

The acetic anhydride filtrate (immediately above) was decomposed with water and organic material extracted with ether. Acetic acid was removed by sodium hydrogen carbonate solution. Evaporation of the ether left a yellow resin that partly crystallised. The amount was estimated at 2 mg or 10 % of the starting material. From acetone colourless crystals were obtained, which melted at 230—245°. A mixture with *epifriedelanyl acetate* melted at 230—255°.

epiFriedelanyl benzoate. A small sample of the benzoate from the original alcohol from *Ceratopetalum apetalum*¹ was available. It melted at 250—251°, whilst a mixture with the original benzoate from the lichen material (m. p. 231—232°)² melted at 231—245°, all three taken at the same time. A fresh sample of the benzoate was prepared with benzoyl chloride similarly as the acetate, m. p. 251—252°, $[\alpha]_D + 34^\circ$ (c, 2.19), recrystallised, m. p. 245—247°, $[\alpha]_D + 34^\circ$ (c, 2.06). The dried sample (as above) melted at 246—248°, $[\alpha]_D + 34^\circ$ (c, 1.55).

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1. Jefferies, P. R. *J. Chem. Soc.* **1954** 473.
2. Bruun, T. *Acta Chem. Scand.* **8** (1954) 71.

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The Structure of Liquid Carbon Disulphide

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Several investigators have noted a departure from normal behaviour of liquid carbon disulphide. Hildebrand¹ as early as in 1919 found that the internal pressure calculated from the coefficients of expansion and compressibility gave a comparatively low relative value. Benson² observed that the ratio of the density at the boiling point to the density at the critical point was abnormally large. This he concluded to be due to a dense packing in the liquid structure, arising from the chain-forming tendency of sulphur atoms with

available 3d orbitals. Stavely and Tupman³ in a discussion of entropies of vaporization and internal order in liquids, found the entropy of vaporization of liquid carbon disulphide surprisingly low. According to their general theory, a nearly unrestricted rotation or a low degree of order should be expected in such cases. The Kerr effect, however, indicates a considerable degree of hindrance to free rotation in this liquid, as pointed out by Debye⁴.

Information about the structure of liquid carbon disulphide would consequently be of interest. Hence the electronic radial distribution curve has been determined (at 15° C) for this system. A procedure according to Finbak⁵ was employed. The X-ray intensity measurements have been obtained using MoK α -radiation only. For low scattering angles a Guinier camera was used, permitting observations to be made down to $s = 4\pi(\sin\theta/\lambda) = 1.3 \text{ \AA}^{-1}$. The resulting distribution curve is reproduced in Fig. 1. Maxima are found at 1.55 Å, 4.0 Å, 6.5 Å and 7.6 Å. At about 3.1 Å a superimposed peak can be distinguished.

The peaks at 1.55 Å and 3.1 Å obviously correspond to the C—S and S—S distances within the molecule. They agree very well with the results obtained on gaseous carbon disulphide by X-ray diffraction⁶ and electron diffraction^{7,8}.

The remaining peaks reflect the packing of the molecules. In order to interpret these peaks, a model of the liquid structure will be considered. The molecule itself can be regarded approximately as a cylinder, with a radius r and a length $d + 2r$. Here d is the S—S distance within the molecule. A closepacking of these cylinders requires the volume:

$$V = 2\sqrt{3} r^2(2r + d)$$

Inserting in the formula above the observed liquid volume extrapolated to 0° K⁹, r is found to be 1.85 Å. This value equals the van der Waals radius of sulphur, as tabulated by Pauling¹⁰. At room temperature the formula gives r equal to 2.0 Å and a corresponding packing distance of 4.0 Å for the molecules. The largest peak in the experimental distribution curve occurs at just this distance.

The peaks at 6.5 Å and 7.6 Å are more uncertain because of the experimental errors. The "end to end" packing of the molecules should give a peak at about 7.1 Å according to the previous discussion. The second coordination shell is found at 6.9 Å (and 14.2 Å for the "end to end"

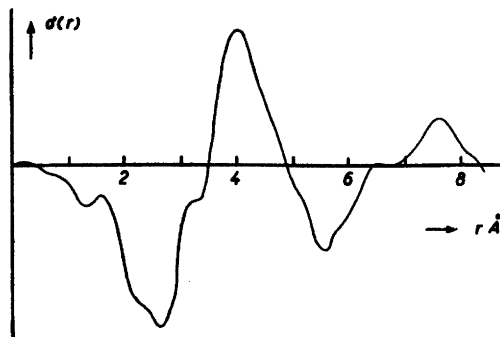


Fig. 1. Electronic radial distribution curve, $\sigma(r)$, for liquid carbon disulphide.

packing). These packing distances are probably not so definite and may very well account for the observed peaks.

Eventually it can be concluded from these considerations that rotation about the two short axes of the molecule is very restricted. Free rotation would have displaced the major peak from 4.0 Å to at least 5.0 Å. The molecules thus tend to orient themselves with their long axis parallel, corresponding to the proposed closepacking.

Any tendency for the molecules to be mutually displaced along the parallel major axes can not be settled by the present experimental distribution function. A crystal structure investigation of solid carbon disulphide would be of great interest in this connection. (The determination by de Smedt¹¹ seems questionable with a C—S distance of 1.77 Å and packing distances varying from about 2.2 Å to 8.0 Å. The result is also inconsistent with symmetry observations by Washer¹².) Kast and Stuart¹³ have discussed various possibilities for the liquid structure. They suggest that the quadrupole moment of the molecule may give rise to parallel displacements as discussed above, (and even to crossed positions of the major molecular axis).

The defect in the entropy of vaporization of liquid carbon disulphide is explained neither by a low degree of order in the structure, nor by unrestricted rotation.

The explanation must be sought in an intermolecular potential energy function differing from normal, as suggested by Frank¹⁴.

1. Hildebrand, J. H. *J. Am. Chem. Soc.* **41** (1919) 1073.
2. Benson, S. W. *J. Phys. & Colloid Chem.* **52** (1948) 1060.
3. Staveley, L. A. K. and Tupman, W. I. *J. Chem. Soc.* **1950** 3597.
4. Debye, P. *Chem. Revs.* **19** (1936) 171.
5. Finbak, Chr. *Acta Chem. Scand.* **3** (1949) 1279.
6. Gajewski, H. *Physik. Z.* **33** (1932) 122.
7. Brockway, L. O. *Revs. Mod. Phys.* **8** 231.
8. Finbak, Chr. and Hassel, O. *Arch. Math. Naturvidenskab* **45** (1942) No. 3.
9. Jacobson, B. and Heedman, P. A. *Acta Chem. Scand.* **7** (1953) 705.
10. Pauling, L. *The Nature of the Chemical Bond*. 2nd. ed. Cornell University Press 1945.
11. de Smedt, J. *Natuurw. Tijdschr.* **8** (1926) 13; *Chem. Abstracts* **21** (1927) 1572, **23** (1929) 2099.
12. Washer, F. E. *Proc. Indiana Acad. Sci.* **45** (1935) 222; *Chem. Abstracts* **31** (1937) 922.
13. Kast, W. and Stuart, H. A. *Physik. Z.* **40** (1939) 714.
14. Frank, H. S. *J. Chem. Phys.* **13** (1945) 493.

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