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# Synthetic High-Pressure Lubricants: Dioctadecyl Trisulfide (I), $C_{36}H_{74}S_3$, and Dioctadecyl Tetrasulfide (II), $C_{36}H_{74}S_4$

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**Abstract.** (I) $M_r = 603{\cdot}30$, triclinic, $P\bar{1}$, $a = 4{\cdot}810\ (4)$, $b = 9{\cdot}596\ (8)$, $c = 43{\cdot}270\ (24)$ Å, $\alpha = 93{\cdot}5\ (1)$, $\beta = 91{\cdot}2\ (1)$, $\gamma = 102{\cdot}9\ (1)°$, $V = 1941{\cdot}9\ (1)$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}03$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 18{\cdot}1$ cm$^{-1}$, $F(000) = 676$, $T = 300$ K, $R = 9{\cdot}2\%$ for 3206 reflections, $S = 1{\cdot}39$. (II) $M_r = 635{\cdot}35$, monoclinic, $C2/c$, $a = 5{\cdot}443\ (6)$, $b = 9{\cdot}427\ (6)$, $c = 78{\cdot}731\ (15)$ Å, $\beta = 90{\cdot}6\ (1)°$, $V = 4039{\cdot}6\ (1)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}04$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 22{\cdot}1$ cm$^{-1}$, $F(000) = 1416$, $T = 300$ K, $R = 8{\cdot}2\%$ for 1588 reflections, $S = 2{\cdot}88$. Structure of (I) was solved by the 'light-atom' method (a combination of direct methods and packing analysis) with the sulfur atoms located in difference maps. Both structures are linear (nonbranched) nonplanar alkyl polysulfides, which exhibit 'anti-wear' properties when used as petroleum additives. (I) has an extended conformation but the chains are not coplanar, while (II) assumes a '*V*' shape.

**Introduction.** Petroleum lubricants currently on the market usually contain several 'anti-wear' additive components to prevent breakdown under extreme load conditions. Sulfurized sperm-whale oil had been a primary source of such additives; however, since enactment of the Endangered Species Act it is no longer available. Substitutes have been sought from renewable (*i.e.* agricultural) sources and since sperm-whale oil itself is made up of monoesters derived mainly from long-chain alcohols and carboxylic acids much research has been centered on long-chain compounds present in plant oils. Sulfurized additives are thought to act in one (or both) of the following ways: (*a*) a tight adsorption of a monolayer of additive on the metal, with a sulfur–metal interaction acting as the linkage; (*b*) the liberation at higher temperatures of reactive sulfur at the metal surface, and the formation of a protective metal sulfide film (Forbes, 1970). This paper reports on the crystal structures of two such materials, dioctadecyl trisulfide (I) and dioctadecyl tetrasulfide (II). (II) has been found to be the better additive, and is as effective as sperm-whale oil.

**Experimental.** Samples of (I) and (II) provided by Dr A. W. Schwab of US Department of Agriculture (Peoria, Illinois). Preliminary note on structure of (II) has been published (Schwab, Gilardi & Flippen-Anderson, 1981). Very thin plates crystallized from slowly evaporating *n*-octanol solutions [$0{\cdot}4 \times 0{\cdot}6 \times 0{\cdot}04$ mm for (I) and $0{\cdot}4 \times 0{\cdot}7 \times 0{\cdot}04$ mm for (II)]. Data collected on Picker FACS-I diffractometer. For (I) $\omega$ step scan, scan width varied to minimize overlap problems along 43 Å axis, 10 s background counts, max. $\sin\theta/\lambda = 0{\cdot}500$ Å$^{-1}$, data collected over $\pm h, k, \pm l$. For (II), two data sets collected due to overlap problems along 78 Å axis, one set $\omega$ step scan, second set $\theta/2\theta$ scan, 10 s background counts, data collected over $\pm h, +k, \pm l$, max. $\sin\theta/\lambda = 0{\cdot}500$ Å$^{-1}$, data sets merged such that $2\theta$ data used if diffraction vector made an angle $>68°$ with closely-spaced $c^*$ axis, otherwise $\omega$ data point used. For (I) 4565 reflections measured, 3986 unique, 3206 observed with $F_o > 3\sigma(F_o)$; for (II), 3449 reflections measured, merged set containing 1789 unique, 1588 observed with $F_o > 3\sigma(F_o)$; standard reflections $\bar{1}38$, $\bar{1},4,10$, 228 (I) and $0,\bar{2},13$, $0\bar{6}5$, 406 (II) monitored every 100 measurements, random intensity variations of $\pm 2{\cdot}5\%$ (I) and $3{\cdot}0\%$ (II). Lattice parameters determined from 13 (I) and 12 (II) centered reflections; corrections for Lorentz and polarization, not for absorption. Structure of (II) with one-half molecule in asymmetric unit solved by routine application of symbolic addition procedure (Karle & Karle, 1966). Solution of (I) was not routine and was finally accomplished by 'light-atom' method. Data set for (I) contained a subcell that could be quantitatively identified prior to structure solution. In this case it was noticed that a large superlattice in the diffraction pattern was formed by the strongest reflections ($|E| > 2{\cdot}5$). This well-defined lattice is the reciprocal of the real-space sublattice. During initial attempts to solve the structure with centric direct methods, *E* maps showed two interpenetrating versions of this hydrocarbon sublattice, and it was difficult to decide which peaks were correctly placed and which were spurious. This same hydrocarbon sublattice is prominent in the Patterson map. To solve the trisulfide structure, subcell parameters taken from an *E* map were used to generate strictly regular, but unrelated, stacks of chains in each half of the cell (*i.e.* the space group was

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degraded to $P1$). Gaps of approximately 4 Å were left between the ends of these stacks with no atoms indentified as sulfurs. The stacks of chains were then shifted relative to one another in three dimensions, while a low-resolution $R$ factor (500 low-angle data) was monitored. The best chain model gave an $R$ of 0·28 with no sulfurs included. The model was then kept fixed, while various weak peaks from difference maps were tested. When two sulfurs were finally located the remaining four started to show clearly in difference maps. A center was then apparent and the origin was shifted to return to space group $P\bar{1}$. In view of the difficulties in clarifying the structure, a retrospective analysis of the phase determination was made. It is interesting to note that the direct-methods phase indications for this crystal are mathematically reliable and correct. None of the top 120 $E$'s was incorrectly phased and, of the top 500 $\sum_2$ interactions, only one was incorrect. Usually, this amount of phase information would be sufficient to provide a well-resolved image of the entire molecule. Hindsight illustrated the unusual character of this reflection set. The chain direction and plane are well determined by a relatively small number of very strong $E$'s, and these combine only with each other to form many strong phase indications; however, details (such as sulfur atoms) that do not fit into the subcell periodicity only begin to appear when large blocks of weaker reflections are added with correct phases.

(I) refined by sparse-matrix restrained least squares (Flippen-Anderson, Gilardi & Konnert, 1983) with hydrogens initially at idealized locations. Parameters refined: atomic coordinates for all atoms, anisotropic temperature factors for non-hydrogen atoms; temperature factors for hydrogens set equal to those of atoms to which they are bonded. (II) refined by full-matrix least squares (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1975). Parameters refined: atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms: hydrogens kept constant at idealized positions with isotropic thermal parameters equal to final isotropic $B$ value for atom to which they are bonded. Two scale factors used, one for $\omega$ data, one for $2\theta$ data. For both molecules function minimized was $\sum w(|F_o|-|F_c|)^2$ where the weights ($w$) were derived from e.s.d.'s of observed intensities with a term added for random errors (0·02 in these cases) (Gilardi, 1973). Scattering factors from *International Tables for X-ray Crystallography* (1974). (I) $R = 9{\cdot}2\%$, $R_w = 10{\cdot}6\%$ for 3206 reflections; (II) $R = 8{\cdot}2\%$, $R_w = 10{\cdot}0\%$ for 1588 reflections; max. $\Delta/\sigma = 0{\cdot}8$ (I), 0·4 (II); final difference Fourier $\Delta\rho$ excursions of 0·31 and −0·36 e Å$^{-3}$ for (I), 0·32 and −0·44 e Å$^{-3}$ for (II).

**Discussion.** Coordinates and $B_{eq}$ values for molecules (I) and (II) are presented in Tables 1 and 2 respectively.* Bond lengths and angles for the two molecules are compared in Table 3. In the tetrasulfide (II), the central S—S bond [2·060 (4) Å] is longer than the terminal S—S bonds [2·018 (3) Å]. The central bond is close to the average value of 2·08 Å selected by Pauling (1960) as a normal S—S single bond, while the shorter terminal S—S bonds may display some slight double-bond character. In the trisulfide (I) the S—S bonds are approximately equal and midway in value between the two different S—S bonds in (II). The C—S bond lengths in both molecules are only slightly less than the normal C—S single bond length of 1·82 to 1·83 Å (Abrahams, 1956). Overall, the C—C bond lengths are significantly shorter than what would be expected [av. = 1·524 (10) Å] and the C—C—C angles are significantly larger than normal [av. = 113·2 (6)°]. Both of these deviations could be due to systematic shifts in the apparent carbon positions caused by large libration about the long-chain axes, but no corrections for libration were made. In both molecules angles around the S atoms are considerably smaller than normal tetrahedral angles [av. = 105·1 (2)°]. In both molecules the chains are not quite planar and exhibit small, but significant, curving. Pertinent torsion angles for both molecules are given in Table 4. The optimal value for torsion angles about S—S bonds is said to be near ±90° (Pauling, 1949; Abrahams, 1956) although observed magnitudes commonly vary over a wide range from 70 to 110°. [In cyclic structures, a larger range has been observed; torsions range from 0° in *cyclo*-heptasulfur (Steudel, Reinhardt & Schuster, 1977) to 135° in cyclic octasulfur cation (Davies, Gillespie, Park & Passmore, 1971).] In (I) one of the C—S—S—S torsional angles is 67·3° and the central S—S—S—S torsional angle in (II) is −65·3°. These values are exceptionally small, especially considering the apparent lack of intramolecular constraints that might cause torsional strain. It is possible that crystal packing forces combine to produce a net torsional strain that reduces the S—S torsions far below optimal values. The terminal C—S—S—S torsion in (II) of −75·9° and the other C—S—S—S torsion in (I), 72·8°, are also considerably less than the optimal value of 90°.

*Packing.* Packing of (I) is illustrated in Fig. 1. The trisulfide moiety has a *trans* configuration (see Schwab *et al.*, 1981, for polysulfide conformation nomenclature) and the molecule is extended overall, although the two octadecyl chains are not coplanar. The crystal structure of the trisulfide contains blocks of atoms that are related by a three-dimensional noncrystallographic periodicity. However, a sublattice that fits hydrocarbon

* Lists of structure factors, anisotropic thermal parameters and hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39711 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and $B_{eq}$ values (with e.s.d.'s in parentheses) for molecule* (I)

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| S(1) | 0·3727 (5) | 0·8721 (1) | 0·52676 (4) | 6·4 (6) |
| S(2) | 0·5192 (4) | 0·7286 (2) | 0·49908 (4) | 6·0 (6) |
| S(3) | 0·1809 (5) | 0·6206 (1) | 0·47191 (4) | 6·6 (6) |
| C(1) | 0·1571 (13) | 0·7681 (6) | 0·5545 (1) | 4·3 (20) |
| C(2) | 0·3198 (14) | 0·6901 (6) | 0·5757 (1) | 5·1 (22) |
| C(3) | 0·1304 (14) | 0·6263 (6) | 0·6020 (1) | 5·2 (22) |
| C(4) | 0·2718 (14) | 0·5409 (6) | 0·6236 (1) | 5·2 (23) |
| C(5) | 0·0855 (14) | 0·4874 (6) | 0·6502 (1) | 5·2 (22) |
| C(6) | 0·2204 (14) | 0·3998 (6) | 0·6719 (1) | 5·2 (22) |
| C(7) | 0·0332 (14) | 0·3495 (6) | 0·6988 (1) | 5·2 (23) |
| C(8) | 0·1664 (14) | 0·2610 (6) | 0·7207 (1) | 5·2 (23) |
| C(9) | −0·0201 (14) | 0·2105 (6) | 0·7478 (1) | 5·4 (23) |
| C(10) | 0·1112 (14) | 0·1220 (6) | 0·7694 (1) | 5·4 (23) |
| C(11) | −0·0766 (14) | 0·0724 (6) | 0·7965 (1) | 5·4 (23) |
| C(12) | 0·0556 (15) | −0·0154 (6) | 0·8183 (1) | 5·7 (24) |
| C(13) | −0·1327 (15) | −0·0646 (6) | 0·8453 (1) | 5·7 (24) |
| C(14) | 0·0010 (16) | −0·1522 (7) | 0·8673 (1) | 6·2 (24) |
| C(15) | −0·1854 (16) | −0·1988 (7) | 0·8945 (1) | 6·5 (26) |
| C(16) | −0·0508 (18) | −0·2839 (7) | 0·9167 (1) | 7·2 (27) |
| C(17) | −0·2361 (20) | −0·3287 (8) | 0·9441 (1) | 9·1 (31) |
| C(18) | −0·1011 (26) | −0·4104 (9) | 0·9668 (2) | 12·3 (38) |
| C(1′) | 0·0982 (12) | 0·7521 (6) | 0·4471 (1) | 4·4 (19) |
| C(2′) | 0·3105 (15) | 0·7941 (6) | 0·4214 (1) | 5·1 (21) |
| C(3′) | 0·1984 (14) | 0·8925 (6) | 0·3998 (1) | 5·1 (23) |
| C(4′) | 0·3955 (14) | 0·9408 (6) | 0·3735 (1) | 5·0 (22) |
| C(5′) | 0·2656 (14) | 1·0315 (6) | 0·3517 (1) | 5·2 (23) |
| C(6′) | 0·4534 (14) | 1·0815 (6) | 0·3251 (1) | 5·2 (22) |
| C(7′) | 0·3211 (14) | 1·1711 (6) | 0·3032 (1) | 5·2 (22) |
| C(8′) | 0·5059 (15) | 1·2210 (6) | 0·2760 (1) | 5·4 (23) |
| C(9′) | 0·3706 (14) | 1·3090 (6) | 0·2544 (1) | 5·3 (22) |
| C(10′) | 0·5565 (15) | 1·3592 (6) | 0·2274 (1) | 5·6 (24) |
| C(11′) | 0·4226 (15) | 1·4476 (6) | 0·2057 (1) | 5·6 (24) |
| C(12′) | 0·6070 (14) | 1·4969 (6) | 0·1787 (1) | 5·5 (23) |
| C(13′) | 0·4715 (15) | 1·5839 (7) | 0·1568 (1) | 5·9 (24) |
| C(14′) | 0·6572 (15) | 1·6331 (7) | 0·1298 (1) | 6·3 (26) |
| C(15′) | 0·5205 (17) | 1·7192 (7) | 0·1079 (1) | 6·8 (26) |
| C(16′) | 0·7032 (17) | 1·7659 (7) | 0·0804 (1) | 7·2 (26) |
| C(17′) | 0·5655 (21) | 1·8528 (9) | 0·0588 (1) | 9·6 (31) |
| C(18′) | 0·7410 (29) | 1·8986 (9) | 0·0312 (2) | 14·0 (42) |

Table 2. *Fractional coordinates and $B_{eq}$ values (with e.s.d.'s in parentheses) for molecule* (II)

Standard deviations are based solely on least-squares results. $B_{eq}$ is as given in Table 1.

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| S(1) | −0·0054 (4) | 0·3967 (3) | 0·27390 (2) | 6·3 (1) |
| S(2) | −0·1081 (4) | 0·2229 (3) | 0·26067 (2) | 6·3 (1) |
| C(1) | 0·2817 (13) | 0·3460 (8) | 0·2833 (1) | 5·5 (2) |
| C(2) | 0·2577 (14) | 0·2366 (8) | 0·2978 (1) | 5·5 (2) |
| C(3) | 0·5012 (14) | 0·2025 (8) | 0·3062 (1) | 5·8 (3) |
| C(4) | 0·4833 (14) | 0·0940 (8) | 0·3209 (1) | 5·6 (2) |
| C(5) | 0·7263 (14) | 0·0636 (8) | 0·3296 (1) | 5·6 (3) |
| C(6) | 0·7053 (14) | −0·0460 (8) | 0·3439 (1) | 5·5 (2) |
| C(7) | 0·9481 (14) | −0·0735 (8) | 0·3531 (1) | 5·6 (2) |
| C(8) | 0·9291 (15) | −0·1823 (8) | 0·3673 (1) | 5·8 (3) |
| C(9) | 1·1714 (14) | −0·2113 (8) | 0·3762 (1) | 5·8 (3) |
| C(10) | 1·1517 (14) | −0·3214 (8) | 0·3903 (1) | 5·6 (2) |
| C(11) | 1·3929 (15) | −0·3486 (8) | 0·3991 (1) | 6·0 (3) |
| C(12) | 1·3735 (14) | −0·4580 (9) | 0·4137 (1) | 6·2 (3) |
| C(13) | 1·6142 (15) | −0·4853 (9) | 0·4228 (1) | 6·3 (3) |
| C(14) | 1·5920 (15) | −0·5936 (9) | 0·4376 (1) | 6·5 (3) |
| C(15) | 1·8325 (16) | −0·6198 (9) | 0·4468 (1) | 7·0 (3) |
| C(16) | 1·8108 (18) | −0·7296 (10) | 0·4612 (1) | 8·0 (3) |
| C(17) | 2·0458 (21) | −0·7517 (11) | 0·4710 (1) | 10·0 (4) |
| C(18) | 2·0303 (26) | −0·8635 (14) | 0·4846 (1) | 14·2 (6) |

atoms in one half of the cell ($c < 0·5$) does not fit similar atoms in the other half ($c > 0·5$), or atoms in the next unit cell. The two sublattices are identical but shifted by a non-sublattice translation.

Table 3. *Bond lengths* (Å) *and angles* (°)

| | Molecule (I) | | Molecule (II) |
|---|---|---|---|
| S(1)–S(2) | 2·023 (3) | | 2·018 (3) |
| S(2)–S(3) {S(2)–S(2′)}$_{II}$ | 2·030 (3) | | 2·060 (4) |
| S(1)–C(1) [S(3)–C(1′)]$_I$ | 1·801 (6) | 1·810 (7) | 1·789 (7) |
| C(1)–C(2) | 1·529 (9) | 1·534 (9) | 1·546 (9) |
| C(2)–C(3) | 1·542 (9) | 1·541 (10) | 1·511 (10) |
| C(3)–C(4) | 1·523 (10) | 1·522 (9) | 1·544 (9) |
| C(4)–C(5) | 1·519 (9) | 1·537 (10) | 1·512 (7) |
| C(5)–C(6) | 1·524 (10) | 1·513 (9) | 1·535 (9) |
| C(6)–C(7) | 1·522 (9) | 1·534 (10) | 1·521 (10) |
| C(7)–C(8) | 1·530 (10) | 1·526 (9) | 1·523 (7) |
| C(8)–C(9) | 1·527 (9) | 1·525 (10) | 1·513 (10) |
| C(9)–C(10) | 1·519 (10) | 1·524 (9) | 1·522 (10) |
| C(10)–C(11) | 1·529 (9) | 1·525 (10) | 1·502 (10) |
| C(11)–C(12) | 1·521 (10) | 1·516 (10) | 1·549 (10) |
| C(12)–C(13) | 1·527 (10) | 1·528 (10) | 1·507 (10) |
| C(13)–C(14) | 1·531 (11) | 1·520 (10) | 1·555 (10) |
| C(14)–C(15) | 1·520 (10) | 1·523 (11) | 1·511 (10) |
| C(15)–C(16) | 1·522 (11) | 1·524 (11) | 1·542 (11) |
| C(16)–C(17) | 1·524 (12) | 1·524 (13) | 1·500 (12) |
| C(17)–C(18) | 1·515 (15) | 1·508 (14) | 1·506 (11) |
| | | | |
| C(1)–S(1)–S(2) [C(1′)–S(3)–S(2)]$_I$ | 105·4 (2) | 104·9 (2) | 103·4 (3) |
| S(1)–S(2)–S(3) {S(1)–S(2)–S(2′)}$_{II}$ | 106·3 (1) | | 105·3 (1) |
| S(1)–C(1)–C(2) | 114·7 (5) | 114·9 (5) | 113·9 (5) |
| C(1)–C(2)–C(3) | 110·7 (6) | 109·7 (6) | 112·7 (6) |
| C(2)–C(3)–C(4) | 114·2 (6) | 113·8 (6) | 114·0 (6) |
| C(3)–C(4)–C(5) | 112·6 (6) | 111·5 (6) | 113·8 (6) |
| C(4)–C(5)–C(6) | 113·7 (6) | 113·4 (6) | 113·0 (6) |
| C(5)–C(6)–C(7) | 112·9 (6) | 113·1 (6) | 113·1 (6) |
| C(6)–C(7)–C(8) | 113·3 (6) | 113·8 (6) | 113·4 (6) |
| C(7)–C(8)–C(9) | 113·6 (6) | 113·2 (6) | 113·5 (6) |
| C(8)–C(9)–C(10) | 113·6 (6) | 113·0 (6) | 113·2 (6) |
| C(9)–C(10)–C(11) | 113·3 (6) | 113·3 (6) | 112·7 (6) |
| C(10)–C(11)–C(12) | 113·3 (6) | 113·2 (6) | 113·1 (6) |
| C(11)–C(12)–C(13) | 113·0 (6) | 113·3 (6) | 113·5 (6) |
| C(12)–C(13)–C(14) | 113·1 (6) | 113·1 (6) | 113·1 (7) |
| C(13)–C(14)–C(15) | 112·8 (6) | 112·8 (6) | 113·2 (7) |
| C(14)–C(15)–C(16) | 112·9 (7) | 113·0 (7) | 113·0 (7) |
| C(15)–C(16)–C(17) | 112·8 (7) | 112·6 (7) | 113·5 (7) |
| C(16)–C(17)–C(18) | 113·8 (8) | 113·6 (9) | 114·1 (9) |

Table 4. *Torsion angles* (°)

E.s.d.'s are 1·1°.

| | Molecule (I) |
|---|---|
| C(3)–C(2)–C(1)–S(1) | 170·2 |
| C(2)–C(1)–S(1)–S(2) | 63·4 |
| C(1)–S(1)–S(2)–S(3) | 72·8 |
| S(1)–S(2)–S(3)–C(1′) | 67·3 |
| S(2)–S(3)–C(1′)–C(2′) | 73·4 |
| S(3)–C(1′)–C(2′)–C(3′) | 173·5 |
| | |
| Minimum (abs) C–C–C–C | 176·6 |
| Maximum (abs) C–C–C–C | 180·0 |
| Av. (abs) C–C–C–C | 179·2 |
| | |
| | Molecule (II) |
| C(3)–C(2)–C(1)–S(1) | −176·4 |
| C(2)–C(1)–S(1)–S(2) | −71·8 |
| C(1)–S(1)–S(2)–S(2′) | −75·9 |
| S(1)–S(2)–S(2′)–S(1′) | −65·3 |
| | |
| Minimum (abs) C–C–C–C | 177·4 |
| Maximum (abs) C–C–C–C | 179·9 |
| Av. (abs) C–C–C–C | 178·9 |

Crystal packing for (II) is illustrated in Figs. 2 and 3. The tetrasulfide moiety exhibits a *trans–trans* geometry and there is a crystallographic twofold axis in the molecule at the center of the central S–S bond. The two octadecyl chains are oriented relative to the twofold axis in such a way as to bend the molecule into the shape of a *V* as opposed to the totally extended conformation found in (I). The packing is composed of columns of parallel molecules stacked along the *b*-axis direction. There are two columns in each cell along the *c*-axis direction with the *V*-shaped molecules going in opposite directions in contiguous columns.

Parameters of the hydrocarbon subcells of (I) and (II) are listed in Table 5. Four other long-chain hydrocarbon structures are also listed to show the typical range of variation in subcell parameters. To facilitate comparison, reduced Niggli cells (*i.e.* cells based on the three shortest non-coplanar lattice translations) were calculated for all structures. The subcells for (I) and (II) fit well with those found for the other long-chain compounds, all of whose subcells were described as triclinic parallel by the original authors. Segerman (1965) pointed out that these cells are all close to monoclinic in geometry and symmetry, and would indeed be monoclinic were it not for a shear force produced by chain-end effects in packing. Parameters for the larger pseudomonoclinic cells are also given for (I) and (II) in Table 5.

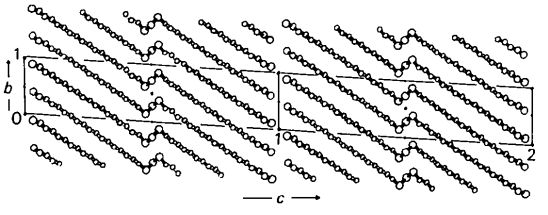


Fig. 1. Packing diagram for dioctadecyl trisulfide (I) viewed down the *a* axis. The diagram was drawn with *ORTEP* Johnson, 1965).

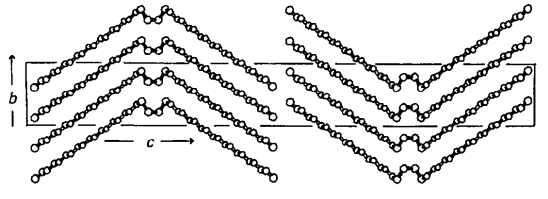


Fig. 2. Packing diagram for dioctadecyl tetrasulfide (II) viewed down the *a* axis.

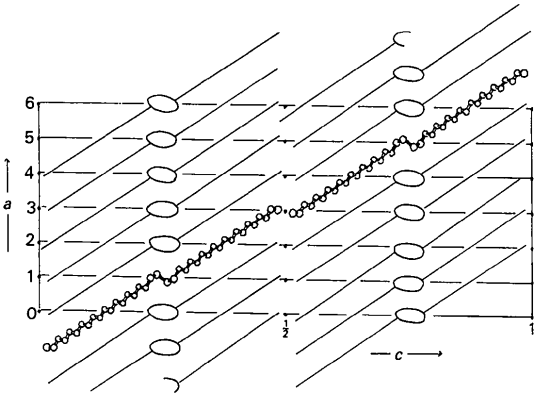


Fig. 3. Packing diagram for (II) viewed down the *b* axis. Each molecule is extended through four unit cells in the *a*-axis direction. An identical layer of molecules, shifted by ½ (**a** + **b**) has been omitted for clarity.

Table 5. *Cell parameters for selected long-chain subcells* (Å *and* deg)

| Compound | *a* | *b* | *c* | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|---|
| | Triclinic ($P\bar{1}$, reduced cell) | | | | | |
| Trisulfide (I) | 2·54 | 4·25 | 4·81 | 70·9 | 90·0 | 74·0 |
| Tetrasulfide (II) | 2·54 | 4·16 | 4·77 | 74·4 | 89·4 | 74·0 |
| 16-DL-Me-C18* (Abrahamsson, 1958) | 2·56 | 4·47 | 4·79 | 69·1 | 86·8 | 73·8 |
| 14-DL-Me-C18† (Abrahamsson, 1959*a*) | 2·57 | 4·37 | 5·00 | 65·0 | 78·7 | 75·2 |
| 2-DL-Me-C18‡ (Abrahamsson, 1959*b*) | 2·50 | 4·24 | 5·08 | 65·4 | 87·5 | 75·1 |
| Trilaurin§ (Vand & Bell, 1951) | 2·45 | 4·23 | 5·12 | 68·5 | 89·0 | 74·6 |
| | Pseudo-monoclinic (*B*2/*m*) | | | | | |
| Trisulfide (I) | 8·33 | 4·81 | 2·54 | 90·0 | 86·8 | 108·5 |
| Tetrasulfide (II) | 8·00 | 4·77 | 2·54 | 90·6 | 88·2 | 106·0 |
| Trilaurin | 8·15 | 5·12 | 2·45 | 91·0 | 91·4 | 117·0 |

* DL-16-Methyloctadecanoic acid.
† DL-14-Methyloctadecanoic acid.
‡ DL-2-Methyloctadecanoic acid.
§ Trilauroylglycerol.

In (I) there are three intermolecular approaches less than van der Waals separations, two S–S approaches [S(1)···S(1) at 3·516 (4) Å and S(3)···S(3) at 3·655 (4) Å] and one S···C approach [S(2)···C(1′) at 3·593 (7) Å]. In (II) there are no intermolecular approaches less than 3·95 Å.

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# Sulfoconjugation of Dopamine. The Structures of Dopamine-*O*-sulfates, $C_8H_{11}NO_5S$

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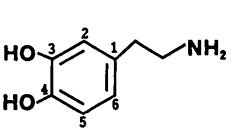
**Abstract.** 4-(2-Aminoethyl)-2-hydroxyphenyl hydrogen sulfate (dopamine-4-*O*-sulfate): $M_r = 233{\cdot}24$, monoclinic, $P2_1/n$, $a = 9{\cdot}866\ (5)$, $b = 10{\cdot}454\ (4)$, $c = 19{\cdot}799\ (5)$ Å, $\beta = 95{\cdot}78\ (2)°$, $V = 2031{\cdot}4$ Å$^3$, $Z = 8$, $D_x = 1{\cdot}525$, $D_m$(flotation in $CHCl_3/C_3H_6Br_2$) = $1{\cdot}52\ (1)$ Mg m$^{-3}$, Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 3{\cdot}054$ mm$^{-1}$, $F(000) = 488$, $T = 298$ K, $R = 0{\cdot}041$, $wR = 0{\cdot}050$ for 2799 observations, $I \geq 3\sigma(I)$. 5-(2-Aminoethyl)-2-hydroxyphenyl hydrogen sulfate (dopamine-3-*O*-sulfate): $M_r = 233{\cdot}24$, monoclinic, $P2_1/c$, $a = 8{\cdot}706\ (5)$, $b = 12{\cdot}749\ (7)$, $c = 9{\cdot}214\ (3)$ Å, $\beta = 102{\cdot}97\ (4)°$, $V = 996{\cdot}5$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}555$, $D_m$(flotation in $CHCl_3/C_3H_6Br_2$) = $1{\cdot}55\ (1)$ Mg m$^{-3}$, Mo $K\alpha$ radiation, $\mu = 3{\cdot}113$ mm$^{-1}$, $F(000) = 244$, $T = 273$ K, $R = 0{\cdot}043$, $wR = 0{\cdot}052$ for 1530 observations, $I \geq 3\sigma(I)$. Both dopamine sulfate molecules crystallize as zwitterions. The two crystallographically independent molecules comprising the dopamine-4-*O*-sulfate asymmetric unit are conformational isomers. The disposition of the ethylamine side chains differs in all three molecules; two of these differ considerably from conformations normally observed in crystal structures of dopamine derivatives, *i.e.* $\tau_1$ for one dopamine-4-*O*-sulfate molecule is $-47{\cdot}4°$ and $\tau_1$ for the dopamine-3-*O*-sulfate molecule is $62{\cdot}9°$. There is extensive hydrogen bonding observed in both structures including intramolecular hydrogen bonding between the ionized sulfate group and the phenolic hydroxyl. The intramolecular hydrogen bonds are accompanied by very short phenolic C—OH distances ranging from 1·349–1·364 Å.

**Introduction.** Sulfoconjugation is an important metabolic pathway determining the fate and pharmacological action of ingested phenolic substances. Among the three catecholamines of pharmacological significance, dopamine (DA) (1) is sulfoconjugated to the highest degree and has the highest affinity toward phenolsulfotransferase (PST). The latter exists in human brain and converts DA to its *O*-sulfates; the ratio of DA-3-*O*- to DA-4-*O*-sulfate is about 4:1 (Renskers, Feor & Roth, 1980). A relatively high percentage of the DA-*O*-sulfates as compared to other catecholamine sulfoconjugates has been isolated from human urine. Because of the presence of DA-*O*-sulfates in brain and other vital peripheral organs (Elchisak & Carlson, 1982), these substrates have attracted considerable attention regarding the possible physiological role of the sulfate esters of catecholamines in general. Jenner & Rose (1973) were the first to demonstrate the *in vitro* conversion of DA to its 3- and 4-*O*-sulfates using preparations from rat liver and brain and, as part of this study, they described a one-step synthesis of the two DA-*O*-sulfates. For the past ten years this procedure has been employed for the preparation of DA-*O*-sulfates which have been used in pharmacological studies. We repeated the Jenner procedure and in addition to the two DA-*O*-sulfates we isolated four additional hitherto unknown products. These have been found to be nuclear sulfonic acid products resulting from alternate modes of sulfonation and will be reported elsewhere (Jain & Kaiser, 1984).

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