

MOLECULAR STRUCTURE OF F_2POPF_2 : AN ELECTRON DIFFRACTION STUDY

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ABSTRACT

The most important geometric parameters and associated uncertainties (2σ) determined for F_2POPF_2 are the distances (r_g) $P-O = 1.631 \pm 0.010$ Å, $P-F = 1.568 \pm 0.004$ Å, and angles $POP = 135.2 \pm 1.8^\circ$, $OPF = 97.6 \pm 1.2^\circ$, and $FPF = 99.2 \pm 2.4^\circ$. Amplitudes of vibration were also found. The large POP angle and relatively short P—O bond length are consistent with a significant degree of $p\pi-d\pi$ 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, F_2POPF_2 , 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 $p\pi$ electrons from the bridge oxygen. Uncertainties concerning $p\pi-d\pi$ 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 F_2POPF_2 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 F_2POPF_2 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 r^3 sector. Plates were developed with Kodak HRP developer at $68^\circ F$ 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

Experimental conditions

Camera distance (cm)	21.141	11.125
Sample pressure (torr)	30	30
Exposure time (sec)	6–7	20–25
Beam current (μA)	0.56	0.53
Throat diameter of Pt nozzle (cm)	0.017	0.017

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, $I_0(s)$, 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 \AA^{-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 \AA for the shrinkage corrections for all non-bonded distances.

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MOLECULAR MODEL

The observed infrared spectrum of F_2POPF_2 indicated the existence of a P—O—P linkage in this compound [1]; ^{31}P and ^{19}F NMR spectra showed clearly that two fluorines are bound to each phosphorus [1]. Subsequently, temperature-dependent NMR investigations of F_2POPF_2 suggested that it is non-rigid in solution [12]. At an early stage of this investigation it appeared that F_2POPF_2 exists in more than one conformation in the gas phase. Since there are no distinct peaks beyond 3.1 Å in the preliminary $f(r)_{exp}$ 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

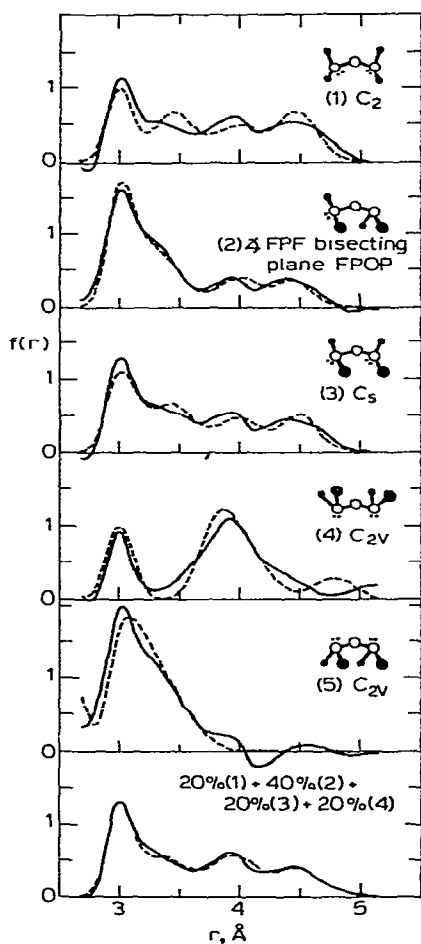


Fig. 1. Experimental (solid curves) and calculated (dashed curves) radial distribution functions of F_2POPF_2 for five rotational isomers and one selected mixture. Experimental curves vary with model because they are based on theoretical intensities in the range $0 < s < 5.5$.

—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 FPOP 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 C_s 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 2

Standard deviations between observed and calculated molecular intensity and radial distribution functions of F₂POPF₂ for various assumed isomeric concentrations

Assumed isomer concentration	$\sigma(I)/I^a$	$\sigma[f(r)]^b$
30 % isomer 1 + 50 % isomer 2 + 20 % isomer 3	0.897	0.041
20 % isomer 1 + 60 % isomer 2 + 20 % isomer 3	0.907	0.039
20 % isomer 1 + 40 % isomer 2 + 20 % isomer 3 + 20 % isomer 4	0.899	0.037

^aStandard deviation in ppt of the composite molecular intensity.

^bStandard deviation between experimental and calculated radial distribution function.

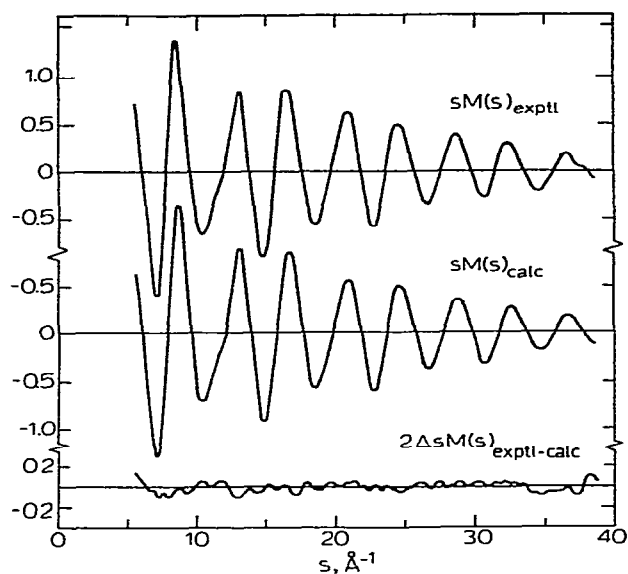


Fig. 2. Experimental and calculated molecular intensity functions for F_2POPF_2 . $\Delta sM(s) = sM(s)_{\text{exp}} - sM(s)_{\text{calc}}$.

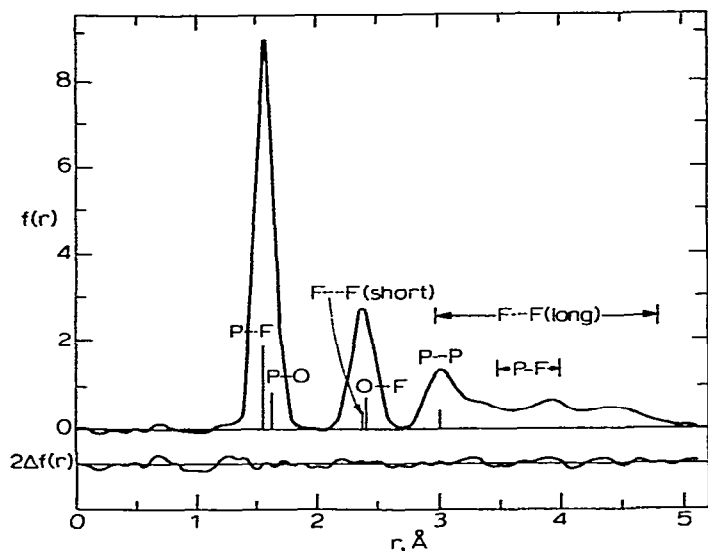


Fig. 3. Experimental radial distribution function for F_2POPF_2 . $\Delta f(r) = f(r)_{\text{exp}} - f(r)_{\text{calc}}$.

coefficients for the molecular parameters are shown in Table 4.

The primary differences between our analysis and that reported by Arnold and Rankin [3] 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 (2σ)

	Present work	Arnold and Rankin ^b	
		Model B	Model C
$r(\text{P—O})$	1.631(10)	1.598(18)	1.534(12)
$r(\text{P—F})$	1.568(4)	1.571(10)	1.598(8)
$\angle \text{POP}$	135.2 (18)	137.5 (23)	145.1 ^c
$\angle \text{OPF}$	97.6 (12)	98.6 ^c	98.8 (6)
$\angle \text{FPF}$	99.2 (24)	99.2 (23)	98.5 ^c
$l(\text{P—O})$	0.039(12)	0.047 ^c	0.047 ^c
$l(\text{P—F})$	0.041(6)	0.045 ^c	0.045 ^c
$l(\text{O} \cdots \text{F})$	0.076(12)	0.081(12)	0.085(12)
$l(\text{F} \cdots \text{F})_{\text{gem}}$	0.079(24)	0.069 ^d	0.072 ^d
$l(\text{P} \cdots \text{P})$	0.085(6)	0.230(100)	0.098(28)
$l(\text{P} \cdots \text{F})$	0.147(26)	0.070 ^c	{ 0.049(36) 0.050 ^c
$l(\text{F} \cdots \text{F})$	0.143(30)	{ 0.280 ^c 0.185 ^c	{ 0.228(70) 0.240 ^c 0.185 ^c

^aDistances (r_g basis) in Å, angles in deg.^bRef. 3.^cRefined in earlier cycle, fixed in last cycle.^dTied to $l(\text{O} \cdots \text{F})$.

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_2PPF_2 [14] and $\text{F}_2\text{P}(\text{NCH}_3)\text{PF}_2$ [15].

The observed P—O—P angle 135.2° , is similar to those found in $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (angle POP $\approx 131\text{--}138^\circ$) [16] and $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (angle POP = 130.2°) [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 $\text{P}_2\text{O}_7^{4-}$ 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 $p\pi\text{--}d\pi$ 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 F₂POPF₂

	r_{P-O}	r_{P-F}	<POP	<OPF	<FPF	l_{P-O}	l_{P-F}	$l_{O...F}$	$l_{F...F}^b$	$l_{P...P}$	$l_{P...F}$	$l_{F...F}^c$	R
r_{P-O}	1.0	-0.88	-0.70	0.09	0.14	-0.89	-0.96	-0.01	-0.16	-0.04	0.00	-0.14	-0.44
r_{P-F}		1.0	0.62	-0.11	-0.08	0.97	0.90	0.00	0.16	0.06	0.00	0.12	0.52
\angle POP			1.0	-0.57	-0.55	0.63	0.67	0.03	0.31	0.08	-0.11	0.40	0.32
\angle OPF				1.0	0.91	-0.12	-0.11	-0.08	-0.40	-0.08	0.07	-0.19	-0.14
\angle FPF					1.0	-0.10	-0.13	-0.36	-0.12	-0.05	0.03	-0.17	-0.12
l_{P-O}						1.0	0.93	0.13	0.17	0.07	0.00	0.13	0.60
l_{P-F}							1.0	0.01	0.18	0.07	0.00	0.14	0.61
$l_{O...F}$								1.0	-0.83	-0.03	0.07	0.00	0.04
$l_{F...F}$ (short)									1.0	0.07	-0.09	0.10	0.17
$l_{P...P}$										1.0	-0.06	0.26	0.13
$l_{P...F}$											1.0	0.00	0.01
$l_{F...F}$ (long)												1.0	0.11
R													1.0

^aMatrix 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 $l_{F...F}$ (short)

^c $l_{F...F}$ (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 $P \cdots F$ amplitudes of vibration (0.05 \AA) suggested quite rigid conformers. A closely related molecule $F_2P(NCH_3)PF_2$ studied by Hedberg et al. [15] yielded a definitive conformational answer because of the additional information provided by the "handle" associated with the $N-CH_3$ bond. Hedberg et al. found a fairly rigid conformation ($l_{P \cdots F} = 0.07 \text{ \AA}$) corresponding to our model (4), perhaps stabilized by interactions between the PF_2 groups and the methyl group. Note that, whereas PF_2 groups in model (4) are in eclipsed conformations in F_2POPF_2 , in $F_2P(NCH_3)PF_2$ 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 $F_2P(NCH_3)PF_2$, and because of a regular, spurious ripple through the Arnold and Rankin radial distribution which correlates with their sharp $P \cdots F$ 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 OCl_2 [20], F_2POPF_2 and $F_3SiOSiF_3$ [21]. This behavior is consistent with a $p\pi-d\pi$ bonding model in which the extent of the π -bonding increases from OCl_2 to F_2POPF_2 to $F_3SiOSiF_3$. The observed behavior closely resembles the case of NCl_3 [22] and $N(SiH_3)_3$ [23] in which analogous experimental evidence also indicated that the $p\pi-d\pi$ delocalization in $N(SiH_3)_3$ was greater than that in NCl_3 . Also correlating with such π -delocalization is the planar bonding around nitrogen in $F_2P(NCH_3)PF_2$ [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 F_2POPF_2 , then, provides one more illustration supporting the $p\pi-d\pi$ bonding picture of Cruickshank [18].

TABLE 5

A comparison of bond length and bond angle in X—O—X molecule where X = Cl, PF₂, or SiF₃

Molecule	ClOCl ^a	F ₂ POP _F ₂	F ₃ SiOSiF ₃ ^b
r(O—X) (Å)	1.700	1.631	1.580
Single bond value for r(O—X) ^c (Å)	1.68 _s	1.71	1.76
Contraction (Å)	-0.01 _s	0.079	0.180
∠XOX (deg.)	111	135.2	155.7
Number of lone pairs of electrons on 2nd row elements	3	1	0

^aRef. 20.^bRef. 21.^cCalculated by the Schomaker—Stevenson equation [19].

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