

tendencies, leading to close Cl...Cl contacts, and plays a key role in the packing of the structure. The positions of hydrogen chloride (two per formula unit) in the structure need comment. The two H⁺ that are to be accounted for in this structure are very close to Cl(1). Difference Fourier maps showed an electron density peak of height 0.69 e Å⁻³ indicating a weakly held dimeric (HCl)₂ species with short H—Cl(1) distances of 1.78 (15) and 1.85 (12) Å. Compounds containing hydrochloride of crystallization have been reported previously (Wells, 1979). This placement of H⁺ would also explain the slightly larger Cl—Cl separation of 3.027 (10) Å between the chloride ions in comparison with the 2.956 (10) Å separation between the two chlorines of the (HCl)₂ dimer.

The ptu ligands are planar to within ±0.056 (5) Å. The mean C—S distance in the ptu ligands is 1.72 (2) Å. The pairs C(1)—N(1) and C(1)—N(2) and C(8)—N(3) and C(8)—N(4) are nearly equal. These indicate that the ptu moiety in the complex is present exclusively in thione form with the molecular parameters close to those observed in the structures of free ptu ligand (Form, Raper & Downie, 1976), Te(ptu)₄Cl₂·2HCl (Rout *et al.*, 1984*a*), Te(tu)₂(ptu)₂·Cl₂ (Rout, Seshasayee, Aravamudan & Sowrirajan, 1984*b*) and TeCl₄(ptu)₂·dioxane (Deuten, Schnabel & Klar, 1979). The ligand in all these cases is present exclusively in thione form.

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2,2',3,3',4,4',5,5'-Octakis(trifluoromethylthio)-2,2'-bi-2H-pyrrole, C₁₆F₂₄N₂S₈

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Abstract. $M_r = 932.665$, monoclinic, $P2_1/c$, $a = 0.71 \text{ nm}^{-1}$, $F(000) = 908$, room temperature, $R = 8.285 (5)$, $b = 16.656 (8)$, $c = 11.431 (7) \text{ Å}$, $\beta = 0.077$, 1162 observed reflections. The crystals contain centrosymmetric dimeric molecules, the five-membered rings being joined by a C—C bond of $1.51 (2) \text{ Å}$. $98.86 (5)^\circ$, $V = 1559 (2) \text{ Å}^3$, $Z = 2$, $D_x = 1.987 (2) \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ Å}$, $\mu =$

S—C(*sp*³) is 1.86 (1) Å and the average S—C(*sp*²) distance is 1.76 (2) Å. Intermolecular contacts are normal.

Table 1. Atom coordinates and isotropic temperature factors (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U/U_{eq}</i>
N	-0.0612 (9)	0.4924 (5)	0.3373 (6)	0.052 (2)
C(1)	0.031 (1)	0.4739 (5)	0.4540 (8)	0.043 (2)
C(2)	0.010 (1)	0.3822 (6)	0.4706 (8)	0.049 (3)
C(3)	-0.089 (1)	0.3579 (6)	0.3753 (8)	0.054 (3)
C(4)	-0.127 (1)	0.4261 (7)	0.2963 (8)	0.054 (3)
C(5)	0.276 (2)	0.5074 (9)	0.313 (1)	0.080 (4)
C(6)	0.192 (2)	0.246 (1)	0.547 (2)	0.106 (5)
C(7)	-0.347 (2)	0.2669 (9)	0.400 (1)	0.091 (4)
C(8)	-0.244 (2)	0.5136 (8)	0.098 (1)	0.087 (4)
F(1)	0.2068 (9)	0.5706 (6)	0.2600 (8)	0.140 (4)
F(2)	0.2250 (9)	0.4473 (6)	0.2425 (7)	0.127 (4)
F(3)	0.4385 (9)	0.5153 (5)	0.3131 (7)	0.132 (4)
F(4)	0.213 (1)	0.2472 (4)	0.4392 (8)	0.123 (4)
F(5)	0.319 (1)	0.2276 (6)	0.621 (1)	0.181 (5)
F(6)	0.084 (1)	0.1861 (5)	0.5555 (9)	0.165 (5)
F(7)	-0.4462 (9)	0.3219 (5)	0.3597 (8)	0.124 (4)
F(8)	-0.320 (1)	0.2756 (5)	0.5160 (8)	0.130 (4)
F(9)	-0.422 (1)	0.1965 (5)	0.383 (1)	0.167 (5)
F(10)	-0.3113 (9)	0.5695 (5)	0.1563 (6)	0.104 (3)
F(11)	-0.327 (1)	0.5098 (5)	-0.0116 (6)	0.124 (4)
F(12)	-0.0947 (9)	0.5382 (5)	0.0906 (6)	0.112 (4)
S(1)	0.2520 (3)	0.4944 (2)	0.4615 (3)	0.069 (1)
S(2)	0.1097 (4)	0.3377 (2)	0.5993 (3)	0.080 (1)
S(3)	-0.1638 (4)	0.2602 (2)	0.3364 (3)	0.090 (1)
S(4)	-0.2514 (4)	0.4149 (2)	0.1588 (3)	0.082 (1)

Table 2. Bond distances (Å) and angles (°)

A prime indicates the symmetry transformation $-x, 1-y, 1-z$.

C(1)—C(1')	1.51 (2)	C(8)—S(4)	1.79 (1)
C(1)—N	1.46 (1)	C(5)—F(1)	1.30 (1)
C(1)—C(2)	1.55 (1)	C(5)—F(2)	1.31 (1)
C(2)—C(3)	1.32 (1)	C(5)—F(3)	1.35 (1)
C(3)—C(4)	1.45 (1)	C(6)—F(4)	1.27 (2)
C(4)—N	1.29 (1)	C(6)—F(5)	1.28 (2)
C(1)—S(1)	1.86 (1)	C(6)—F(6)	1.36 (2)
C(2)—S(2)	1.738 (9)	C(7)—F(7)	1.27 (1)
C(3)—S(3)	1.77 (1)	C(7)—F(8)	1.32 (1)
C(4)—S(4)	1.75 (1)	C(7)—F(9)	1.33 (2)
C(5)—S(1)	1.75 (1)	C(8)—F(10)	1.32 (1)
C(6)—S(2)	1.80 (2)	C(8)—F(11)	1.33 (1)
C(7)—S(3)	1.78 (1)	C(8)—F(12)	1.32 (1)
C(1')—C(1)—N	109.3 (7)	S(1)—C(5)—F(3)	105.9 (9)
C(1')—C(1)—C(2)	115.2 (7)	S(2)—C(6)—F(4)	115 (1)
C(1')—C(1)—S(1)	107.3 (6)	S(2)—C(6)—F(5)	108 (1)
C(2)—C(1)—N	105.5 (7)	S(2)—C(6)—F(6)	108 (1)
C(2)—C(1)—S(1)	107.7 (6)	S(3)—C(7)—F(7)	116 (1)
S(1)—C(1)—N	112.0 (6)	S(3)—C(7)—F(8)	113 (1)
C(1)—C(2)—C(3)	105.4 (8)	S(3)—C(7)—F(9)	107 (1)
C(1)—C(2)—S(2)	118.4 (6)	S(4)—C(8)—F(10)	114 (1)
C(3)—C(2)—S(2)	136.2 (8)	S(4)—C(8)—F(11)	106 (1)
C(2)—C(3)—C(4)	108.6 (9)	S(4)—C(8)—F(12)	114 (1)
C(2)—C(3)—S(3)	129.4 (8)	F(1)—C(5)—F(2)	105 (1)
C(4)—C(3)—S(3)	121.9 (7)	F(1)—C(5)—F(3)	107 (1)
C(3)—C(4)—N	114.0 (8)	F(2)—C(5)—F(3)	108 (1)
C(3)—C(4)—S(4)	120.9 (8)	F(4)—C(6)—F(5)	115 (2)
S(4)—C(4)—N	125.1 (8)	F(4)—C(6)—F(6)	105 (1)
C(1)—N—C(4)	106.4 (8)	F(5)—C(6)—F(6)	105 (1)
C(1)—S(1)—C(5)	103.7 (5)	F(7)—C(7)—F(8)	107 (1)
C(2)—S(2)—C(6)	103.6 (6)	F(7)—C(7)—F(9)	109 (1)
C(3)—S(3)—C(7)	97.2 (6)	F(8)—C(7)—F(9)	104 (1)
C(4)—S(4)—C(8)	101.5 (6)	F(10)—C(8)—F(11)	108 (1)
S(1)—C(5)—F(1)	116 (1)	F(10)—C(8)—F(12)	107 (1)
S(1)—C(5)—F(2)	115 (1)	F(11)—C(8)—F(12)	108 (1)

Introduction. An attempt to prepare pyrrole dimers by the reaction of the Ag salt of 2,3,4,5-tetrakis(trifluoromethylthio)pyrrole (Dorn, Eggenberg, Gerstenberger, Haas, Niemann & Zobrist, 1979) yielded a diamagnetic, colorless compound (I) whose solutions turn red and paramagnetic upon long exposure to light. This behavior and the fact that the ¹⁹F NMR spectrum was inconsistent with a 1,1'-bipyrrole prompted this X-ray study.

Experimental. *D_m* not measured. Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo *K*α radiation. Crystal 0.5 × 0.3 × 0.2 mm elongated along [021]. Cell constants refined from 69 Bragg angles (7 < θ < 18°). 3778 reflections (0.5 < θ < 27.4°; *hkl*, $\bar{h}\bar{k}l$) measured with the variable-speed ω-2θ scan technique; 3492 unique but only 1162 with *F_o* > 1.5σ(*F_o*) were deemed observed and used in the refinement. Data corrected for Lp and the 12% decay of the three monitor reflections. Structure solved by multisolution direct methods and refinement on *F* to *R* = 0.077 and *wR* = 0.075 with only S and F atoms assigned anisotropic thermal parameters; weighting scheme *w*⁻¹ = σ²(*F*) + 0.0004*F*² where σ(*F*) = [σ²(*I*) + 0.0004*I*²]^{1/2}/2*FLP*; *S* = 1.99; |Δ/σ|_{max} < 0.2; densities in final difference Fourier synthesis between 0.6 [near S(1)] and -0.4 e Å⁻³. Dispersion-corrected relativistic Hartree-Fock scattering factors (*International Tables for X-ray Crystallography*, 1974) used for all atoms. No correction for absorption or secondary extinction. Computer programs include *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. Atomic parameters are listed in Table 1 while bond lengths and angles are given in Table 2.* The numbering scheme is defined in Fig. 1.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39945 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

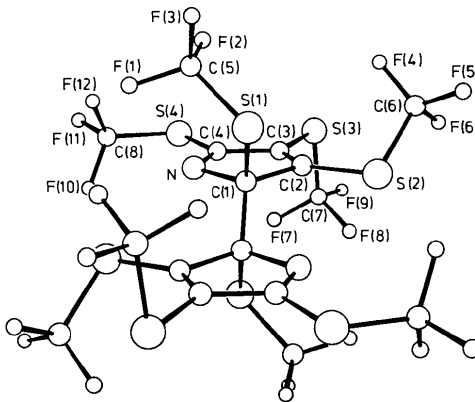


Fig. 1. Perspective drawing of (I) with arbitrary atom sizes.

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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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