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The Structure of the Condensation Product of Acetone and *N*-Phenylhydroxylamine and of the Corresponding Free Radical

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BANFIELD and KENYON[1] proposed that the structure of the condensation product formed from acetone solutions of *N*-phenylhydroxylamine was either (I) or (II). Their main arguments were based on the molecular formula, shown by Beakmann and Scheiber[2] to be $C_{18}H_{22}N_2O_2$, and the fact that the action of aqueous hydrochloric acid on the product produced 2,4′-chloroanilino-2-methylpentan-4-one.

The n.m.r. spectrum of a chloroform solution includes an AX-system: δ 3·09 and 2·12 (J_{AX} 14 Hz), which shows no change when the temperature is raised from 33·5° to 60°. These absorptions would correspond to the methylene protons in structure (I) or (II). Had the product been (II), the non-equivalence of the methylene protons would have been due to restricted rotation. Molecular models and a study of related structures suggest that in fact such a rotational barrier would not be sufficiently large to account for the observed n.m.r. behaviour. On the basis of structure (I), the non-equivalence of the methylene protons would have been due to the asymmetry of the adjacent carbon atom. The observed coupling constant is very high for protons in such a situation, since free rotation about the appropriate C–C bond is expected. However, these observations are reasonably explained in terms of a different structure, (III). The remaining part of the n.m.r. spectrum is equally well accounted for by any of the three structures.

Complete confirmation of structure (III) has been obtained by an *X*-ray crystallographic determination.

The crystals were obtained from an ethanol solution and a preliminary study showed that two types of crystal were present in the same batch. Both types were well-formed monoclinic prisms but the smaller crystals were mostly of one type and the larger ones of the second type. Their unit cell dimensions were as follows:

type 1 (small crystals, prism axis = c) a = 12·45, b = 13·25, c = 10·18 Å, β = 97·7°, D_m = 1·188;
type 2 (large crystals, prism axis = b) a = 13·67, b = 7·37, c = 16·09 Å, β = 94·8°, D_m = 1·193.

In both cases the systematically absent reflections were $h0l$ when $h + l$ is odd and $0k0$ when k is odd; thus the space group is $P2_1/n$ and $Z = 4$, and $M = 298$.

Three-dimensional *X*-ray diffraction data (2317 independent reflections) were collected for the type 1 crystals (Cu-K_α radiation) and the signs of 196 reflections were obtained by the method of symbolic addition.[3] The 22 highest peaks from a three-dimensional "E" Fourier synthesis gave a molecular structure consistent with (III). The co-ordinates of the 22 peaks were obtained from the Fourier synthesis and were used to calculate structure factors for all the 2317 observed reflections. The R value was 0·43 but this fell to 0·17 after 5 cycles of least-squares refinement with isotropic temperature parameters. Probable

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hydrogen co-ordinates were included in the structure-factor calculations at this stage and further cycles of least-squares refinement, now with anisotropic temperature parameters, reduced R to 0·125. The molecular structure was confirmed by means of a three-dimensional F_0 Fourier synthesis with all the observed structure factors. The bond-lengths and bond angles were as expected for structure (III) with the exception of one short bond in a benzene ring. Previous experience suggests that the R value should be lower than 0·125 and it is possible that there is some disorder in the crystal lattice. The molecule is flexible and it is probable that its shape in the type 2 crystals is different from that in type 1.

The i.r. spectra of (III) and of the Banfield and Kenyon radical ($C_{18}H_{21}N_2O_2$) are identical, except for the absence of O–H vibrations in the latter. Consequently the radical must have the structure (IV).

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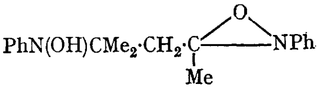
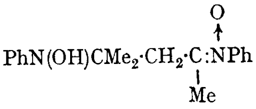
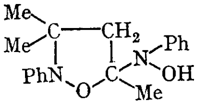


(I)

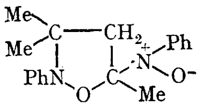


$\mathrm{PhN(OH)CMe_2{\cdot}CH_2{\cdot}\underset{Me}{C}{:}\overset{\overset{O}{\uparrow}}{N}Ph}$

(II)



(III)



(IV)

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[3] J. Karle and I. Karle, "Computing Methods in Crystallography," ed. J. Rollett, Pergamon Press, Oxford, 1965.