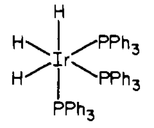
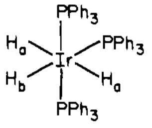
fashion, then the dihydride species III which initially forms rearranges to give the observed product, V. An alternative explanation to account for the observed product is the oxidative addition of H_2 to an iridium species other than $Ir(PPh_3)_2(acac)$, possibly via loss of phosphine prior to oxidative addition.

During the course of the reaction of **16** + H_2, several other hydride resonances are observed in the −8 to −14 ppm region of the ^1H NMR spectrum. If the iridium(I) bis(phosphine) complex, **16**, is prepared in situ from Ir(COD)(acac) + PPh_3 under H_2, these hydride resonances are much more evident. On the basis of the observed coupling constants as determined through selective homonuclear decoupling, we identify these additional hydride resonances as belonging to the *fac* and *mer* isomers of the iridium(III) trihydride complex, $IrH_3(PPh_3)_3$, shown as structures VI and VII, respectively.


VI


VII

In the ^1H NMR spectrum of the facial isomer, VI, the equivalent hydrides appear as a complex multiplet centered at −11.38 ppm, which contain a large trans-phosphorus coupling of 120 Hz and a smaller cis-phosphorus coupling of ca. 18 Hz. The spectrum of the meridional isomer, VII, exhibits two complex multiplets at −10.2 and −12.1 ppm. The H_b multiplet (−12.1 ppm) contains a large trans-phosphorus coupling of 116 Hz and $J_{cis\text{-}P}$ of 22 Hz, while proton H_a gives rise to an apparent quartet with a cis-phosphorus coupling of 16 Hz.[19] Comparison of the hydride spectra of VI and VII with the spectra of the closely related iridium complexes $IrH_3(PEt_2Ph)_3$ and $IrH_3(PEt_3)_3$[20] confirms our structural assignments.

The formation of these iridium(III) trihydride complexes, VI and VII, requires the loss of the acac ligand from the metal center. The presence of free triphenylphosphine facilitates this displacement and increases the amount of $IrH_3(PPh_3)_3$ formed during the reaction H_2 + Ir(COD)(acac) + PPh_3. These same iridium hydride complexes, VI and VII, are observed during the reaction of the binuclear iridium complex **8** with H_2 and PPh_3. It is thus apparent that both the binucleating bis(β-diketonate) ligand, xyl(acac)$_2$, and the simple bidentate ligand, acac, are easily displaced by H_2 as well as by H^+. These observations, together with our results on the activity and stability of the rhodium complexes $Rh(P(OPh)_3)_2(acac)$[16] and $(Rh(P(OPh)_3)_2)_2(xyl(acac)_2)$, indicate that a binuclear framework using xyl(acac)$_2$ complexes of Rh and Ir will not be maintained during simple catalytic reactions such as olefin hydrogenation and hydroformylation.

Acknowledgment. We wish to thank the National Science Foundation (Grants CHE 80-11974 and CHE 83-08064) and the Office of Naval Research for support of this work. A generous loan of precious metal salts from Johnson Matthey Co., Inc., is also gratefully acknowledged. B.C.W. acknowledges a Sherman Clarke Fellowship.

Registry No. **1**, 89890-61-9; **2**, 89890-62-0; **3**, 89890-63-1; **4**, 89890-64-2; **5**, 89890-65-3; **6**, 89890-66-4; **7** (monomer), 89890-67-5; **7** (dimer), 89890-76-6; **8**, 89890-68-6; **9**, 89890-69-7; **10**, 89890-70-0; **11**, 89890-71-1; **12**, 89890-72-2; **13**, 89890-73-3; **14**, 12154-84-6; **15**, 14023-80-4; **16**, 89890-74-4; **17**, 89890-75-5; **18**, 64625-61-2; $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$, 12112-67-3; $Rh_2(COD)_2(\mu\text{-}Cl)_2$, 12092-47-6; *fac*-$IrH_3(PPh_3)_3$, 18660-46-3; *mer*-$IrH_3(PPh_3)_3$, 18660-47-4; C_3H_6, 115-07-1.

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(19) Irradiation of the resonance due to H_a results in the complete disappearance of the resonance due to H_b. This suggests that the hydride ligands in *mer*-$IrH_3(PPh_3)_2$ interconvert at room temperature. On the basis of the frequency separation between the two resonances of 720 Hz, the rate of exchange must be slower than 1.4×10^{-3} s, but this interconversion must be faster than the rate of relaxation (T_1) of the hydride ligands in order to cause the saturation of both H_a and H_b during the decoupling experiment.

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Altruism Revisited: Gas Electron Diffraction Study of Tris(trifluoromethyl)phosphine Oxide, $OP(CF_3)_3$, and ab Initio Molecular Orbital Calculations on $X_3C\text{–}Y$ and $X_3C\text{–}Y(O)$ Systems (X = H, F; Y = PH_2, SH, Cl)

COLIN J. MARSDEN

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The molecular structure of tris(trifluoromethyl)phosphine oxide, $OP(CF_3)_3$, has been investigated by gas-phase electron diffraction. Principal structural parameters, with uncertainties (2σ) in parentheses, are r_g(C–F) = 1.336 (2) Å, r_g(P–C) = 1.897 (4) Å, r_g(P═O) = 1.476 (8) Å, ∠O–P–C = 114.2 (0.4)°, ∠C–P–C = 104.3 (0.4)°, ∠P–C–F = 110.4 (0.2)°, and ∠F–C–F = 108.5 (0.2)°. CF_3 groups appear to be tilted by 1.9 (1.2)° away from the P═O bond and twisted by 16.2 (2.0)° away from a staggered conformation. Shrinkage corrections and amplitudes of vibration, which agreed satisfactorily with measured amplitudes, were calculated from an approximate force field. The vibrational spectrum was extended to low frequencies to include some bending modes previously unreported. Phosphorus–carbon bonds are substantially longer than in $OP(CH_3)_3$, and the lengthening is greater than that found for $P(CF_3)_3$. The concept of "altruistic bonding", involving the 3d orbitals on phosphorus, previously advanced to account for the long P–C bonds in $P(CF_3)_3$, is examined in the light of extensive ab initio MO calculations on CH_3 and CF_3 derivatives of phosphorus, sulfur, and chlorine.

Introduction

In a recent reinvestigation of the structure of $P(CF_3)_3$,[1] the P–C bond length was confirmed to be appreciably greater than that in $P(CH_3)_3$. This observation provided another example of the curious striking trends in $(F_3)C\text{–}X$ bond distances,[2,3] which are shorter than $(H_3)C\text{–}X$ if X is highly electronegative but longer if X is of moderate to low electronegativity.

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0020-1669/84/1323-1703$01.50/0

Following examination of literature bond lengths and the results of semiempirical molecular orbital calculations, a rationalization was proposed[1] of the unexpected behavior of CF_3 compounds, under the title of "altruistic covalent interaction". This term was coined to indicate that the influence of the 3d orbitals on P in $P(CF_3)_3$ might be to *weaken* the P–C bonding, while enhancing the C–F bonding. Analogous interactions in $P(CH_3)_3$ would be expected to be of no importance.

Since the energy gap between 3p and 3d orbitals on P is thought to be a sensitive function of the effective nuclear charge and since the magnitude of an altruistic interaction would depend on the energy separation between 3d and other orbitals, one might anticipate that the magnitude of the P–C bond lengthening in $OP^{V}(CF_3)_3$ would differ from that in $P^{III}(CF_3)_3$. To test this prediction, we have undertaken a determination of the structure of $OP(CF_3)_3$ by gas electron diffraction and present the results here.

On the basis of ab initio molecular orbital calculations, recent criticism has been expressed[4] of the altruistic concept, at least insofar as it is applied to $P(CF_3)_3$. However, these calculations used only a minimal basis set, with very limited geometry optimization, and their reliability may thus be questioned. We have performed an extensive series of calculations using the split-valence basis 3-21G$^{(*)}$, which has been shown[5] to reproduce satisfactorily geometries for second-row compounds in a wide range of oxidation states. In an attempt to assess the significance, if any, of the altruistic effect, we have completely optimized, by gradient techniques, the structures of CH_3PH_2, CH_3SH, CH_3Cl, CF_3PH_2, CF_3SH, CF_3Cl, $CH_3P(O)H_2$, $CH_3S(O)H$, $CH_3S(O)_2H$, $CF_3P(O)H_2$, $CF_3S(O)H$, and $CF_3S(O)_2H$.

Experimental Section

A sample of $OP(CF_3)_3$ was prepared by the oxidation of $P(CF_3)_3$ with NO_2 at room temperature[5,6] and purified by distillation in the vacuum system. The purity of the product was established by measurement of its vapor pressure [Found at 0 °C (203 torr, lit.[5] 201 torr)] and gas-phase molecular weight (found 257, $OP(CF_3)_3$ requires 254) and by checking its gas-phase infrared spectrum,[5,6] which showed no evidence of any impurities.

Electron diffraction data were recorded on Kodak Electron Image plates, using the Balzers' K.D.G2 unit at UMIST, England, at nominal nozzle-to-plates distances of 100, 50, and 19 cm. The sample was maintained at −45 °C, while the nozzle was at room temperature. Calibration with benzene vapor established an electron beam wavelength of 0.056 75 Å, corresponding to an accelerating voltage of 44.7 keV. Initial data processing was performed at UMIST, following procedures described elsewhere.[7] Data from three plates were averaged at each camera distance. The "uphill curves" s^4I_{TOT} were then "leveled" by dividing through by the atomic scattering calculated from the form factors of Schafer et al.[8] so as to yield the molecular scattering $M(s)$. A composite data set, covering the range $1.6 < s < 37.94$ Å^{-1} and interpolated in units of $\Delta s = \pi/10$, was prepared by blending together the sets from the three different camera distances. Diagonal weight matrices, whose elements were proportional to s, were used in the least-squares intensity refinements; standard deviations quoted for the derived parameters have been augmented to incorporate estimates of the influence of correlation between adjacent data points[9] and subjective estimates of the uncertainties introduced by the nonrigorous treatment of amplitudes influenced by torsional motions. Radial distribution functions were calculated by using a damping factor of $\exp(-0.0012\ s^2)$. Anharmonicity constants were taken to be 2.0 Å^{-1} for bonded distances and 1.0 Å^{-1} for nonbonded distances. It was established that changing these assumed values by as much as 50% produced insignificant changes in the derived structural or vibrational parameters.

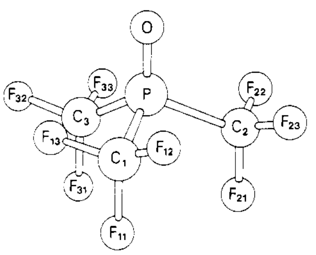

Figure 1. Perspective view of the molecule $OP(CF_3)_3$, showing the atomic numbering scheme used.

Table I. Structural Results for $OP(CF_3)_3$[a]

		obsd amplitude	calcd amplitude	K	parameter no.
$r(P{=}O)$	1.476 (8)	0.038 (8)	0.035	0.0053	r_1, l_1
$r(P–C)$	1.897 (4)	0.053 (4)	0.054	0.0033	r_2, l_2
$r(C–F)$	1.336 (2)	0.043 (3)	0.045	0.0292	r_3, l_3
$\angle(O–P–C)$	114.2 (0.4)				$\angle_1$
$\angle(C–P–C)^b$	104.3 (0.4)				
$\angle(P–C–F)$	110.4 (0.2)				$\angle_2$
$\angle(F–C–F)^b$	108.5 (0.2)				
$\angle CF_3$ tilt	−1.9 (1.2)				$\angle_3$
$\angle CF_3$ twist	16.2 (2.0)				$\angle_4$
$r(O\cdots F_{11})$	3.926	0.072 (15)	0.077	0.0112	l_4
$r(O\cdots F_{12})$	3.352	0.108 (18)	0.148	0.0134	
$r(O\cdots F_{13})$	3.092	0.101 (18)	0.141	0.0159	l_5
$r(O\cdots C)$	2.839	0.054 (14)	0.071	0.0048	l_6
$r(P\cdots F_{11})$	2.694	0.086 (5)	0.075	0.0161	
$r(P\cdots F_{12})$	2.659	0.085 (5)	0.074	0.0162	l_7
$r(P\cdots F_{13})$	2.644	0.085 (5)	0.074	0.0164	l_7
$r(C\cdots C)$	2.993	0.078^c	0.078	0.0033	
$r(C_1\cdots F_{21})$	3.097	0.162^c	0.162	0.0150	
$r(C_1\cdots F_{31})$	3.409	0.181^c	0.181	0.0111	
$r(C_1\cdots F_{22})$	4.127	0.096 (15)	0.089	0.0085	
$r(C_1\cdots F_{33})$	4.145	0.088 (15)	0.081	0.0087	l_8
$r(C_1\cdots F_{23})$	3.480	0.28 (7)	0.180	0.0108	
$r(C_1\cdots F_{32})$	3.153	0.27 (7)	0.174	0.0138	l_9
$r(F_{11}\cdots F_{12})$	2.170	0.060 (3)	0.055	0.0494	l_{10}
$r(F_{11}\cdots F_{21})$	3.034	0.26^c	0.26	0.0281	
$r(F_{11}\cdots F_{22})$	4.447	0.21 (5)	0.20	0.0137	
$r(F_{11}\cdots F_{33})$	4.383	0.157 (50)	0.154	0.0153	l_{11}
$r(F_{11}\cdots F_{23})$	4.136	0.28^c	0.28	0.0104	
$r(F_{11}\cdots F_{32})$	3.173	0.33^c	0.33	0.0155	
$r(F_{12}\cdots F_{22})$	4.436	0.20 (6)	0.164	0.0141	l_{12}
$r(F_{12}\cdots F_{33})$	5.183	0.106 (20)	0.091	0.0110	l_{13}
$r(F_{12}\cdots F_{23})$	3.167	0.28^c	0.28	0.0248	
$r(F_{13}\cdots F_{23})$	4.559	0.23 (6)	0.191	0.0134	
$\sigma(I)/I^d$	0.0011				

[a] Distances (r_g), rms parallel amplitudes (l_α), and perpendicular amplitude corrections (K) in Å; angles ($\angle_\alpha$) in deg. Calculated l and K values are for 295 K. Parenthesized values are 2σ, in units of the least significant digit, and include estimates of possible systematic errors and data correlation effects. [b] Not an independent variable. [c] Not varied in least-squares refinement. [d] Mean fractional standard deviation of diffraction intensity points.

Computational Procedures

All molecular orbital calculations used the program GAUSSIAN 80[10] and the basis set 3-21G$^{(*)5}$, in which d functions are added to second-row atoms only. The five pure d functions were used, rather than the six second-order functions used elsewhere,[5] which are equivalent to five d functions plus an extra s-type function. We call attention to the fact that this slight change in basis can lead to appreciable changes in optimized geometries, of the order of 0.005 Å in bond lengths involving carbon and chlorine, sulfur, or phosphorus. As might

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Table II. Correlation Matrix for $OP(CF_3)_3$[a]

	r_1	r_2	r_3	$\angle_1$	$\angle_2$	$\angle_3$	$\angle_4$	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	R[b]
σ	0.0025	0.0014	0.00040	0.15	0.059	0.37	0.48	0.0029	0.0017	0.00069	0.0059	0.0072	0.0047	0.0015	0.0060	0.029	0.00077	0.017	0.023	0.0086	0.0061
r_1	100																				
r_2	−20	100																			
r_3	38	−45	100																		
$\angle_1$	−37	23	−16	100																	
$\angle_2$	23	−65	59	−4	100																
$\angle_3$	13	−11	−5	21	−2	100															
$\angle_4$	−1	−14	−8	−17	−8	29	100														
l_1	15	−2	0	−11	−1	0	2	100													
l_2	7	3	4	−5	−4	−2	−1	−1	100												
l_3	35	−9	13	−30	6	−4	1	48	2	100											
l_4	5	1	2	10	2	3	−5	2	0	4	100										
l_5	0	−6	−7	−31	−14	−17	−4	3	2	8	−11	100									
l_6	3	3	4	16	9	16	−6	−2	2	1	3	5	100								
l_7	22	−9	4	8	8	74	11	4	1	11	6	−16	39	100							
l_8	7	2	−3	16	−4	22	13	2	0	4	53	−14	6	19	100						
l_9	21	21	18	−27	17	−52	−60	3	3	12	7	−13	0	−20	−14	100					
l_{10}	21	−9	10	−24	5	−6	2	6	−1	22	2	8	0	4	2	8	100				
l_{11}	−6	1	−16	33	−14	53	28	−1	−2	−7	12	−16	9	35	31	−42	−7	100			
l_{12}	15	0	17	−52	10	−50	−18	4	3	16	0	20	−11	−30	−12	43	−14	−88	100		
l_{13}	1	−1	0	2	0	1	0	0	0	1	−1	0	1	1	−1	−2	1	−3	1	100	
R	51	−13	19	−52	8	−11	2	18	9	54	6	16	4	17	6	22	42	−14	30	2	100

[a] All entries, except for the standard deviations, have been multiplied by 100. Units for σ are Å for bond lengths and vibrational amplitudes and deg for angles. Numbering of parameters follows from Table I. [b] Index of resolution, dimensionless.

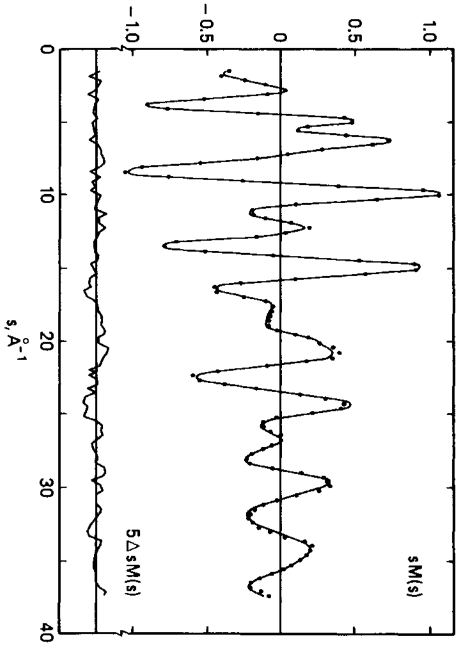

Figure 2. Observed (dots) and calculated (full line) molecular scattered intensities for $OP(CF_3)_3$ and weighted differences.

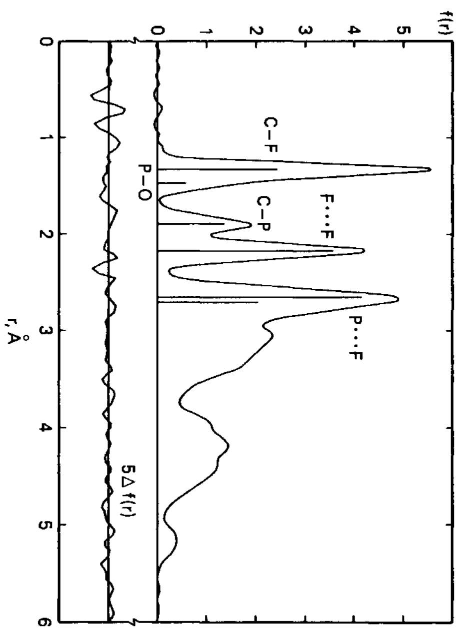

Figure 3. Observed and difference radial distribution function for $OP(CF_3)_3$.

be expected, since the six d functions imply a bigger, more complete s p basis than do the five, their use shortens bonds. All geometry optimizations used gradient techniques.[11]

Structure Analysis

A perspective view of $OP(CF_3)_3$ is presented in Figure 1, illustrating the atomic numbering scheme used. C_3 molecular symmetry was assumed, with local C_{3v} symmetry for the CF_3 groups. Seven geometrical parameters are thus required to define the structure. These were chosen to be the C–F, P=O, and P–C bond lengths, the O–P–C and P–C–F bond angles, an angle α describing the tilt of the CF_3 groups, and an angle β defining their conformation. A nonzero value of α indicates that the local C_3 axis of the C_1F_3 group is not colinear with the P–C bond but lies in the OPC_1 plane, such that F_{11} is closer to P than are F_{12} or F_{13} if α is positive. The angle β measures the rotation of the CF_3 groups about their C_3 axes away from the staggered conformation, for which β is zero. Under C_3 molecular symmetry, no significance is attached to the sign of β.

Observed and final calculated values of the molecular intensity fraction $sM(s)$ for $OP(CF_3)_3$ are displayed in Figure 2. Seven distinct peaks may be seen in the radial distribution function, shown in Figure 3, and an optimist could be excused for discerning at least three additional shoulders. It was evident at the outset that it would not be possible satisfactorily to refine amplitudes of vibration for all 27 different internuclear distances in $OP(CF_3)_3$. The published force field for

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(11) P. Pulay in "Modern Theoretical Chemistry", Vol. 4, Schaefer, H. F., Ed., Plenum Press, New York, 1977, Chapter 4.

$P(CF_3)_3$[1] was extended and slightly adjusted, empirically, so as to reproduce the observed vibrational frequencies for $OP(CF_3)_3$,[6] permitting the calculation of vibrational amplitudes. Since the existing vibrational data for $OP(CF_3)_3$ do not extend below 250 cm^{-1}, the Raman spectrum of liquid $OP(CF_3)_3$ was recorded to permit observation of the bending modes at phosphorus. Peaks were seen at 106 (dp) and 137 (p) cm^{-1}, which were accordingly assigned as the antisymmetric and symmetric C–P–C bending motions, respectively.

Unfortunately, the CF_3 torsional vibrations were not directly observed, nor have any combination bonds been convincingly assigned that involve them. Yet these torsional motions make the biggest contribution to many nonbonded amplitudes. To overcome this problem, we calculated both parallel and perpendicular amplitudes assuming various fixed values of the C–P torsional force constant in the range 0.06–0.12 mdyn Å rad^{-2}. We then performed a series of least-squares refinements, applying appropriate shrinkage corrections, and calculated amplitudes for those distances whose amplitudes could not be satisfactorily refined. The best fit to the intensity data was obtained for an assumed C–P torsional force constant of 0.080 mdyn Å rad^{-2}, which is equivalent, assuming the adequacy of a threefold cosine potential, to a barrier to rotation of 2.6 kcal $mol.^{-1}$ From a consideration of the change in the quality of the fit to the diffraction data as the C–P torsional force constant was varied, it was possible to derive an estimate of the uncertainty in that force constant value, assuming that random error theory is applicable. The resulting 95% confidence limits are ±0.014 mdyn Å rad^{-2}, but we feel it prudent to multiply these by a factor of at least 2 in view of the assumptions involved and the correlated residuals typical for electron diffraction data. This force constant implies CF_3 torsional frequencies of 44 (E) and 42 (A_1) cm^{-1}, in a region where direct detection is difficult, given their expected low intensities in either the infrared or Raman spectrum.

From inspection of Figure 3, it can be seen that the C–F- and C–P-bonded distances, as well as the 1,3 F···F and P···F distances, are well determined, as are their respective amplitudes of vibration. The P=O distance, however, although of appreciable scattering power, is not well resolved from the C–F distances, appearing as a scarcely perceptible shoulder. It is thus largely determined from the many nonbonded distances involving O, and its uncertainity is correspondingly larger than for the C–F or C–P distances.

Information on the O–P–C bond angle and the conformation of the CF_3 groups must be extracted from the rather diffuse features appearing in the radial distribution function at distances greater than 3 Å. The areas and positions of the peaks at 4.08 and 5.07 Å establish that the CF_3 groups are close to staggered with respect to the P=O bond. Several attempts were made to find least-squares minima different from that reported, by starting refinements from a variety of initial parameter values, but all were without success.

Since a nonzero angle of tilt α produces a broadening of the P···F peak at 2.67 Å in the radial distribution function, the value of α is correlated with the amplitude for the P···F distances. In tests in which the tilt angle was fixed at zero, the quality of the fit to the diffraction intensity data worsened by about 20%, and the resulting vibrational amplitude for the P···F distance increased appreciably, giving poorer agreement with the spectroscopically calculated value. It is felt, therefore, that despite the problem of parameter correlation a nonzero tilt angle appears probable. It is noteworthy that in $P(CF_3)_3$ the CF_3 tilt angle is about $2^1/_2$ times larger than the value found here,[1] *and* in the *opposite* direction. These observations are consistent with the idea[12] that these small distortions result from the asymmetry of nonbonded interactions about the P atoms in $OP(CF_3)_3$ and $P(CF_3)_3$.

In the final requirements it proved possible to vary independently the surprisingly large number of 13 amplitudes of vibration. The values obtained are in satisfactory agreement with those calculated spectroscopically, considering the uncertainties associated with the least-squares results, the nonrigorous treatment of torsional motions adopted here, and the approximations involved in the calculation of amplitudes by standard methods. As the rms torsional amplitude of the CF_3 groups is estimated to be about 13°, the use of "small-amplitude" theory[13] is not really appropriate.

Discussion of Electron Diffraction Results

The main emphasis in the experimental part of this work was to permit a four-way comparison to be made of the structures of $OP(CF_3)_3$ and $P(CF_3)_3$ with those of $OP(CH_3)_3$[14] and $P(CH_3)_3$.[15] We start by contrasting the two phosphines with their oxides. We ask whether the replacement of the phosphorus lone pair by a double bond to oxygen has the same structural consequences for $P(CF_3)_3$ as for $P(CH_3)_3$. In the methyl case, the C–P–C angle increases from 98.6 (0.3) to 104.1 (0.3)°, while the P–C bond length is reduced substantially from 1.846 (3) to 1.809 (1) Å. Both these observations can be rationalized by using VSEPR terminology;[16] the phosphorus lone pair exerts a greater effective repulsion on the P–C-bonded pairs than do the P=O pairs. Semiquantitative molecular orbital arguments[17,18] can also account for these changes, using quite different language. It has been shown how, in group 5 compounds ER_3 (E = N, P, As, etc.), a more electronegative group R leads to a smaller angle R–E–R. Since the electronegativity of phosphorus is effectively increased by the addition of the double bond to oxygen, the influence on bond angles is equivalent to that produced by decreasing the electronegativity of R, so the R–E–R bond angle is increased. The increased electronegativity, or higher effective nuclear charge, of phosphorus in the phosphine oxide also leads to more compact valence orbitals and, thus, reduced bond lengths to P in the phosphine oxide.

We have found the C–P–C angle in $OP(CF_3)_3$ to be 104.3 (0.1)°, or 7.1° greater than in $P(CF_3)_3$.[1] Thus, the angular changes produced by converting the phosphine to phosphine oxide are greater, in the same direction, for $P(CF_3)_3$ than for $P(CH_3)_3$. However, the P–C distance of 1.897 (2) Å reported here for $OP(CF_3)_3$ is only marginally less than that of 1.904 (3) Å in $P(CF_3)_3$,[1] and one cannot claim that these two values are significantly different. Now both the VSEPR[13] and MO[17,18] arguments predict that bond angle and bond length changes occur together. As the P–C bonds in $P(CF_3)_3$ are already long, 0.058 Å longer than in $P(CH_3)_3$,[15] those in $OP(CF_3)_3$ exceed the $OP(CH_3)_3$ value[14] by the even greater amount of 0.088 Å.

If the long P–C bonds in $P(CF_3)_3$ are due to an altruistic interaction,[1] it appears that such an interaction is present to greater degree in $OP(CF_3)_3$. This implies that the 3d orbitals on phosphorus are more energetically accessible in $OP(CF_3)_3$ than in $P(CF_3)_3$, consistent with the idea that the greater effective nuclear charge on P^V in the oxide will lower the energy gap between 3p and 3d. Related, and more extreme,

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Table III. C–Y Bond Lengths, ab Initio and Experimental, for Some CH_3–Y and CF_3–Y Molecules (Å)

	CH_3–Y			CF_3–Y		
Y	3-21G	3-21G$^{(*)}$	exptl	3-21G	3-21G$^{(*)}$	exptl
Cl	1.892	1.812	1.778[a]	1.835	1.742	1.752[b]
SH	1.894	1.828	1.819[c]	1.852	1.779	1.801[d]
PH_2	1.910	1.861	1.858[e]	1.898	1.841	1.904[f]
S(O)H	1.869	1.801	~1.81[g]	...	1.801	~1.88[h]
$S(O)_2H$	1.827	1.755	~1.77[i]	1.858	1.782	~1.86[j]
$P(O)H_2$	1.846	1.802	~1.80[k]	1.870	1.817	~1.90[l]

[a] Reference 33. [b] Reference 34. [c] Reference 35. [d] Reference 36. [e] Reference 37. [f] Reference 38. [g] See ref 39. [h] See ref 19. [i] See ref 40. [j] See ref 20. [k] See ref 14. [l] See this work.

cases of long bonds involving CF_3 have been found in S^{IV} and S^{VI} derivatives such as $OS(CF_3)_2$[19] or $O_2S(CF_3)Cl$.[20] We can see no possibility that nonbonded interactions are responsible for the long P–C bonds in $OP(CF_3)_3$, since there are no uncomfortably close contacts involving O, F, or C atoms.

The P═O distance in $OP(CF_3)_3$ has been found here to be 1.476 (4) Å, indistinguishable from the value of 1.476 (1) Å reported for $OP(CH_3)_3$.[14] A clear general trend has been apparent until now, in which the P═O bond in OPX_3 is shortened by electronegative substituents X; compare OPF_3[21] [1.435 (2) Å] and $OPCl_3$[21] [1.447 (2) Å] with $OP(CH_3)_3$ already mentioned. Since CF_3 is generally considered to have an effective electronegatively similar to that of chlorine, the value of 1.476 (4) Å determined here in $OP(CF_3)_3$ seems anomalously large. Now similar behavior has been found in related sulfur compounds such as $OS(CF_3)_2$[19] in which the S═O distance of 1.469 (4) Å is substantially greater than in OSF_2[22] [1.416 (1) Å] or $OSCl_2$[23] [1.443 (6) Å]. These observations, together with those already noted on P–CF_3 and S–CF_3 bond lengths, show that the structural influence of CF_3 is strangely complex and not consistent with a one-dimensional concept of electronegativity.

Molecular Orbital Calculations

Two series of compounds were studied by ab initio MO techniques, in further comparisons of CF_3–Y and CH_3–Y structures. We were particularly anxious to discover whether the altruistic hypothesis,[1] originally advanced on the basis of extended Hückel wave functions, to account for the long bonds in $P(CF_3)_3$ and related species, is supported by the more rigorous ab initio procedures. The basis set 3-21G$^{(*)}$[5] was initially adopted as a compromise between computational cost and accuracy. At the suggestion of a reviewer, geometries were also optimized by using the smaller 3-21G basis,[24] which contains no polarization functions. Important structural results, from both ab initio calculations and experiment, are presented in Table III for a range of CH_3–Y and CF_3–Y systems. Strictly speaking, the experimental results are variously r_g, r_s, etc., parameters, while ab initio values refer to the equilibrium geometry, but one does not anticipate that these usually minor differences will materially affect the points at issue here. Some of the molecules studied ab initio such as $CF_3S(O)H$ have not been structurally characterized and may even be unknown; their choice was based on computing economy. However, it was established that, at the 3-21G$^{(*)}$ level, the difference between the optimized S–C bond lengths in $CF_3S(O)H$ and $CF_3S(O)F$ does not exceed a few thousandths of an angstrom. Thus, any conclusions reached concerning the S–C bond in $CF_3S(O)H$ from our calculations should also be valid for other species such as $(CF_3)_2S(O)$, which have been studied experimentally.

The results of the ab initio calculations can be analyzed in several different ways. We start by discussing the relative performances of the 3-21G and 3-21G$^{(*)}$ basis sets. From inspection of Table III, we see that CH_3–Y bond lengths are appreciably too long in *all* cases at the 3-21G level. For CF_3–Y systems, distances are substantially overestimated for CF_3Cl and CF_3SH but are satisfactory for CF_3PH_2, $CF_3P(O)H_2$, and $CF_3S(O)_2H$. An optimized 3-21G geometry for $CF_3S(O)H$ could not be obtained, due to unsormountable SCF convergence problems. Although not evident from Table III, the description of Y═O bonds is quite inadequate at the 3-21G level, calculated bond distances being too long by 0.15–0.2 Å. Thus, from several points of view, the 3-21G basis has failed to give an acceptable account of the structures of the compounds under discussion here.

Addition of polarization functions to Y alone gives the 3-21G$^{(*)}$ basis, whose use results in substantial CH_3–Y bond shortening, producing results in fairly satisfactory agreement with experiment for all six molecules studied. Y═O distances are now also calculated to acceptable accuracy (for present purposes, acceptable accuracy here implies deviations from experiment no greater than 0.02 Å). Observations of this type are scarcely original to the present work. The importance of adding polarization functions to second-row atoms has long been known,[5,25,26] if successful geometry prediction is required. Although the energy lowering produced by polarization functions is most pronounced for hypervalent molecules, their use still yields significant changes in geometry for low oxidation states such as Cl_2 where they are in no way needed as "hybridization functions".[5,27] It should not be thought that the small s,p basis used is responsible for the substantial geometrical differences between 3-21G and 3-21G$^{(*)}$, since very similar changes are produced by adding polarization functions to a much larger 11,7/6,4 basis.[28]

Use of the 3-21G$^{(*)}$ basis shortens CF_3–Y bond distances by an amount that consistently is slightly greater than that found for the CH_3–Y analogues resulting in mixed agreement with experiment (see Table III). Satisfactory C–Y distances are predicted for CF_3Cl and CF_3SH, but the long C–Y bonds in CF_3PH_2 and in all the hypervalent species are not reproduced at all. However, as we are not here concerned so much with the exact reproduction of experimental results, but more with the understanding of sysematic trends, it may be more valuable to concentrate attention on the quantity Δ, defined as the bond length difference $r(CH_3\text{–}Y) - r(CF_3\text{–}Y)$. Experimental results, followed by 3-21G and 3-21G$^{(*)}$ predictions, in thousandths of an angstrom are as follows: Y = Cl, 26 (58, 70); Y = SH, 19 (38, 49); Y = PH_2, −46 (12, 10); Y = S(O)H, −70 (not available, 0); Y = $S(O)_2H$, −90 (−29, −27); Y = $P(O)H_2$, −100 (−24, −15). Experimental uncertainties are not more than a few thousandths of an angstrom for the first three pairs of compounds but may be two- or even three-hundredths of an angstrom for those molecules involving double bonds to oxygen, since the exact compounds studied have not usually been structurally characterized. Thus, CF_3–Y distances are consistently underestimated, relative to CH_3–Y, by both basis sets used. The discrepancies for the hypervalent compounds are rather greater than those in normal oxidation states, in which latter category the phosphine is less well treated

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than either the sulfide or chloride. In an absolute sense, the 3-21G set, with satisfactory C–Y bond distances in only three of the 12 compounds studied, performs less well than 3-21G$^{(*)}$, which "passed", with eight successes. However, in predicting the *differences* between CH_3–Y and CF_3–Y distances, which are the primary concern here, neither set performed at all satisfactorily.

It is illuminating to examine two pairs of examples in more detail, to show that arguments based solely on population analyses[29] should be viewed with caution. A consistent, satisfying picture is obtained from the 3-21G$^{(*)}$ wave functions for CH_3Cl and CF_3Cl, for which the C–Cl bond overlap populations are 0.331 and 0.391, respectively. The increase in CF_3Cl arises entirely from π interactions between $2p_{x,y}$ on C and $3p_{x,y}$ on Cl (taking z as the C–Cl direction), indicating a modest double-bond character for the C–Cl linkage in CF_3Cl and neatly rationalizing its reduced length (Table III). Involvement of d orbitals is but slight. Their contribution to the C–Cl bond overlap population is less than 0.02 for either molecule, while their total occupation is only 0.037 e in CF_3Cl and 0.027 e in CH_3Cl.

However, the 3-21G$^{(*)}$ results for CH_3PH_2 and CF_3PH_2 give an unexpected *positive* correlation between optimized bond length and overlap population, rather than the inverse relationship that might appear self-evident. While the calculated C–P distance is slightly shorter in CF_3PH_2 than CH_3PH_2, contrary to experiment, the C–P bond overlap population is 0.522 for CH_3PH_2 but only 0.340 for CF_3PH_2. Analysis of the participation of the 3d orbitals on P does not support the altruistic hypothesis,[1] since they increase the P–C overlap from 0.188 (3-21G) to 0.340 (3-21G$^{(*)}$) in CF_3PH_2, a greater increase than that of 0.432–0.522 found for CH_3PH_2.

In summary, we can say that the ab initio calculations have had not more than very limited success in reproducing bond length patterns in CF_3/CH_3–Y systems, failing utterly to predict the strikingly long CF_3–Y bonds in CF_3PH_2 and the hypervalent species involving $CF_3P(O)$, $CF_3S(O)$, and $CF_3S(O)_2$ systems. This failure was both disappointing and unexpected, given the success already reported for geometry optimization using the 3-21G$^{(*)}$ basis on molecules in a range of oxidation states.[5] Several different possibilities suggest themselves. It may be that the s,p basis in 3-21G is simply too small, especially for oxygen and fluorine, or polarization functions may be needed on other atoms besides those in the second row or, given the large number of electron-rich atoms, the Hartree–Fock method itself may be inadequate, necessitating inclusion of the correlation energy. All these improvements in ab initio technique naturally lead to major increases in computing requirements but are currently being pursued.

Since our ab initio calculations have not reproduced the interesting long CF_3–Y bond distances, they naturally are unable to contribute any understanding of the causes of these long bonds. It has been suggested[13] that, in the cases of $(CF_3)_2SO$, the long C–S bonds are caused by repulsions between the substantial net positive charges present on both sulfur and carbon. However, at present we feel that a split-valence basis should be able to account for such effects adequately, and we are inclined to feel that the real reason for the long bonds lies elsewhere. The question as to whether 3d orbitals on phosphorus or sulfur can act in an altruistic[1] or "counterintuitive"[30] manner, so as to weaken the C–P or C–S bonds, has unfortunately not been satisfactorily answered by this work. This suggestion has recently been attacked by Whangbo and Stewart,[4] on the basis of ab initio calculations using the minimal STO-3G[31] and STO-3G$^{(*)25}$ bases, both of which reproduced the long C–P bonds in CF_3P compounds. Both CH_3–P and CF_3–P bonds were shortened by inclusion of d functions on phosphorus, as was found in our work, leading Whangbo and Stewart to remark[4] that there is no altruistic action of the 3d orbitals in CF_3–P compounds.

It may appear paradoxical that calculations using a minimal basis (STO-3G) have had more success for geometry prediction in this area than those using a split-valence basis (3-21G). However, this behavior is not found in general.[24,32] The quality of ab initio calculations is often judged on energy criteria, since the coefficients of atomic orbitals in the LCAO–SCF formalism are themselves determined by the variational principle of energy lowering. Our energies are lower than those of Whangbo and Stewart[4] by the not inconsiderable amounts of 12 870 kJ mol^{-1} for CF_3PH_2 and 6059 kJ mol^{-1} for CH_3PH_2. It is worth noting that orbital exponents in the STO-3G basis are "scaled" by substantial amounts,[31] so as most effectively to reproduce observed standard molecular geometries, whereas the 3-21G basis, except for hydrogen, uses exponents that are optimized for free atoms.[24] Thus, while the STO-3G basis is often efficacious for geometry prediction, it may be that its slight semiempirical character reduces the value and reliability of any interpretation of its wave functions. So we suggest that Whangbo and Stewart[4] have not established conclusively that altruistic behavior of the phosphorus 3d orbitals does not occur. Likewise, we have certainly failed to show that it does, or even may, occur, and at present the theoretical evidence is against the idea. The causes of the long CF_3–P, CF_3–P(O), and CF_3–S(O) bonds remain to be identified.

Conclusions

We have determined the structure of $OP(CF_3)_3$ by gas electron diffraction. The most striking feature is that the C–P bonds are almost 0.1 Å longer than in $OP(CH_3)_3$.[14] One interpretation is that altruistic bonding is more pronounced in $OP(CF_3)_3$ than in $P(CF_3)_3$.[1] Ab initio calculations on a range of CH_3 and CF_3 derivatives using the 3-21G and 3-21G$^{(*)}$ bases suprisingly failed to predict the long CF_3–P and CF_3–S bonds in compounds for which the altruistic hypothesis was proposed. More elaborate calculations are under way.

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Registry No. $OP(CF_3)_3$, 423-01-8; CH_3Cl, 74-87-3; CH_3SH, 74-93-1; CH_3PH_2, 593-54-4; $CH_3S(O)H$, 62965-22-4; $CH_3S(O)_2H$, 17696-73-0; $CH_3P(O)H_2$, 7187-92-0; CF_3Cl, 75-72-9; CF_3SH, 1493-15-8; CF_3PH_2, 420-52-0; $CF_3S(O)H$, 306-79-6; $CF_3S(O)_2H$, 34642-42-7; $CF_3P(O)H_2$, 89726-00-1.

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