* $\text{C}_9\text{H}_{14}\text{O}_4$

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Abstract. $M_r = 186.2$, monoclinic, $P2_1/c$, $a = 6.554(1)$, $b = 7.297(3)$, $c = 20.983(4) \text{ Å}$, $\beta = 95.69(2)^\circ$, $V = 998.6(5) \text{ Å}^3$, $Z = 4$, $D_x = 1.238(6)$, $D_m = 1.229 \text{ Mg m}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.70926 \text{ Å}$, $\mu = 0.10 \text{ mm}^{-1}$, $F(000) = 400$, m.p. 334 K , final $R = 0.064$

* erythro-3-Methoxymethyl-3,5-dimethyl-1-oxacyclohexane-2,6-dione.

for 2227 unique reflexions measured at room temperature. The oxacyclohexane ring has a half-boat conformation with C(4) at the tip. The dihedral angle between the planes of the sp^2 bonds of C(2) and C(6) is $7.9(5)^\circ$. The average distances in the 1-oxacyclohexane-2,6-dione fragment are C=O $1.19(2)$, C—O $1.38(3)$, C(sp^2)—C(sp^3) $1.49(3)$, C(sp^3)—C(sp^3) $1.51(3) \text{ Å}$.