

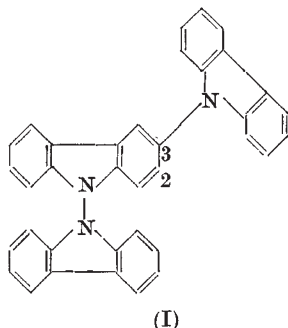
## CHEMISTRY

## Tricarbazyl

OXIDATION of carbazole with potassium permanganate in boiling acetone was reported in 1921 (ref. 1) to yield two crystalline products, (A) and (B), and an amorphous product. One of these crystalline products, (A), was later shown<sup>2</sup> to be 9,9'-dicarbazyl, and the other, (B), which was thought<sup>1</sup> to be a dicarbazyl on the basis of a cryoscopic molecular weight determination in benzene, was shown not to be identical with synthetic specimens of 1,1'-(ref. 3), 3,3'-(ref. 4) and 3,9'-(ref. 5) dicarbazyls. It was, however, proposed<sup>6</sup> that (B) might be either 1,3'- or 1,9'-dicarbazyl.

A recent paper<sup>7</sup> describing investigations of the oxidative dimerization of carbazole in various solvents prompts this report of structural investigations which have been carried out on the aforementioned compound (B), which has been prepared from carbazole by a method previously described<sup>1</sup>.

The mass spectrum (mass spectra were recorded on an A.E.I. MS 9 spectrometer by Dr. J. M. Wilson) of compound (B) exhibits a molecular ion peak at  $m/e = 497$ , which, therefore, contrary to the previous proposal<sup>1</sup>, shows it to be a tricarbazyl for which structure (I) is proposed on the basis of the following evidence.



(a) The mass spectrum of compound (A), 9,9'-dicarbazyl<sup>2</sup>, which has a molecular ion peak at  $m/e = 332$ , shows the expected very easy fragmentation across the N—N bond to give a base-peak at  $m/e = 166$ . By comparison, the mass spectrum of (B) indicates, as well as a molecular ion peak at  $m/e = 497$ , the very easy loss of one carbazyl group (presumably by N—N bond scission as occurred in 9,9'-dicarbazyl) to give a base-peak at  $m/e = 331$ . Further fragmentation of the stronger C<sub>3</sub>—N bond then affords much weaker peaks at  $m/e = 167$  and 166.

(b) The infra-red spectrum (infra-red spectra were recorded in 'Nujol' on a Perkin Elmer model 237 spectrophotometer) of (B) shows no absorption in the N—H stretching region, indicating that the carbazole N-atoms must take part in the bonds between the three carbazole units. The complete spectrum is also very similar to that of 9,9'-dicarbazyl, but, unlike the latter spectrum, it exhibits a medium-strong band at  $\nu_{\max} = 812 \text{ cm}^{-1}$  and a weak band at  $\nu_{\max} = 879 \text{ cm}^{-1}$ , indicative of a 1,2,4-tri-substituted benzene nucleus<sup>8</sup>, which therefore supports the attachment of the third carbazole unit to the 9,9'-dicarbazyl unit in (B) at either C<sub>2</sub> or C<sub>3</sub>.

(c) That this linkage is between N—C<sub>3</sub> as shown in (I) and not between N—C<sub>2</sub> is supported by the observations<sup>9</sup> that C<sub>3</sub> in carbazole is more reactive than C<sub>2</sub>.

Attempts to verify chemically structure (I) by selective reductive cleavage of the N—N bond to afford carbazole and 3,9'-dicarbazyl<sup>5</sup> have not been successful, prob-

ably due to the low solubility of (B) (ref. 1). Treatment with concentrated hydriodic acid at 150° C in a sealed tube for 15 h gave, contrary to previous observations<sup>2</sup>, only carbazole.

B. ROBINSON

Department of Pharmacy,  
University of Manchester.

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<sup>3</sup> Macrae, T. F., and Tucker, S. H., *J. Chem. Soc.*, 1520 (1933).

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<sup>5</sup> Nelmes, M. C., and Tucker, S. H., *J. Chem. Soc.*, 1523 (1933).

<sup>6</sup> Campbell, N., and Barclay, B. M., *Chem. Revs.*, 40, 359 (1947).

<sup>7</sup> Kuroki, M., *Yuki Gosei Kagaku Kyokai Shi.*, 23, 447 (1965); *Chem. Abs.*, 63, 4238 (1965).

<sup>8</sup> Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, 65 (Methuen, London, 1960).

<sup>9</sup> Maitland, P., and Tucker, S. H., *J. Chem. Soc.*, 1388 (1927). Freudenberg, W., in *Heterocyclic Compounds*, edit. by Elderfield, R. C., 3, 291 (Chapman and Hall, London; Wiley, New York, 1952). Sumpter, W. C., and Miller, F. M., in *Heterocyclic Compounds with Indole and Carbazole Systems*, edit. by Weissberger, A., 70 (Interscience, London and New York, 1954).

### Crystal Structure of the Benzene *tris(o-Phenylenedioxy) Phosphonitrile Trimer Complex*

A DESCRIPTION of the inclusion compound *tris(o-phenylenedioxy) phosphonitrile trimer* has already been reported<sup>1</sup> which includes some preliminary crystallographic data and a short discussion of the possible arrangements of the molecular architecture. This communication describes a partial structure determination in two dimensions of the complex with benzene.

The crystals were hexagonal, unit cell  $a = 11.68 \text{ \AA}$ ,  $c = 10.077 \text{ \AA}$ ; space group either  $P6_3$  or  $P6_3/m$ . The measured density of 1.395 g/c.c. is consistent with two molecules of the trimer and about one benzene molecule in the unit cell. The intensities of seventy-four independent  $hk0$  reflexions were visually estimated, corrected for  $Lp$  factors and used to calculate the Patterson projection  $P(u,v)$ .

As reported in ref. 1, the two trimers must either be sited on the six-fold axis or one on each of the triad axes, but simple packing considerations show that only the sites on the three-fold axes lead to a structure containing suitable channels. The vector line of the *o*-phenylenedioxy group was obtained from the Patterson map, and a Fourier map based on a trial structure showed well-resolved atoms of the trimer arranged so that six trimers form one channel per unit cell around the benzene molecule which is sited at the origin. Initially the  $R$  value was high (> 40 per cent), but marked improvement was obtained ( $R$  fell to 21 per cent) when the trimer was moved through a small angle around the triad axis (the

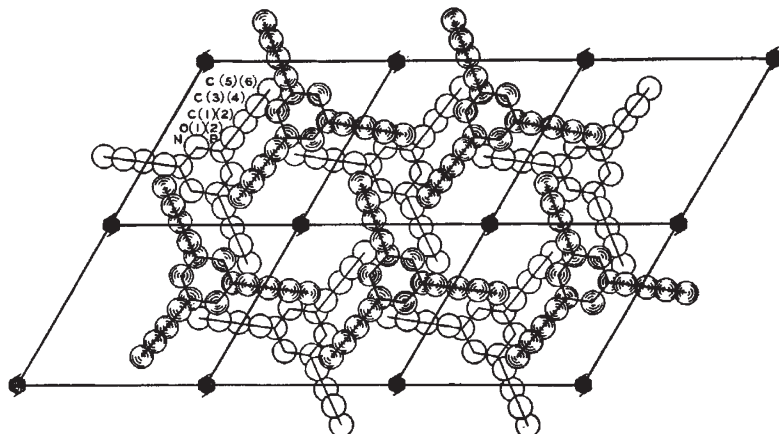


Fig. 1. (00.1) Projection showing channels parallel to six-fold axis