Table 3. *Possible hydrogen-bonding and salt-bridging contacts between asymmetric units*

The table lists (*a*) interatomic distances between asymmetric units less than 3·0 Å and (*b*) possible ion/ion electrostatic interactions less than 3·5 Å. The symmetry operators 3 and 4 are $-x, y+\frac{1}{2}, -z$ and $\frac{1}{2}-x, y, \frac{1}{2}-z$, respectively.

Residue *I*		Residue *J*		Distance (Å)	Symmetry
(*a*) Interatomic distances					
Gly15*A*	O	Gln113*A*	Nε2	2·8	3
Asn66*A*	Nδ2	Gln128*A*	Oε2	2·7	3
Gln91*A*	Nε1	Glu148	O	2·8	4
Gly15*B*	O	Gln113*B*	Nε2	2·7	3
Asn66*B*	Nδ2	Gln128*B*	Oε2	2·9	3
Glu148*B*	O	Gln91*A*	Oε1	2·8	4
(*b*) Electrostatic interactions					
Lys16*A*	Nζ	Glu109*A*	Oε1	3·2	3
Glu18*A*	Oε2	Arg31*A*	Nη1	3·4	3
Glu18*A*	Oε2	Arg31*A*	Nη2	3·3	3
Lys63*A*	Nζ	Asp126*A*	Oδ2	3·3	3
Lys16*B*	Nζ	Glu109*B*	Oε2	3·2	3
Glu18*B*	Oε2	Arg31*B*	Nη1	3·2	3

the Patterson maps; (3) there is a paucity of close contacts between the molecules in the pig myoglobin crystal so that there are very few intermolecular vectors contributing to the observed Patterson function.

The manipulation of the gene encoding pig myoglobin for high-level expression of recombinant protein and the determination of an atomic resolution structure from crystals of this material provide a basis for detailed structure–function studies. This work is now being extended in two directions. Firstly, we have introduced a number of amino-acid substitutions into the protein by oligonucleotide-directed mutagenesis to probe the roles of individual side chains in the protein. The properties of the mutant proteins will be examined both kinetically and structurally. Secondly, we are extending the X-ray structural studies to higher resolution for both the wild-type and mutant proteins from which crystals have been grown.

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Structures of Six Terminally Substituted [*n*]Staffanes, *n* = 1–4

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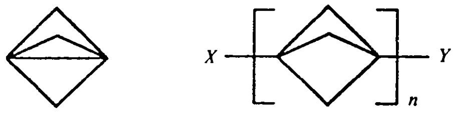
Abstract

1,3-Diacetylbicyclo[1.1.1]pentane (2), $C_9H_{12}O_2$, M_r = 152·19, monoclinic, $C2/m$ (No. 12), a = 11·691 (4), b = 6·624 (4), c = 5·807 (2) Å, β = 112·40 (2)°, V = 415·8 (3) Å^3, D_x = 1·22 g cm^{-3}, Z = 2, Mo $K\alpha$, λ = 0·71073 Å, μ = 0·7912 cm^{-1}, $F(000)$ = 164, T = 163 K, R = 0·0703 for 310 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. Methyl [2]staffane-3-carboxylate (3), $C_{12}H_{16}O_2$, M_r = 192·26, monoclinic, $P2_1/m$ (No. 11), a = 5·793 (2),

$b = 8{\cdot}690\,(3)$, $c = 11{\cdot}111\,(2)$ Å, $\beta = 96{\cdot}13\,(1)°$, $V = 556{\cdot}1\,(3)$ Å^3, $D_x = 1{\cdot}15$ g cm^{-3}, $Z = 2$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}7156$ cm^{-1}, $F(000) = 208$, $T = 163$ K, $R = 0{\cdot}0680$ for 971 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. 3,3′-Dibromo[2]staffane (4), $C_{10}H_{12}Br_2$, $M_r = 292{\cdot}02$, orthorhombic, *Pnma* (No. 62), $a = 22{\cdot}886\,(5)$, $b = 8{\cdot}2075\,(12)$, $c = 5{\cdot}6336\,(10)$ Å, $V = 1058{\cdot}2\,(3)$ Å^3, $D_x = 1{\cdot}83$ g cm^{-3}, $Z = 4$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 75{\cdot}35$ cm^{-1}, $F(000) = 568$, $T = 223$ K, $R = 0{\cdot}0534$ for 960 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. 3,3′-Bis(acetylthio)[2]staffane (5), $C_{14}H_{18}O_2S_2$, $M_r = 282{\cdot}42$, triclinic, $P\bar{1}$ (No. 2), $a = 7{\cdot}418\,(2)$, $b = 10{\cdot}916\,(3)$, $c = 11{\cdot}098\,(3)$ Å, $\alpha = 61{\cdot}09\,(2)$, $\beta = 78{\cdot}39\,(2)$, $\gamma = 78{\cdot}21\,(2)°$, $V = 764{\cdot}5\,(4)$ Å^3, $D_x = 1{\cdot}23$ g cm^{-3}, $Z = 2$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 3{\cdot}261$ cm^{-1}, $F(000) = 300$, $T = 223$ K, $R = 0{\cdot}0700$ for 2314 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. 3,3″-Bis(acetylthio)[3]staffane (6*a*), $C_{19}H_{24}O_2S_2$, $M_r = 348{\cdot}52$, triclinic, $P\bar{1}$ (No. 2), $a = 12{\cdot}017\,(6)$, $b = 13{\cdot}359\,(5)$, $c = 14{\cdot}544\,(5)$ Å, $\alpha = 99{\cdot}56\,(3)$, $\beta = 112{\cdot}85\,(3)$, $\gamma = 106{\cdot}58\,(3)°$, $V = 1958\,(2)$ Å^3, $D_x = 1{\cdot}18$ g cm^{-3}, $Z = 4$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}663$ cm^{-1}, $F(000) = 744$, $T = 298$ K, $R = 0{\cdot}0762$ for 3650 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. 3,3″-Bis(acetylthio)[3]staffane (6*b*), $C_{19}H_{24}O_2S_2$, $M_r = 348{\cdot}52$, orthorhombic, *Fdd*2 (No. 43), $a = 20{\cdot}017\,(3)$, $b = 19{\cdot}283\,(4)$, $c = 9{\cdot}939\,(2)$ Å, $V = 3836\,(1)$ Å^3, $D_x = 1{\cdot}21$ g cm^{-3}, $Z = 8$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}718$ cm^{-1}, $F(000) = 1488$, $T = 298$ K, $R = 0{\cdot}0584$ for 838 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. 3,3‴-Bis(acetylthio)[4]staffane (7), $C_{24}H_{30}O_2S_2$, $M_r = 414{\cdot}62$, triclinic, $P\bar{1}$ (No. 2), $a = 5{\cdot}7153\,(10)$, $b = 11{\cdot}839\,(2)$, $c = 17{\cdot}819\,(3)$ Å, $\alpha = 101{\cdot}780\,(14)$, $\beta = 90{\cdot}556\,(14)$, $\gamma = 102{\cdot}021\,(15)°$, $V = 1152{\cdot}7\,(4)$ Å^3, $D_x = 1{\cdot}19$ g cm^{-3}, $Z = 2$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}361$ cm^{-1}, $F(000) = 444$, $T = 173$ K, $R = 0{\cdot}0900$ for 2733 reflections $\{F_o \geq 4[\sigma(F_o)]\}$. The crystal structures of six terminally substituted [*n*]staffanes [(2)–(7)] are reported. They exhibit a very close nonbonded transannular distance between the bridgehead C atoms, ranging from 1·821 (9) Å in (4) to 1·902 (6) Å in (6*b*), with an average of 1·871 (1) Å. The intercage bridgehead–bridgehead bond length is uncommonly short with an average of about 1·48 (2) Å, shorter by 0·06 Å than normal C_{sp^3}—C_{sp^3} bonds. The high strain of the bicyclo[1.1.1]pentane cage is apparent from the intracage bond angles, which vary from 85·1 (2)° in (6*a*) to 88·8 (2)° in (4) at the bridgehead. The angle at the bridging methylenes ranges from 72·2 (3)° in (4) to 77·5 (3)° in (6*a*). Meshed packing of the bicyclic cages occurs in (6*a*) and (7). For one molecule, 3,3″-bis(acetylthio)[3]staffane (6), two polymorphs are observed.

Introduction

Terminally functionalized oligomers of [1.1.1]-propellane (1), called [*n*]staffanes for short, are of interest as spacers and molecular construction elements, as liquid crystals, and as rigid-rod surfactants (Friedli, Kaszynski, & Michl, 1989; Kaszynski, Friedli & Michl, 1988, 1990; Kaszynski & Michl, 1988; Michl, Kaszynski, Friedli, Murthy, Yang, Robinson, McMurdie & Kim, 1989). We report the crystal structures of six of these compounds [(2)–(7)], with $n = 1$–4.



(1) (2)–(9)

	n	
(2)	1	$X = Y =$ COMe
(3)	2	$X =$ COOMe, $Y =$ H
(4)	2	$X = Y =$ Br
(5)	2	$X = Y =$ SCOMe
(6*a*)	3	$X = Y =$ SCOMe, form I
(6*b*)	3	$X = Y =$ SCOMe, form II
(7)	4	$X = Y =$ SCOMe
(8)	2	$X = Y =$ SMe
(9)	2	$X = Y = SO_2Me$

Preliminary information on the crystal structures of (3) (Kaszynski & Michl, 1988; Michl *et al.*, 1989), (4) (Kaszynski *et al.*, 1990; Michl *et al.*, 1989), (5) (Kaszynski *et al.*, 1990; Michl *et al.*, 1989) and (6*a*) (Friedli *et al.*, 1989; Kaszynski, Friedli & Michl, 1988, 1990; Kaszynski & Michl, 1988; Michl *et al.*, 1989) has appeared, as has a full report (Bunz, Polborn, Wagner & Szeimies, 1988) on (8) and (9). Related structures from our laboratory have also been published elsewhere: [3]- and [4]staffanes (Murthy, Hassenrück, Lynch & Michl, 1989), and 1,4-bis([1]staff-1-yl)cubane (Hassenrück, Murthy, Lynch & Michl, 1990).

X-ray (Clauss, Wilson, Buchanan, Pierpont & Hendrickson, 1983; Irngartinger, Nixdorf & Reimann, 1984; Padwa, Shefter & Alexander, 1968; Potekhin, Maleev, Kurkutova, Struchkov, Surmina, Kozmin & Zefirov, 1987; Potekhin, Maleev, Struchkov, Surmina, Kozmin & Zefirov, 1988) and electron diffraction (Almenningen, Andersen & Nyhus, 1971; Chiang & Bauer, 1970) structures as well as microwave (Cox & Harmony, 1970; McRae, Cohen, Sponsler & Dougherty, 1986) structural information on bicyclo[1.1.1]pentanes ([1]staffanes) have been in the literature for some time, and the chief characteristics of this strained bicyclic skeleton are well established: The C1C2C3 angle is very small (~74°) and the transannular inter-bridgehead separation remarkably short (~1·85 Å). The geometry at the bridgehead C, with a C2C1C4 angle of ~87°, is strikingly similar to that in cubane. The two electron diffraction studies in the parent hydrocarbon disagree as to whether the symmetry is D_{3h}

Table 1. *Data-collection and structure-refinement details*

	(2)	(3)	(4)	(5)	(6*a*)	(6*b*)	(7)
(*a*) Data collection							
Scan rate (° min^{-1})	3–6	3–6	4–8	3–6	4–8	5	3–6
Scan range, ω (°)	1	1	1·5	1	1	1	1·3
Max. decay correction (on I) (%)	NA	3·3	17·8	< 2	4	< 3	3
Check reflections	$\bar{1}\bar{1}1$; $00\bar{1}$	100; 040 $00\bar{4}$; $\bar{1}\bar{2}\bar{1}$	$\bar{2}\bar{3}\bar{2}$; 160 040; $\bar{5}0\bar{2}$	030; $\bar{1}\bar{2}\bar{3}$ $0\bar{3}\bar{3}$; 212	$\bar{4}\bar{1}\bar{4}$; $0\bar{6}0$ $10\bar{3}$; 031	313; $31\bar{3}$ $3\bar{1}3$; $\bar{3}13$	$1\bar{1}3$; $\bar{1}\bar{1}2$ $0\bar{2}\bar{4}$; $02\bar{3}$
2θ max. (°)	50	50	60	60	50	55	60
Reflections measured	765	2735	3488	6044	7985	2463	8280
Unique reflections	398	1367	1633	4467	6901	1161	5300
R_{int}	0·027	0·023	0·034	0·037	0·018	0·058	0·024
Range of h,k,l	0→13 −7→7 −6→6	−1→7 −2→11 −14→14	0→32 0→11 −7→7	−2→10 −15→15 −15→15	−1→15 −16→16 −18→18	−26→26 0→24 0→24	−5→8 −16→16 −26→26
Transmission-factor range	NA	0·9780–0·9881	0·1833–0·2862	NA	0·8774–0·9679	NA	NA
Crystal dimensions (mm)	0·16 × 0·16 × 0·20	0·17 × 0·30 × 0·87	0·24 × 0·30 × 0·67	0·16 × 0·34 × 0·48	0·12 × 0·19 × 0·38	0·20 × 0·38 × 0·50	0·03 × 0·18 × 0·28
(*b*) Structure refinement							
Reflections used	310	971	960	2314	3650	838	2733
Unobserved reflections	88	396	673	2153	3251	323	2567
No. of variables	38	109	91	217	439	116	349
R, wR	0·0703, 0·0703	0·0680, 0·0606	0·0534, 0·0491	0·0700, 0·0662	0·0762, 0·0752	0·0584, 0·0548	0·0900, 0·0805
R_{all}, wR_{all}	0·0876, 0·0711	0·0940, 0·0620	0·107, 0·0584	0·134, 0·0743	0·135, 0·0826	0·0913, 0·0708	0·156, 0·0896
Goodness of fit	2·961	3·699	1·456	1·786	1·940	1·594	1·961
Max. $\lvert\Delta/\sigma\rvert$	< 0·1	< 0·1	< 0·1	< 0·1	< 0·1	< 0·1	0·12
Max. peak (e Å^{-3})	0·66	0·31	1·42	0·48	0·45	0·32	0·84

(Almenningen *et al.*, 1971) or D_3, with twisted CH_2 groups (Chiang & Bauer, 1970). *Ab initio* calculations (Balaji & Michl, 1988, 1989; Jackson & Allen, 1984; Newton & Schulman, 1972; Politzer & Jayasuriya, 1986; Wiberg, 1983; Wiberg & Wendoloski, 1982) generally favor local D_{3h} symmetry. Our interest is in the examination of the higher members of the [*n*]staffane series.

Although we have prepared and individually isolated pure [*n*]staffane derivatives up to $n = 6$ (Friedli *et al.*, 1989; Murthy, Hassenrück, Lynch & Michl, 1989; Kaszynski *et al.*, 1990; Kaszynski & Michl, 1988; Michl *et al.*, 1989), we have so far not succeeded in growing suitable single crystals with *n* larger than 4. Fortunately, already the lower [*n*]staffane derivatives described here provide an excellent idea of the structure of these molecular staffs and some information on their packing in the solid state. The results are also likely to be relevant for the insoluble higher molecular weight poly[1.1.1]-propellane solid, available only in a polydisperse form (Murthy, Hassenrück, Lynch & Michl, 1989; Kaszynski & Michl, 1988; Schlüter, 1989). The straight yet somewhat flexible chain structure and high strain-energy content make this polymer quite unique.

Experimental

Details of data collection and structure refinement for all structures are summarized in Table 1. Data for (2) and (3) were collected at 163 K on a Syntex $P2_1$ diffractometer using a Syntex LT-1 low-temperature device. Data for (4), (5), forms I and II of (6) [(6*a*) and (6*b*)], and (7) were collected on a Nicolet *R*3 diffractometer. Data for (6*a*) and (6*b*) were collected at room temperature, data for (4) and (5) (both at 223 K) and (7) (173 K) were collected using a Nicolet LT-2 low-temperature device. All data were collected using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å) using the ω-scan technique. Except as otherwise noted, non-H atoms were refined with anisotropic thermal parameters. All structures were refined using *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0{\cdot}5kI^{-1/2} \times \{[\sigma(I)]^2 + (0{\cdot}02I)^2\}^{1/2}$. The intensity, I, is given by $(I_{\text{peak}} - I_{\text{background}}) \times$ (scan rate), 0·02 is a factor to downweight intense reflections and to account for instrument instability, and k is the correction for Lp effects, decay and absorption (when applied). $\sigma(I)$ is estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times \text{(scan rate)}]$. The details of the individual structure refinements are described below. Scattering factors for the non-H atoms are from Cromer & Mann (1968) with anomalous-dispersion corrections taken from Cromer & Liberman (1970). The scattering factors for the H atoms are from Stewart, Davidson & Simpson (1965); the linear absorption coefficient was obtained from *International Tables for X-ray Crystallography* (1974). Data reduction for (2) and (3) was performed as described in Riley & Davis (1976). Decay corrections for (2) and (3) were carried out according to Henslee & Davis (1975). Data reduction and decay corrections for (4), (5), (6*a*), (6*b*) and (7) were performed using *SHELXTL-Plus* (Sheldrick, 1987). Thermal ellipsoid plots and space-filling plots were all generated using *SHELXTL-Plus*. The least-squares-planes program was supplied by Cordes (1983), and other computer programs used may be found in reference 11 of Gadol & Davis (1982).

Crystals of (2) grew in clusters of long needles by sublimation. A thermal ellipsoid plot of (2) showing bond lengths and angles is shown in Fig. 1. The data crystal was cut into a colorless block. Lattice parameters were obtained by least-squares refinement of 29 reflections with $14{\cdot}9 < 2\theta < 33{\cdot}0°$. Systematically absent reflections revealed a *C*-centered monoclinic cell consistent with space groups *C*2, *Cm* or *C*2/*m*. Intensity statistics indicated that the structure was centrosymmetric. The structure was solved by direct methods (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) in space group *C*2/*m*, which requires the molecule to lie around a position of 2/*m* symmetry, and therefore to be disordered. The C and O atoms of the acetyl group and the bridgehead atoms of the bicyclo[1.1.1]pentane group lie on a mirror. The methylene C atoms are disordered about four orientations: two where a methylene C atom lies on a mirror (C5, Wyckoff position *i*) and two where a methylene carbon lies on a twofold axis (C7, Wyckoff position *h*). The disordered C atoms were refined with isotropic thermal parameters. Refinement of site-occupancy factors indicated the four orientations should be of equal weight. H atoms were calculated in ideal positions and refined riding on the appropriate C atom with isotropic thermal parameters set to 1·2 × *U* of the C atom. Because the observed disorder could be the result of refinement in artificially high symmetry, refinement was also performed in space groups *C*2 and *Cm*. In both space groups, the fourfold disorder was observed. The *wR* in the *C*2 refinement was 0·0745 and this model could be rejected. The *wR* for *Cm* was 0·0593. Even though Hamilton's test (Hamilton, 1965) indicated that this model is superior to that obtained in *C*2/*m*, down to the 0·5% confidence level, the results of the latter refinement are reported because of the unacceptably wide scatter in bond lengths and angles for chemically equivalent atoms in the *Cm* refined model. For example, the bridgehead C-to-methylene C bond lengths range from 1·38 (2) to 1·68 (2) Å in *Cm* and from 1·52 (1) to 1·58 (1) Å in *C*2/*m*, while the angles between these atoms range from 80 (1) to 95 (1)° in *Cm* and from 87·5 (6) to 88·9 (7)° in *C*2/*m*. Positional and thermal parameters for (2) are listed in Table 2.

Table 2. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms of* $C_9H_{12}O_2$ (2)

For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the *i*th and *j*th direct-space unit-cell vectors. Atoms C5, C6, C7 and C8 were refined with isotropic thermal parameters.

	x	*y*	*z*	*U*
C1	0·3097 (5)	0·0	0·8062 (9)	0·053 (2)
C2	0·2155 (4)	0·0	0·5470 (9)	0·037 (2)
O3	0·2433 (3)	0·0	0·3653 (6)	0·052 (2)
C4	0·0831 (4)	0·0	0·5183 (8)	0·033 (2)
C5	−0·029 (2)	0·0	0·273 (4)	0·034 (6)
C6	0·0156 (13)	0·162 (2)	0·623 (3)	0·032 (4)
C7	0·0	0·180 (3)	0·5	0·043 (7)
C8	−0·027 (2)	−0·099 (3)	0·303 (3)	0·038 (4)

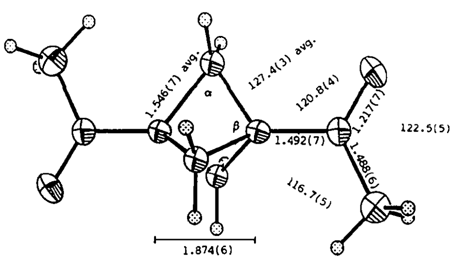


Fig. 1. View of (2) showing one orientation of the molecule. Thermal ellipsoids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown except for the intracage angles: $\alpha = 74{\cdot}2\ (4)°$ avg.; $\beta = 88{\cdot}1\ (4)°$ avg. All indicated cage bond lengths and angles are averages of six values.

Colorless needles of (3) were obtained by sublimation. A thermal ellipsoid plot of (3) with bond lengths and angles is shown in Fig. 2. Lattice parameters were obtained by least-squares refinement of 44 reflections with $22{\cdot}1 < 2\theta < 33{\cdot}8°$. Systematically absent reflections were consistent with space groups $P2_1$ or $P2_1/m$. Intensity statistics indicated the correct space group was $P2_1/m$. The structure was solved by direct methods (Main *et al.*, 1978). The C and O atoms of the methoxycarbonyl group and the bridgehead atoms of the bicyclo[1.1.1]pentane moiety lie on a mirror. The methylene C atoms of both bicyclo[1.1.1]pentane groups were found to be disordered about two orientations. Minor components had refined site-occupancy factors of 30 (2)% for C6*B* and C7*B* and 40 (2)% for C10*B* and C11*B*. C6, C11, C6*B* and C11*B* lie on a mirror. H atoms were

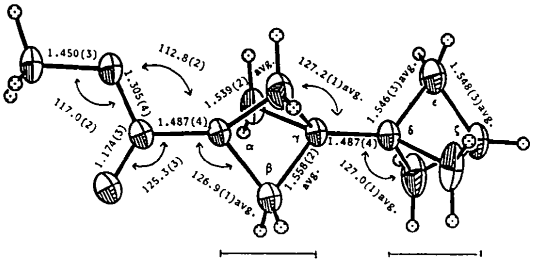


Fig. 2. View of (3) showing the major component of the disordered structure. The methoxycarbonyl group, bridgehead C atoms, and two bridging C atoms lie on a mirror plane. Thermal ellipsoids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown, except for the intracage angles: $\alpha = 87\ (1)°$ avg.; $\beta = 74{\cdot}3\ (1)°$ avg.; $\gamma = 86{\cdot}7\ (1)°$ avg.; $\delta = 86{\cdot}6\ (1)°$ avg.; $\varepsilon = 74{\cdot}5\ (1)°$ avg.; $\zeta = 87{\cdot}1\ (1)°$ avg. All indicated cage bond lengths and angles are averages of six values. The angle between lines drawn through the terminal bridgehead C atoms and the midpoint of the bicyclic core is 178·8 (2)°.

Table 3. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms of* $C_{12}H_{16}O_2$ (3)

For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	U
C1	1·0457 (5)	0·25	−0·2546 (2)	0·0689 (14)
O2	0·9972 (3)	0·25	−0·1292 (2)	0·0599 (8)
C3	0·7794 (5)	0·25	−0·1092 (2)	0·0571 (12)
O4	0·6285 (4)	0·25	−0·1886 (2)	0·151 (2)
C5	0·7485 (5)	0·25	0·0220 (2)	0·0448 (10)
C6	0·5155 (8)	0·25	0·0729 (4)	0·062 (2)
C7	0·8325 (7)	0·1276 (4)	0·1153 (2)	0·0573 (13)
C8	0·7012 (4)	0·25	0·1860 (2)	0·0426 (10)
C9	0·6559 (5)	0·25	0·3146 (2)	0·0463 (10)
C10	0·5152 (11)	0·1282 (6)	0·3746 (4)	0·083 (2)
C11	0·8253 (12)	0·25	0·4268 (5)	0·086 (4)
C12	0·5918 (6)	0·25	0·4761 (3)	0·0648 (13)
C6*B*	0·933 (2)	0·25	0·1369 (8)	0·071 (5)
C7*B*	0·611 (2)	0·1266 (11)	0·0956 (6)	0·067 (3)
C10*B*	0·734 (2)	0·1272 (10)	0·4179 (5)	0·091 (4)
C11*B*	0·423 (2)	0·25	0·3718 (8)	0·091 (6)

calculated in idealized positions and refined riding on the appropriate C atom with isotropic thermal parameters set to $1·2 \times U_{eq}$ of the C atom. Refinement in space group $P2_1$ resulted in the same disordered structure but with slightly more scatter in the C—C bond lengths of the bicyclo[1.1.1]pentane moiety [range 1·43 (3)–1·68 (4) Å in $P2_1$ and 1·434 (9)–1·611 (9) Å in $P2_1/m$]. Positional and thermal parameters are listed in Table 3.

Crystals of (4) grew as colorless blocks by sublimation. A thermal ellipsoid plot of (4) containing bond lengths and angles is shown in Fig. 3. Lattice parameters were obtained by least-squares refinement of 30 reflections with $27·5 < 2\theta < 30·7°$. The systematically absent reflections are consistent with space groups *Pnma* and $Pn2_1a$ (the standard setting is $Pna2_1$, No. 33). The structure was solved by direct methods (*SHELXTL-Plus*, Sheldrick, 1987) The molecule lies on a mirror at $y = \frac{1}{4}$. H-atom positions were obtained from a ΔF map and refined with isotropic thermal parameters. Positional and thermal parameters for (4) are listed in Table 4.

Table 4. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms of* $C_{10}H_{12}Br_2$ (4)

For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	U
Br1	0·55682 (3)	0·25	0·7100 (2)	0·0464 (4)
Br2	0·18381 (3)	0·25	1·2042 (2)	0·0438 (3)
C1	0·4777 (3)	0·25	0·8249 (14)	0·035 (3)
C2	0·4316 (2)	0·3812 (9)	0·7715 (11)	0·036 (2)
C3	0·4581 (3)	0·25	1·088 (2)	0·039 (3)
C4	0·4023 (3)	0·25	0·9311 (13)	0·030 (2)
C5	0·3411 (3)	0·25	1·0145 (13)	0·027 (2)
C6	0·2861 (3)	0·25	0·8530 (14)	0·036 (3)
C7	0·3107 (2)	0·3819 (9)	1·1695 (11)	0·036 (2)
C8	0·2651 (3)	0·25	1·1093 (13)	0·031 (2)

Colorless plates of (5) were obtained by sublimation. A thermal ellipsoid plot of (5) is shown in Fig. 4. Lattice parameters were obtained by least-squares refinement of 26 reflections with $22·4 < 2\theta < 27·5°$. The structure was solved with *SHELXTL-Plus* (Sheldrick, 1987). Methyl-group H atoms were calculated in idealized positions. Other H atoms were obtained from a ΔF map and all were refined with isotropic thermal parameters. Positional and thermal parameters for (5) are listed in Table 5.

Two crystallographic forms of 3,3″-bis(acetylthio)-[3]staffane, (6*a*) and (6*b*), were isolated. (6*a*) grew as thin, colorless plates upon sublimation (393 K) of a sample composed primarily of 3,3″-bis(acetylthio)-[3]staffane. Lattice parameters were obtained by least-squares refinement of 41 reflections with $14·0 < 2\theta < 23·7°$. The structure was solved by direct methods (*SHELXTL-Plus*, Sheldrick, 1987). Crystals of (6*a*) are triclinic, space group $P\bar{1}$ (No. 2), containing two molecules per asymmetric unit. The relative orientation of the acetylthio groups is nearly *anti* in one molecule [referred to as molecule 1 of (6*a*) with atoms labelled C1 through C23] and nearly *syn* in the other (molecule 2). A stereoview thermal ellipsoid

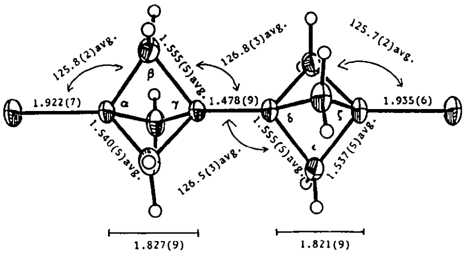


Fig. 3. View of (4) showing one orientation of the molecule. Thermal ellipsoids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown, except for the intracage angles: α = 72·3 (2)° avg.; β = 89·2 (2)° avg.; γ = 88·3 (2)° avg.; δ = 88·0 (2)° avg.; ε = 73·1 (2)° avg.; ζ = 89·6 (2)° avg. All indicated cage bond lengths and angles are averages of three values. The angle between the axes drawn through the terminal Br atoms and the midpoint of the bicyclic core is 177·6 (2)°.

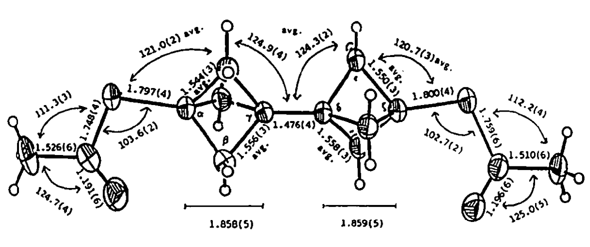


Fig. 4. View of (5) showing one orientation of the molecule. Thermal ellipsoids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown, except for the intracage angles: α = 88·2 (2)° avg.; β = 73·5 (1)° avg.; γ = 87·6 (2)° avg.; δ = 87·6 (2)° avg.; ε = 73·7 (1)° avg.; ζ = 88·2 (2)° avg. All indicated cage bond lengths and angles are averages of six values. The angle between the axes drawn through the S atoms and the midpoint of the bicyclic core is 170·94 (9)°.

Table 5. *Fractional coordinates and equivalent isotropic thermal parameters* ($\AA^2$) *for the non-*H *atoms of* $C_{14}H_{18}O_2S_2$ (5)

For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the *i*th and *j*th direct-space unit-cell vectors.

	x	*y*	*z*	*U*
C1	0·4630 (7)	0·3571 (7)	0·1897 (5)	0·090 (3)
C2	0·2784 (6)	0·3571 (5)	0·2802 (4)	0·068 (2)
O3	0·1682 (5)	0·4587 (4)	0·2617 (3)	0·108 (2)
S4	0·24647 (14)	0·18753 (10)	0·41291 (11)	0·0608 (5)
C5	0·0213 (5)	0·2119 (4)	0·5010 (4)	0·047 (2)
C6	−0·0610 (6)	0·3207 (4)	0·5554 (5)	0·050 (2)
C7	−0·0458 (5)	0·0957 (4)	0·6436 (4)	0·050 (2)
C8	−0·1708 (5)	0·2294 (5)	0·4557 (4)	0·052 (2)
C9	−0·2080 (5)	0·2182 (3)	0·6043 (3)	0·041 (2)
C10	−0·3883 (5)	0·2144 (3)	0·6906 (3)	0·043 (2)
C11	−0·5674 (5)	0·3225 (4)	0·6569 (4)	0·051 (2)
C12	−0·4218 (5)	0·2021 (5)	0·8394 (4)	0·051 (2)
C13	−0·5148 (6)	0·0962 (4)	0·7475 (5)	0·053 (2)
C14	−0·6127 (5)	0·2009 (4)	0·8041 (4)	0·049 (2)
S15	−0·83205 (14)	0·17202 (11)	0·91209 (11)	0·0588 (5)
C16	−0·8688 (6)	0·3063 (4)	0·9622 (4)	0·059 (2)
O17	−0·7627 (4)	0·3905 (4)	0·9242 (4)	0·090 (2)
C18	−1·0469 (6)	0·3009 (5)	1·0578 (5)	0·076 (3)

plot of molecule 1 of (6*a*) is shown in Fig. 5. Table 6 details bond lengths and angles for molecules 1 and 2 of (6*a*). The methylene C atoms of the terminal bicyclo[1.1.1]pentane moieties of molecule 1 were disordered about two principal orientations which are differentiated in the atom list (Table 6) by the label *A* by the appropriate C atom. Site-occupancy factors refined to 76 (1)% for C6, C7 and C8, and 65·3 (9)% for C16, C17 and C18. These atoms were refined with isotropic thermal parameters. All H atoms were calculated in idealized positions and refined riding on the appropriate C atom. The methylene H atoms of molecule 1 had *U*'s set to 1·2 × *U* of the C atom; other H-atom *U*'s were free. Positional and thermal parameters for (6*a*) are listed in Table 7.

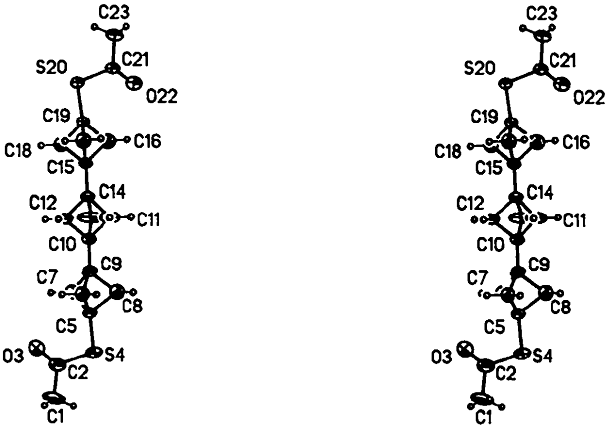


Fig. 5. Stereoview of (6*a*) showing the atom-labelling scheme for the major component of molecule 1. Thermal ellipsoids are scaled to the 30% probability level. The angle between the axes containing the terminal S atoms and the midpoint of the tricyclic core is 177·8 (1)° in molecule 1 and 178·7 (1)° in molecule 2.

Table 6. *Bond lengths* (Å) *and angles* (°) *for the non-*H *atoms of* $C_{19}H_{24}O_2S_2$ (6*a*)

1	2	3	1—2	1—2—3
C2	C1		1·495 (13)	
O3	C2	S4	1·189 (7)	122·1 (7)
O3	C2	C1		122·9 (8)
S4	C2	C1	1·730 (8)	115·0 (5)
C5	S4	C2	1·783 (5)	103·2 (3)
C6	C5	C7	1·506 (9)	89·5 (5)
C6	C5	C8		87·5 (6)
C6	C5	S4		127·6 (6)
C7	C5	C8	1·534 (11)	87·0 (6)
C7	C5	S4		130·0 (5)
C8	C5	S4	1·564 (11)	121·9 (3)
C6*A*	C5	C7*A*	1·57 (2)	95·5 (13)
C6*A*	C5	C8*A*		82·1 (12)
C6*A*	C5	S4		130·0 (10)
C7*A*	C5	C8*A*	1·40 (4)	83·(2)
C7*A*	C5	S4		128·0 (9)
C8*A*	C5	S4	1·66 (3)	121·5 (9)
C9	C5	S4	1·869 (7)	175·5 (4)
C9	C6	C5	1·539 (12)	75·7 (5)
C9	C7	C5	1·555 (10)	74·5 (5)
C9	C8	C5	1·576 (7)	73·0 (4)
C10	C9	C6*A*	1·465 (7)	125·6 (7)
C10	C9	C7*A*		133·0 (14)
C10	C9	C8*A*		123·8 (12)
C10	C9	C6		127·9 (5)
C10	C9	C7		127·9 (6)
C10	C9	C8		127·5 (5)
C10	C9	C5		179·1 (5)
C6*A*	C9	C7*A*	1·57 (3)	93·(2)
C6*A*	C9	C8*A*		83·4 (14)
C7*A*	C9	C8*A*	1·48 (2)	82·(2)
C8*A*	C9		1·63 (3)	
C6	C9	C7		87·5 (6)
C6	C9	C8		85·9 (5)
C7	C9	C8		85·8 (5)
C11	C10	C12	1·525 (11)	85·8 (4)
C11	C10	C13		84·3 (6)
C11	C10	C9		128·3 (5)
C12	C10	C13	1·503 (6)	84·8 (5)
C12	C10	C9		128·4 (5)
C13	C10	C9	1·515 (12)	129·5 (5)
C14	C10	C9	1·893 (7)	179·2 (5)
C14	C11	C10	1·514 (9)	77·1 (5)
C14	C12	C10	1·511 (10)	77·8 (4)
C14	C13	C10	1·515 (8)	77·3 (5)
C15	C14	C11	1·468 (7)	129·6 (6)
C15	C14	C12		127·6 (4)
C15	C14	C13		128·9 (6)
C15	C14	C10		178·3 (4)
C11	C14	C12		85·9 (5)
C11	C14	C13		84·7 (5)
C12	C14	C13		84·6 (6)
C16	C15	C17	1·520 (12)	85·5 (6)
C16	C15	C18		88·2 (6)
C16	C15	C14		128·3 (4)
C17	C15	C18	1·557 (10)	86·2 (5)
C17	C15	C14		128·3 (7)
C18	C15	C14	1·536 (10)	126·3 (6)
C16*A*	C15	C17*A*	1·58 (2)	84·8 (8)
C16*A*	C15	C18*A*		87·9 (11)
C16*A*	C15	C14		129·8 (7)
C17*A*	C15	C18*A*	1·620 (12)	82·8 (9)
C17*A*	C15	C14		127·2 (8)
C18*A*	C15	C14	1·54 (2)	128·5 (7)
C19	C15	C14	1·881 (7)	179·2 (5)
C19	C16	C15	1·518 (8)	76·5 (5)
C19	C17	C15	1·546 (14)	74·6 (6)
C19	C18	C15	1·558 (12)	74·9 (5)
S20	C19	C16*A*	1·781 (5)	129·1 (8)
S20	C19	C17*A*		120·3 (5)
S20	C19	C18*A*		127·6 (9)
S20	C19	C16		132·5 (6)
S20	C19	C17		126·7 (5)
S20	C19	C18		123·8 (4)
S20	C19	C15		175·2 (4)
C16*A*	C19	C17*A*	1·51 (2)	88·9 (11)
C16*A*	C19	C18*A*		92·2 (9)
C17*A*	C19	C18*A*	1·57 (2)	85·8 (11)
C18*A*	C19		1·50 (2)	
C16	C19	C17		86·0 (6)
C16	C19	C18		87·5 (5)
C17	C19	C18		85·8 (6)
C21	S20	C19	1·714 (7)	104·3 (3)
O22	C21	C23	1·180 (7)	122·3 (7)

Table 6 (*cont.*)

1	2	3	1—2	1—2—3
O22	C21	S20		121·8 (6)
C23	C21	S20	1·485 (10)	115·8 (4)
C25	C24		1·508 (10)	
O26	C25	S27	1·192 (9)	123·3 (5)
O26	C25	C24		123·8 (7)
S27	C25	C24	1·745 (8)	112·9 (6)
C28	S27	C25	1·785 (6)	103·6 (3)
C29	C28	C30	1·539 (10)	88·1 (4)
C29	C28	C31		88·1 (5)
C29	C28	S27		121·1 (4)
C30	C28	C31	1·541 (6)	88·7 (4)
C30	C28	S27		128·9 (4)
C31	C28	S27	1·536 (11)	129·1 (4)
C32	C28	S27	1·866 (8)	174·6 (4)
C32	C29	C28	1·562 (8)	74·0 (4)
C32	C30	C28	1·555 (8)	74·1 (3)
C32	C31	C28	1·567 (8)	74·0 (5)
C33	C32	C29	1·464 (7)	128·0 (6)
C33	C32	C30		125·9 (3)
C33	C32	C31		128·8 (6)
C33	C32	C28		178·5 (4)
C29	C32	C30		86·8 (5)
C29	C32	C31		86·2 (5)
C30	C32	C31		87·1 (5)
C34	C33	C35	1·538 (8)	86·7 (5)
C34	C33	C36		86·8 (4)
C34	C33	C32		126·2 (5)
C35	C33	C36	1·550 (8)	87·0 (5)
C35	C33	C32		129·9 (3)
C36	C33	C32	1·553 (8)	126·3 (6)
C37	C33	C32	1·887 (7)	177·3 (4)
C37	C34	C33	1·541 (9)	75·6 (4)
C37	C35	C33	1·559 (6)	74·7 (3)
C37	C36	C33	1·550 (11)	74·9 (4)
C38	C37	C34	1·476 (7)	126·9 (5)
C38	C37	C35		127·3 (5)
C38	C37	C36		128·6 (5)
C38	C37	C33		178·7 (5)
C34	C37	C35		86·3 (4)
C34	C37	C36		86·8 (5)
C35	C37	C36		86·8 (4)
C39	C38	C40	1·563 (10)	87·1 (4)
C39	C38	C41		86·6 (5)
C39	C38	C37		127·5 (5)
C40	C38	C41	1·557 (6)	87·4 (4)
C40	C38	C37		128·7 (5)
C41	C38	C37	1·546 (11)	125·7 (5)
C42	C38	C37	1·864 (7)	178·4 (5)
C42	C39	C38	1·547 (9)	73·6 (4)
C42	C40	C38	1·537 (9)	74·1 (3)
C42	C41	C38	1·540 (8)	74·3 (5)
S43	C42	C39	1·792 (6)	121·0 (5)
S43	C42	C40		129·4 (3)
S43	C42	C41		129·2 (5)
S43	C42	C38		174·5 (4)
C39	C42	C40		88·4 (5)
C39	C42	C41		87·3 (4)
C40	C42	C41		88·3 (5)
C44	S43	C42	1·766 (8)	102·8 (3)
O45	C44	C46	1·181 (10)	123·2 (8)
O45	C44	S43		123·4 (6)
C46	C44	S43	1·511 (12)	113·4 (6)

Table 7. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms of* (6*a*) ($C_{19}H_{24}O_2S_2$): *molecule* 1 (C1–C23) *and molecule* 2 (C24–C46)

For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the *i*th and *j*th direct-space unit-cell vectors. Methylene C atoms of the terminal staffanes of molecules 1 were refined using isotropic thermal parameters. These atoms are C6, C7, C8, C6*A*, C7*A*, C8*A*, C16, C17, C18, C16*A*, C17*A* and C18*A*

	x	*y*	*z*	*U*
C1	0·0215 (9)	0·8157 (9)	−0·0520 (7)	0·123 (7)
C2	0·1302 (7)	0·7931 (6)	0·0241 (5)	0·084 (4)
O3	0·2364 (6)	0·8621 (4)	0·0801 (5)	0·161 (4)
S4	0·0886 (2)	0·65942 (14)	0·02832 (13)	0·0861 (9)
C5	0·2366 (5)	0·6620 (4)	0·1266 (4)	0·058 (3)
C6	0·2958 (8)	0·7120 (7)	0·2438 (5)	0·059 (2)
C7	0·3743 (7)	0·6982 (7)	0·1352 (5)	0·063 (2)
C8	0·2530 (7)	0·5545 (6)	0·1469 (6)	0·069 (2)
C6*A*	0·345 (2)	0·756 (2)	0·230 (2)	0·048 (6)
C7*A*	0·320 (3)	0·612 (2)	0·113 (2)	0·073 (7)
C8*A*	0·236 (2)	0·591 (2)	0·210 (2)	0·083 (8)
C9	0·3840 (5)	0·6537 (4)	0·2291 (4)	0·051 (3)
C10	0·4999 (5)	0·6487 (4)	0·3105 (4)	0·049 (3)
C11	0·5067 (6)	0·5880 (7)	0·3913 (6)	0·124 (5)
C12	0·6175 (6)	0·7418 (5)	0·3994 (5)	0·132 (4)
C13	0·5987 (7)	0·6047 (7)	0·2994 (5)	0·130 (6)
C14	0·6489 (5)	0·6428 (4)	0·4174 (4)	0·051 (3)
C15	0·7665 (5)	0·6416 (4)	0·5007 (4)	0·048 (3)
C16	0·8054 (9)	0·5443 (7)	0·5142 (7)	0·071 (3)
C17	0·8124 (9)	0·6744 (8)	0·6212 (6)	0·068 (3)
C18	0·9089 (8)	0·7093 (7)	0·5290 (7)	0·061 (2)
C16*A*	0·7816 (14)	0·5921 (14)	0·5945 (12)	0·056 (4)
C17*A*	0·8945 (15)	0·7470 (13)	0·5889 (13)	0·061 (4)
C18*A*	0·8700 (15)	0·601 (2)	0·4898 (11)	0·071 (5)
C19	0·9184 (5)	0·6403 (4)	0·6062 (4)	0·054 (3)
S20	1·06887 (15)	0·65084 (13)	0·70725 (13)	0·0869 (9)
C21	1·0363 (6)	0·5226 (5)	0·7219 (5)	0·079 (4)
O22	0·9330 (6)	0·4504 (5)	0·6695 (5)	0·191 (4)
C23	1·1472 (7)	0·5077 (7)	0·8026 (6)	0·092 (4)
C24	−0·6676 (8)	1·3580 (6)	−1·0559 (5)	0·085 (5)
C25	−0·5885 (7)	1·3282 (5)	−0·9633 (4)	0·064 (3)
O26	−0·4735 (5)	1·3517 (4)	−0·9282 (4)	0·102 (3)
S27	−0·68360 (14)	1·25347 (14)	−0·91386 (12)	0·0731 (9)
C28	−0·5702 (5)	1·2204 (4)	−0·8138 (4)	0·052 (3)
C29	−0·6137 (6)	1·1545 (6)	−0·7480 (5)	0·075 (4)
C30	−0·4483 (6)	1·2985 (5)	−0·7112 (4)	0·067 (3)
C31	−0·4944 (7)	1·1477 (5)	−0·8243 (4)	0·069 (4)
C32	−0·4644 (5)	1·1801 (4)	−0·7061 (4)	0·047 (3)
C33	−0·3797 (5)	1·1515 (4)	−0·6198 (3)	0·047 (3)
C34	−0·2313 (5)	1·1839 (5)	−0·5773 (5)	0·065 (3)
C35	−0·3863 (6)	1·0371 (4)	−0·6080 (4)	0·065 (3)
C36	−0·3523 (6)	1·1878 (5)	−0·5035 (4)	0·064 (4)
C37	−0·2656 (5)	1·1218 (4)	−0·5055 (3)	0·046 (3)
C38	−0·1748 (5)	1·0981 (4)	−0·4174 (4)	0·048 (3)
C39	−0·2088 (6)	1·0319 (6)	−0·3463 (5)	0·068 (4)
C40	−0·0514 (6)	1·1804 (5)	−0·3156 (4)	0·068 (3)
C41	−0·0926 (7)	1·0299 (5)	−0·4257 (4)	0·067 (4)
C42	−0·0602 (5)	1·0650 (4)	−0·3089 (4)	0·053 (3)
S43	0·0367 (2)	1·02589 (14)	−0·20341 (11)	0·0747 (9)
C44	0·1846 (6)	1·0552 (5)	−0·2118 (5)	0·077 (4)
O45	0·2062 (5)	1·0982 (5)	−0·2711 (4)	0·123 (4)
C46	0·2796 (8)	1·0170 (8)	−0·1378 (6)	0·104 (5)

Crystals of (6*b*) grew as colorless prisms by sublimation of a sample composed primarily of 3,3‴-bis(acetylthio)[4]staffane, *i.e.* under sublimation conditions 50 K higher than the 393 K normally needed for (6*a*). A thermal ellipsoid plot containing bond-length and bond-angle information is given in Fig. 6. Crystals of (6*b*) are orthorhombic, space group *Fdd*2. Lattice parameters were obtained by least-squares refinement of 50 reflections with 20·6 < 2θ < 27·5°. The structure was solved by direct methods (*SHELXTL-Plus*, Sheldrick, 1987). The molecule lies perpendicular to a crystallographic twofold axis which passes through the molecule at C11. The *z* coordinate of S4 was fixed to define the origin along the twofold axis. The H atoms were obtained from a ΔF map and refined with isotropic thermal parameters. Positional and thermal parameters for (6*b*) are listed in Table 8.

Colorless plates of (7) were grown by sublimation. Crystals of (7) are triclinic, space group $P\bar{1}$. Lattice parameters were obtained by least-squares refinement of 50 reflections with 16·1 < 2θ < 27·9°. There are two crystallographically independent molecules per asymmetric unit. However, each independent molecule lies around an inversion center. Molecule 1 (Fig. 7) lies around an inversion center at 0·5, 0·5, 0·5 while molecule 2 (Fig. 8) lies around an inversion center at 1, 0, 0·5. The structure was solved by direct methods (*SHELXTL-Plus*, Sheldrick, 1987). The methyl H atoms were calculated in idealized positions while all other H atoms were obtained from a ΔF map. All H atoms were refined with isotropic thermal parameters. Positional and thermal parameters for (7) are listed in Table 9.*

Table 8. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms of* $C_{19}H_{24}O_2S_2$ (6*b*)

For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	U
C1	0·4119 (3)	−0·0326 (5)	0·3884 (13)	0·111 (4)
C2	0·3370 (3)	−0·0358 (4)	0·4080 (7)	0·069 (2)
O3	0·3066 (2)	−0·0856 (3)	0·4428 (6)	0·102 (2)
S4	0·29957 (6)	0·04441 (7)	0·36765	0·0649 (5)
C5	0·2124 (2)	0·0257 (2)	0·3762 (7)	0·046 (2)
C6	0·1671 (3)	0·0151 (4)	0·4979 (7)	0·066 (2)
C7	0·1732 (2)	−0·0319 (3)	0·3038 (7)	0·062 (2)
C8	0·1602 (2)	0·0773 (3)	0·3214 (8)	0·063 (2)
C9	0·1202 (2)	0·0134 (2)	0·3763 (6)	0·046 (2)
C10	0·0473 (2)	0·0048 (2)	0·3749 (7)	0·0473 (15)
C11	0·0	0·0	0·2504 (8)	0·054 (3)
C12	−0·0055 (2)	0·0547 (3)	0·4362 (7)	0·064 (2)

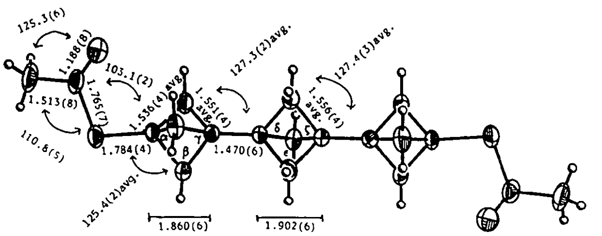


Fig. 6. View of (6*b*) showing one orientation of the molecule. Thermal elliposids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown, except for the intracage angles: α = 87·9 (2)° avg.; β = 74·2 (2)° avg.; γ = 86·9 (2)° avg.; δ = 86·4 (2)° avg.; ε = 75·4 (3)° avg. All indicated values are averages of three values. The angle between lines drawn through the terminal S atoms and the midpoint of the tricyclic core is 178·6 (1)°.

Results

The results for the molecular structures of (2)–(5) are presented in Figs. 1–4, respectively. The results for the two crystalline modifications of 3,3″-bis(acetylthio)[3]staffane, (6*a*) and (6*b*), are shown in Figs. 5 and 6; the results for (7) are in Figs. 7 and 8. Full data for average intracage and intercage bond lengths and angles are collected in Tables 10(*a*) and 10(*b*), respectively. Because of the many similarities between the bicyclic cages of the six structures, they are discussed jointly. Molecular-packing diagrams for (6*a*) are shown in Figs. 9 and 10, emphasizing the gear-like meshing and the typical six-nearest-neighbor arrangement, respectively.

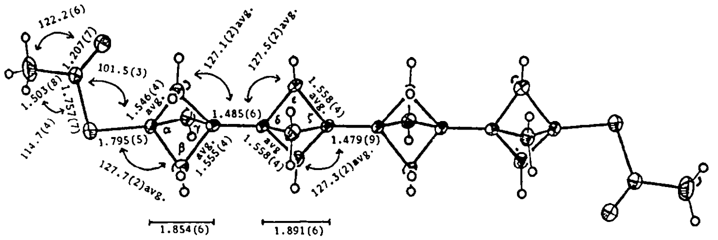


Fig. 7. View of (7) showing one orientation of molecule 1. Thermal ellipsoids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown, except for the intracage angles: α = 87·9 (3)° avg.; β = 73·9 (2)° avg.; γ = 87·1 (2)° avg.; δ = 86·6 (2)° avg.; ε = 75·1 (2)° avg.; ζ = 86·9 (2)° avg. All indicated cage bond lengths and angles are averages of three values. The angle between lines drawn through the S atoms and the midpoint of the molecule is 180° by symmetry.

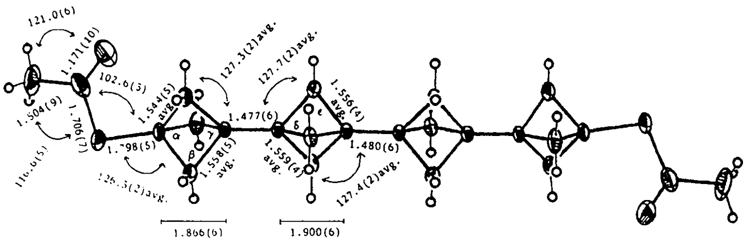


Fig. 8. View of (7) showing one orientation of molecule 2. Thermal ellipsoids are scaled to the 30% probability level. Bond lengths (Å) and angles (°) are shown, except for the intracage angles: α = 88·4 (2)° avg.; β = 73·5 (2)° avg.; γ = 87·5 (2)° avg.; δ = 87·0 (2)° avg.; ε = 74·7 (2)° avg.; ζ = 87·1 (2)° avg. All indicated cage bond lengths and angles are averages of three values. The angle between lines drawn through the S atoms and the midpoint of the molecule is 180° by symmetry.

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* Tables of anisotropic thermal parameters, H-atom positions and thermal parameters, bond distances and angles, torsion angles for the non-H atoms, least-squares-planes data, structure-factor amplitudes, figures showing single views, and unit-cell packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52563 (237 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 9. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for non-*H *atoms of* (7) ($C_{24}H_{30}O_2S_2$): *molecule* 1 (C1–C14) *and molecule* 2 (C15–C28)

For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* \times \mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	U
C1	0·291 (2)	1·1038 (6)	0·9582 (4)	0·101 (4)
C2	0·3475 (14)	1·0142 (6)	0·8920 (4)	0·069 (3)
O3	0·4942 (14)	1·0414 (4)	0·8498 (4)	0·166 (4)
S4	0·1862 (3)	0·8729 (2)	0·88169 (9)	0·0635 (7)
C5	0·2882 (9)	0·7990 (5)	0·7938 (3)	0·035 (2)
C6	0·2408 (13)	0·8130 (6)	0·7116 (3)	0·047 (3)
C7	0·1981 (12)	0·6643 (5)	0·7642 (3)	0·044 (2)
C8	0·5418 (10)	0·7823 (6)	0·7718 (3)	0·042 (2)
C9	0·3680 (8)	0·7086 (4)	0·7030 (2)	0·027 (2)
C10	0·4205 (8)	0·6338 (4)	0·6309 (2)	0·026 (2)
C11	0·2332 (10)	0·5583 (6)	0·5668 (3)	0·036 (2)
C12	0·5438 (11)	0·5259 (5)	0·6196 (3)	0·034 (2)
C13	0·5751 (11)	0·6729 (5)	0·5648 (3)	0·035 (2)
C14	0·4788 (8)	0·5378 (4)	0·5367 (2)	0·025 (2)
C15	0·6749 (13)	0·6002 (5)	0·9373 (3)	0·075 (3)
C16	0·7045 (10)	0·5055 (5)	0·8699 (3)	0·040 (2)
O17	0·6346 (7)	0·5042 (3)	0·8055 (2)	0·055 (2)
S18	0·8547 (3)	0·40029 (14)	0·89212 (8)	0·0508 (7)
C19	0·8765 (9)	0·3127 (4)	0·7986 (3)	0·032 (2)
C20	1·0189 (11)	0·3514 (5)	0·7312 (3)	0·034 (2)
C21	0·9943 (12)	0·2051 (6)	0·7871 (3)	0·040 (2)
C22	0·6748 (9)	0·2388 (5)	0·7393 (3)	0·035 (2)
C23	0·9134 (8)	0·2169 (4)	0·7052 (3)	0·027 (2)
C24	0·9447 (8)	0·1382 (4)	0·6314 (3)	0·028 (2)
C25	1·1835 (10)	0·1114 (6)	0·5984 (3)	0·036 (2)
C26	0·8758 (11)	0·1515 (5)	0·5489 (3)	0·034 (2)
C27	0·8354 (11)	0·0041 (5)	0·6044 (3)	0·034 (2)
C28	0·9849 (8)	0·0393 (4)	0·5368 (3)	0·027 (2)

Discussion

The bicyclo[1.1.1]*pentane ring systems*

The basic structural unit of [*n*]staffanes remains nearly constant in all of the environments examined (Table 10*a*). The most remarkable feature is the short non-bonded distance between the two bridgehead C atoms, about 1·87 Å. In (4), with electronegative atoms in the bridgehead positions, this distance is shortened further to 1·83 Å, probably the shortest non-bonded C—C distance known. The effect of substituents on bicyclo[1.1.1]pentane is known from experiments (Potekhin *et al.*, 1987, 1988) and calculations (Wiberg, 1985) for several examples of electron donors and acceptors. This effect can be readily understood in terms of Bent's rules (Bent, 1961): in the case of (4), the orbital used by C in the C—Br bond has an increased *p* character, forcing the three bridgehead C—C bonds to be more nearly coplanar. The non-bonded distances in the central cages of [*n*]staffanes are somewhat longer than in bicyclo[1.1.1]pentanes, with an average of 1·89 (3) Å.

We have not been able to resolve the controversy (Almenningen *et al.*, 1971; Chiang & Bauer, 1970) surrounding the exact positions of the H atoms.

Molecular architecture

The sequential arrangement of the bicyclo[1.1.1]pentane cages produces nearly linear structures (Table 10*b*) with a length increment of 3 1/3 Å. Deviations from strict linearity are small and attributable to the need to accommodate the terminal substituents in the crystal lattice. This is especially noticeable in the acetylthio series [(5)–(7)].

The remarkably short intercage C—C bonds, 1·47–1·48 Å, also follow Bent's rules (Bent, 1961) and reflect the state of hybridization (Della, Cotsaris, Hine & Pigou, 1981; Maksić, Klasinc & Randić, 1966; Newton & Schulman, 1972) of the bridgehead C atoms. The three 127° intercage CCC valence angles are best accommodated by the use of valence orbitals with a high degree of *p* character for the endocyclic bonds, leaving an unusually high degree of *s* character for the exocyclic valence orbital. As a result, one expects a shortened exocyclic C—C bond with a stretching force constant higher and a bending force constant lower than usual, and similar properties for the bridgehead C—H bond. This explanation

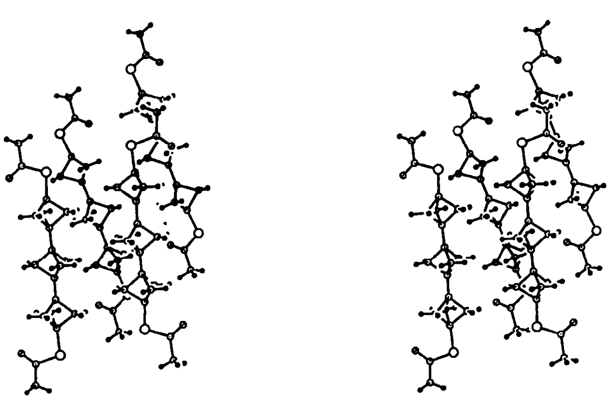


Fig. 9. Stereoview of (6*a*) illustrating close packing within pairs of molecule 1 and also pairs of molecule 2.

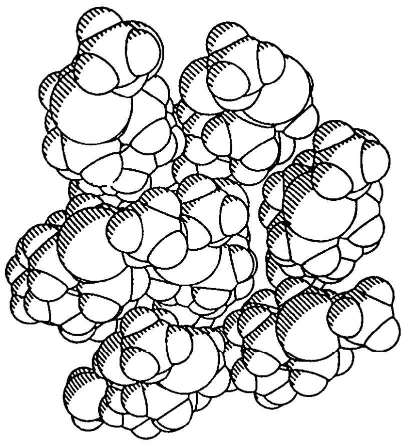
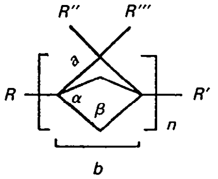


Fig. 10. Space-filling drawing looking down the long axis of (6*a*). The six-nearest-neighbor hexagonal packing forms a helical arrangement of molecules 1 and 2 with interlocking of bicyclic cages between like members of pairs.

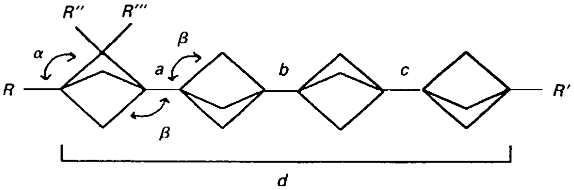
Table 10. *Bond lengths* (Å) *and angles* (°) *of* [*n*]*staffane derivatives*

(*a*) Intracage bond lengths and angles



R	*R'*	*R''*	*R'''*	Form	*n*	Cage No.[a]	α (°)[b]	β (°)[c]	*a* (Å)[b]	*b* (Å)	Ref.
SAc	SAc	H	H	Mol. 1	4	1,4	87·4 (2)	73·9 (2)	1·550 (3)	1·865 (6)	1
						2,3	86·7 (2)	75·1 (2)	1·558 (3)	1·899 (6)	
SAc	SAc	H	H	Mol. 2	4	1,4	88·0 (2)	73·4 (2)	1·549 (3)	1·854 (6)	1
						2,3	87·0 (2)	74·7 (2)	1·558 (3)	1·891 (6)	
H	H	H	H		4	1,4	86·9 (2)	74·8 (2)	1·552 (3)	1·886 (9)	2
						2,3	87·0 (1)	74·7 (2)	1·555 (3)	1·888 (6)	
SAc	SAc	H	H	(I)	3	1	86·3 (1)[d]	74·2 (3)[b]	1·551 (1)[d]	1·869 (7)	1
				Mol. 1		2	85·1 (2)[d]	77·5 (3)[b]	1·511 (4)[d]	1·893 (7)	
				anti		3	86·9 (2)[d]	75·4 (3)[b]	1·540 (1)[d]	1·881 (7)	
SAc	SAc	H	H	(I)	3	1	87·6 (2)	74·0 (2)	1·551 (3)	1·864 (7)	1
				Mol. 2		2	86·7 (2)	75·0 (2)	1·550 (3)	1·887 (7)	
				syn		3	87·5 (2)	74·0 (2)	1·549 (3)	1·866 (8)	
SAc	SAc	H	H	(II)	3	1,3	87·4 (1)	74·2 (2)	1·544 (3)	1·860 (6)	1
				anti		2	86·3 (4)	75·4 (3)	1·557 (6)	1·902 (6)	
H	H	H	H		3	1,3	87·0 (3)	74·7 (4)	1·536 (5)	1·866 (9)	2
						2	86·4 (3)	75·9 (4)	1·555 (3)	1·869 (9)	
SAc	SAc	H	H	*syn*	2	1	87·8 (1)	73·7 (1)	1·550 (2)	1·858 (5)	1
						2	87·9 (1)	73·5 (1)	1·554 (2)	1·859 (5)	
SMe	SMe	H	H	*anti*	2	1,2	87·2 (1)	73·9 (1)	1·549 (1)	1·861 (4)	3
SO_2Me	SO_2Me	H	H	*anti*	2	1,2	88·0 (1)	73·2 (1)	1·553 (2)	1·856 (5)	3
Br	Br	H	H		2	1	88·7 (2)	72·3 (3)	1·548 (5)	1·827 (9)	1
						2	88·8 (2)	72·2 (3)	1·545 (5)	1·821 (9)	
COOMe	H	H	H		2	1	87·1 (1)[d]	74·4 (1)[b]	1·538 (3)[d]	1·871 (4)	1
						2	86·6 (1)[d]	75·0 (2)[b]	1·547 (2)[d]	1·871 (4)	
CCl_3	H	H	H		2	1	87·6 (6)	73·87 (7)	1·554 (1)	1·868 (2)	4
						2	87·1 (1)	74·5 (1)	1·550 (1)	1·876 (3)	
H	H	H	H		1	1	88·0[e]	73·3 (1)	1·545 (6)	1·845	5
							87·5 (2)[e]	74·2 (2)	1·557 (2)	1·874 (4)	6
Ac	Ac	H	H		1	1	88·1 (4)	74·2 (4)	1·546 (7)	1·874 (6)	1
f	*f*	H	H		1	1	86·55 (31)	75·32 (38)	1·531 (5)	1·858 (4)	7
Cl	H	H	H		1	1	87·92	73·47 (5)	1·545 (2)	1·850	8
g	H	H	H		1	1	87·1 (1)	74·6 (1)	1·555 (2)	1·884 (3)	9
COOH	Me	H	H		1	1	87·3 (1)	74·2 (1)	1·551 (1)	1·873 (2)	10
H	H	Ph	*h*		1	1	86·5 (4)[i,j]	74·9 (7)[i]	1·554 (10)[i,k]	1·890 (14)	11
							86·2 (5)[k,l]	75·7 (5)[i]	1·540 (7)[j,l]		
H	H	=O			1	1	83·3[e]	79·8[i]	1·524[i,k]	1·955	12
							85·5[e]	76·9[l]	1·573[j,l]		
COOH	Me	Cl	Cl		1	1	85·9 (1)[i,j]	76·9 (2)[i]	1·530 (2)[i,k]	1·903 (3)	13
						2	86·1 (1)[k,l]	75·3 (1)[l]	1·557 (2)[k,l]		
H	H	$O(CH_2)O$[m]			1	1	*n*	*n*	*n*	1·923	14

(*b*) Intercage bond lengths and angles



R	*R'*	*R''*	*R'''*	Form	*n*[o]	α (°)[p] β (°)[p]	γ (°)[q]	*a*,*b*,*c* (Å)	*d* (Å)	Ref.
SAc	SAc	H	H	(7)	4	126·3 (2)	180·0	1·477 (6) *a*,*c*	11·957 (7)	1
				Mol. 1		127·5 (1)		1·481 (8) *b*		
SAc	SAc	H	H	(7)	4	127·7 (2)	180·0	1·485 (6) *a*,*c*	11·938 (7)	1
				Mol. 2		127·3 (1)		1·480 (9) *b*		
H	H	H	H		4	127 (3)	180·0	1·473 (6) *a*,*c*	11·992 (7)	2
						127·6 (1)		1·498 (8) *b*		
SAc	SAc	H	H	(6*a*)	3	125·2 (2)	177·8 (1)	1·465 (7) *a*	8·576 (8)	1
				Mol. 1		127·4 (1)		1·468 (8) *b*		
				anti						
SAc	SAc	H	H	(6*a*)	3	127·0 (2)	178·7 (1)	1·464 (7) *a*	8·553 (8)	1
				Mol. 2		127·6 (1)		1·476 (7) *b*		
				syn						
SAc	SAc	H	H	(6*b*)	3	125·4 (2)	178·6 (1)	1·470 (6) *a*	8·561 (6)	1
				anti		127·3 (2)		1·470 (6) *b*		
H	H	H	H		3	127·2 (4)	180·0	1·458 (8) *a*,*b*	8·515 (8)	2
						127·5 (2)				

Table 10 (*cont.*)

R	*R*′	*R*″	*R*‴	Form	*n*[o]	α (°)[p] β (°)[p]	γ (°)[q]	*a*,*b*,*c* (Å)	*d* (Å)	Ref.
SAc	SAc	H	H	(5) *syn*	2	120·9 (2) 124·4 (2)	170·94 (9)	1·476 (4)	5·189 (5)	1
SMe	SMe	H	H	(8), *anti*	2	126·9 (1)	178·7 (1)	1·480 (3)	5·20	3
SO_2Me	SO_2Me	H	H	(9), *anti*	2	126·8 (1)	179·7 (1)	1·469 (6)	5·18	3
Br	Br	H	H	(4)	2	125·8 (1) 126·7 (2)	177·6 (2)	1·478 (9)	5·124 (9)	1
COOMe	H	H	H	(3)	2	126·9 (1) 127·1 (1)	178·8 (2)	1·480 (4)	5·221 (4)	1
CCl_3	H	H	H		2	126·3 (2) 127·3 (1)	177·3 (1)	1·483 (2)	5·224 (2)	4
H	H	H	H		1	120	*n*	*r*	1·845	5
						n	*n*	*r*	1·874	6
Ac	Ac	H	H	(2)	1	127·4 (3)	179·9 (4)	*r*	1·874 (6)	1
f	*f*	H	H		1	127·7 (2) *n*	*n*	*r*	1·858 (4)	7
Cl	H	H	H		1	126·2	*n*	*r*	1·850	8
g	H	H	H		1	127·6 (1) *n*	*n*	*r*	1·884 (3)	9
COOH	Me	H	H		1	127·1 (1) *n*	*n*	*r*	1·873 (2)	10
H	H	Ph	*h*		1	*n*	*n*	*r*	1·890 (14)	11
H	H	=O			1	*n*	*n*	*r*	1·955	12
COOH	Me	Cl	Cl		1	127·3 (2)[i] *n* 128·4 (1)[l] *n*	*n*	*r*	1·903 (3)	13
H	H	$O(CH_2)O$[m]			1	*n*	*n*	*r*	1·923	14

Notes: (*a*) Numbered from the left end of the formula shown. (*b*) Average of six values except where specified otherwise. (*c*) Average of three values except where specified otherwise. (*d*) Average of twelve values. (*e*) Calculated from data reported in the references. (*f*) $CO_2Ti(C_5H_5)_2$. (*g*) 4-([1]Staff-1-yl)cubyl. (*h*) O—CO—NH—*p*-C_6H_4Br. (*i*) Values involving a substituted bridge. (*j*) Average of four values. (*k*) Average of two values. (*l*) Values involving an unsubstituted bridge. (*m*) The other two bridges are substituted by one methoxycarbonyl group each in an *anti* relationship. (*n*) Data not reported. (*o*) Number of bicyclic rings. (*p*) α is the average of all the exocyclic *R*—C—C angles, β is the average of all the exocyclic intercage C—C—C angles. (*q*) The angle between axes drawn through the substituent atoms in the terminal bridgehead positions and the midpoint of the [*n*] staffane core. (*r*) Not applicable.

References: (1) This work. (2) Murthy, Hassenrück, Lynch & Michl (1989). (3) Bunz *et al.* (1988). (4) Murthy, Lynch, Hassenrück & Michl (1990). (5) Chiang & Bauer (1970). (6) Almenningen *et al.* (1971). (7) Clauss *et al.* (1983). (8) Cox & Harmony (1970). (9) Hassenrück, Murthy *et al.* (1990). (10) Potekhin *et al.* (1987). (11) Padwa *et al.* (1968). (12) McRae *et al.* (1986). (13) Potekhin *et al.* (1988). (14) Irngartinger *et al.* (1984).

of the remarkably short length of the intercage C—C bond in staffanes also accounts for the even shorter C—C bond in bicubyl derivatives (Gilardi, Maggini & Eaton, 1988; Hassenrück, Radziszewski, Balaji, Murthy, McKinley, David, Lynch, Martin & Michl, 1990); both results were initially predicted on the basis of molecular-mechanics calculations (Ermer & Lex, 1987), and also agree with the more recent semiempirical (Bunz *et al.*, 1988; Murthy, Hassenrück, Balaji & Michl, 1989), and *ab initio* (Murthy, Hassenrück, Balaji & Michl, 1989) calculations. The expected unusually high C—C stretching 'accordion' mode has just been identified in the parent hydrocarbons at ~1370 cm^{-1} (Murthy, Hassenrück, Balaji & Michl, 1989; Murthy, Hassenrück, Lynch & Michl, 1989), in good agreement with the calculations, which also predict an ususually soft bending mode in the far IR region (Michl *et al.*, 1989; Murthy, Hassenrück, Balaji & Michl, 1989), not yet observed experimentally.

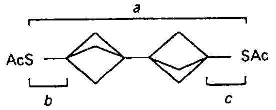
The high degree of *s* character in the exocyclic valence orbital is likely to have other important consequences. The lack of directionality in the interactions of the *s* component of the hybrid with the valence orbitals of other atoms probably contributes to the remarkable efficiency with which the two 'back lobes' of the two exocyclic bridgehead orbitals of the bicyclo[1.1.1]pentane cage interact with each other, as reflected in the large transannular NMR coupling constants through one (Della, Kasum & Kirkbride, 1987; Wiberg & Connor, 1966) or more cages (Kaszynski & Michl, 1988; Michl *et al.*, 1989), and in the strength of the central bond in [1.1.1]-propellane (Wiberg, 1983). After all, in the limit of pure *s* character, the 'front' and the 'back' of the bridgehead orbital would be equivalent.

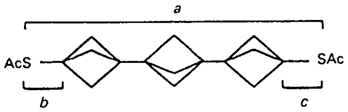
The mutual orientation of the neighboring bicyclo[1.1.1]pentane cages in the linear sequence tends to be staggered, as expected. The calculated (Murthy, Hassenrück, Balaji & Michl, 1989) barrier to internal rotation is small, less than 9 kJ mol^{-1}, and this accounts for the significant deviations from exact bond staggering found in some of our structures, most notably (6*a*). We believe that these are imposed on the molecules by the need to accommodate the end groups in the crystal lattice and do not reflect the conformational preferences of an isolated molecule.

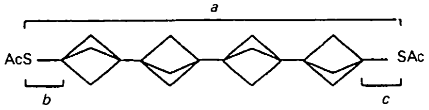
End-group conformations

In the case of end groups possessing a threefold symmetry axis, such as CH_3, one would expect a threefold barrier and a preferred staggered conformation not only along the length of the staffane

Table 11. *Dihedral and torsional angles in* $3,3^{(n-1)}$*-bis(acetylthio)[n]staffanes*







	Dihedral angles (°)*	Torsional angles (°)†	
	a	*b*‡	*c*‡
(5)	47·1 (1)‡	−49·3 (4)	−71·1 (5)
		−166·9 (4)	58·4 (4)
		78·1 (4)	74·0 (3)
(6*a*)	177·2 (3)§	74·5 (7)	−27·9 (9)
Mol. 1		−54·7 (7)	96·5 (7)
syn		−170·9 (7)	−150·6 (6)
(6*a*)	14·4 (5)§	179·4 (5)	167·4 (5)
Mol. 2		63·6 (7)	−75·8 (7)
anti		−64·5 (6)	52·7 (5)
(6*b*)	144·2 (2)§	75·2 (5)	
anti		−53·8 (6)	
		−168·0 (5)	
(7)	180‡	−70·0 (6)	
Mol. 1		176·3 (5)	
		59·8 (6)	
(7)	180‡	65·0 (5)	
Mol. 2		−179·2 (4)	
		−61·2 (6)	

* Angle between the planes defined by each acetylthio group.

† Angle between the planes defined by the (i) methylene C atom, bridgehead C atom and S atom, and (ii) bridgehead C atom, S atom, and carbonyl C.

‡ Ideal angles are 180 and 60°.

§ Ideal angles are 120 and 0°.

structure, but also with respect to rotation around the terminal exocyclic bond. For terminal substituents such as CH_2X, one would then expect rotational isomerism. In even [*n*]staffanes (*n* even) the relative orientations of the C—*X* bonds could be staggered, *gauche* (dihedral angle 60°), or staggered, *anti* (180°). In odd [*n*]staffanes (*n* odd), they could be eclipsed, *syn* (0°), or eclipsed, *gauche* (120°), *cf.* Fig. 11.

Planar terminal groups such as —S*X* may either prefer to orient the S—*X* bond so as to bisect the C—C—C angle on the terminal bridgehead atom (ideal torsion angles ± 60, 180°) or prefer to orient it so as to eclipse one of its three C—C bonds (ideal torsion angles 0, ± 120°). In the $3,3^{(n-1)}$bis(acetylthio)[*n*]staffane series the former orientation is favored; a list of the dihedral and torsional angles for $n = 2-4$ is given in Table 11.

Internal disorder

Rotational disorder within the rods in (3) and in (6*a*) results in imperfectly staggered or even nearly eclipsed conformations for some molecules. In (3), the relevant torsional angles are 0° as required by symmetry, while in (6*a*) they range from − 13 (2)° for C6*A*—C9—C10—C12 to 5 (2)° for C7*A*—C9—C10—C13. Disorder is also observed in (2). Molecules of (2) lie around a position of $2/m$ symmetry with the acetyl groups lying in the mirror. The methylene bridges are accordingly disordered.

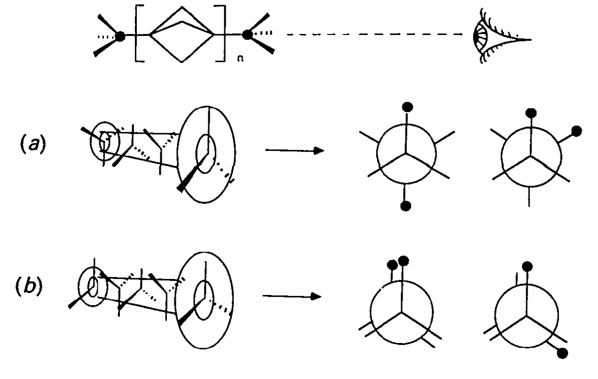


Fig. 11. Idealized axial view of disubstituted [*n*]staffanes showing two preferred conformations for even *n* (*a*) and odd *n* (*b*) using extended projections (all cages and end groups shown) and pseudo-Newman projection (only end groups shown).

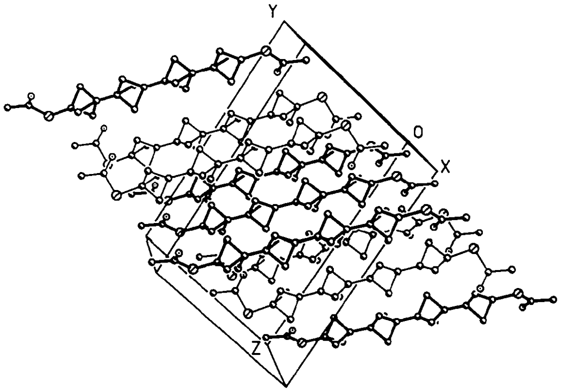


Fig. 12. Unit cell of (7) showing the meshed packing of like pairs of molecules. Molecules pack in parallel layers with each layer containing either molecule 1 or molecule 2. Molecules 2 are drawn with thicker bonds for clarity. Three molecules of the center layer, two of the next layer, and one of the outside layers are shown in this oblique view.

Crystal packing and intermolecular interactions

A glimpse of the geometrical arrangement favored for intermolecular interactions between staffane cores is offered by the crystal structures of (7) and of the two conformers of (6*a*). In the crystal of (7), the long axes of the molecules are arranged parallel, 5·380 (10) or 5·524 (10) Å apart for pairs of the two unique molecules, and mutually displaced so as to mesh, positioning the bicyclo[1.1.1]pentane cages of one between those of the other (Fig. 12). In the crystal of (6*a*), the *anti* and *syn* conformers are arranged pairwise meshed in a plane, with axes within each pair nearly parallel and separated by 6·010 (11) and 5·857 (11) Å, respectively, as shown in the stereoview in Fig. 9. Similar meshing has also been found in the [3]- and [4]staffanes (Murthy, Hassenrück, Lynch & Michl, 1989). The results suggest an effective van der Waals diameter of about 5·5 Å for the substituted [*n*]staffane rod.

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