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What Makes the Huge $^{31}P-^{31}P$ Coupling Constants in $S(PF_2)_2$ and $Se(PF_2)_2$ Vary So Much with Temperature?

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The enormous temperature dependence of the $^2J_{PP}$ coupling constants in $S(PF_2)_2$ and $Se(PF_2)_2$ has been explained by a theoretical investigation of their conformations and NMR coupling constants. In contrast, the coupling in $O(PF_2)_2$ is almost invariant. Gas electron diffraction data for $S(PF_2)_2$ have been reinterpreted. The results show that two conformers, with C_s and C_{2v} symmetry, exist for the S and Se compounds. The C_s and C_{2v} conformers have very different $^2J_{PP}$ coupling constants (−12.6 and 395.2 Hz for $S(PF_2)_2$ at B3LYP/aug-cc-pVQZ) and thermal interconversion of these conformers explains the experimental behavior.

Introduction

The bis(difluorophosphino) compounds of group 16, $O(PF_2)_2$ (**1**), $S(PF_2)_2$ (**2**) and $Se(PF_2)_2$ (**3**), have been the focus of a number of structural studies. The interest in these compounds lay in the large and highly temperature-dependent $^{31}P-^{31}P$ geminal coupling constants, $^2J_{PP}$, that occur in **2** and **3** but not in **1**. Ruldoph and Newmark studied $^2J_{PP}$ as a function of temperature for compound **2** in solution and found that it changed from 392.2 Hz at 153 K to 274.1 Hz at 304 K.[1] Similar results were found for compound **3**,[2] but compound **1** was only "slightly temperature dependent" with a value of 4 Hz at 300 K.[1,3] The other coupling constants in **2** and **3** show relatively small temperature dependence.

Several explanations for the temperature dependence have been suggested. A change in the average P−Y−P (Y = S, Se) angle could have an effect on the interactions between the phosphorus lone pairs. Alternatively, torsional motions of the PF_2 groups could disrupt the P⋯P lone pair interactions. However, a number of authors[1,2] state that is it unlikely that these effects could account for the large magnitudes of the effects seen in **2** and **3** and suggest that the presence of multiple conformers, whose relative abundances change with temperature, would best explain the experimental behavior. All three compounds have been the subject of structure determinations using gas electron diffraction (GED). Two such studies of compound **1** have been carried out. The first, by Arnold and Rankin,[4] determined a single C_1 conformer. A second study with higher resolution by Bartell et al. suggested a mixture of four conformers, with C_2, C_1, C_s and C_{2v} symmetries,[5] which are shown as conformers i−iv in Figure 1. The later studies of compounds **2** and **3** fitted structures similar to Bartell's conformer (iv).[6] With these results suggesting that only **1**, which displayed little temperature dependence, has multiple conformations, there would seem to be little support for the argument that interconversion of conformers accounts for the temperature dependence of the coupling constants. However, the fitting of multiple conformations is particularly sensitive to the long-range F⋯F distances and to amplitudes of vibration, which could not be refined or accurately calculated when the previous studies were performed. We therefore decided to study the structures and NMR behavior of **1**−**4** using ab initio and density-functional theory (DFT) calculations. We have also reanalyzed the original GED data for compound **2** using the latest refinement methods, to determine whether multiple conformers are present in the gas phase. The GED data for **3** are no longer available in a suitable format for reanalysis.

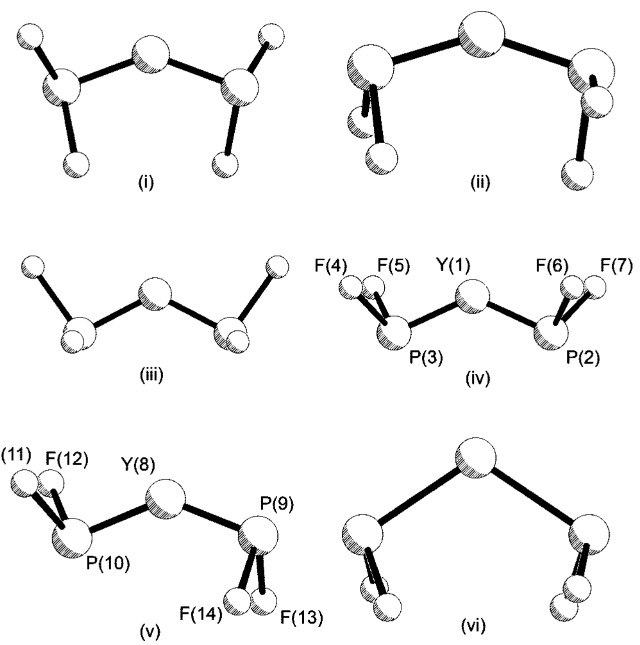

Figure 1. Six possible conformers, (i)−(vi), of $Y(PF_2)_2$ [where Y = O (**1**), S (**2**) and Se (**3**)]. Conformers i−iv are those from Bartell et al.[5]

Methods

Calculations. Ab initio and DFT calculations of **1**−**3** were carried out using the Gaussian 03 program.[7] As well as considering the four conformers used in the previous studies, another potential C_s structure, conformer v in Figure 1, was considered. Trial geometries of conformers iv and v for all three compounds were optimized using the HF, B3LYP[8] and MP2[9] levels of theory. The 6-31G(d)[10] basis set and the correlation-consistent basis sets of Dunning and co-workers,[11] aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ, were used. Attempts were made to optimize trial structures of conformers i and iii.

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However, for all compounds at the HF/aug-cc-pVDZ and MP2/6-31G(d) levels of theory these starting geometries optimized to the C_{2v} structure of conformer iv. An optimization of a trial geometry of conformer ii was also performed for each compound. Although conformer ii optimized successfully for **1**, for **2** and **3** it collapsed to a C_2 conformer, shown as conformer vi in Figure 1. At each level of theory, except MP2/aug-cc-pVQZ, and for each optimized geometry, harmonic frequencies were calculated to give zero-point energy corrections to the computed energies at room temperature (298 K). For S(PF$_2$)$_2$ a cubic frequency calculation[12] was performed for conformers iv and v at the B3LYP/6-31G(d) level of theory to obtain distance corrections and amplitudes of vibration using the SHRINK program.[13] This therefore allowed the $r_{a3,1}$ GED structure to be refined. For more information on the type of refinement used, see McCaffrey et al.[14] NMR spin−spin coupling calculations[15] were performed using the GIAO method[16] at the HF, B3LYP and PW91[17] levels of theory for **2** and the B3LYP level of theory for **1** and **3**.

Gas Electron Diffraction. The GED study of compound **2** used the diffraction patterns previously collected[6] on the Edinburgh diffraction apparatus.[18] The scattering intensities, which had been recorded on Kodak Electron Image plates, were measured using an Epson Expression 1680 Pro flatbed scanner and converted to mean optical densities using a method described elsewhere.[19] The data were then reduced and analyzed using the ed@ed v. 3.0 least-squares refinement program,[20] employing the scattering factors of Ross et al.[21] The weighting points for the off-diagonal weight matrix, correlation parameters, and scale factors are shown in Table S1 (Supporting Information).

Results and Discussion

Calculated Stability of Conformers of 1−3. Geometry optimizations show that several conformers might exist for each compound. In the case of compound **1** structures of conformers ii, iv and v were successfully optimized. The theoretical values for the conformer ratios may not be perfect, but at all levels of theory appreciable amounts of all three conformer were predicted. At lower levels of theory the conformers were reasonably similar in relative energies, differing at most by 2−3 kJ mol^{-1}. At higher levels of theory the doubly degenerate C_s conformer (v) was the most stable, with the calculated relative abundances of (ii):(iv):(v), at 298 K, being 0.065:0.858:0.077, at the B3LYP/aug-cc-pVQZ level of theory. This is in stark contrast to the findings of Bartell et al., who determined a ratio of 0.2:0.4:0.2:0.2 for conformers i−iv. In that previous refinement only three possible ratios were considered and the authors state that "little quantitative significance can be attached to these concentrations", in part because F···F distances and amplitudes were not refined. Also the C_s conformer (v) was not considered in any previous study of **1** (or **2** or **3**).

The calculations suggest that three conformers may exist for **2** and **3** as well. However, the calculated free energies show that only the C_{2v} and C_s conformers, (iv) and (v), are likely to be found in significant proportions in the gas phase. The C_2 conformer is highly unfavored with B3LYP and the larger basis sets. For compound **2**, conformer vi is over 9.0 kJ mol^{-1} less stable than the other two conformations at the B3LYP/aug-cc-pVQZ level of theory, making up only 1.4% of the gas at room temperature. For compound **3** it is more than 100 kJ mol^{-1} less stable. This is not that surprising as conformer vi results in the shortest F···F distances. Such a small amount would be unlikely to be detectable by GED or NMR experiments.

TABLE 1: Relative Free Energies of the C_{2v} and C_s Conformers of S(PF$_2$)$_2$ and Se(PF$_2$)$_2$ at 298 K in kJ mol^{-1} [a]

	6-31G(d)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
		S(PF$_2$)$_2$		
HF	7.98	1.61	−1.44	−1.76
B3LYP	6.48	1.25	−7.63	−1.45
MP2	8.41	2.92	−10.95	
		Se(PF$_2$)$_2$		
HF	4.88	0.85	−1.61	−1.77
B3LYP	4.73	1.37	−6.85	0.28
MP2	6.08	2.08	−11.94	

[a] $\Delta G = G_{C_{2v}} - G_{C_s}$.

It should be noted that the relative stabilities of conformers have a significant basis set dependence. This is demonstrated in Table 1, which shows the relative free energies, $\Delta G = G_{C_{2v}} - G_{C_s}$, of conformers iv and v of **2** and **3** at various combinations of levels of theory and basis set. Each of the optimized structures represented a true minimum on its potential-energy surface, apart from those of the C_s conformers of **2** and **3** at the MP2/aug-cc-pVTZ level of theory. These both feature a single imaginary frequency, although they are small in magnitude and most likely arise from an issue of convergence with respect to the basis set used. Free-energy calculations could not be performed at the MP2/aug-cc-pVQZ level, but such calculations should be in reasonable agreement with the B3LYP/aug-cc-pVQZ results as the two yield similar values for the smaller basis sets. For compound **2** the B3LYP/aug-cc-pVQZ conformer ratio, (vi):(iv):(v), is 0.014:0.466:0.520 at 298 K. At the temperature of the GED experiment, 273 K, the ratio of (iv):(v) becomes 0.499:0.501. For compound **3** the conformer ratio, (iv):(v), at the same level of theory is 0.691:0.309 at 298 K. The general trend of the results for compounds **2** and **3** indicates that there are likely to be at least two conformers, (iv) and (v), present in the gas phase.

NMR Calculations. The calculated values of $^2J_{PP}$ and $^1J_{PF}$ at a number of levels of theory are given in Table 3 for the three possible conformers of **1−3** along with the experimental values near room temperature. Though the theoretical results suggest only two conformations are likely for **2** and **3**, a small amount of a third conformer could have a significant impact on the experimental NMR values if its coupling constant was substantially different from those of the other conformers. As expected from the results of the geometry optimizations, there is some dependence of the coupling constants on the basis set. In general, the $^1J_{PF}$ values agree well with those from experiment and between different conformers. However, the $^2J_{PP}$ values vary dramatically between the conformations. The C_{2v} value is much larger than the values for the other conformers, especially in **2** and **3**. The large temperature dependence of the experimental $^2J_{PP}$ value for these compounds could be explained by changes in the thermal populations of the conformations, as the NMR experiment would yield the average coupling constant if the interconversion was a fast process. The NMR experiments do not show more than one set of resonances, even at the lowest temperature, so the barrier is small enough for fast interconversion on the NMR time scale. Molecules all in the same conformation could not account for the observed behavior, as detailed in the introduction. We would expect less temperature dependence in the case of **1** due to the smaller $^2J_{PP}$ coupling constant and low abundance of its C_{2v} conformation. Taking the conformer ratios and theoretical coupling constants at the B3LYP/aug-cc-pVQZ level, we expect $^2J_{PP}$ for **1** to be −2.3 Hz at room temperature; this is close to the experimental value

TABLE 2: Refined ($r_{a3,1}$) and Calculated (r_e) Geometric Parameters for $S(PF_2)_2$ from a Re-evaluation of the Original GED Data[a,b]

	parameter	$r_{a3,1}$	r_e[c]	restraint
		Independent		
p_1	r(P−F) average	156.4(2)	158.5	
p_2	r(P−F) difference 1	0.4(5)	0.5	0.5(5)
p_3	r(P−F) difference 2	0.2(5)	0.1	0.1(5)
p_4	r(S−P) average	211.9(2)	212.4	
p_5	r(S−P) difference 1	−1.0(5)	−1.1	−1.1(5)
p_6	r(S−P) difference 2	−1.7(5)	−1.6	−1.6(5)
p_7	∠(S−P−F) average	100.4(2)	99.1	
p_8	∠(S−P−F) difference 1	2.2(7)	2.5	2.5(7)
p_9	∠(S−P−F) difference 2	0.8(5)	0.7	0.7(5)
p_{10}	∠(F−P−F) mean	98.1(3)	96.4	
p_{11}	∠(P−S−P) average	94.6(4)	96.1	96.1(10)
p_{12}	∠(P−S−P) difference	6.6(5)	5.9	5.9(6)
p_{13}	proportion of C_{2v} conformer	0.87(5)	0.98 [d]	
		Dependent		
p_{14}	r[P(2)−F(6)]	156.4(2)	158.4	
p_{15}	r[P(10)−F(12)]	156.2(5)	158.3	
p_{16}	r[P(9)−F(13)]	156.8(5)	158.9	
p_{17}	r[S(1)−P(2)]	211.6(2)	212.1	
p_{18}	r[S(8)−P(9)]	211.1(5)	213.7	
p_{19}	r[S(8)−P(10)]	213.3(5)	211.5	
p_{20}	∠[S(1)−P(2)−F(6)]	100.1(2)	98.7	
p_{21}	∠[S(8)−P(10)−F(12)]	99.3(5)	98.0	
p_{22}	∠[S(8)−P(9)−F(13)]	102.1(7)	101.0	
p_{23}	∠[P(2)−S(1)−P(3)]	91.3(3)	93.1	
p_{24}	∠[P(9)−S(8)−P(10)]	97.9(6)	99.0	

[a] For original GED refinement see ref 6. [b] Distances (r) are in pm and angles (∠) are in degrees. See text for parameter definitions and Figure 1 for the atom numbering. The figures in parentheses are the estimated standard deviations of the last digits. [c] Refers to MP2/aug-cc-pVQZ calculations. [d] Refers to MP2/aug-cc-pVTZ calculations.

TABLE 3: $^2J_{PP}$ and $^1J_{PF}$ Coupling Constants of $O(PF_2)_2$, $S(PF_2)_2$ and $Se(PF_2)_2$ in Hz

	C_{2v}		C_s		C_1	
	$^1J_{PF}$	$^2J_{PP}$	$^1J_{PF}$	$^2J_{PP}$	$^1J_{PF}$	$^2J_{PP}$
			$O(PF_2)_2$			
experiment[a]	−1358	4				
B3LYP/aug-cc-pVDZ	−1226.5	110.8	−1142.6	−8.9	−1005.3	13.0
B3LYP/aug-cc-pVTZ	−1388.7	110.6	−1312.2	−14.2	−1365.8	42.3
B3LYP/aug-cc-pVQZ	−1472.1	102.8	−1381.8	−16.1	−1432.0	54.7
			$S(PF_2)_2$			
experiment[b]	−1307.3	274.1				
HF/aug-cc-pVQZ	−1156.8	288.2	−1180.4	−9.3		
PW91PW91/aug-cc-pVDZ	−1127.7	380.1	−1089.2	−7.2	−1155.6	−18.4
B3LYP/aug-cc-pVDZ	−1117.3	343.1	−1092.0	−7.5	−1153.6	−5.4
B3LYP/aug-cc-pVTZ	−1294.6	385.5	−1276.4	−8.8	−1330.5	13.2
B3LYP/aug-cc-pVQZ	−1373.2	395.2	−1364.8	−12.6	−1408.9	16.1
			$Se(PF_2)_2$			
experiment[c]	−1305	232				
B3LYP/aug-cc-pVDZ	−1100.2	302.6	−1082.0	−4.4	−1140.0	−21.7
B3LYP/aug-cc-pVTZ	−1283.3	347.9	−1272.8	−5.9		
B3LYP/aug-cc-pVQZ	−1359.4	342.8	−1353.4	−10.4		

[a] 300 K.[1,3] [b] Values at 304 K for a 9% solution in $CFCl_3$.[1] [c] 300 K.[2]

of 4 Hz.[3] Any lowering of the temperature could only result in a small change in the coupling constant as the C_s conformer becomes 100% abundant. The theoretical results do not give an explanation of why the C_{2v} and C_s conformers have such different coupling constants, but it seems likely that it originates from the overlap of the phosphorus lone pairs in the C_{2v} conformers. The small experimental values of $^2J_{PP}$ for compound **1** relative to those for **2** and **3** arise first because the value for conformer iv is much smaller than those for the S and Se analogs and second because the abundance of the conformers is much smaller. Both of these factors are consequences of the wide P−O−P angle [135(2)°][5] relative to P−S−P [93.1(3)°] and P−Se−P [94.6(8)°].[6]

The theoretical values of $^2J_{PP}$ for the conformers of **2** and **3** can be used together with the observed value to estimate the amount of each conformer present in solution:

$$ {}^2J_{PP}^{C_{2v}} n_{C_{2v}} + {}^2J_{PP}^{C_s} n_{C_s} = {}^2J_{PP}^{C_{2v}} n_{C_{2v}} + {}^2J_{PP}^{C_s}(1 - n_{C_{2v}}) = {}^2J_{PP}^{obs} \qquad (1) $$

where n_{C_x} is the population of C_x conformer present. The contribution of the C_2 conformer has been neglected, as its coupling constant is similar to that of the C_s and its population

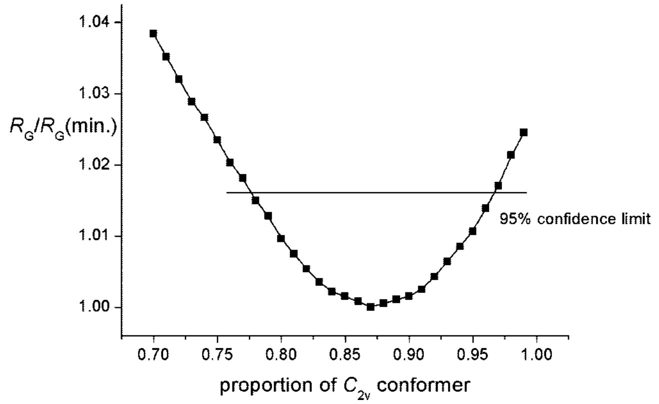

Figure 2. Plot of R_G/R_G (min) against the proportion of C_{2v} conformer in the GED refinement.

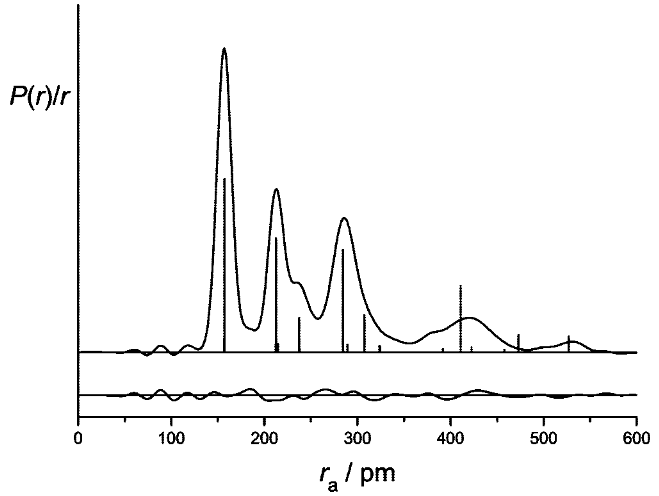

Figure 3. Experimental and theoretical-minus-experimental radial-distribution curves for the GED refinement of $S(PF_2)_2$. Before Fourier inversion, the data were multiplied by $s \exp(-0.00002s^2)/(Z_F - f_F)(Z_P - f_P)$.

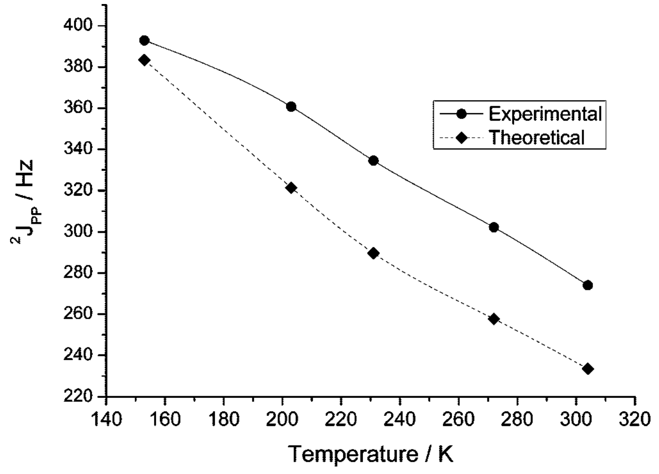

Figure 4. Experimental and theoretical temperature dependence of $^2J_{PP}$.

is likely to be very small. For **2** at 304 K, eq 1 yields 70.3% C_{2v} conformer, whereas for **3** this equates to 68.6% of C_{2v} conformer being present. The values agree poorly with the conformer populations calculated from the free energies, particularly for **3**, but we might expect there to be uncertainty in the free energies, especially given their strong basis-set dependence. There are a number of methods for determining more accurate free energies,[22] but we have not performed these, as the aim of the present work is to explore the potential for multiple conformers and the theoretical results do suggest the presence of two conformers in the *gas phase*. It should be stressed that the experimental NMR values were recorded in solution, where solvation effects may change the relative free energies of the two conformations. Rudolph and Newmark studied solutions of **2** with concentrations ranging from 100 to 1 mol % in $CFCl_3$ and found that the coupling constants were identical within experimental uncertainties.[1] This suggests that the interactions of $S(PF_2)_2$ with other $S(PF_2)_2$ molecules and with $CFCl_3$ molecules in solution are either identical or, as is more likely, negligible.

The difference in the conformer ratios as determined from the theoretical free energies and eq 1 leads one to expect poor agreement between the experimental and theoretical temperature dependence of $^2J_{PP}$. The free energy difference can be estimated from the experimental $^2J_{PP}$ value at different temperatures using the theoretical $^2J_{PP}$ values of conformers iv and v:

$$\Delta G = -kT \ln\left(2 \times \frac{n_{C_{2v}}}{n_{C_s}}\right) \qquad (2)$$

where the factor of 2 takes into account the double degeneracy of the C_s conformer. These free energies can be used to give a reasonable idea of the expected temperature dependence of $^2J_{PP}$. This temperature dependence is plotted along with the experimental values for compound **2** in Figure 4. Although the two curves are offset, they show that the experimental behavior can be reasonably explained by the change in the relative populations of two conformers. The experimental values also suggest that the theoretical coupling constant is too small. The calculated $^2J_{PP}$ values for **2** do seem to be converging toward a larger value. If reinvestigation of the compound could be performed at lower temperatures then we would expect $^2J_{PP}$ to plateau as all of the C_s conformer converts to C_{2v}.

Gas Electron Diffraction Refinement of $S(PF_2)_2$. Following the comprehensive computational study described above, which identified conformers of $S(PF_2)_2$ with both C_{2v} and C_s symmetries, it was decided to attempt to fit both of these conformers to the original GED data. As the theoretical calculations suggested that the C_2 conformer would be present only in very small amounts, it was decided not to include this conformer in the GED model. To write the model describing two conformers, three different PF_2 groups must be described (the PF_2 groups in the C_{2v} conformer are related through symmetry). The three P−F distances that were required were included as the average of the three (weighted to account for the fact that the P−F distance in the C_{2v} conformer appears twice as often) and two corresponding differences (p_{1-3}). The individual P−F distances, numbered using the scheme shown in Figure 1, were therefore constructed using the following equations:

$$r[P(2)-F(6)] = p_1 - p_2/4 + p_3/3 \qquad (3)$$

$$r[P(10)-F(12)] = p_1 - p_2/4 + 2p_3/3 \qquad (4)$$

$$r[P(9)-F(13)] = p_1 + 3p_2/4 \qquad (5)$$

In an identical manner the three S-P distances were formed using the average of the three and differences between them (p_{4-6}), as too were the S−P−F angles (p_{7-9}). As the F−P−F angles differed very little between the three distinct types of PF_2 group, a single value was used in the refinement model (p_{10}). Finally, the two P−S−P angles were described by the average of the two and the difference between them (p_{11-12}). A nongeometrical parameter was also included in the model to define the amount of C_{2v} conformer present. After performing the refinement with this parameter fixed at the value calculated at the B3LYP/aug-cc-pVTZ level, the experimental value was determined by systematically stepping through values to see where the minimum R factor lay. The uncertainty on this value was then estimated using Hamilton's statistical tables.[23] This plot is shown in Figure 2, where the horizontal line represents the 95% confidence limit (1.016), corresponding to 2σ. All independent geometric parameters were refined by least squares, to the values given in Table 2. Parameters that could otherwise not be refined were restrained using the SARACEN method,[24] to values calculated at the MP2/aug-cc-pVQZ level. Additionally, nine amplitudes or groups of amplitudes of vibration were refined, some subject to SARACEN restraints. (See Table S2 in the Supporting Information for a list of amplitudes of vibration.) The success of the refinement can be assessed numerically using the final R factor, which was $R_G = 0.079$ ($R_D = 0.054$), and visually using the goodness of fit of the radial-distribution and difference curves as seen in Figure 3 and the molecular-scattering intensity curves (Figure S1, Supporting Information). The least-squares correlation matrix is given in Table S3 (Supporting Information) and coordinates for the final GED structures and for the calculated structures (MP2/aug-cc-pVQZ) are in Tables S4 and S5 (Supporting Information), respectively.

The GED refinement indicates that 87(5)% of the molecules are in the C_{2v} conformation and that remainder in the C_s form in the gas phase, at room temperature, supporting the results of the geometry and NMR calculations.

Conclusions

The present work has reinvestigated compounds **1**−**3** in an effort to understand the large temperature dependence of the $^2J_{PP}$ spin−spin coupling constants of **2** and **3** in solution. The ab initio and DFT calculations suggest that two conformers of **2** and **3** are likely to coexist and that thermal interconversion of these explains the observed NMR behavior, as they have vastly different $^2J_{PP}$ coupling constants. The calculations have been augmented with a rerefinement of the GED data of **2**, which fits best with the two calculated conformers being present in the gas phase, in contrast to the orginal refinement, which did not consider the C_s conformation. The calculations also suggest that compound **1** is likely to consist of three conformers, (ii), (iv) and (v), in the gas phase and not conformers (i)−(iv) as found previously from GED.[5]

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Supporting Information Available: Tables of experimental parameters for the GED analysis of **2** (Table S1), refined and calculated root-mean-squared amplitudes of vibration (u), associated r_a distances and $r_a - r_e$ distance corrections (Table S2), the least-squares correlation matrix (Table S3), GED and MP2/aug-cc-pVQZ molecular coordinates (Tables S4 and S5) and molecular-intensity scattering and difference curves (Figures S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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