MOLECULAR STRUCTURE OF F₂POPF₂: AN ELECTRON DIFFRACTION STUDY

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ABSTRACT

The most important geometric parameters and associated uncertainties (2σ) determined for F₂POPF₂ are the distances (r₁) P—O = 1.631 ± 0.010 Å, P—F = 1.568 ± 0.004 Å, and angles POP = 135.2 ± 1.8°, OPF = 97.6 ± 1.2°, and FPF = 99.2 ± 2.4°. Amplitudes of vibration were also found. The large POP angle and relatively short P—O bond length are consistent with a significant degree of pπ—dπ bonding. Our structure interpretation differs from an earlier one reported by Arnold and Rankin in the relative P—O and P—F bond lengths and in the conclusion that the molecule exists in a distribution of not very rigid, probably staggered, conformers instead of one fairly rigid structure.

INTRODUCTION

Bis(difluorophosphino)ether, F₂POPF₂, was first synthesized by Rudolph et al. who also investigated the infrared and nuclear magnetic resonance spectra [1]. The fluorine substituents make the phosphorus a good candidate for accepting pπ electrons from the bridge oxygen. Uncertainties concerning pπ—dπ bonding between first-row elements and second-row elements with outer d orbitals made it worthwhile to acquire information about the molecular structure of the substance, for bond angles and bond lengths are considered to be useful in diagnosing π-bonding. After our study was completed [2] the results of another electron diffraction study of F₂POPF₂ were published [3]. Because our data extended to a significantly higher scattering angle and because the structural parameters deduced were somewhat different, we report our findings in the following.

EXPERIMENTAL

A sample of F₂POPF₂ was synthesized according to the procedure of Rudolph et al. [1] and stored at liquid nitrogen temperature. Diffraction patterns were taken of the vapor at room temperature on 4 × 5 in. Kodak Electron Image plates using an electron diffraction apparatus [4, 5] equipped with an r³ sector. Plates were developed with Kodak HRP developer at 68 °F for 3 min. The experimental conditions under which the diffraction patterns
were recorded using 40 kV incident electrons are given in Table 1.

**TABLE 1**

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>21.141</th>
<th>11.125</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camera distance (cm)</td>
<td>21.141</td>
<td>11.125</td>
</tr>
<tr>
<td>Sample pressure (torr)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Exposure time (sec)</td>
<td>6–7</td>
<td>20–25</td>
</tr>
<tr>
<td>Beam current (μA)</td>
<td>0.56</td>
<td>0.53</td>
</tr>
<tr>
<td>Throat diameter of Pt nozzle (cm)</td>
<td>0.017</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Optical densities, $A$, measured with a digital microphotometer while spinning the plates, were converted to exposures, $E$, by the expression

$$E = A(1 + 0.1A + 0.0133A^2 + 0.002A^3).$$

Five plates from the 21 cm and four plates from the 11 cm camera distances with absorbances between 0.25 and 0.9 were averaged and used in the structure analysis.

**ANALYSIS OF DATA**

Experimental intensities were corrected for the measured sector irregularities and extraneous scattering before being leveled by division by the theoretical atomic intensity. The atomic scattering factors used were the tabulated elastic scattering factors of Schafer et al. [6] and the inelastic scattering factors [7] of Tavard et al. and Cromer in all phases of the analysis.

Experimental and calculated molecular intensities and radial distribution functions were calculated as described elsewhere [8–10]. Tabulations of the scattering variable $s$, experimental leveled intensity, $I_o(s)$, and background intensity, $B(s)$, for the two camera distances are available from ASIS*. The indices of resolution were 0.845 and 0.804 for the 21 and 11 cm camera distances respectively. Although these values are somewhat low, they are comparable to values for other molecules obtained with the same batch of plates. Radial distribution functions, $f(r)$, were computed using a damping factor of $\exp(-0.0015 s^2)$. Anharmonicity constants of 2.0 Å$^{-1}$ were adopted for all bonded and non-bonded distances. Crude corrections were made for Bastiansen–Morino shrinkage effects [11] in least squares analyses of the intensities by adopting the value of 0.002 Å for the shrinkage corrections for all non-bonded distances.

*See NAPS document # 02589 for 1 page of 1. Order from ASIS/NAPS, c/o Microfiche Publications, 305 East 46th Street, New York, N.Y. 10017. Remit with order for each NAPS document number $1.50 for microfiche or $5.00 for photocopies for up to 30 pages; and 15¢ per page for each additional page over the first 30 pages. Make checks payable to Microfiche Publications.
The observed infrared spectrum of $\text{F}_2\text{POPF}_2$ indicated the existence of a $\text{P}–\text{O}–\text{P}$ linkage in this compound [1]; $^{31}\text{P}$ and $^{19}\text{F}$ NMR spectra showed clearly that two fluorines are bound to each phosphorus [1]. Subsequently, temperature-dependent NMR investigations of $\text{F}_2\text{POPF}_2$ suggested that it is non-rigid in solution [12]. At an early stage of this investigation it appeared that $\text{F}_2\text{POPF}_2$ exists in more than one conformation in the gas phase. Since there are no distinct peaks beyond 3.1 Å in the preliminary $f(r)_{\text{exp}}$ curve, several plausible molecular conformations were considered in the structural analysis. Because the diffraction data provide marginal information about the conformations, no attempt was made to optimize the torsional angles for

Fig. 1. Experimental (solid curves) and calculated (dashed curves) radial distribution functions of $\text{F}_2\text{POPF}_2$ for five rotational isomers and one selected mixture. Experimental curves vary with model because they are based on theoretical intensities in the range $0<s<5.5$. 

MOLECULAR MODEL
—PF₂ groups. Only the five conformers shown in Fig. 1 were adopted for further investigation.

The conformers (1)—(3) and (5) may be envisaged as various configurations in which bond pairs and localized lone pairs on each atom are staggered with respect to bond pairs and lone pairs on adjacent atoms. Staggered configurations are commonly encountered when single bonds are present. Conformers (1) and (3) contain virtually co-planar FPOPF links and (2) contains a planar FPOP group. Conformer (4) eclipses bond pairs by lone pairs. It is to be expected that fairly large amplitudes of vibration occur about the P—O bonds. Since these were not explicitly built into the models their effects are absorbed into atom-pair amplitudes of vibration and skeletal parameters.

The conformational investigation was carried out by comparing the experimental intensities with calculated intensity functions corresponding to various concentrations of rotational isomers. A least squares procedure optimized structural parameters (except for torsional angles which were fixed) but not concentrations. The P—F and F—F (long) non-bonded distances were each assigned a single skeletal amplitude of vibration and all O—P—F valency angles were assumed to be equal to preserve local C₃ symmetry for the —OPF₂ groups.

RESULTS

Experimental and calculated radial distribution functions for the five individual rotational isomers of F₂POPF₂ and for one selected mixture are compared in Fig. 1 for the r = 2.7 to 5.1 Å region. Isomers (4) and (5) individually give the least satisfactory account of the experimental data. Standard deviations between experimental and calculated distribution functions based on various isomeric concentrations are given in Table 2. All mixtures in Table 2 give acceptable representations of the data and markedly better representations than given by any of the single conformations by itself. Little quantitative significance can be attached to these concentrations because, among other reasons, no attempt was made to optimize the angles of internal rotation for each isomer. The sensitivity of the distribution to the assumed dihedral angles was not investigated. Experimental and calculated molecular intensities, sM(s) and radial distribution functions, f(r) are compared in Figs. 2 and 3 respectively. In each of these comparisons the calculated functions were based on parameters derived from least squares analyses of the composite intensity with a composition of 40 % isomer 2, 20 % isomer 1, 3 and 4 respectively. Table 3 gives the corresponding structural parameters and their estimated standard errors which were derived from a least squares analysis of diffracted intensities. Both random and systematic errors [5] were included in calculated standard errors. In the course of the least squares refinements, a diagonal weight matrix was adopted with elements proportional to the square of the scattering variable s. The corresponding correlation
<table>
<thead>
<tr>
<th>Assumed isomer concentration</th>
<th>( \sigma(I)/I^a )</th>
<th>( \sigma[f(r)]^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 % isomer 1 + 50 % isomer 2 + 20 % isomer 3</td>
<td>0.897</td>
<td>0.041</td>
</tr>
<tr>
<td>20 % isomer 1 + 60 % isomer 2 + 20 % isomer 3</td>
<td>0.907</td>
<td>0.039</td>
</tr>
<tr>
<td>20 % isomer 1 + 40 % isomer 2 + 20 % isomer 3 + 20 % isomer 4</td>
<td>0.899</td>
<td>0.037</td>
</tr>
</tbody>
</table>

\(^a\)Standard deviation in ppt of the composite molecular intensity.

\(^b\)Standard deviation between experimental and calculated radial distribution function.
coefficients for the molecular parameters are shown in Table 4.

The primary differences between our analysis and that reported by Arnold and Rankin [33] are in the treatment of conformations and in the ranges of data (3<s<28, A&R; 4<s<39, Y, R&B). Instead of working with a distribution of conformers with fixed dihedral angles, Arnold and Rankin
**TABLE 3**

Structure parameters\(^a\) and estimated errors (2\(\sigma\))

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Arnold and Rankin(^b)</th>
<th>Model B</th>
<th>Model C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r(P-O))</td>
<td>1.631(10)</td>
<td>1.598(18)</td>
<td>1.534(12)</td>
<td></td>
</tr>
<tr>
<td>(r(P-F))</td>
<td>1.568(4)</td>
<td>1.571(10)</td>
<td>1.598(8)</td>
<td></td>
</tr>
<tr>
<td>(\angle{POP})</td>
<td>135.2 (18)</td>
<td>137.5 (23)</td>
<td>145.1(^c)</td>
<td></td>
</tr>
<tr>
<td>(\angle{OPF})</td>
<td>97.6 (12)</td>
<td>98.6(^c)</td>
<td>98.8 (6)</td>
<td></td>
</tr>
<tr>
<td>(\angle{FPF})</td>
<td>99.2 (24)</td>
<td>99.2 (23)</td>
<td>98.5(^c)</td>
<td></td>
</tr>
<tr>
<td>(l(P-O))</td>
<td>0.039(12)</td>
<td>0.047(^c)</td>
<td>0.047(^c)</td>
<td></td>
</tr>
<tr>
<td>(l(P-F))</td>
<td>0.041(6)</td>
<td>0.045(^c)</td>
<td>0.045(^c)</td>
<td></td>
</tr>
<tr>
<td>(l(O \cdots F))</td>
<td>0.076(12)</td>
<td>0.081(12)</td>
<td>0.085(12)</td>
<td></td>
</tr>
<tr>
<td>(l(F \cdots F))</td>
<td>0.079(24)</td>
<td>0.069(^d)</td>
<td>0.072(^d)</td>
<td></td>
</tr>
<tr>
<td>(l(P \cdots P))</td>
<td>0.085(6)</td>
<td>0.230(100)</td>
<td>0.098(28)</td>
<td></td>
</tr>
<tr>
<td>(l(P \cdots F))</td>
<td>0.147(26)</td>
<td>0.070(^e)</td>
<td>0.049(36)</td>
<td>0.050(^c)</td>
</tr>
<tr>
<td>(l(F \cdots F))</td>
<td>0.143(30)</td>
<td>(0.280(^c)</td>
<td>(0.298(70))</td>
<td>(0.240(^c)</td>
</tr>
</tbody>
</table>

\(^a\)Distances (\(r_g\) basis) in Å, angles in deg.
\(^b\)Ref. 3.
\(^c\)Refined in earlier cycle, fixed in last cycle.
\(^d\)Tied to \(l(O \cdots F)\).

worked with a single conformer and optimized dihedral angles. They report two separate least squares minima, one for conformation B and one for conformation C.

**DISCUSSION**

The P—F bond length, F—P—F angle and P—F amplitude of vibration found in the present study closely resemble those in PF\(_3\) [13], F\(_2\)PPF\(_2\) [14] and F\(_2\)P(NCH\(_3\))PF\(_2\) [15].

The observed P—O—P angle 135.2\(^o\), is similar to those found in \(\beta\)-Ca\(_2\)P\(_2\)O\(_7\) (angle POP \(\approx\) 131—138\(^o\)) [16] and Na\(_4\)P\(_2\)O\(_7\), 10H\(_2\)O (angle POP = 130.2\(^o\)) [17]. The observed P—O bond length (1.631 Å) is also comparable to the lengths of 1.615 Å [16] and 1.612 Å [17] observed for the bridging oxygens in the above compounds as well as to a value of 1.64 Å predicted by Cruickshank [18] for P\(_2\)O\(_5\)\(^-\)ion. The observed P—O bond length is much less than the value of 1.71 Å calculated from the Schomaker—Stevenson equation [19] for a single P—O bond, suggesting that the two lone pairs on oxygen may be involved in \(p_\pi—d_\pi\) bonding to the phosphorus atoms.

The above evidence implies that refinement B rather than refinement C of Arnold and Rankin [3] corresponds to the more likely model, at least in bond lengths, despite the fact that its standard deviation is less favorable.
### TABLE 4

Matrix of correlation coefficients\(^a\) for \(\text{F}_2\text{POP}_2\)

<table>
<thead>
<tr>
<th></th>
<th>(r_{\text{PO}})</th>
<th>(r_{\text{PF}})</th>
<th>(r_{\text{OP}})</th>
<th>(r_{\text{OF}})</th>
<th>(r_{\text{FP}})</th>
<th>(r_{\text{FO}})</th>
<th>(r_{\text{OPF}})</th>
<th>(r_{\text{OPF}})</th>
<th>(r_{\text{OPF}})</th>
<th>(r_{\text{OPF}})</th>
<th>(r_{\text{OPF}})</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_{\text{PO}})</td>
<td>1.0</td>
<td>-0.88</td>
<td>-0.70</td>
<td>0.09</td>
<td>0.14</td>
<td>-0.89</td>
<td>-0.96</td>
<td>-0.01</td>
<td>-0.16</td>
<td>-0.04</td>
<td>0.00</td>
<td>-0.14</td>
</tr>
<tr>
<td>(r_{\text{PF}})</td>
<td></td>
<td>1.0</td>
<td>0.62</td>
<td>-0.11</td>
<td>-0.08</td>
<td>0.97</td>
<td>0.90</td>
<td>0.00</td>
<td>0.16</td>
<td>0.06</td>
<td>0.00</td>
<td>0.12</td>
</tr>
<tr>
<td>(r_{\text{OP}})</td>
<td></td>
<td></td>
<td>1.0</td>
<td>-0.57</td>
<td>-0.55</td>
<td>0.63</td>
<td>0.67</td>
<td>0.03</td>
<td>0.31</td>
<td>0.08</td>
<td>-0.11</td>
<td>0.40</td>
</tr>
<tr>
<td>(r_{\text{OF}})</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.91</td>
<td>-0.12</td>
<td>-0.11</td>
<td>-0.08</td>
<td>-0.40</td>
<td>-0.08</td>
<td>0.07</td>
<td>-0.19</td>
</tr>
<tr>
<td>(r_{\text{FP}})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>-0.10</td>
<td>-0.13</td>
<td>-0.36</td>
<td>-0.12</td>
<td>-0.05</td>
<td>0.03</td>
<td>-0.17</td>
</tr>
<tr>
<td>(r_{\text{FO}})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.93</td>
<td>0.13</td>
<td>0.17</td>
<td>0.07</td>
<td>0.00</td>
<td>0.13</td>
</tr>
<tr>
<td>(r_{\text{OPF}})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.01</td>
<td>0.18</td>
<td>0.07</td>
<td>0.00</td>
<td>0.14</td>
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<tr>
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<td>1.0</td>
<td>-0.83</td>
<td>-0.03</td>
<td>0.07</td>
<td>0.00</td>
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<tr>
<td>(r_{\text{OPF}})</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>-0.09</td>
<td>0.10</td>
<td>0.17</td>
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<tr>
<td>(r_{\text{OPF}})</td>
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<td></td>
<td>1.0</td>
<td>-0.06</td>
<td>0.26</td>
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<tr>
<td>(r_{\text{OPF}})</td>
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<td>0.00</td>
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<tr>
<td>(R)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(^a\)Matrix elements are given by \(\rho_{ij} = B_{ij}/(B_{ii}B_{jj})^{1/2}\) where the notation corresponds to that of O. Bastiansen, L. Hedberg and K. Hedberg, J. Chem. Phys., 27 (1957) 1311.

\(^b\)\(r_{\text{OPF}}\) (short)

\(^c\)\(r_{\text{OPF}}\) (long)
Concerning conformational rigidity, our data are indicative of a broad
distribution of rotational isomers in view of the rather diffuse distribution of
distances we find in the region 3<r<4.5 (see Figs. 1 and 2). In this respect
our radial distribution function is quite different from that reported by
Arnold and Rankin (see their Fig. 2). Their rather small derived P⋯F
amplitudes of vibration (0.05 Å) suggested quite rigid conformers. A closely
related molecule F₂P(NCH₃)PF₂ studied by Hedberg et al. [15] yielded a
definitive conformational answer because of the additional information
provided by the “handle” associated with the N—CH₃ bond. Hedberg et al.
found a fairly rigid conformation (l_p⋯F = 0.07 Å) corresponding to our
model (4), perhaps stabilized by interactions between the PF₂ groups and the
methyl group. Note that, whereas PF₂ groups in model (4) are in eclipsed
conformations in F₂POPF₂, in F₂P(NCH₃)PF₂ they are staggered with respect
to the N—C bond and, accordingly, the closely related oxygen and nitrogen
derivatives are very different in conformational possibilities. Further
accentuating the difference is the fact that the P—N—P angle (116°) is much
smaller than the P—O—P angle (135°) by virtue of the additional bond around
nitrogen. A resolution of the discrepancy between our analysis and that of
Arnold and Rankin will require additional information. Because the rigid
Arnold and Rankin conformations are not very similar to that of the fairly
rigid F₂P(NCH₃)PF₂, and because of a regular, spurious ripple through the
Arnold and Rankin radial distribution which correlates with their sharp
P⋯F peaks, we favor, tentatively, our own interpretation.

The most interesting information provided by our analysis is tabulated in
Table 5 where it is evident that the X—O—X angle and the X—O bond length
contraction both increase in the series OCl₂ [20], F₂POPF₂ and F₃SiOSiF₃
[21]. This behavior is consistent with a pπ—dπ bonding model in which the
extent of the π-bonding increases from OCl₂ to F₂POPF₂ to F₃SiOSiF₃. The
observed behavior closely resembles the case of NCl₃ [22] and N(SiH₃)₃ [23]
in which analogous experimental evidence also indicated that the pπ—dπ
delocalization in N(SiH₃)₃ was greater than that in NCl₃. Also correlating
with such π-delocalization is the planar bonding around nitrogen in
F₂P(NCH₃)PF₂ [15]. It is worthy of note that the above observations are in
agreement with Cruickshank’s contention [18] that lone pairs of electrons
on second row elements will reduce the π-bonding power of the d
orbitals. The case of F₂POPF₂, then, provides one more illustration supporting the
pπ—dπ bonding picture of Cruickshank [18].
### TABLE 5

A comparison of bond length and bond angle in X-O-X molecule where X = Cl, PF$_2$, or SiF$_3$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>ClOCl$^a$</th>
<th>F$_2$POPF$_2$</th>
<th>F$_3$SiOSiF$_3$$_b^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(O-X) (Å)</td>
<td>1.700</td>
<td>1.681</td>
<td>1.580</td>
</tr>
<tr>
<td>Single bond value for r(O-X)$^c$ (Å)</td>
<td>1.68, 1.71</td>
<td>1.71</td>
<td>1.76</td>
</tr>
<tr>
<td>Contraction (Å)</td>
<td>-0.015</td>
<td>0.079</td>
<td>0.180</td>
</tr>
<tr>
<td>$\angle$ XOX (deg.)</td>
<td>111</td>
<td>135.2</td>
<td>155.7</td>
</tr>
<tr>
<td>Number of lone pairs of electrons on 2nd row elements</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$Ref. 20.

$^b$Ref. 21.

$^c$Calculated by the Schomaker—Stevenson equation [19].
REFERENCES