An Electron Diffraction Investigation of the Molecular Structure of Fluoro-*N*,*N*'-dimethyl-1,2,3,4-diazadiphosphetidine, $(F_3PNCH_3)_2$, in the Vapour Phase

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The structure investigation of $(F_3PNCH_3)_2$ was started in order to study the bonding arrangement at the phosphorus atom when it takes part in a ring formation. The compound was prepared by Schmutzler.[1] Spectroscopic investigations have shown that the ring in $(F_3PNCH_3)_2$ is planar.[2,3] The infrared and Raman spectra were recorded from solution.

The experimental data for the electron diffraction study of $(F_3PNCH_3)_2$ were taken at three camera distances, approximately 130, 48, and 19 cm, and combined to give a molecular intensity function in the *s*-range 1.25–44.00 Å^{-1}.

The bond distances and angles in the molecule were determined by comparing the experimental radial distribution (RD) function [4] with corresponding calculated functions based on a series of molecular models till the best agreement was obtained, shown in Fig. 1. Except for the peak complex at about 2.9 Å which contains mainly the P···C distances, all peaks on the RD curve contain contributions from a large number of distances. All bond distances (except C–H) contribute to one peak at about 1.6 Å.

The preliminary structure parameters are given in Fig. 2. In agreement with the spectroscopic investigators we find that

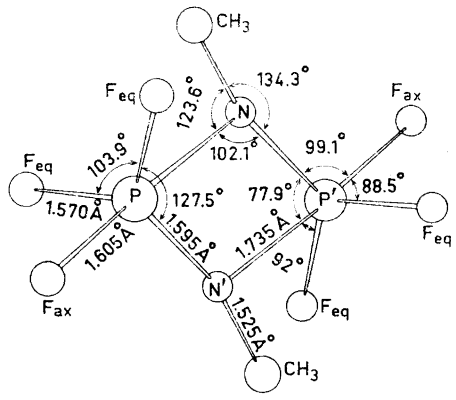

Fig. 2. Preliminary structure of $(F_3PNCH_3)_2$.

the ring is planar. Further we find that the methyl carbons lie in the plane of the ring. The arrangement at the phosphorus atom is a distorted trigonal bipyramid with one axial and one equatorial nitrogen atom and one axial and two equatorial fluorine atoms. The axial fluorine atom lies in the plane of the ring. The angle $F_{eq}PF_{eq}$ is bisected by the plane of the ring. The correspondence between experimental and theoretical RD curves is not quite satisfactory, but it is certainly better than the correspondence obtained for any of the other models that were tried. The calcula-

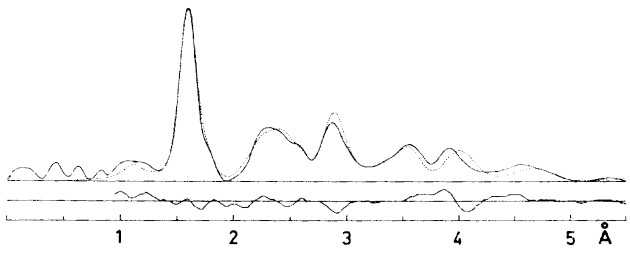

Fig. 1. $(F_3PNCH_3)_2$. Experimental (————) and theoretical (– – – –) radial distribution functions. $B = 0.0009$.

tion showed that the theoretical RD curve is very sensitive to even small changes in the angular parameters. We therefore consider the preliminary parameters to be close to the final ones, though we intend to refine the structure further using least-squares refinement. The agreement between the experimental auto-correlation power spectrum (APS) [5] and the corresponding theoretical curve based on the bond distances determined from the RD function is quite good.

The angular parameters for the ring and methyl carbons in $(F_3PNCH_3)_2$ are in good agreement with the corresponding parameters of $(Cl_3PNCH_3)_2$ [6] and $(PhF_2PNCH_3)_2$ [7] determined by Hoard and Jacobsen and Cox and Corey, respectively, using the X-ray crystallographic technique. The P—F bond lengths in $(F_3PNCH_3)_2$ and $(PhF_2PNCH_3)_2$ are not significantly different. While there is good agreement between the present values for the P—N bond distances with those found in the two crystal structures, we find a considerably longer C—N bond in $(F_3PNCH_3)_2$, 1.52 Å, compared to 1.475 Å in $(Cl_3PNCH_3)_2$ and 1.44 Å in $(PhF_2PNCH_3)_2$. Theoretical RD curves calculated using the values determined for comparable bond distances in $(Cl_3PNCH_3)_2$ and $(PhF_2PNCH_3)_2$ are definitely not in agreement with our experimental RD curve.

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1. Schmutzler, R. *Chem. Commun.* **1965** 19.
2. Downs, A. J. *Chem. Commun.* **1967** 628.
3. Chapman, A. C., Holmes, W. S., Paddock, N. L. and Searle, H. T. *J. Chem. Soc.* **1961** 1825.
4. Almenningen, A., Bastiansen, O., Haaland, A, and Seip, H. M. *Angew. Chem.* **4** (1965) 819.
5. Trætteberg, M. and Bonham, R. A. *J. Chem. Phys.* **42** (1965) 587.
6. Hoard, L. G. and Jacobsen, R. A. *J. Chem. Soc.* **A 9** (1966) 1203.
7. Cox, J. W. and Corey, E. R. *Chem. Commun.* **1967** 123.

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Evidence Suggesting Independent Pathways for the Synthesis of Rat Liver Fatty Acids from Acetyl-CoA and Malonyl-CoA Respectively

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We have previously shown [1] that an addition of citrate to rat liver homogenates will result in a specific enhancement of the synthesis of myristic acid from (^{14}C) acetate. Recent work by Smith and Dils [2] and Bartley and co-workers [3] has demonstrated a connection between the size of the available malonyl-CoA pool and the pattern of the fatty acids synthesized, small malonyl-CoA concentrations favouring the formation of shorter chained fatty acids such as myristic acid. In the paper by Bartley and co-workers [3] it is suggested that our findings may be due to the gradual synthesis and utilization of malonyl-CoA when acetate or acetyl-CoA are the precursors, the available malonyl-CoA pool thus being small at any given time.

In the present investigation we have studied the effect of adding malonyl-CoA to a rat liver homogenate which is synthesizing fatty acids from acetate or acetyl-CoA. The results show, that this does not lead to any relatively reduced synthesis of myristic acid. It seems that there are independent pathways for fatty acid synthesis from acetyl-CoA and malonyl-CoA, respectively.

Experimental. Liver tissue was taken from two mature albino rats. The homogenization medium was 0.05 M phosphate buffer pH = 7.0 containing 0.01 M $MgCl_2$, 0.02 M nicotinamide and 0.10 M sucrose. The ratio between liver (g) and medium (ml) was 1 to 2.5. Cell debris and nuclei were removed by centrifugation at 800 *g* for 10 min.

The incubation media contained further 0.001 M NADH and 0.001 M NADPH besides K-citrate and precursors as specified. No extra ATP was added, to avoid mitochondrial decarboxylation of (^{14}C) malonyl-CoA as described by Nakada *et al.*[4] (1-^{14}C) acetate and (1,3-$^{14}C_2$) malonyl-CoA were obtained from NEN Chem-