# The Structure of the *NN*-Diethyldithiocarbamate Ion in the Trihydrate Sodium Salt

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THOUGH many metal *NN*-dialkyldithiocarbamates have been studied by *X*-ray diffraction analysis, no information is yet available on the geometry of any of the free *NN*-dialkyldithiocarbamate ions. Sodium *NN*-diethyldithiocarbamate trihydrate seemed to provide a suitable case of a free ligand molecule in an essentially ionic environment, and we therefore determined its structure by three-dimensional *X*-ray techniques.

$Na(S_2CNEt_2),3H_2O$ crystallizes from acetone as stout prisms without losing its water of crystallization; $a = 7{\cdot}591 \pm 0{\cdot}010$, $b = 28{\cdot}632 \pm 0{\cdot}015$, $c = 10{\cdot}470 \pm 0{\cdot}010$ Å; $U = 2275{\cdot}6$ Å$^3$; $D_m = 1{\cdot}313 \pm 0{\cdot}003$ g.cm.$^{-3}$ (by flotation); $Z = 8$, $D_c = 1{\cdot}315$ g.cm.$^{-3}$; $F(000) = 965{\cdot}0$. Space group: *Pbca* from systematic absences. Cu-$K_\alpha$ radiation ($\lambda$ taken as 1·5418 Å), $\mu = 42{\cdot}8$ cm.$^{-1}$. Data derived from Weissenberg photographs using an improved version of Christ's method.[1] Limits of error given in the form of maximum error.

A total of 1555 independent non-zero structure amplitudes were obtained from visual estimates of photographic Weissenberg records. The structure was solved by means of a direct phase-determining procedure based on the iterative application of Sayre's equation,[2] a method similar to the symbolic addition procedure of Karle and Karle,[3] and refined by anisotropic block diagonal least-squares methods to a *R* value of 0·079.[4] Further refinement is in progress.

The structure consists of infinite layers of co-ordination polyhedra of sodium ions, extending parallel to the *ac* plane, and connected on both sides with layers of organic anions. Adjacent organic layers are held together solely by the van der Waals forces between the non-polar ends of the anions. Similar double-layer structures are typical of a number of the alkaline salts of organic acids, mainly fatty acids.

The sodium ion is situated at the centre of a distorted octahedron of five water molecules (at distances ranging from 2·360 to 2·486 Å) and one sulphur atom (at $3{\cdot}052_3$ Å). The other sulphur atom of the anion is outside the sodium co-ordination sphere, being situated at $4{\cdot}151_3$ Å away from the sodium ion. The octahedra share one edge in pairs; each pair in turn shares four corners with four adjacent pairs, giving rise to the infinite layer.

Six hydrogen bonds occur, and five of them are of the type S···H–O, with sulphur–oxygen distances ranging from 3·249 to 3·355 Å. Four out of the six hydrogen atoms involved have actually been located on the difference map.†

Details of the geometry of the *NN*-diethyldithiocarbamate ion at the present stage of refinement are given in the Figure. The main points of interest are:

(i) The ion is planar (apart from the terminal methyl groups) within ±0·04 Å, the small (but significant) deviations from planarity being indicative of a small torsion (2—3°) about the C(1)–N bond. A similar feature was observed in tetraethylthiuramdisulphide.[4]

(ii) The sulphur–carbon and carbon($sp^2$)-nitrogen bonds all have high double-bond character.

(iii) The difference in length between the S(1)–C(1) and the S(2)–C(1) bonds, 2·6 $\sigma$, is only possibly

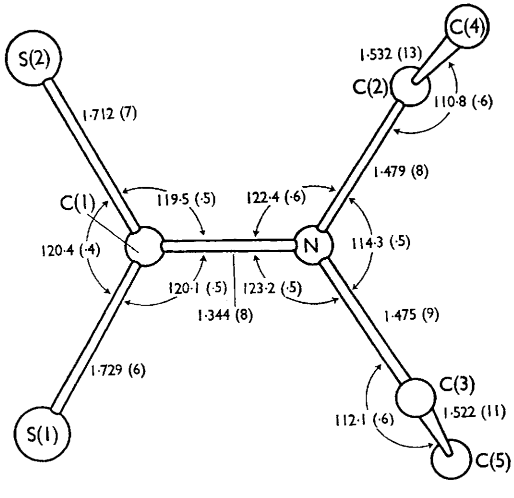

FIGURE. *Bond distances* (Å) *and angles* (*degrees*) *in the* NN-*diethyldithiocarbamate ion. Values in parentheses are estimated standard deviations.*

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† The contributions from 14 out of the 16 hydrogen atoms, as located on a difference Fourier map, have been taken into account.

significant, in spite of the fact that S(1) is within the sodium co-ordination sphere and S(2) is not. This is consistent with the ionic character of the Na–S(1) interaction.

(iv) The three angles at C(1), which are opposite to three bonds all with high double bond character, are all equal to 120°, within experimental error.

(v) Of the three angles at the nitrogen atom, one, C(2)–N–C(3), is remarkably less than the other two. This fact, which was reported, but not pointed out, in all the metal *NN*-diethyldithiocarbamates studied so far, and also in tetraethylthiuram disulphide,[4] seems to be scarcely dependent on the size of the alkyl groups, and is probably due to the peculiar position of the C(2)–N–C(3) angle, which is opposite to a bond with a high double-bond character, whilst the other two angles at the same atom are opposite to practically single bonds. A similar situation occurs in a number of organic compounds with $sp^2$-hybridized carbon or nitrogen atoms, such as ethylene and substituted ethylenes, ketones, *NN*-dimethylamides, thioamides, carboxylic acids and esters, in which angles less than 120° have been reported to be opposite to double or partially double bonds.

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