Inorg. Chem. **1986**, *25*, 3177–3181

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Gas-Phase Structures of Perfluoro-2-phosphapropene, $CF_3P{=}CF_2$, and Its Cyclic Dimer, $(CF_3PCF_2)_2$[†]

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Received February 12, 1986

The geometric structures of $CF_3P{=}CF_2$ and its cyclic dimer $(CF_3PCF_2)_2$ have been determined by gas electron diffraction. The following geometric parameters (r_a values) were derived for $CF_3P{=}CF_2$: P=C = 1.690 (5) Å, P—C = 1.901 (4) Å, C—P=C = 108.8 (8)°; C(sp^2)—F = 1.313 Å (assumed on the basis of ab initio calculations), C(sp^3)—F = 1.342 (5) Å, FCF (methyl) = 106.3 (10)°, P=C—F$_{cis}$ = 125.3 (10)°, P=C—F$_{trans}$ = 122.9 (38)°. The four-membered PCPC ring of the dimer is strongly puckered (puckering angle θ = 35.4 (12)°), and CPC = 77.6 (8)°. The CF_3 groups (C–F = 1.341 (2) Å and FCF = 107.7 (6)°) point in axial and equatorial directions, respectively (trans position). The endo and exo P–C bonds (P–C$_1$ = 1.895 (11) Å, P–C$_2$ = 1.905 (21) Å) are equal within their experimental uncertainties (2σ values including a possible scale error of 0.1%). For the methylene groups, the C–F bond lengths were set equal to the methyl bonds (1.341 (2) Å) and FCF = 106.4 (17)°.

Introduction

The actual and continuing interest in unsaturated compounds consisting of elements of the second and following rows of the periodic table is demonstrated by a series of excellent reviews[2-5] concerning the study of small labile molecules in the gas phase and interstellar space as well as investigations aimed at the preparation of EE′ multiple bonds stabilized by bulky substitutents. In spite of the rapid expansion in both fields during the last 10 years the number of unshielded phosphaalkene compounds is still very limited. Analogous to the procedure used by Johnson and Lovas[6] for the production of methanimine, $HN{=}CH_2$, the parent species $HP{=}CH_2$ and the substituted derivatives $ClP{=}CH_2$ and $HP{=}CF_2$ were detected in the pyrolysis of CH_3PH_2, CH_3PCl_2, and CF_3PH_2, respectively.[7] These phosphaalkenes, similar to methanimine, are unstable species, which could not be isolated as pure compounds. They were characterized in the gas phase under low pressure by microwave spectroscopy. The chemistry of the small phosphaalkene $CF_3P{=}CF_2$ dates back to 1965, when it was postulated as an intermediate species in the methanolysis of $(CF_3)_2PH$.[8] It was discussed as the primary product formed by the decomposition of $(CH_3)_3M'P(CF_3)_2$ compounds (M′ = Si, Ge, Sn) yielding $(CH_3)_3M'F$ and $(CF_3PCF_2)_x$ polymers[9,10] as well as in the BF_3-catalyzed destruction of $H_3SiP(CF_3)_2$ leading to the cyclic dimer.[11] $CF_3P{=}CF_2$ was later trapped from the base reaction of $(CF_3)_2PH$ with methanol/sodium methoxide and identified by NMR spectroscopy.[12] Burg[13] obtained the pure compound by low-pressure pyrolysis of the cyclic dimer or trimer, and it proved to be stable in the gas phase at room temperature. A more suitable procedure has been developed recently by Grobe et al.[14] applying the low-pressure thermolysis to $(CH_3)_3SnP(CF_3)_2$. This novel route produces $CF_3P{=}CF_2$ in almost quantitative yield and high purity, so that physical measurements could be completed and chemical reactivity studies could be performed.[1,15-17] In this paper we report the gas-phase structures of $CF_3P{=}CF_2$ and its cyclic dimer, *trans*-$(CF_3PCF_2)_2$.

Experimental Section

Preparation of Compounds. (a) Perfluoro-2-phosphapropene. A 5-mmol sample of $(CH_3)_3SnP(CF_3)_2$ is passed through a pyrolysis tube of 250-mm length and 18-mm diameter at 300 °C and 10^{-3} torr. Unreacted $(CH_3)_3SnP(CF_3)_2$ is condensed in a cold trap at −78 °C and repeatedly fed through the hot zone until the conversion to $CF_3P{=}CF_2$ is complete. The pure phosphaalkene is collected at −196 °C, whereas the less volatile polyadduct $((CH_3)_3SnF)_n$ separates out immediately behind the hot zone. The purity of the product was tested by mass spectrometry and by ^{19}F NMR measurements in toluene-d_8. The sample used for the electron diffraction study contained less than 1% $(CF_3)_2PH$ due to hydrolysis of the tin compound. The solvent toluene-d_8 was removed from the sample by trap-to-trap condensation at 10^{-3} torr (−78/−196 °C).

(b) *trans*-1,3-Bis(trifluoromethyl)-1,3-diphosphaperfluorocyclobutane. For the preparation of the trans dimer of $CF_3P{=}CF_2$ a 30% solution of the pure monomer in deuteriochloroform, $CDCl_3$, is kept at 25 °C for 4 days. Only about 6% of the monomer is transformed to the *cis*-1,3-diphospha- and the *trans*-1,2-diphosphacyclobutane derivatives in addition to a mixture of trimers under these conditions, whereas 94% of the starting compound undergoes (2+2) cycloaddition with formation of the trans 1,3-dimer. The trimeric species and the less volatile *trans*-1,2-diphosphacyclobutane are removed by fractional condensation at 10^{-3} torr. The trans 1,3-dimer is obtained in about 98% purity, containing mainly the cis 1,3-conformer and only traces of the trans 1,2-species.

Electron Diffraction. The scattering intensities were recorded with the Balzers Gas Diffractograph KD-G2[18] at two camera distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The samples were kept at −85 °C (monomer) and −15 °C (dimer). The stainless steel inlet system and nozzle were at room temperature. The camera pressure never exceeded 10^{-5} torr. The exposure times were 5–8 s and 20–35 s for the long and short camera distances, respectively. The electron wavelength was calibrated by ZnO diffraction patterns. Two plates for each compound and camera distance were analyzed by the usual procedures.[19] The averaged molecular intensities in the ranges $1.4 < s < 17$ and $8 < s < 35$ Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figures 1 and 2.

Structure Analyses

Preliminary structural models were obtained from the radial distribution functions and refined by least-squares analyses. A diagonal-weight matrix[19] was applied to the intensities, and scattering amplitudes and phases of J. Haase[20] were used.

[†] Reactive E=C (*p–p*) Systems. 7.

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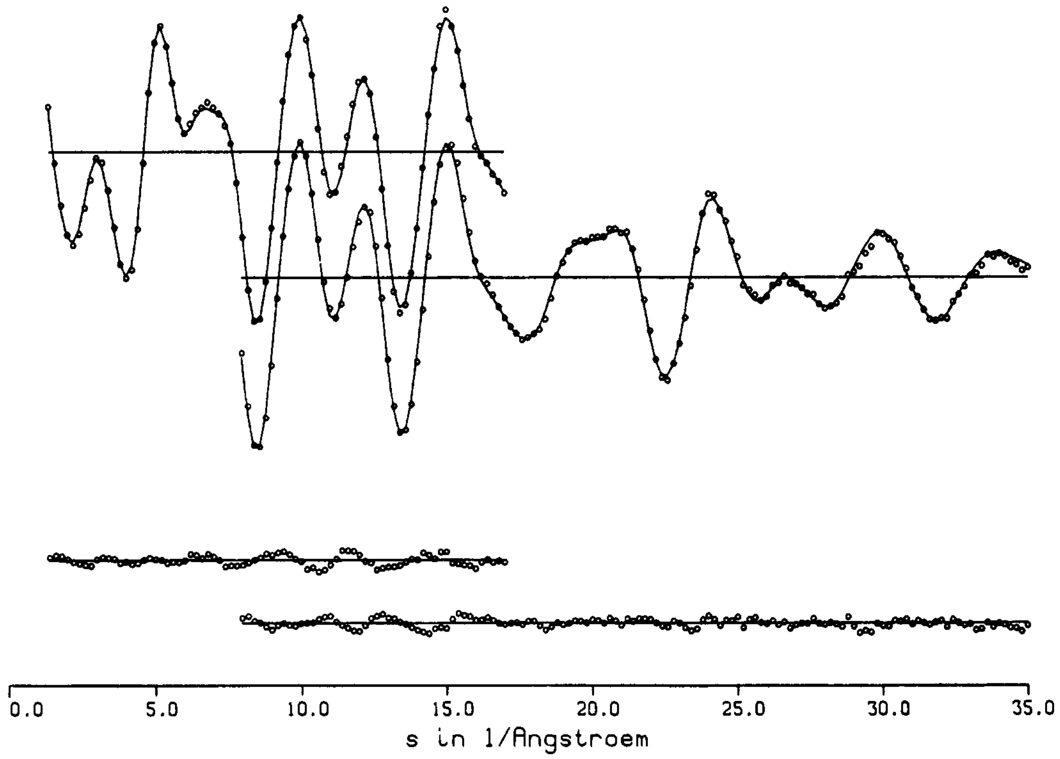

Figure 1. Experimental (···) and calculated (—) molecular intensities and differences for $CF_3P{=}CF_2$.

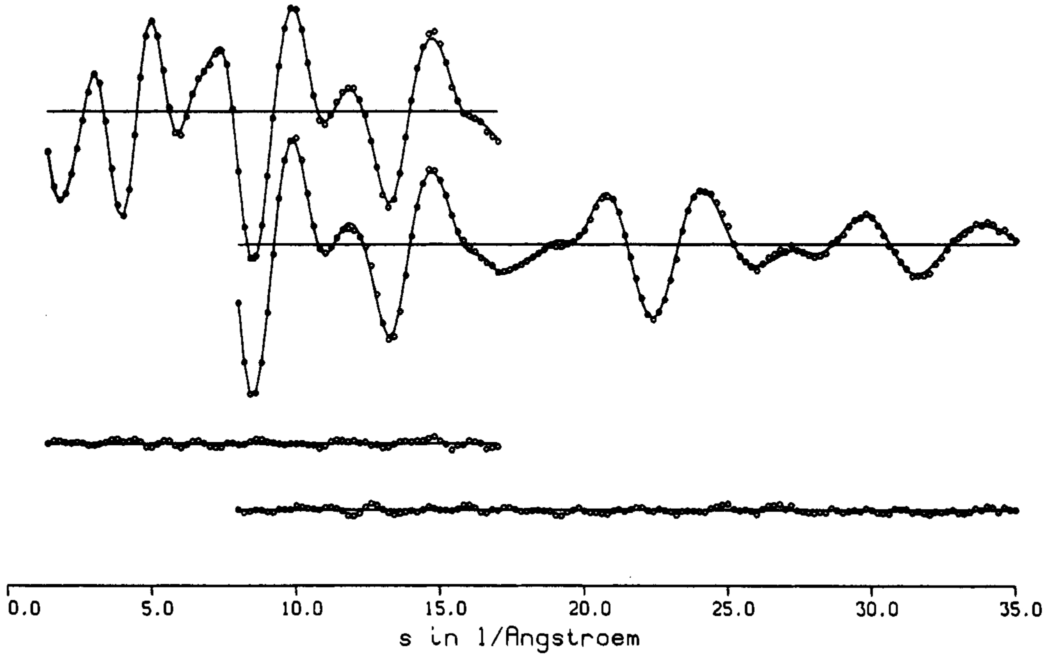

Figure 2. Experimental (···) and calculated (—) molecular intensities and differences for $(CF_3PCF_2)_2$.

$CF_3P{=}CF_2$. The analysis of the radial distribution curve (Figure 3) demonstrates that the CF_3 group eclipses the P=C double bond; i.e., it staggers the phosphorus lone pair. Assuming C_{3v} symmetry for the CF_3 group, the structure of $CF_3P{=}CF_2$ is characterized by nine geometric parameters: four bond lengths, four bond angles, and a possible tilt angle between the C_3 axis of CF_3 and the P–C bond direction. Since a preliminary least-squares analysis resulted in a value for this tilt angle, which was smaller than its standard deviation (1.2 (2.1)°), this parameter was set to zero in the following refinements. Assuming a "rigid" molecular model, small differences between the experimental and calculated radial distribution curves existed in the region $4.7 < r < 5.4$ Å. These discrepancies could be reduced with a "nonrigid" model assuming a large-amplitude CF_3 torsional motion with a threefold potential. Refinements with different but fixed values for the torsional barrier resulted in an optimum value of $V_0 = 4.7 \pm 2.4$ kJ mol^{-1}. The sum of the errors squared was reduced by 13% relative to the case of the "rigid" model. The closely spaced $C(sp^2)$–F and $C(sp^3)$–F distances correlate strongly with the C–F vibrational amplitude, which was assumed to be equal for both types of bonds. Ab initio calculations (6–31 G * basis sets) for $HN{=}CH_2$, $HP{=}CH_2$, and their various fluorinated species[21]

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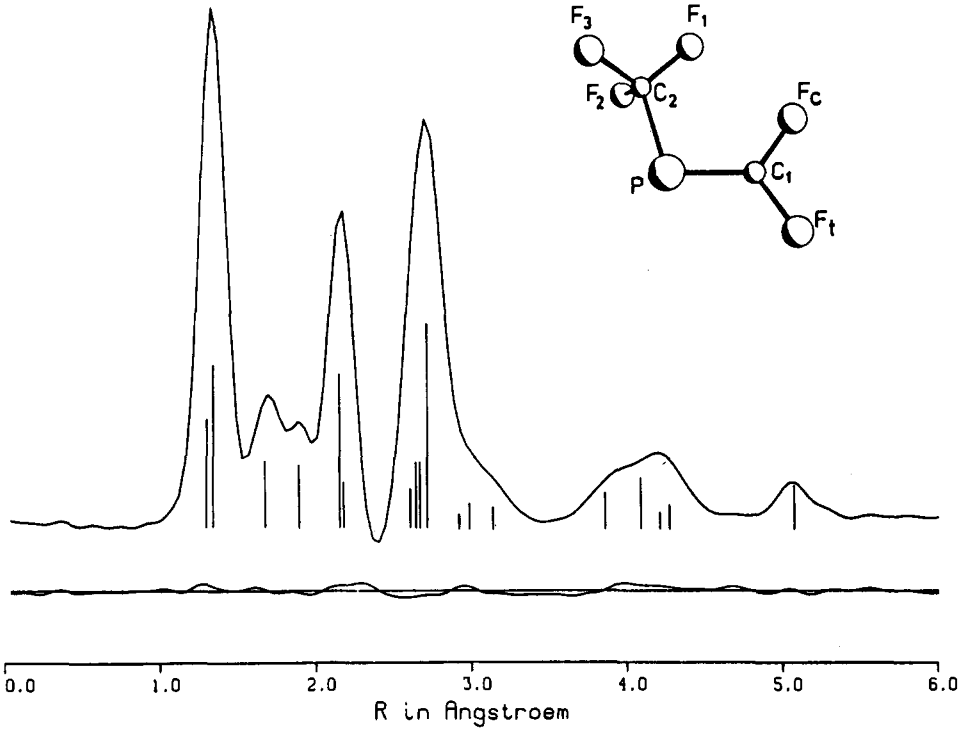

Figure 3. Experimental radial distribution function and difference curve for $CF_3P{=}CF_2$. The vertical lines indicate the positions of the interatomic distances. The labeling is evident from Table I.

result in $C(sp^2)$–F bond lengths of 1.295 Å for $HP{=}CF_2$ and $FP{=}CF_2$. If these values are corrected for systematic differences between theoretical r_e values and experimental r_a distances by comparing calculated and experimental values for $FN{=}CF_2$,[22] r_a values of 1.313 Å are estimated for these bonds in the phosphaalkenes. In the final least-squares analysis the $C(sp^2)$–F distances in $CF_3P{=}CF_2$ were constrained to this value. Systematic errors, which this assumption may introduce in other geometric parameters, were estimated by varying this value by ±0.01 Å. Assumptions made for vibrational amplitudes are evident from Table I. Seven geometric parameters and 11 vibrational amplitudes were refined simultaneously. Correlation coefficients with values larger than |0.6| are listed in Table II, and the final results are summarized in Table I. A strong three-way correlation exists between the FCF angles in the CF_3 group (p_5), the PC_1F_t angle (p_7), and the F··F vibrational amplitude (l_4). If the geminal F··F amplitudes are constrained to spectroscopic values derived for similar compounds (0.053 Å for $F_c{\cdot\cdot}F_t$ in $FN{=}CF_2$[22] and 0.057 Å for $F_l{\cdot\cdot}F_2$ in $P(CF_3)_3$[23]), the correlation p_5/p_7 reduces to −0.84. These constraints have a marginal effect on the fit between experimental and calculated intensities, and all parameters remain the same within their standard deviations.

$(CF_3PCF_2)_2$. Analysis of the radial distribution curve (Figure 4) results in a strongly puckered PCPC ring with the CF_3 groups in axial and equatorial directions, respectively. Both CF_3 groups stagger the ring bonds. The least-squares analyses were based on a "rigid" model assuming C_{3v} symmetry for the CF_3 groups and equal angles between the exo P–C bonds and the CPC planes of the ring (i.e., $C_1PC_2 = C_1P'C_2'$; see Figure 4 for atom numbering). Preliminary refinements of tilt angles for the CF_3 groups and rocking angles for the CF_2 groups resulted in values that were smaller than their standard deviations, and these parameters were set to zero in the following calculations. The C–F bond lengths in the CF_3 and CF_2 groups were set equal. Comparison with other compounds indicate that such bond lengths are very similar: 1.340 (3) or 1.342 (5) Å for CF_3 groups in $P(CF_3)_3$[23] or $CF_3P{=}CF_2$ and 1.344 (2) Å for the CF_2 group in $\overline{SCF_2SCF_2}$.[24] The value obtained for the C–F vibrational amplitude (0.042 (3) Å) furthermore justifies this assumption. A larger value for this amplitude would be expected if these bond distances were strongly different. Separate refinement of the endo and exo P–C bond lengths ($P{-}C_1$ and $P{-}C_2$) causes strong correlations between some parameters, resulting in large standard deviations. Independent of the starting values ($P{-}C_1 < P{-}C_2$ or $P{-}C_1 > P{-}C_2$), the refined endo bond lengths were always shorter than the exo bond lengths, but the difference is smaller than the combined error limits. The vibrational amplitudes were grouped according to their type and distance (see Table III). In the final analysis eight geometric parameters and 10 vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.6|: $p_2/p_3 = -0.97$, $p_2/l_2 = 0.68$, $p_3/l_2 = -0.68$, $p_2/l_4 = -0.77$, $p_3/l_4 = 0.76$, $p_7/l_3 = 0.80$, $p_8/l_3 = 0.82$. The final results are summarized in Table III.

Table I. Results of Electron Diffraction Analysis for CF_3PCF_2

(a) Geometric Parameters (r_a, Å; Angles, deg)[a]

$C_1{-}F$	1.313[b]		C_1PC_2	108.8 (8)	p_4
$C_2{-}F$	1.342 (5)	p_1	$F_1C_2F_2$	106.3 (10)	p_5
$P{=}C$	1.690 (5)	p_2	PC_1F_c	125.3 (10)	p_6
$P{-}C$	1.901 (4)	p_3	PC_1F_t	122.9 (38)	p_7

(b) Interatomic Distances (Å) and Vibrational Amplitudes[c]

$C_1{-}F$	1.31	0.043 (2)	l_1	$P{\cdot\cdot}F_1$	2.71	0.087 (14)	l_6
$C_2{-}F$	1.34			$C{\cdot\cdot}C$	2.92	0.070 (24)	l_7
$P{=}C$	1.69	0.050 (9)	l_2	$C_1{\cdot\cdot}F_1$	2.98		
$P{-}C$	1.90	0.048 (10)	l_3	$C_2{\cdot\cdot}F_c$	3.14		
$F_1{\cdot\cdot}F_2$	2.15	0.053 (9)	l_4	$C_1{\cdot\cdot}F_2$	3.85	0.069 (20)	l_8
$F_c{\cdot\cdot}F_t$	2.17			$F_c{\cdot\cdot}F_2$	4.09	0.102 (24)	l_9
$F_c{\cdot\cdot}F_1$	2.61	0.100[d]		$C_2{\cdot\cdot}F_t$	4.18	0.088 (37)	l_{10}
$P{\cdot\cdot}F_t$	2.64	0.074 (15)	l_5	$F_t{\cdot\cdot}F_1$	4.29		
$P{\cdot\cdot}F_c$	2.67			$F_2{\cdot\cdot}F_t$	5.05	0.053 (14)	l_{11}

(c) Agreement Factors

$R_{50} = 0.056$ $R_{25} = 0.093$

[a] Error limits are 2σ values and include systematic errors due to the assumption for C_1–F. [b] Not refined in the least-squares analyses but varied by ±0.01 Å. [c] Error limits are 3σ values. [d] Not refined.

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Table II. Correlation Coefficients Larger than |0.6| for CF_3PCF_2

p_7/p_5	-0.93	p_5/l_6	-0.83	p_5/l_5	-0.74	p_5/l_4	-0.92
p_5/l_{10}	-0.65	p_7/p_6	0.81	p_7/l_5	0.78	p_7/l_4	0.91
l_6/l_4	0.82	l_5/l_4	0.68	l_4/l_{10}	0.62		

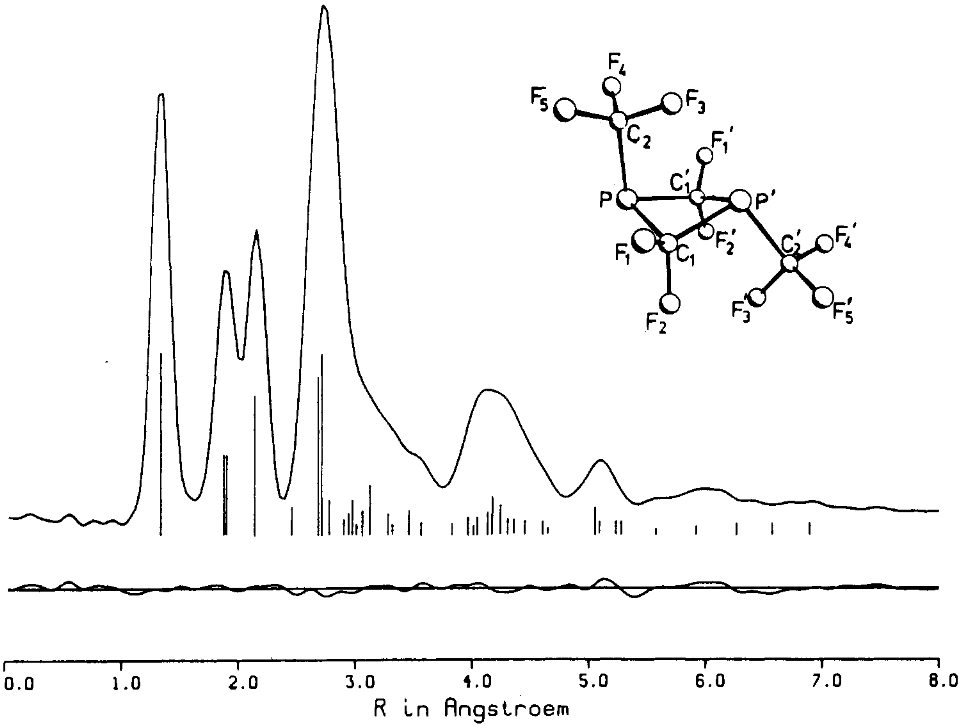

Figure 4. Experimental radial distribution function and difference curve for $(CF_3PCF_2)_2$. The vertical lines indicate the positions of the interatomic distances. Distances with contributions Z_iZ_j/r_{ij} less than 20 have been omitted. The labeling is evident from Table III.

If a small amount of the cis conformer with both CF_3 groups in equatorial positions (2%) is included in the model, the *R* factors increase marginally and the geometric parameters remain unchanged. We estimate that the amount of the cis conformer in our sample was indeed less than that indicated by the ^{19}F NMR spectra, since several days elapsed between the NMR and electron diffraction experiments and the cis species slowly inverts to the trans form at room temperature.

Discussion

The most interesting geometric parameter in $CF_3P{=}CF_2$ is the P=C double-bond length with a value of 1.690 (5) Å. This bond is longer by about 0.02 Å than in the parent compound $HP{=}CH_2$, where a microwave study resulted in a value of 1.673 (2) Å.[25] Also, for the partially fluorinated species, $HP{=}CF_2$[7] and $FP{=}CH_2$,[3] P=C bond lengths of 1.67 Å have been derived from rotational constants, whereby most other geometric parameters had to be assumed. The ab initio calculations, however, predict *shortening* of the P=C double bond by about 0.02 Å with fluorination at P and *lengthening* by about the same amount with fluorination at C or perfluorination. It can be shown that these trends in the P=C bonds are compatible with the experimental rotational constants, if the assumptions for other geometric parameters are adjusted according to the calculated values.[21] Thus the observed lengthening of P=C in $CF_3P{=}CF_2$ relative to $HP{=}CH_2$ is in good agreement with trends predicted by ab initio calculations. It is interesting to point out that fluorination affects the P=C and N=C bonds differently. Whereas perfluorination lengthens the P=C bond in phosphaalkene, the N=C bond is not affected (1.273 (4) Å in $HN{=}CH_2$[26] and 1.274 (6) Å in $FN{=}CF_2$[22]). This observation can be rationalized by the different polarities of N=C and P=C bonds resulting from the different electronegativities of N and P.

Table III. Results of Electron Diffraction Analysis for $(CF_3PCF_2)_2$

(a) Geometric Parameters (r_a, Å; Angles, deg)[a]

$(C-F)_{av}$	1.341 (2)	p_1	θ^c	35.4 (12)	p_5
$(P-C)_{av}$	1.898 (3)		α^d	105.0 (7)	p_6
$P-C_1$	1.895 (11)	p_2	$C_1PC_2{}^b$	101.7 (11)	
$P-C_2$	1.905 (21)	p_3	$F_3C_2F_4$	107.7 (6)	p_7
C_1PC_1'	77.6 (8)	p_4	$F_1C_1F_2$	106.4 (17)	p_8
$PC_1P'^b$	95.6 (6)				

(b) Interatomic Distances (Å) and Vibrational Amplitudes[e]

C-F	1.34	0.042 (3)	l_1	$P'{\cdot\cdot}F_3$	2.70	0.109 (24)	l_5
$P-C_1$	1.89	0.055 (4)	l_2	$P{\cdot\cdot}F_3'$	4.01		
$P-C_2$	1.91			$P'{\cdot\cdot}F_4$	4.25		
$F_1{\cdot\cdot}F_2$	2.15	0.054 (4)	l_3	$P{\cdot\cdot}F_4'$	5.05		
$F_3{\cdot\cdot}F_4$	2.16			C··F	(2.90–3.13)	0.18 (3)	l_6
$P{\cdot\cdot}F_3$	2.70	0.100 (6)	l_4	C··F	(3.46–3.58)	0.18[f]	
$P{\cdot\cdot}F_1$	2.73			C··F	(3.85–4.17)	0.28 (11)	l_7
$C_1{\cdot\cdot}C_1'$	2.38	0.080[f]		C··F	(4.60–6.03)	0.20[f]	
P··P'	2.81			F··F	(2.42–3.26)	0.30 (9)	l_8
$C_1{\cdot\cdot}C_2$	2.95	0.120[f]		F··F	(3.98–4.64)	0.21 (11)	l_9
$C_2{\cdot\cdot}C_2'$	5.14			F··F	(5.08–5.25)	0.37 (14)	l_{10}
$P'{\cdot\cdot}C_2$	3.32	0.110[f]		F··F	(6.28–6.93)	0.30[f]	
$P{\cdot\cdot}C_2'$	4.16						

(c) Agreement Factors

$R_{50} = 0.054$ $R_{25} = 0.071$

[a] Error limits are 2σ values and include possible scale error of 0.1%. [b] Dependent parameter. [c] Puckering angle. [d] Angle PC_2/C_1PC_1'. [e] Error limits are 3σ values. [f] Not refined.

X-ray studies for phosphaalkenes with large substituents[2,4,27] report P=C double-bond lengths between 1.68 and 1.72 Å. The P–C single bond length in $CF_3P{=}CF_2$ is typical for P–CF_3 compounds such as in $P(CF_3)_3$ (1.904 (7) Å[23]). Similarly, long P–C bonds have been reported for acylphosphines (1.86–1.89 Å[4]), whereas P–CH_3 bonds are shorter (e.g., 1.846 (3) Å in $P(CH_3)_3$[28]).

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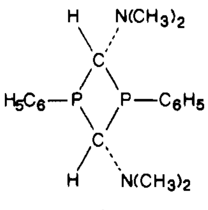
The $C{-}P{=}C$ angle (108.8 (8)°) is considerably larger than these phosphorus valence angles in $HP{=}CH_2$ (97.4 (4)° [25]) or $ClP{=}CH_2$ (103.0 (7)° [29]) and may be interpreted as a consequence of steric interactions. A similar CPC angle of 106.7 (1)° has been reported for bis((trimethylsilyl)sulfano)methylenephenylphosphine.[27]

In the dimeric species, $(CF_3PCF_2)_2$, the strong puckering of the four-membered CPCP ring ($\theta = 35.4\ (12)°$) and the very small CPC ring angle of 77.6 (8)° are striking. Similar rings containing large substituents, such as **1**,[30] **2**,[31] and **3**,[32] have smaller puckering angles in the crystal or are planar as in the case of **3**. The reported CPC angles in these compounds range from 83–87°. The exo P–C bonds in $(CF_3PCF_2)_2$ are again typical for $P{-}CF_3$ bonds (see above) and are considerably longer than these P–C bonds in **1** and **2** (1.83–1.84 Å). The endo P–C bond lengths in $(CF_3PCF_2)_2$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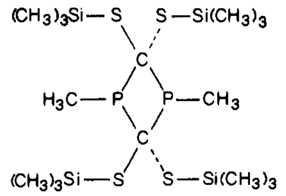
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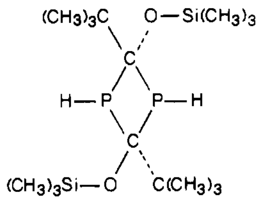
3

are very similar to these bonds in **1**–**3** (1.87–1.91 Å).

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Registry No. $CF_3P{=}CF_2$, 72344-34-4; *trans*-$(CF_3PCF_2)_2$, 37896-36-9; $(CH_3)_3SnP(CF_3)_2$, 39185-13-2.

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EPR Evidence for an Unexpected Symmetric Dinuclear Species Present in the Lattice of an Asymmetric Dinuclear Copper Complex

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Received February 24, 1986

The low-temperature single-crystal EPR spectra of $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ (I: dien = diethylenetriamine; ox = oxalato; tmen = *N,N,N′,N′*-tetramethylethylenediamine) revealed that the paramagnetic species that caused the deviation of the magnetic susceptibility from the Bleaney–Bowers equation is a spin triplet containing two equivalent copper ions. The comparison of the magnetic properties of the impurity with those reported in the literature for similar compounds leads us to suggest that $[(dien)Cu(ox)Cu(dien)]^{2+}$ species are present in the lattice.

Introduction

The presence of paramagnetic species, often called impurities, in the lattice of dinuclear copper(II) complexes is well-established, evidence arising from both EPR and magnetic susceptibility measurements.[2-6] In fact, in the EPR spectra beyond the signals attributable to the $S = 1$ coupled state, quite often signals of $S = {}^1/_2$ species are observed. Generally the **g** tensors of the $S = {}^1/_2$ species are practically identical with those of the triplet.

In the temperature dependence of the magnetic susceptibility of antiferromagnetically coupled pairs both a maximum and a minimum are observed: the former is due to the coupling between the ions; the latter is attributed to the presence of the paramagnetic impurity, which is generally associated with defective dinuclear units in which one of the two copper ions is missing, but, to our knowledge, no attempt has ever been made to proceed to a detailed characterization of the nature of the impurity.

Recently three of us reported[7] the synthesis of an asymmetric dinuclear copper(II) complex of formula $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ (I: dien = diethylenetriamine; ox = oxalato; tmen = *N,N,N′,N′*-tetramethylethylenediamine), in which the two inequivalent copper ions are antiferromagnetically coupled, with a singlet–triplet separation of 75.5 cm^{-1}. The magnetic data revealed the presence of a paramagnetic species, which determined the value of the magnetic susceptibility below 25 K. The asymmetric nature of the complex in this case poses some problems about the possible nature of the impurity, since, with the above explanation, two different defective complexes might be formed. By recording the low-temperature EPR spectra of I, we found that the paramagnetic species corresponds to a spin triplet. We characterized this impurity by single-crystal EPR spectroscopy, and we report here the results of such analysis in order to show how this species is symmetric and presumably rather different from the parent compound.

Experimental Section

A blue-violet precipitate of I was formed immediately when equimolar methanolic solutions of $[Cu(dien)](ClO_4)_2$ and $Cu(tmen)(ox)\cdot 4H_2O$ were mixed.[7,8] The solid was dissolved in warm water, and EPR-suitable

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