Discussion of the structure

Atomic positions consistent with the electron-density maps of both projections are given in Table 1, and in Tables 2 and 3 are compared the observed and calculated structure amplitudes for the $h0l$ and $0kl$ zones. The agreement residual $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ is 0·18 for the $h0l$ zone, and 0·20 for the $0kl$ zone. These figures do not consider accidentally absent reflexions (two for $h0l$, one for $0kl$) which according to the calculations should have been just visible.

The minimum distance of approach between neighbouring molecules varies from 3·4 Å to 3·8 Å.

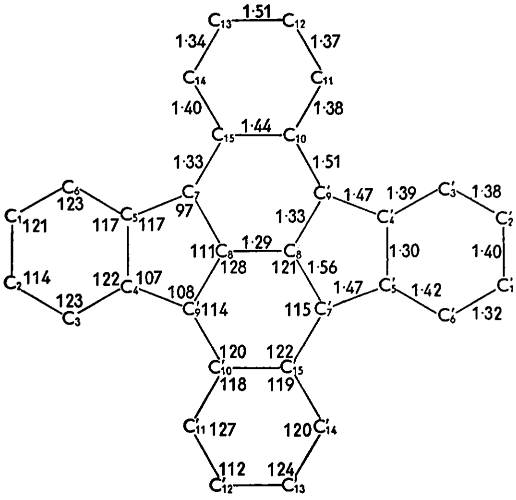

Fig. 2. Diagrammatic representation of the molecule, showing bond lengths (in Ångström units) and angles (in degrees).

The atomic positions quoted are consistent with a molecule in which both the naphthacene and the phenyl groups are effectively planar. The plane of one makes an angle of about 8° with that of the other, and the line of intersection contains the atoms C_4–C_5.

A diagrammatic representation of the molecule is given in Fig. 2; the average C–C bond length is 1·40 Å, and individual bond lengths range from 1·29 Å to 1·56 Å. The variation gives some indication of the probable accuracy of the atomic positions, and suggests that the statement concerning the departure of the molecule from planarity should be treated with some reserve.

The accuracy of the atomic positions is limited by the quality of the X-ray data, and by the poor resolution in the (100) projection. Some of the individual atoms might be resolved in the (101) projection, but three-dimensional methods would probably be necessary to determine the atomic positions accurately.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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The crystal structure of *n*-dodecylammonium chloride and bromide.

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N-mono-n-alkyl substituted ammonium halides are of interest because of their monolayer behaviour and polymorphism, which suggests different kinds of packing of long hydrocarbon chains, and because the lower members possess interesting tetragonal high-temperature forms which are thought to exhibit some kind of chain rotation.

The shorter members of the series were studied first by Hendricks and others and more recently by King &

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Lipscomb (1950*a*, *b*) whose findings differed on some points from those of Hendricks. For the longer members, Wyckoff (1930) gives some long spacings, that for *n*-dodecylammonium iodide being 31·24 Å.

Crystals of *n*-dodecylammonium chloride and bromide were studied by X-ray diffraction, using an automatic variable-temperature moving-film powder camera and single-crystal techniques.

The chloride, on heating to 75° C., undergoes a transition at 59° C. to another monoclinic or triclinic form with a double sheet arrangement. On cooling, there is again a transition at 59° C., evidently not back to the previous form but to a form with a slightly different long spacing.

The bromide on heating from room temperature to 85° C. exhibits at least three transitions at about 57, 61, and 72° C. which can be detected by the change of the powder pattern in a moving-film variable-temperature powder camera. On cooling back to room temperature, further transitions are observed. The chloride and the bromide melt at about 200° C.

Good crystals of the chloride and of the bromide were grown from ethanol at room temperature. The unit-cell dimensions were obtained from rotation and Weissenberg photographs using Ni-filtered Cu *Kα* radiation. The results are:

n - *Dodecylammonium chloride.* — Molecular formula $C_{12}H_{25}NH_3Cl$. Molecular weight 221·5. The crystal is monoclinic with

$$a = 5{\cdot}68,\ b = 7{\cdot}16,\ c = 17{\cdot}86\ \text{Å},\ \beta = 91{\cdot}2^\circ,$$
$$d(001) = 17{\cdot}86\ \text{Å}.$$

Two molecules per unit cell. Density calc. 1·034 g.cm.$^{-3}$. Absences: $0k0$ when k odd. Possible space groups: C_{2h}^2–$P2_1/m$, C_2^2–$P2_1$, the latter appearing the more probable, having two equivalent positions. This space group has no centre of symmetry, but a Fourier projection along the *b* axis has a centre of symmetry.

n - *Dodecylammonium bromide.* — Molecular formula $C_{12}H_{25}NH_3Br$. Molecular weight 266·36. The crystal is monoclinic with

$$a = 6{\cdot}06,\ b = 7{\cdot}02,\ c = 35{\cdot}8\ \text{Å}.,\ \beta = 91{\cdot}6^\circ,$$
$$d(001) = 35{\cdot}8\ \text{Å}.$$

Four molecules per unit cell. Density calc. 1·162 g.cm.$^{-3}$. Density meas. 1·183 g.cm.$^{-3}$ at 22° C. Absences: $h0l$ when l odd, $0k0$ when k odd. Space group: C_{2h}^5–$P2_1/c$.

It is to be noted that the moving-film photographs of the chloride and bromide are very similar as regards general appearance and detailed distribution of intensities up to high-order reflexions. However, the first-layer *b*-axis bromide photographs show in certain regions some extra reflexions which do not seem to be caused by accidental twinning and which require the *c* axis of the unit cell to be doubled, and these are definitely absent for the chloride. This also affects the choice of the space group, so that we have an example of two crystals which are very nearly isomorphous, but yet have different unit cells and space groups.

Intensities of reflexions for both compounds were estimated visually by the multiple-film technique and for the bromide were corrected for absorption. Normal Lorentz and polarization factors were applied and the moduli of the structure factors were obtained on a relative scale.

For the chloride, the approximate *z* co-ordinates of the atoms were first obtained from a one-dimensional Fourier projection on the *c* axis. The *x* co-ordinates were then obtained by constructing masks for the (109), $(2,0,\overline{13})$ and $(30\bar{4})$ planes, which are very strong. Using the *z* co-ordinates, the structure factors of these planes were found to be positive. A preliminary Fourier projection along the *b* axis resolves individual atoms, the atomic arrangement being very similar to that of the bromide.

For the bromide, the moving-film photographs clearly show that the bromine scattering predominates, except at points corresponding to the sub-lattice of the hydrocarbon chains (Vand, 1951). From the nodes where the bromine contribution decreased to zero, it was possible to obtain the bromine co-ordinates by inspection. They are:

$$x_{\text{Br}}/a = 0{\cdot}256,\ y_{\text{Br}}/b = 0{\cdot}225,\ z_{\text{Br}}/c = 0{\cdot}0156\,.$$

As bromine scattering was predominantly phase-determining, a Fourier projection along the *b* axis could be prepared which included all the structure factors of which the sign was reasonably certain. This projection revealed the bromine atom and the hydrocarbon chains. The bromine atom appeared elliptical, suggesting anisotropic thermal motion. This anisotropy was further confirmed by analysing the general decrease of observed structure factors in different directions of reciprocal space.

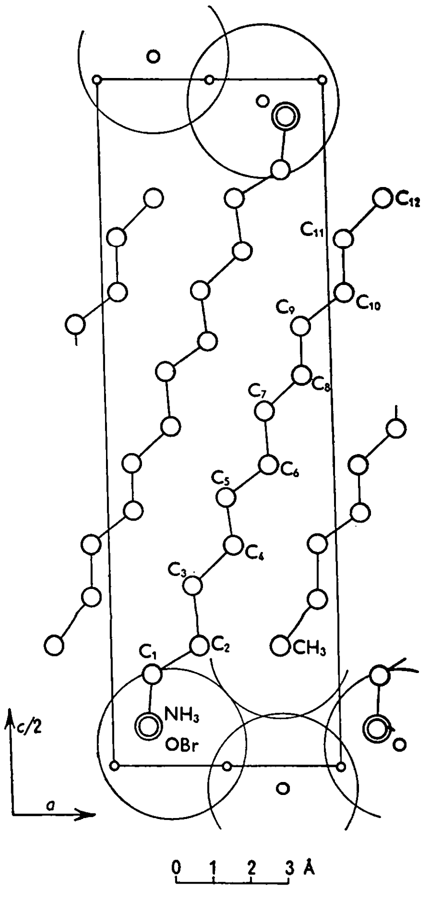

Fig. 1.

As the Fourier projection showed some disturbing diffraction ripples round the bromine atom due to finite termination of the series, a second Fourier difference projection was prepared with the bromine contributions subtracted. This projection shows much better resolution of the carbon atoms. The structure is shown schematically in Fig. 1. The angle of tilt of the chains is $\tau = 66°$. The subcell is nearly orthorhombic with $a_s = 5{\cdot}52$, $b_s = 7{\cdot}02$, $c_s = 2{\cdot}50$ Å.

The co-ordinates obtained from this projection, referring to all the atoms falling within one asymmetric unit (one-quarter unit cell) but belonging to parts of three separate molecules, are:

Atom	x/a	z/c	Atom	x/a	z/c
Br	0·256	0·0156	C_6	0·7205	0·2165
N	0·161	0·0278	C_7	0·2911	0·2438
C_1	0·1968	0·0650	C_8	0·1129	0·2178
C_2	0·4003	0·0860	C_9	0·1179	0·1800
C_3	0·3737	0·1258	C_{10}	0·9315	0·1550
C_4	0·5563	0·1520	C_{11}	0·9320	0·1163
C_5	0·5270	0·1902	C_{12}	0·7580	0·0900

The consideration of this projection shows that the NH_3^+ groups lie about 0·5 Å out of the planes occupied by the halide ions. This agrees with a similar displacement observed by King & Lipscomb (1950*b*) for the low-temperature form of *n*-propylammonium chloride.

It is to be noted that the particular crystalline form of the *n*-dodecylammonium chloride and the bromide are approximately isomorphous and have the C–N bond at roughly 90° to the 001 plane, which is near to the value for *n*-propylammonium chloride (space group C_{2h}^3–$C2/m$). All the three structures, however, are representatives of three different space groups.

In order to obtain more complete information on the packing of the hydrocarbon chains, it will be necessary to prepare the other projections of the unit cell.

We wish to thank Professors J. Monteath Robertson and P. D. Ritchie for great interest in this investigation, and C. J. McCron for help in the evaluation of data for the hydrochloride.

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Neutron-diffraction study of the structure of the *A*-form of the rare earth sesquioxides.

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(*Received 23 April 1953*)

In the course of experiments on the paramagnetic scattering of neutrons by rare earth ions, the results of which are reported elsewhere (Koehler & Wollan, 1953), neutron-diffraction data from powdered samples of La_2O_3, Pr_2O_3 and Nd_2O_3 of normal isotopic constitution and Nd_2O_3 enriched in Nd^{142}, Nd^{144} and Nd^{146} were obtained which provide direct evidence in confirmation

Table 1. *Values of* $j|F|^2$ *for* La_2O_3*-type structures*

	Pauling model	Zachariasen model
	2 La in $\pm(\frac{1}{3}, \frac{2}{3}, u)$ 2 O in $\pm(\frac{1}{3}, \frac{2}{3}, v)$ 1 O in $(0, 0, 0)$	2 La in $\pm(\frac{1}{3}, \frac{2}{3}, u)$ 3 O in $(v, v, 0;\ \bar{v}, v, 0;\ v, \bar{v}, 0)$
Index	$u = 0{\cdot}25,\ v = 0{\cdot}65$	$u = 0{\cdot}25,\ v = 0{\cdot}25$
001	0·0207	6·06
100	$6f_M^2$	$6f_M^2-6{\cdot}96f_M+2{\cdot}02$
002	$8f_M^2-1{\cdot}77f_M+0{\cdot}0982$	$8f_M^2-13{\cdot}9f_M+6{\cdot}07$
101	$36f_M^2-33{\cdot}8f_M+18{\cdot}1$	$36f_M^2+4{\cdot}04$
102	$12f_M^2+18{\cdot}2f_M+18{\cdot}2$	$12f_M^2+13{\cdot}9f_M+4{\cdot}04$
003	5·66	6·06
110	$24f_M^2+41{\cdot}8f_M+18{\cdot}2$	$24f_M^2-13{\cdot}9f_M+10{\cdot}1$
111	0·124	20·2
103	$36f_M^2+12{\cdot}9f_M+7{\cdot}37$	$36f_M^2+4{\cdot}04$
200	$6f_M^2$	$6f_M^2+6{\cdot}96f_M+2{\cdot}02$
112	$48f_M^2-10{\cdot}6f_M+0{\cdot}589$	$48f_M^2+27{\cdot}8f_M+20{\cdot}2$
201	$36f_M^2-33{\cdot}8f_M+18{\cdot}1$	$36f_M^2+4{\cdot}04$
004	$8f_M^2-2{\cdot}89f_M+0{\cdot}257$	$8f_M^2+13{\cdot}9f_M+6{\cdot}06$

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* This work constitutes part of a dissertation submitted to the University of Tennessee, Knoxville, Tennessee, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.