# Crystal Phases of Dodecyl Sulfates Obtained from Aqueous Solutions: Structure of the Rubidium Salt

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**Abstract.** Rubidium dodecyl sulfate, $Rb^+.C_{12}H_{25}O_4S^-$, $M_r = 350.86$, triclinic, $P\bar{1}$, $a = 7.137$ (2), $b = 7.492$ (2), $c = 30.685$ (10) Å, $\alpha = 96.26$ (2), $\beta = 90.57$ (2), $\gamma = 84.91$ (2)°, $V = 1624.5$ (8) Å³, $Z = 4$, $D_x = 1.43$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 33.5$ cm⁻¹, $F(000) = 728$, $R = 0.057$ for 4665 independent reflections. The molecules form a lamellar structure with alternate polar and apolar regions. Monolayers with facing polar heads are held together tightly by Coulombic forces whereas weak van der Waals interactions are present in the tail-to-tail apolar region. The hydrocarbon chains are tilted on the polar plane but do not interdigitate each other. At variance with the sodium salt crystal phases, no water molecule is present in this crystal phase.

**Introduction.** The knowledge of the structure of micellar aggregates is necessary for the comprehension of their chemical and physical properties and related phenomena. The available models of micellar aggregates in aqueous solution do not give satisfactory accounts of the experimental data and often give rise to contradictions (Dill, Koppel, Cantor, Dill, Bendedouch & Chen, 1984; Menger & Doll, 1984). In fact the techniques employed so far have not been able to provide precise information on the micellar structure.

There are micellar systems which change to solid phases (gels, fibers and crystals) by variation of thermodynamic parameters such as concentration, temperature or ionic strength. In the case where the solid and liquid phases give rise to X-ray intensity minima or maxima in the same regions of the diffraction angle, it is reasonable to suppose that similar structural subunits characterize them. Then, the structural model obtainable from the study of the solid phase can be checked in the investigation of micellar aggregates (Campanelli, Candeloro De Sanctis, Giglio & Petriconi, 1984; Conte, Di Blasi, Giglio, Parretta & Pavel, 1984; Esposito, Zanobi, Giglio, Pavel & Campbell, 1987; Esposito, Giglio, Pavel & Zanobi, 1987; Giglio, Loreti & Pavel, 1988).

With the aim of obtaining models to be successively tested in the study of micellar solutions with different techniques we have undertaken the elucidation of crystalline phases of dodecyl sulfates which can be grown from aqueous solutions at a concentration above the critical micellar concentration (Coiro, Mazza & Pochetti, 1986; Coiro, Manigrasso, Mazza & Pochetti, 1987; Coiro, Mazza & Pochetti, 1987). Furthermore, since the micellar growth is very sensitive to the nature of the counterion (Missel, Mazer, Carey & Benedek, 1982), in order to investigate the effect of the counterion on the molecular aggregation of surfactants we are also examining the crystal packing of the same anionic amphiphile with different cations. Here we report the crystal structure of rubidium dodecyl sulfate (RDS).

**Experimental.** The title compound was prepared by sulfation of 1-dodecanol with chlorosulfonic acid; the product obtained was then neutralized with rubidium hydroxide (McIntire, Chiappardi, Casselberry & Blount, 1982). RDS was purified by repeated crystallizations from ethanol and water. Single crystals in the form of colourless prisms were obtained from water.

A crystal of $0.8 \times 0.5 \times 0.4$ mm was mounted on an automatic Syntex $P2_1$ diffractometer equipped with graphite monochromator and Mo $K\alpha$ radiation. The unit-cell parameters were determined from a least-squares fit of the angular settings of 15 reflections in the range $12 < \theta < 24°$. Because of the X-ray decay three different crystals of about the same dimensions as that used for crystal data were successively used to complete the intensity data collection.

Three data sets at increasing intervals of $\theta$ were recorded by the $\theta$–$2\theta$ scan technique, with a scan rate varying in the interval $29.3$–$1.0$ min⁻¹ up to a maximum $2\theta$ value of $56°$. Background counts were taken for a time equal to half of the scan time. For each set of data, $\varphi$-scan curves obtained for two reflections with $\chi \sim 90°$ were used to take care of anisotropy of absorption and the correction for X-ray decay was performed by three standard reflections (020, 003 and $1\bar{1}5$) measured after every 100, which showed a steady decrease: when their intensities were less than 40% of

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their initial value a new crystal was mounted for intensity data collection. The three sets of data were subsequently scaled by averaging the intensities of common reflections. After merging equivalent reflections, $R_{int}$ was 0·08. A total of 4665 independent reflections with $I \geq 2·5\sigma(I)$ were obtained ($h$ −9→9, $k$ −9→9, $l$ 0→40), and corrected for Lorentz and polarization factors. 2013 unobserved reflections.

The structure was solved by the semiinvariant representation package *SIR* (Cascarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985) using 400 reflections with the largest $E$'s (> 1·89) and 100 reflections with the smallest $E$'s (< 0·057). For the convergence–divergence and phase expansion processes, 4000 triplets, 13 two-phase semiinvariants and seven one-phase semiinvariants accepted as known phases, among the strongest, were used. The $E$ map computed with the phases of the second set having the highest figures of merit revealed molecular fragments: the location of all the non-H atoms was completed by Fourier recycling.

After isotropic and anisotropic refinement of the heavy atoms by block-diagonal least-squares method, all the H atoms were found from successive $\Delta F$ syntheses: their positional parameters were varied in the last cycles of refinement keeping fixed their isotropic temperature factors deduced from the carrier atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (a + |F_o| + c|F_o|^2)^{-1}$ with $a$ and $c$ equal to $2F_{o(min)}$ and $2/F_{o(max)}$, respectively. The atomic scattering factors were corrected for anomalous dispersion. In the last refinement cycle $(\Delta/\sigma)_{max}$ was 0·2 and 0·3 for the positional and thermal parameters of the methyl groups respectively, while much smaller values were obtained for the parameters of the other atoms. The maximum and minimum heights in the final Fourier difference synthesis were 0·2 and −0·1 e Å⁻³, respectively. The final $R$ and $wR$ were 0·057 and 0·082, respectively, and $S = 0·4$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were carried out on the DG ECLIPSE MV/8000 II of the CNR Research Area (Montelibretti) using local programs (Camalli, Capitani, Cascarano, Cerrini, Giacovazzo & Spagna, 1986). The final atomic parameters are reported in Table 1.*

**Discussion.** Bond lengths and angles found for the two independent anions are reported in Fig. 1. For each sulfate group the ester S—O bond is longer than the other S—O bonds and all the O—S—O valence angles are larger than those involving the ester O atom. These

Table 1. *Final fractional coordinates and $B_{eq}$ values of the non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}(Å^2)$ |
|---|---|---|---|---|
| Rb(1) | 0·0876 (1) | 0·2204 (1) | 0·03531 (2) | 2·99 (2) |
| S(1) | −0·0141 (2) | 0·2971 (2) | −0·0765 (1) | 2·90 (4) |
| O(11) | 0·1197 (8) | 0·2045 (7) | −0·1153 (2) | 3·8 (1) |
| O(12) | −0·1589 (8) | 0·4101 (8) | −0·0959 (2) | 4·7 (2) |
| O(13) | −0·0825 (7) | 0·1461 (7) | −0·0582 (2) | 3·6 (1) |
| O(14) | 0·1047 (8) | 0·3986 (7) | −0·0465 (2) | 3·9 (1) |
| C(11) | 0·167 (1) | 0·320 (1) | −0·1484 (3) | 4·1 (2) |
| C(12) | 0·352 (1) | 0·239 (1) | −0·1684 (3) | 4·1 (2) |
| C(13) | 0·404 (1) | 0·334 (1) | −0·2083 (3) | 4·1 (2) |
| C(14) | 0·599 (1) | 0·258 (1) | −0·2260 (3) | 4·3 (2) |
| C(15) | 0·652 (1) | 0·338 (1) | −0·2677 (3) | 4·5 (2) |
| C(16) | 0·848 (1) | 0·263 (1) | −0·2845 (3) | 4·6 (2) |
| C(17) | 0·902 (1) | 0·330 (1) | −0·3269 (3) | 4·8 (3) |
| C(18) | 1·097 (1) | 0·256 (2) | −0·3436 (4) | 5·5 (3) |
| C(19) | 1·146 (2) | 0·324 (2) | −0·3865 (3) | 5·5 (3) |
| C(110) | 1·341 (2) | 0·254 (2) | −0·4036 (4) | 5·9 (3) |
| C(111) | 1·387 (2) | 0·320 (3) | −0·4469 (4) | 8·0 (5) |
| C(112) | 1·580 (2) | 0·251 (3) | −0·4649 (6) | 9·3 (6) |
| Rb(2) | 0·5080 (1) | 0·2726 (1) | −0·05118 (2) | 3·17 (2) |
| S(2) | 0·6055 (2) | 0·2026 (2) | 0·0640 (1) | 2·81 (4) |
| O(21) | 0·4612 (6) | 0·1123 (6) | 0·0924 (2) | 3·0 (1) |
| O(22) | 0·7451 (8) | 0·2713 (8) | 0·0933 (2) | 4·4 (2) |
| O(23) | 0·6748 (7) | 0·0551 (7) | 0·0325 (2) | 3·6 (1) |
| O(24) | 0·4917 (8) | 0·3417 (7) | 0·0438 (2) | 4·1 (1) |
| C(21) | 0·394 (1) | 0·216 (1) | 0·1334 (3) | 3·3 (2) |
| C(22) | 0·230 (1) | 0·133 (1) | 0·1492 (3) | 3·5 (2) |
| C(23) | 0·158 (1) | 0·229 (1) | 0·1931 (3) | 3·8 (2) |
| C(24) | −0·022 (1) | 0·159 (1) | 0·2084 (3) | 4·2 (2) |
| C(25) | −0·091 (1) | 0·240 (1) | 0·2530 (3) | 4·1 (2) |
| C(26) | −0·273 (1) | 0·167 (1) | 0·2668 (3) | 4·7 (2) |
| C(27) | −0·341 (1) | 0·244 (1) | 0·3130 (3) | 4·2 (2) |
| C(28) | −0·522 (1) | 0·171 (2) | 0·3255 (3) | 5·2 (3) |
| C(29) | −0·587 (1) | 0·246 (2) | 0·3721 (3) | 4·9 (3) |
| C(210) | −0·768 (1) | 0·176 (2) | 0·3856 (3) | 5·4 (3) |
| C(211) | −0·830 (2) | 0·255 (2) | 0·4323 (4) | 7·1 (4) |
| C(212) | −1·010 (2) | 0·181 (3) | 0·4459 (5) | 9·4 (5) |

structural features may be ascribed to the negative charge equally shared among the three non-ester O atoms, as already observed for the monoclinic and triclinic phases of sodium dodecyl sulfate (SDS) (Coiro, Mazza & Pochetti, 1986; Coiro, Manigrasso, Mazza & Pochetti, 1987).

The conformation of both independent hydrocarbon chains is almost completely *trans*-planar: the largest deviations from planarity in the two chains are shown from the sequences C(12)—C(13)—C(14)—C(15) and C(21)—C(22)—C(23)—C(24) with torsion angles of 175·7 (7) and 174·6 (7)°, respectively. In Table 2 the torsion angles giving the orientation of the polar heads with respect to the hydrocarbon chains are compared: the sign convention is that of Klyne & Prelog (1960). The unit cell contains four RDS molecules: the two independent hydrocarbon chains run nearly parallel to each other. Views of the crystal packing at the $ac$ and the $bc$ planes are shown in Fig. 2($a$) and ($b$) respectively. The chains lie almost on the $ac$ plane with a tilting angle of only 1(1)°, form an angle of 43(1)° with the $bc$ plane, and arrange themselves in a lamellar structure with alternately polar and apolar portions which extend into the $ab$ plane. Lamellar structures have already been found for the variously hydrated crystal phases of SDS; namely the (1:8) water:SDS-

ratio phase (Sundell, 1977), the hemihydrate phase (Coiro, Mazza & Pochetti, 1986) and the mono-hydrate phase (Coiro, Manigrasso, Mazza & Pochetti, 1987). At variance with these Na salts, no water molecule is present in the polar region of RDS crystals which, therefore, are characterized by strong Coulom-bic interactions without screening of water molecules.

From Fig. 2 it can be seen that the sulfate groups of adjacent molecules belonging to the same monolayer are displaced alternately from the *ab* plane giving rise to a rippled surface: such surfaces have already been noted for the SDS crystal phases where more than one independent molecule is present in the asymmetric unit.

The Rb ions are distributed among sulfate groups within each layer and their coordination with the O atoms of different-facing polar heads is shown in Fig. 3. Rb(1) forms ten contacts, ranging from 2·911 (3) to 3·292 (3) Å, with the O atoms of six different polar heads, three of which belong to the first molecule of the asymmetric unit, and the remaining three to the second one. Rb(2) forms nine contacts, ranging from 2·874 (3) to 3·426 (3) Å, with the O atoms of five different polar heads, two of which belong to one independent

molecule and the other three to the other one. The distance between the two Rb ions is 4·098 (1) Å. O(14), O(24) and O(23$^{iv}$), belonging to three different polar heads, are simultaneously coordinated to the two Rb ions. The angles O···Rb···O around each ion are reported in Table 3, where it can be noted that no regular arrangement of O atoms occurs.

Weak van der Waals interactions characterize the apolar region composed of two facing monolayers where the parallel hydrocarbon chains make an angle of 46(1)° with the *ab* plane. Although better packing conditions should be realized through this chain tilting, no energetically strong contact is formed.

The shortest contact in the tail-to-tail region is 3·99 (2) Å and occurs between the C(112) and C(212) at *x* + 3, *y*, *z*−1 methyl groups. In contrast to the Na salts, the two independent hydrocarbon chains have their mean planes almost perpendicular to each other, as shown in Fig. 4 where a view of the mean plane of one of the two chains is presented. A side view of the chains belonging to the same monolayer is given in Fig. 5. Molecules with equally oriented hydrocarbon-chain planes are aligned along the **a** and **b** directions, whereas
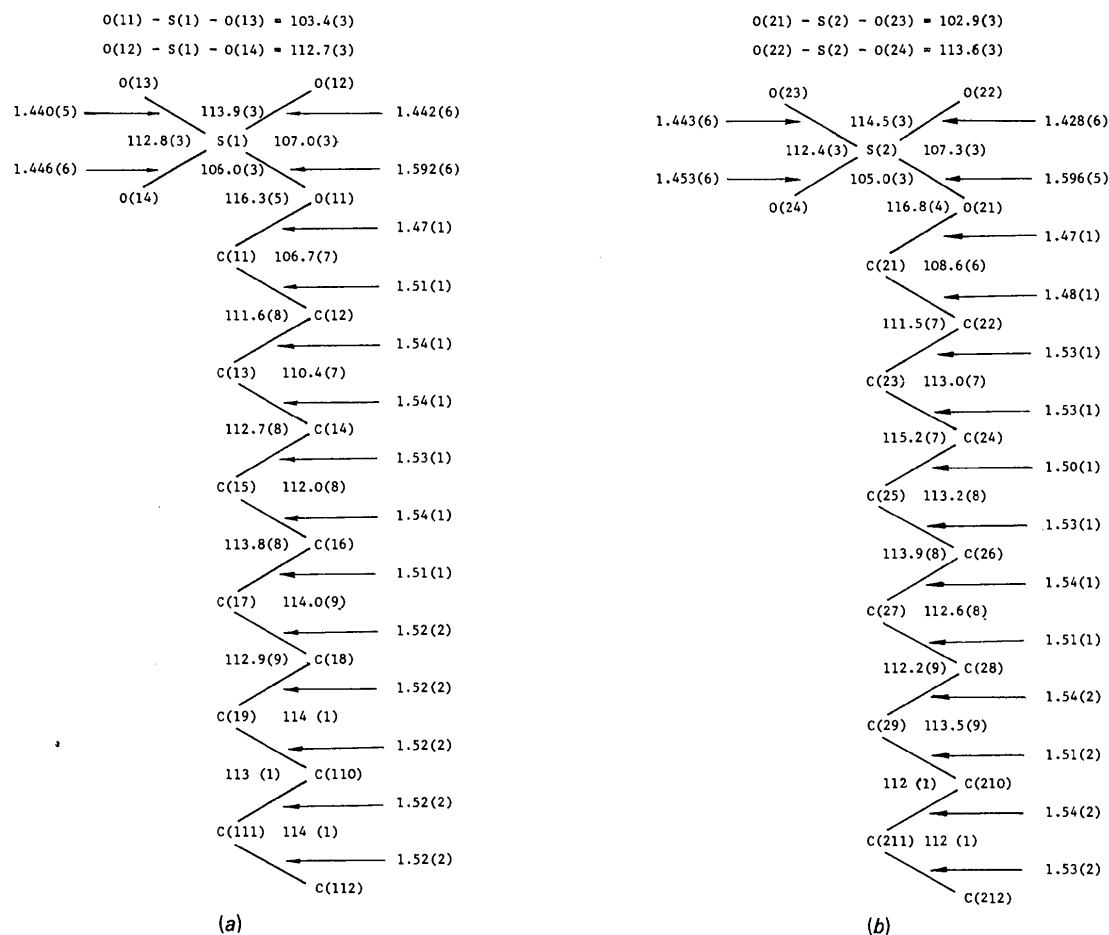


(a)　　　　　　　　　　　　　　　(b)

Fig. 1. Atomic numbering, valence bond lengths (Å) and angles (°) of the two independent RDS anions. E.s.d.'s are in parentheses.

## Table 2. *Relevant torsion angles* (°) *of the two independent anions with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(11)–O(11)–S(1)–O(12) | 41·9 (6) | C(21)–O(21)–S(2)–O(22) | 46·5 (5) |
| C(11)–O(11)–S(1)–O(13) | 162·5 (5) | C(21)–O(21)–S(2)–O(23) | 167·6 (5) |
| C(11)–O(11)–S(1)–O(14) | −78·6 (6) | C(21)–O(21)–S(2)–O(24) | −74·6 (5) |
| C(12)–C(11)–O(11)–S(1) | 154·8 (5) | C(22)–C(21)–O(21)–S(2) | 166·5 (5) |
| C(13)–C(12)–C(11)–O(11) | 172·0 (7) | C(23)–C(22)–C(21)–O(21) | 177·3 (6) |

along the diagonals, hydrocarbon-chain planes alternate perpendicular to each other. So far each molecule is surrounded by six others arranged in a hexagonal array similar to that observed for the SDS crystal phases. The

## Table 3. *The* O···Rb···O *angles* (°) *occurring around each* Rb *ion*

E.s.d.'s are in the range 0·1–0·2°.

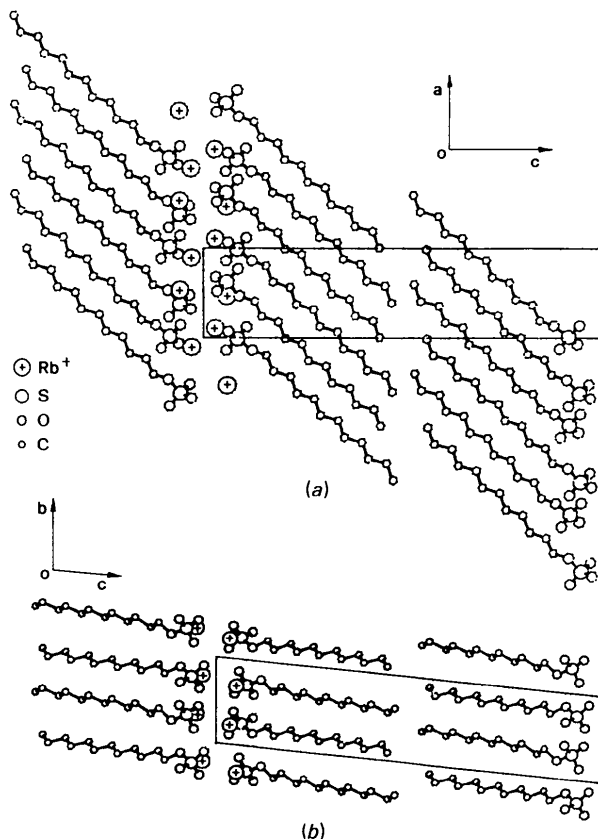| | | | |
|---|---|---|---|
| O(12$^i$)···Rb(1)···O(13) | 132·3 | O(11)···Rb(2)···O(12$^v$) | 116·1 |
| O(12$^i$)···Rb(1)···O(13$^{ii}$) | 130·4 | O(11)···Rb(2)···O(13$^v$) | 135·0 |
| O(12$^i$)···Rb(1)···O(14) | 91·9 | O(11)···Rb(2)···O(14) | 44·0 |
| O(12$^i$)···Rb(1)···O(14$^i$) | 44·9 | O(11)···Rb(2)···O(21$^{iv}$) | 71·2 |
| O(12$^i$)···Rb(1)···O(21) | 76·0 | O(11)···Rb(2)···O(23) | 129·5 |
| O(12$^i$)···Rb(1)···O(22$^{iii}$) | 78·4 | O(11)···Rb(2)···O(23$^{iv}$) | 67·7 |
| O(12$^i$)···Rb(1)···O(23$^{iii}$) | 121·3 | O(11)···Rb(2)···O(24) | 123·2 |
| O(12$^i$)···Rb(1)···O(23$^{iv}$) | 136·1 | O(11)···Rb(2)···O(24$^{vi}$) | 101·7 |
| O(12$^i$)···Rb(1)···O(24) | 60·9 | O(12$^v$)···Rb(2)···O(13$^v$) | 47·0 |
| O(13)···Rb(1)···O(13$^{ii}$) | 96·1 | O(12$^v$)···Rb(2)···O(14) | 132·0 |
| O(13)···Rb(1)···O(14) | 46·4 | O(12$^v$)···Rb(2)···O(21$^{iv}$) | 99·7 |
| O(13)···Rb(1)···O(14$^i$) | 91·6 | O(12$^v$)···Rb(2)···O(23) | 108·1 |
| O(13)···Rb(1)···O(21) | 140·9 | O(12$^v$)···Rb(2)···O(23$^{iv}$) | 145·0 |
| O(13)···Rb(1)···O(22$^{iii}$) | 102·9 | O(12$^v$)···Rb(2)···O(24) | 116·4 |
| O(13)···Rb(1)···O(23$^{iii}$) | 65·1 | O(12$^v$)···Rb(2)···O(24$^{vi}$) | 65·3 |
| O(13)···Rb(1)···O(23$^{iv}$) | 63·1 | O(13$^v$)···Rb(2)···O(14) | 178·6 |
| O(13)···Rb(1)···O(24) | 118·5 | O(13$^v$)···Rb(2)···O(21$^{iv}$) | 72·4 |
| O(13$^{ii}$)···Rb(1)···O(14) | 136·9 | O(13$^v$)···Rb(2)···O(23) | 65·8 |
| O(13$^{ii}$)···Rb(1)···O(14$^i$) | 145·9 | O(13$^v$)···Rb(2)···O(23$^{iv}$) | 103·9 |
| O(13$^{ii}$)···Rb(1)···O(21) | 69·8 | O(13$^v$)···Rb(2)···O(24) | 97·2 |
| O(13$^{ii}$)···Rb(1)···O(22$^{iii}$) | 80·8 | O(13$^v$)···Rb(2)···O(24$^{vi}$) | 103·1 |
| O(13$^{ii}$)···Rb(1)···O(23$^{iii}$) | 63·6 | O(14)···Rb(2)···O(21$^{iv}$) | 107·3 |
| O(13$^{ii}$)···Rb(1)···O(23$^{iv}$) | 69·2 | O(14)···Rb(2)···O(23) | 115·5 |
| O(13$^{ii}$)···Rb(1)···O(24) | 110·3 | O(14)···Rb(2)···O(23$^{iv}$) | 76·6 |
| O(14)···Rb(1)···O(14$^i$) | 68·3 | O(14)···Rb(2)···O(24) | 84·1 |
| O(14)···Rb(1)···O(21) | 122·7 | O(14)···Rb(2)···O(24$^{vi}$) | 76·7 |
| O(14)···Rb(1)···O(22$^{iii}$) | 122·1 | O(21$^{iv}$)···Rb(2)···O(23) | 78·7 |
| O(14)···Rb(1)···O(23$^{iii}$) | 105·1 | O(21$^{iv}$)···Rb(2)···O(23$^{iv}$) | 46·7 |
| O(14)···Rb(1)···O(23$^{iv}$) | 73·7 | O(21$^{iv}$)···Rb(2)···O(24) | 118·6 |
| O(14)···Rb(1)···O(24) | 80·3 | O(21$^{iv}$)···Rb(2)···O(24$^{vi}$) | 159·3 |
| O(14$^i$)···Rb(1)···O(21) | 120·8 | O(23)···Rb(2)···O(23$^{iv}$) | 62·2 |
| O(14$^i$)···Rb(1)···O(22$^{iii}$) | 65·1 | O(23)···Rb(2)···O(24) | 44·6 |
| O(14$^i$)···Rb(1)···O(23$^{iii}$) | 90·2 | O(23)···Rb(2)···O(24$^{vi}$) | 118·6 |
| O(14$^i$)···Rb(1)···O(23$^{iv}$) | 141·9 | O(23$^{iv}$)···Rb(2)···O(24) | 81·4 |
| O(14$^i$)···Rb(1)···O(24) | 94·7 | O(23$^{iv}$)···Rb(2)···O(24$^{vi}$) | 149·6 |
| O(21)···Rb(1)···O(22$^{iii}$) | 110·0 | O(24)···Rb(2)···O(24$^{vi}$) | 81·8 |
| O(21)···Rb(1)···O(23$^{iii}$) | 129·3 | O(22$^{iii}$)···Rb(1)···O(24) | 134·8 |
| O(21)···Rb(1)···O(23$^{iv}$) | 77·8 | O(23$^{iii}$)···Rb(1)···O(23$^{iv}$) | 102·6 |
| O(21)···Rb(1)···O(24) | 44·6 | O(23$^{iii}$)···Rb(1)···O(24) | 173·8 |
| O(22$^{iii}$)···Rb(1)···O(23$^{iii}$) | 44·8 | O(23$^{iv}$)···Rb(1)···O(24) | 75·8 |
| O(22$^{iii}$)···Rb(1)···O(23$^{iv}$) | 144·3 | | |



Fig. 2. (a) and (b) show views of the crystal packing of RDS molecules at the *ac* and the *bc* planes respectively.

Symmetry code: (i) −x, 1−y, −z; (ii) −x, −y, −z; (iii) x−1, y, z; (iv) 1−x, −y, −z; (v) 1+x, y, z; (vi) 1−x, 1−y, −z.
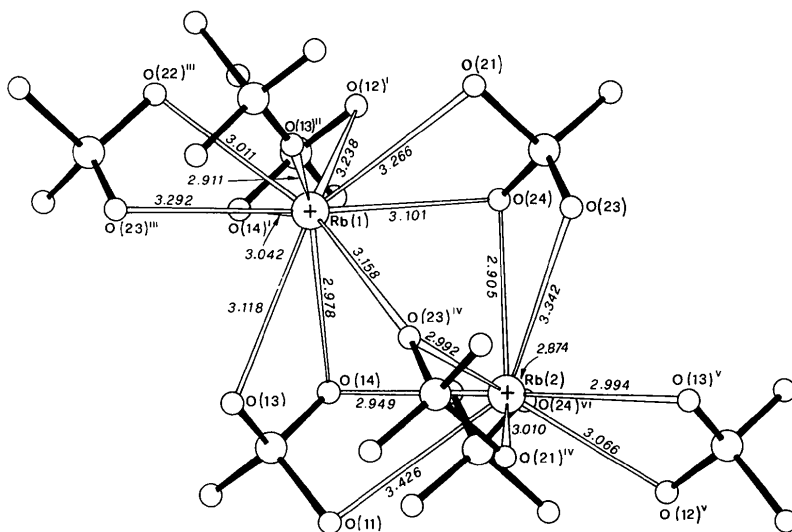


Fig. 3. The coordination of the two independent Rb ions to the surrounding O atoms of the polar heads. Empty and filled bonds represent Rb···O interactions (Å) and S—O bonds respectively. E.s.d.'s are in the range 0·003–0·005 Å. The symmetry code is the same as that in Table 3.

distance of 3·97 (2) Å between the atoms C(12) and C(21) of the molecule at $-x+1$, $-y$, $-z$, and that of 4·63 (2) Å between the atoms C(18) and C(15) of the molecule at $x+1$, $y$, $z$, are the shortest interatomic contacts between hydrocarbon chains having perpendicular and parallel orientations of their mean planes, respectively.

By inspection of Table 4, where some relevant parameters characterizing the SDS and RDS crystal phases are compared, it appears that there is a close similarity between the RDS and the SDS monoclinic phase as far as the average area per polar head, the lamellar thickness and the chain tilting are concerned. Since the Rb ion has an ionic radius larger than that of the Na ion, the similar values indicate that a better packing energy for the hydrocarbon chains is realized in RDS. This statement is supported by the interchain contacts which are slightly smaller for RDS than for the SDS monoclinic crystal phase.
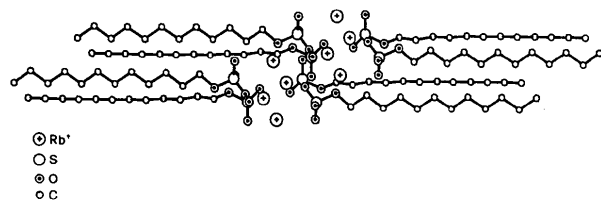


Fig. 4. The relative orientation of the hydrocarbon chains viewed on the mean plane of one of the two.
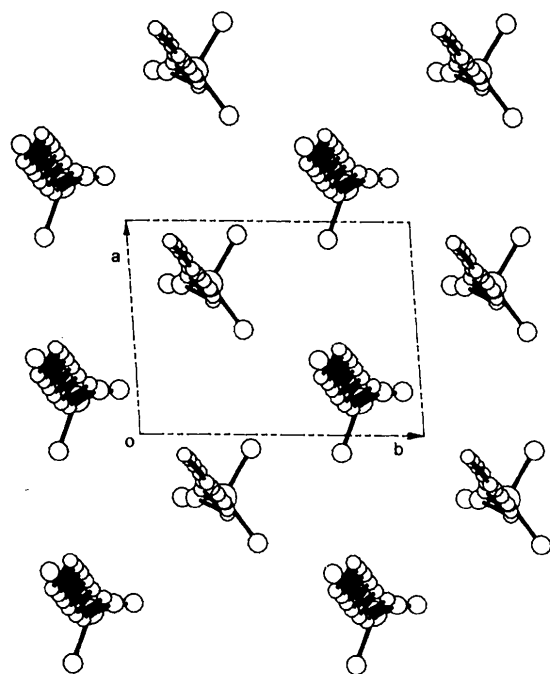


Fig. 5. The packing of the hydrocarbon chains belonging to the same monolayer viewed almost along the chain axis. The cations are not shown.

Table 4. *Some relevant geometrical parameters of SDS and RDS crystal phases*

| Crystal phase | Average area per polar head ($Å^2$) | Lamellar thickness (Å) | Chain tilting angle(°) plane $ac$ | plane $ab$ |
|---|---|---|---|---|
| SDS:H₂O 8:1 (MS) | 20·9 | 38·8 | 4–7 | 79 |
| SDS:H₂O 1:1 (T) | 29·5 | 28·9 | 40 | 40 |
| SDS:H₂O 2:1 (M) | 25·8 | 30·8 | 15 | 46 |
| RDS | 26·6 | 30·7 | 1 | 46 |

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