is quite stable in accord with its covalent character.) The siloxanes, as a class, have 'abnormally' low boiling points and low temperature coefficients of viscosity. The seeming contradiction between the idea of a highly polar siloxane skeleton and the observed low inter-molecular forces is resolved by assuming a low barrier to free rotation of CH_3 groups about siloxane bonds. The 'softness' of the bond angles, plus the favourable geometry reducing steric interactions of attached groups, should result in a negligible barrier to free rotation about the siloxane bonds in linear polymers. Consequently, the low boiling points and temperature coefficients of viscosity may be attributed to free rotation preventing chains from packing sufficiently closely for the short-range intermolecular forces to become strongly operative.

The kind assistance of Mr Eric Asp in the taking of the X-ray pictures is acknowledged. We are grateful to Mr J. Kilfoyle for tracing the drawings, and to Miss Charlotte Cherry for helping in the construction of a set of Beevers-Lipson strips.

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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. Rapid publication will be facilitated if the contributions are without illustrations.

The crystal structure of kalsilite. By G. F. CLARINGBULL and F. A. BANNISTER. *British Museum (Natural History), London, S.W. 7, England*

Kalsilite, the simplest of the three known polymorphous forms of $KAlSiO_4$, was isolated in minute quantities from volcanic rocks of S.W. Uganda in 1942 (Bannister & Hey, 1942) and synthesized in the laboratory for the first time in 1947 (Rigby & Richardson, 1947). Its unit-cell contents, dimensions and space group when determined by chemical analysis and single-crystal photographs revealed an obvious relationship to hexagonal tridymite, nepheline and kaliophilite (Bannister & Hey, 1931). In cell dimensions ($a = 5·17$, $c = 8·67$ A.) and space group ($C6_32$) kalsilite is, however, more closely related to $BaAl_2O_4$ ($a = 5·21$, $c = 8·76$ A.) (Wallmark & Westgren, 1937) which Nowacki (1942) pointed out is almost identical in crystal structure and parameter values with $KLiSO_4$ ($a = 5·13$, $c = 8·60$ A.) (Bradley, 1925; Ewald & Hermann, 1931).

Nagelschmidt recently sent us crystals of $KLiSO_4$ and also powder photographs of $KLiSO_4$ and artificial kalsilite showing the essential identity of their crystal structures. We have now obtained photometer records of our own powder photographs of kalsilite, $BaAl_2O_4$ and $KLiSO_4$ which confirm these suggestions of identity. The differences between the almost identical photometer curves for kalsilite and $KLiSO_4$ and the curve for $BaAl_2O_4$ can be attributed to the difference in the atomic scattering factors for the potassium and barium ions.

The comparison of calculated and estimated intensities for kalsilite establishes its structure type as $H2_8$ (Gottfried, 1940) and establishes parameter values. The (Si, Al)O_2 tetrahedral framework of kalsilite and the corresponding frameworks AlO_2 and LiO_2, SO_2 of $BaAl_2O_4$ and $KLiSO_4$ are derived from hexagonal tridymite, SiO_2, structure type $C10$. The (Si, Al)–O–(Si, Al) linkages between the tetrahedra along the c axis are straight as in tridymite. All other linkages, which in tridymite are also straight, have in kalsilite an approximately tetrahedral angle near to 109° 28'. The cavities in this modified tridymite structure are occupied by the large potassium ions.

Buerger (1946) has confirmed that the crystal structure of nepheline, $KNa_3Al_4Si_4O_{16}$, is based upon a tridymite-like framework, but the distortion is not confined to tetra-hedral rotations in the c plane as in the $H2_8$ framework, and cavities of two sizes are developed which are occupied by the sodium and potassium ions respectively. The crystal structure of kaliophilite ($a = 26·94, c = 8·55$ A., space group $C6_32$) (Lukesh & Buerger, 1941), which has not yet been worked out in detail, is probably a multiple kalsilite structure. The c dimension is perceptibly less for kalio-philite than for kalsilite, possibly indicating slight flexing of the (Si, Al)–O–(Si, Al) linkages lying parallel to the c axis.
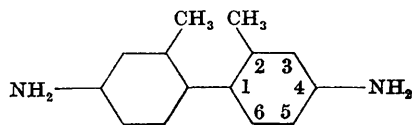
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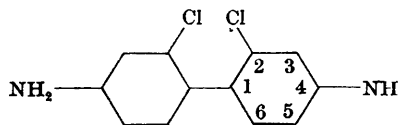## The structure of 3:3′-dichlorobenzidine. By J. TOUSSAINT*. *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*
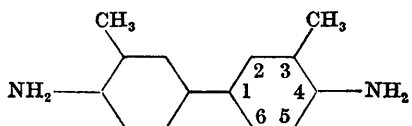
Analysis of the structures of *m*-tolidine dihydrochloride (Hargreaves & Taylor, 1941) and of 2:2′-dichlorobenzidine (Smare, 1942) has shown that in each of these molecules (I, II) the phenyl rings are rotated from the *cis*-planar configuration through approximately 36° in opposite

for both chlorine atoms of the molecule; but from these co-ordinates it appears that the chlorine atoms contribute nothing to reflexions ($h0l$) when h is odd, so that in a first Fourier synthesis the positions of these atoms can be used to determine the signs of reflexions ($h0l$) only when
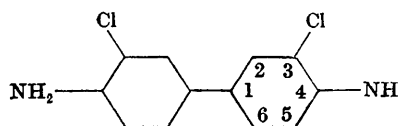

(I)

(II)

(III)

(IV)

directions around the central diphenyl link, so that the angle between the planes of the phenyl rings is approximately 72°. The non-planar configuration arises from the need to allow clearance between the rather large methyl groups or chlorine atoms attached to the rings at positions 2,2′. It would obviously be of interest to compare the configurations of these molecules with those of *o*-tolidine (III) and 3:3′-dichlorobenzidine (IV), for which a completely planar configuration would seem to be likely, whether the molecule is *cis* or *trans*.

The unpublished data of A. Hargreaves and H. F. Kay show that the unit cell of 3:3′-dichlorobenzidine is monoclinic with a 12·5 A., b 3·85 A., c 23·7 A., and β 108°. The cell contains four molecules, the space group is $P2_1/a$, and a special feature of the diffraction patterns is that reflexions ($h0l$) are absent or very weak when h is odd, indicating that the structure has a pseudo-periodicity $\frac{1}{2}a$ in projection on (010). I am indebted to Dr Hargreaves and Mr Kay for permission to use their experimental data, which include the intensities of all ($h0l$) reflexions estimated by eye in the usual way.

The present paper describes the results obtained from these data, in an attempt to complete the analysis of the structure.

From the Patterson projection along the b axis it is possible to determine approximate x and z co-ordinates

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h is even. The usual method of successive approximations, using only terms ($h0l$) with h even, leads to the projection in Fig. 1.
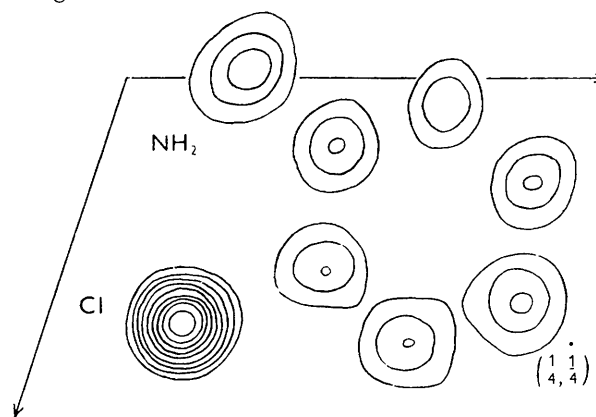

Fig. 1. 3:3′-dichlorobenzidine. Electron density projected on (010)

Since terms ($h0l$) with h odd have been left out of consideration in the calculation of this projection, it represents an 'average' structure having spurious symmetry additional to the true symmetry of the actual structure. The 'molecule' is an 'average' molecule, with a spurious centre of symmetry at $x=\frac{1}{4}a$, $z=\frac{1}{4}c$ (the point marked $\frac{1}{4}$, $\frac{1}{4}$ in