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Molecular Structure and Vibrational Spectrum of $P(CF_3)_3$: A Possible Example of an "Altruistic Covalent Interaction"

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The structure of $P(CF_3)_3$ has been reinvestigated by gas-phase electron diffraction and liquid-phase Raman spectroscopy. A reversed assignment of the skeletal PC_3 bending modes was found to be necessary. Principal structural parameters ($\pm 3\sigma$) are r_g(P–C) = 1.904 (7) Å, r_g(C–F) = 1.340 (3) Å, ∠C–P–C = 97.2 (0.7)°, and ∠F–C–F = 107.5 (0.3)°. Trifluoromethyl groups, in or close to staggered conformations, are tilted by 5.3 (0.9)° from the C–P bonds so as to increase the closest 1–5 F···F distances. Shrinkage corrections and amplitudes of vibration, which agreed well with measured amplitudes, were calculated from a plausible set of valence force constants constructed to reproduce the vibrational frequencies. Phosphorus–carbon bonds are substantially longer than in $P(CH_3)_3$. It is suggested that the lengthening arises, at least in part, from an "altruistic interaction" of the d orbitals on phosphorus with the carbon orbitals, which sacrifices P–C bonding while leading to a strengthening of C–F bonds. Support for this suggestion is provided by EHMO calculations and by the apparently long A–B bond lengths already reported in the literature for ABX_n species for which A contains fairly compact, empty orbitals lying appreciably higher than the valence orbitals of X.

Introduction

Chemists are accustomed to the idea that bond distances between a given pair of atoms change according to the electronic environment of those atoms in various molecules. In particular, it has been observed that the introduction of electronegative atoms or groups into a molecule often tends to shorten adjacent bonds in that molecule. From the many examples available, we may quote the cases of $P(CH_3)_nF_{(5-n)}$,[1,2] $n = 0, 1, 2, 3$, in which the replacement of CH_3 by F shortens the P–C bond lengths from 1.813 through 1.798 (4) to 1.780 (5) Å, and of SOX_2, in which the S=O bond lengths are 1.480 (9), 1.443 (6), 1.4308 (2), 1.420 (3), when $X_2 = (NMe_2)_2$,[3] Cl_2,[4] O,[5] and F_2.[6] It was therefore of interest to observe[7] that the substitution of CF_3 for CH_3 in CH_3–X compounds appears to shorten or lengthen the C–X bond accordingly as X is of high or low to moderate electronegativity. $P(CF_3)_3$[8] and $P(CH_3)_3$[9] provide an outstanding example in which the reported length of the P–C(F$_3$) bond, 1.937 (17) Å, is substantially greater than that of the P–C(H$_3$) bond, 1.846 (3) Å. Since the published structure of $P(CF_3)_3$, based on visual estimation of electron diffraction data, is of uncertain reliability, we decided to redetermine the structure by modern methods. We anticipated that semiempirical calculations on $P(CF_3)_3$ and related compounds might provide some indication of the origin of the bond length pattern, referred to above, which is found for CF_3 derivatives.

Table I. Experimental Conditions for Recording Diffraction Patterns

Camera dist, cm	21.164	11.091
Reservoir temp, °C	−55	−55
Vapor pressure, Torr	25	25
Exposure time, s	7–10	15–20
Beam current, μA	0.48	0.70
Diameter of Pt nozzle, mm	0.25	0.25

Table II. Approximate Shrinkage Corrections, Calculated in Å

$P\cdots F_{11}$	0.0092	$F_{11}\cdots F_{21}$	−0.0264
$P\cdots F_{12}$	0.0075	$F_{11}\cdots F_{22}$	0.0270
$C\cdots C$	0.0018	$F_{11}\cdots F_{23}$	0.0195
$F_{12}\cdots F_{13}$	0.0017	$F_{12}\cdots F_{22}$	0.0316
$F_{11}\cdots C_2$	0.0022	$F_{12}\cdots F_{23}$	−0.0194
$F_{12}\cdots C_2$	0.0054	$F_{13}\cdots F_{22}$	0.0433
$F_{12}\cdots C_3$	0.0233		

Valence Force Field Used[a]

k_R 2.6, k_r 6.0 mdyn/Å
k_α 1.78, k_β 0.81, k_γ 1.7, k_τ 0.08 mdyn Å/rad^2
k_{RR} 0.137, k_{rr} 0.846, k_{Rr} 0.144 mdyn/Å
$k_{\alpha\alpha}$ 0.25, $k_{\gamma\gamma}$ 0.3, $k_{\alpha\beta}$ −0.15 mdyn Å/rad^2
$k_{R\alpha}$ −0.392, $k_{r\alpha}$ 0.14, $k_{r\alpha'}$ 0.67, $k_{r\beta}$ 0.5, $k_{R\gamma}$ 0.15, $k_{R\gamma'}$ 0.25 mdyn/rad

R = C–P bond
r = C–F bond
α = FCF angle
β = PCF angle
γ = CPC angle
τ = torsion angle

[a] All interaction constants not listed were set at zero.

Experimental Section

A sample of $P(CF_3)_3$ was prepared by direct reaction of CF_3I and red phosphorus.[10] That fraction of the products which was retained by a trap at −96 °C, but which passed repeatedly through a trap at −78 °C, was found to be pure, judged by the following criteria: gas-phase molecular weight 238 (calcd 238), vapor pressure at 0 °C (398 Torr) (literature value 400 Torr). No peaks assignable to impurities were observed in the vibrational spectra.

Electron diffraction patterns were recorded on 4 × 5 in. Kodak electron image plates using the diffraction unit at the University of Michigan,[11] at the 21 and 11 cm distances, with an r^3 sector. The sample was maintained in a cold finger at −55 °C, to provide a suitable pressure of about 25 Torr, while the reservoir bulb and nozzle were at room temperature. The incident electrons were accelerated through 40 kV. Full experimental conditions are given in Table I. The photographic plates were developed at 20 °C for 3 min with Kodak HRP developer to which antifog solution had been added. An automated recording microphotometer, with digital output, measured the absorbance of the plates at $^1/_8$-mm intervals, while they were spun about the center of the diffraction pattern. Absorbances were converted to exposures by the following relationship, $E = A(1 + 0.116A + 0.0179A^2 + 0.003\,12A^3)$,[12] in which E and A are respectively the exposure and the absorbance. Experimental intensities were obtained by averaging the data from five plates selected for each camera distance. Intensities were leveled once corrections had been applied for extraneous scattering and for irregularities in the sector opening. Calibration of the sector was performed both optically and from intensity measurements of electrons scattered by rare gas atoms. Atomic elastic and inelastic scattering factors of Schafer, Yates, and Bonham were used.[13] Intensity data for the two camera distances were initially treated separately by a least-squares process which imposed geometrical self-consistency on the internuclear distances. A diagonal weight matrix was used, with weighting proportional to s. The error matrix was modified to include estimates of the influence of correlation between neighboring data points.[11] After the individual background functions had been established and good agreement was obtained between the molecular parameters derived from each camera distance, the two sets of data were blended together. The indices of resolution were 0.88 for the 21 cm data and 0.81 for the 11 cm data. The composite data set, covering the s range 3.1–38.0, was interpolated in units of $\Delta s = \pi/10$. Radial distribution functions were calculated using a damping factor of $\exp(-0.002s^2)$. Anharmonicity constants were taken as 2.0 for all bonded and nonbonded distances. Approximate shrinkages were calculated from the force field discussed

Table III. Observed and Calculated Vibrational Spectra of $P(CF_3)_3$[a] (Frequencies in cm^{-1})

Raman (liquid)		Ir[b] (gas)	Calcd	Sym-	Assign-
Freq	Rel int	Freq	freq	metry	ment
1234 br	1	1235 vvs	1219	E	ν_{12}
1215 br, sh	<<1		1213	A_1	ν_1
1180 dp	2	1189 vvs	1172	E	ν_{13}
1158 sh	<<1	1157 vvs	1158	A_1	ν_2
1119 dp	3	1129, 1134 vvs	1131	E	ν_{14}
786 p	6				$\nu_4 + \tau$
747 p	73	757 s	747	A_1	ν_4
609 p	<1				$\nu_3 + \tau$
571 p	5	573 m	587	A_1	$\nu_3 + \tau$
562 sh	<1	559 s	552	E	ν_{15}
532 dp	1	535 w	535	E	ν_{16}
503 dp	<1				$\nu_{20} + \tau$
489 p	2				$\nu_6 + \tau$
465 dp	20	464 vs	481	E	ν_{20}
451 p	38	455 s	464	A	ν_6
324 dp	1				$\nu_{18} + \tau$
308 p	8				$\nu_5 + \tau$
286 dp	20	280 vvw	274	E	ν_{18}
270 p	100	269 vw	274	A_1	ν_5
250 dp	9	250 w	259	E	ν_{19}
190	<<1				$\nu_7 + \tau$
151 p	4		151	A_1	ν_7
110 dp	7		110	E	ν_{21}
			43	E	ν_{22}
			40	A_2	ν_{11}

[a] Abbreviations used: v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder; p, polarized; dp, depolarized. [b] Reference 14.

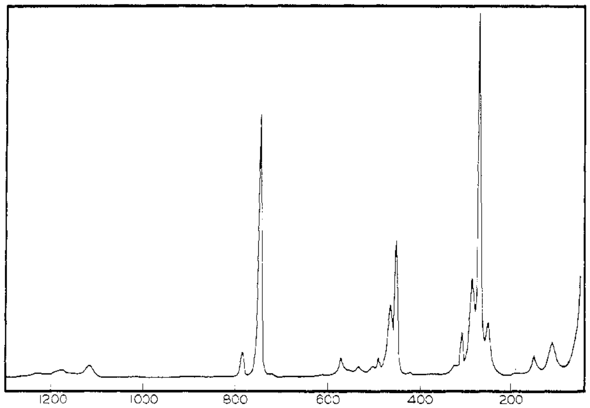

Figure 1. Raman spectrum of liquid $P(CF_3)_3$. Frequency scale in cm^{-1}.

below. They are listed in Table II.

Vibrational Spectrum and Force Field

While recording the Raman spectrum of liquid $P(CF_3)_3$, it became apparent that the published spectrum[14] and assignment are incorrect at low frequency. Measurement of depolarization ratios established that the A_1 skeletal bending mode is at higher frequency than the E mode, the same pattern as observed for $P(CH_3)_3$,[15] but opposite to the original report on $P(CF_3)_3$.[14] The spectrum was rerecorded over the range 50–1300 cm^{-1}, using 4880 Å radiation and a Spex 1401 monochromator. Qualitative depolarization ratios were determined for most bands. Results are presented in Table III and Figure 1. Frequencies are believed accurate to within 2 cm^{-1}, except for a few broad or weak bands. No direct evidence was obtained for the frequencies of the CF_3 torsional modes, either for the liquid or gas. However, a number of weak bands can plausibly be assigned as combinations of the torsional modes and other normal modes, leading to the approximate value of 40 cm^{-1} for the presumed torsional frequency.

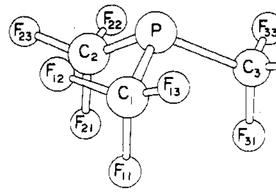

Figure 2. A perspective view of the molecule $P(CF_3)_3$, showing the atom labeling scheme used.

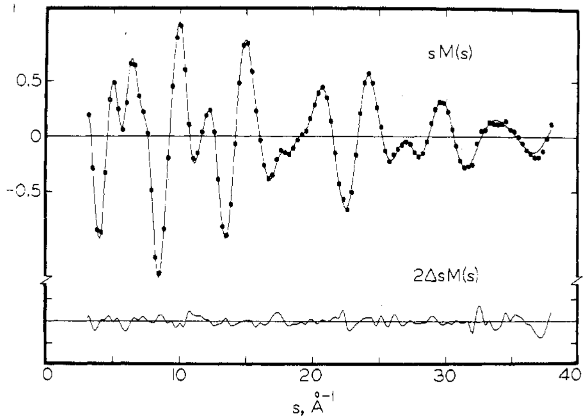

Figure 3. Experimental (filled circles) and best fit calculated (smooth curve) molecular intensity functions for $P(CF_3)_3$. $\Delta sM(s) = sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}$.

The published force field was adjusted empirically to reproduce the observed frequencies. Since the torsional frequency was not observed directly, a value was assumed for the torsional force constant. The observed barrier to rotation in CF_3PH_2 [16] is slightly greater than that in CH_3PH_2,[17] and so for $P(CF_3)_3$ a value of 2.8 kcal/mol was adopted, slightly greater than the value found for $P(CH_3)_3$.[18] The resulting torsional frequencies were calculated as 40 (A_2) and 43 (E) cm^{-1}, values which receive some support from the interpretation of the vibrational spectrum discussed above. Table III lists the observed spectrum and the frequencies calculated by the valence force field adopted. Although exact agreement was not obtained, the discrepancies are in general slight. We feel that any errors in the calculated values of the nonbonded amplitudes of vibration and shrinkages will be small and insignificant compared to the uncertainties introduced by assuming a value of the torsional force constant.

Structure Analysis

The molecular model used assumed C_{3v} symmetry for the PC_3 skeleton and local C_{3v} symmetry for the CF_3 groups. The six geometrical parameters required to describe the structure were taken as the P–C and C–F bond lengths, the C–P–C bond angle, the angle θ between a C–F bond and the threefold axis of the CF_3 group, and angles ϕ and δ, referring to the tilt and twist of the CF_3 groups. A nonzero angle of tilt ϕ indicates that the threefold axes of the CF_3 groups are not collinear with the P–C bonds but lie in the planes defined by P, C, and F_{ax}, such that a positive value increases the P–C–F_{ax} angles by the amount of the angle of tilt. A nonzero value of the angle of twist δ for a given CF_3 group implies that the group is twisted about its threefold axis away from the all-staggered conformation (shown in Figure 2), which was adopted as a starting point in the structure refinement.

Experimental and final calculated molecular intensities are presented in Figure 3, and the experimental radial distribution function is presented in Figure 4. Final values of the bond length and angle parameters calculated are given in Table IV, and the correlation matrix is displayed in Table V. Since the

Table IV. Observed Structural Parameters

	Obsd amplitude, Å	Calcd amplitude, Å	Parameter No.
$r(P–C) = 1.904$ (7) Å	0.056 (8)	0.054	r_1, l_1
$r(C–F) = 1.340$ (3) Å	0.047 (4)	0.045	r_2, l_2
$\angle C–P–C = 97.2$ (0.7)°			
$\angle F–C–F = 107.5$ (0.3)°			
$\angle$Tilt[a] = 5.3 (0.9)°			$\angle_3$
$\angle$Twist[a] = 5.5 (6.0)			$\angle_4$
$r(F_{11}\cdots F_{12})$[b]	0.059 (4)	0.057	l_3
$r(F\cdots P)$	0.079 (8)	0.073	l_4
$r(F_{11}\cdots F_{22})$[b]	0.158 (22)	0.177	l_5
$r(F_{12}\cdots F_{22})$[b]	0.169 (25)	0.180	l_6
$r(F_{12}\cdots F_{33})$[b]	0.103 (29)	0.099	l_7
$r(F_{11}\cdots F_{21})$[b]	0.253 fixed	0.253	
$r(F_{12}\cdots F_{23})$[b]	0.292 fixed	0.292	
$r(F_{11}\cdots F_{32})$[b]	0.320 fixed	0.320	
$r(C_1\cdots F_{22})$[b]	0.097 (22)	0.084	l_8
$r(C_1\cdots F_{21})$[b]	0.171 fixed	0.171	
$r(C_1\cdots F_{23})$[b]	0.193 fixed	0.193	
$r(C\cdots C)$	0.083 fixed	0.083	
$\sigma(I)/\bar{I} = 1.38 \times 10^{-3}$			

[a] See text for definition. [b] Symmetry-related distances assigned same amplitudes. Uncertainties are given in units of last digit quoted. They represent 3σ, where σ includes random errors, suspected systematic errors, and our estimates of the influence of correlation between neighboring data points ($\gamma = 1.4$ Å).[11] Bond lengths are r_g, amplitudes are l_g.

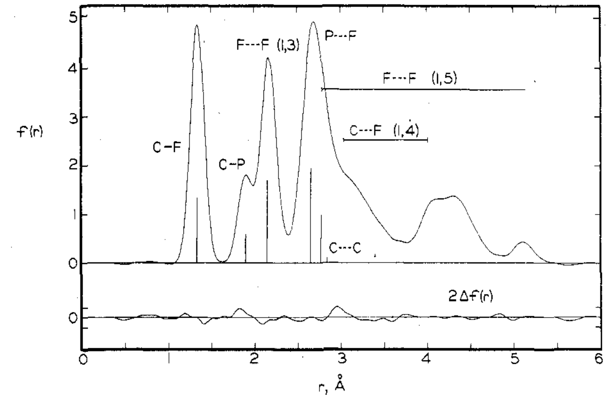

Figure 4. Experimental radial distribution function for $P(CF_3)_3$. $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calcd}}$.

C–F, C–P, and F···F (within a CF_3 group) distances give rise to distinct peaks in the radial distribution function they are well-determined, as are their respective amplitudes of vibration. The P···F distances are the major contributors to the peak at about 2.7 Å; the position and spread of this peak, together with the F···F (geminal) peak, determine not only the angle θ and the P···F amplitude but also the angle of tilt ϕ. Thus the angle of tilt is appreciably correlated with the P···F amplitude of vibration. Refinements in which ϕ was fixed at zero led to residuals almost three times higher than when ϕ was free, so it is felt that the nonzero value of ϕ is real and tolerably well-determined. During these refinements, the $P\cdots F_{i1}$ (i = 1, 2, 3) amplitude was constrained to be 0.003 Å smaller than the $P\cdots F_{i2,3}$ amplitudes, this difference being indicated by the force field calculations. The C–P–C angle and information about the conformation must be deduced from the weaker features in the radial distribution function, at distances greater than 3 Å. The amplitudes involving C···C, C···F, and F···F (1–5 interactions) atom pairs were initially given their calculated values. As the refinements proceeded, more and more amplitudes were allowed to refine freely. If, however, the esd was large, greater than $^1/_3$ of the amplitude's value, the parameter was again fixed at its calculated value. It can be seen from Table IV that the agreement between the calculated and refined amplitude values is satisfactory. Various constraints were applied to the angle of twist δ. Refinements in which all three CF_3 groups were twisted equally in the same direction gave better agreement with the experimental data than when the twists were "scrambled", one group twisted clockwise and one anticlockwise while the third was not twisted at all. The difference in fit, although apparently statistically significant if the dominant errors in the data are randomly distributed, was not large enough to inspire confidence that it was physically significant. The value of δ obtained by refinement varied considerably according to the constraints applied to the less well-determined amplitudes, and it is felt that the data obtained are not able to determine whether the angle of twist is nonzero. It does appear, however, to lie within the range 0–15°.

Discussion

Structural parameters obtained from the previous study of $P(CF_3)_3$[8] were P–C = 1.937 (17) Å, C–F = 1.342 (15) Å, ∠CPC = 99.6 (2.5)°, ∠FCF = 108.5° (assumed). An all-staggered conformation was adopted, and the angle of tilt was assumed to be zero. These values do not differ by more than twice their quoted uncertainties from the more precise results reported here. The C–F bond length in $P(CF_3)_3$ is found to be roughly 0.015 Å greater than in several CF_3–N[19–22]

Table V. Matrix of Correlation Coefficients for $P(CF_3)_3$[a]

	r_1	r_2	$\angle_1$[b]	$\angle_2$[c]	$\angle_3$	$\angle_4$	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8	R[d]
σ	0.0017	0.00048	0.067	0.21	0.23	1.9	0.0020	0.00072	0.00087	0.0024	0.0071	0.0089	0.0093	0.0063	0.0070
r_1	100	−43	−64	13	−30	14	7	−14	−17	−33	8	−1	−2	−1	−24
r_2		100	64	12	−18	−11	1	−9	8	−8	−13	11	0	−5	11
$\angle_1$			100	22	−10	−21	−7	4	6	−2	−20	4	2	−6	4
$\angle_2$				100	−29	−80	−4	−7	−3	−36	−11	−28	7	10	−14
$\angle_3$					100	−4	−3	5	7	78	11	−19	0	13	10
$\angle_4$						100	5	−4	−9	13	11	17	−7	−12	−6
l_1							100	−1	−5	−2	2	3	−1	0	3
l_2								100	24	17	10	10	2	10	53
l_3									100	15	7	7	2	8	44
l_4										100	14	−10	0	13	32
l_5											100	−14	−3	39	20
l_6												100	−7	15	18
l_7													100	−14	3
l_8														100	18
R															100

[a] Matrix elements are given by $\rho_{ij} = (M_x)_{ij}/[(M_x)_{ii}(M_x)_{jj}]^{1/2}$, where M_x is the zeroth-order error matrix.[11] Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100. The numbering of the parameters follows from Table IV, except where noted otherwise. Units for σ are Å for bond lengths and amplitudes of vibration, degrees for angles. [b] Angle θ, see text. [c] Angle between a C–P bond and the C_{3v} axis of PC_3. [d] Index of resolution, dimensionless.

derivatives studied recently. A more or less similar lengthening is found between CF_3Cl[23] and CF_4[24] and between CF_3SH[25] and CF_3OF.[26]

The most striking result of our work is that the P–C bond in $P(CF_3)_3$ is 0.058 Å longer than in $P(CH_3)_3$.[8] In $P_2(CF_3)_4$,[27] a lengthening of 0.059 Å of the P–C bond was reported, compared to the value in $P_2(CH_3)_4$.[28] Despite the presumably greater steric requirements of CF_3 than of CH_3, the C–P–C angle in $P(CF_3)_3$ is slightly smaller than in $P(CH_3)_3$, 97.2 (0.3)° compared with 98.6 (0.3)°. The closest 1–5 F···F distance in $P(CF_3)_3$ is 2.70 Å, equal to the sum of van der Waals radii. If the angle of tilt were zero, but all other parameters unchanged, that F···F distance would be decreased to 2.55 Å and would be further decreased to 2.51 Å if the angle of twist were zero, i.e., in the all-staggered conformation. These considerations suggest that the long P–C bond in $P(CF_3)_3$ is unlikely to be caused by nonbonded repulsions between CF_3 groups, as the molecules $(CF_3)_2NN(CF_3)_2$,[19] $(CF_3)_2NO$,[20] and $(CF_3)_2NOH$[21] have F···F and F···O contacts appreciably shorter than the sum of the van der Waals radii and yet their C–N bonds are shorter than the most nearly comparable $(H_3)C$–N bonds.

A series of EHMO[29] calculations was performed with the aim of gaining some insight into why the P–C bond in $P(CF_3)_3$ is longer than in $P(CH_3)_3$, whereas the C–Cl bond in CF_3Cl is shorter than in CH_3Cl. Ionization potentials for s and p orbitals were those of Basch, Viste, and Gray,[30] adjusted to be consistent with the net atomic charges calculated; the VOIP for the 3d orbitals on P and Cl were taken as −4 and −8 eV for the neutral atoms, respectively, and were adjusted to the atomic charges in a plausible manner to yield −7.7 and −4.9 eV for the two phosphines and −8 and −5 eV for the two chlorides. Neutral-atom exponents were chosen for s and p orbitals,[31] while values of 1.1 and 1.2 were adopted for the 3d orbitals of phosphorus and chlorine, respectively. In order to eliminate the variation of orbital overlap with internuclear distance, the P–C bond lengths in $P(CF_3)_3$ and $P(CH_3)_3$ and the C–Cl distances in CF_3Cl and CH_3Cl were taken as equal. Other geometrical parameters were set at their experimental values.

While the calculated bond overlap populations were found to be fairly sensitive to the parameterization adopted, particularly with respect to the 3d orbitals, it is felt nevertheless that the trends in a series provide useful comparisons. The P–C overlap populations calculated are 0.730 in $P(CF_3)_3$ and 0.753 in $P(CH_3)_3$, if d orbitals are included, but 0.758 and 0.713, respectively, when d orbitals are neglected. It was initially surprising that the introduction of a potentially bonding orbital on phosphorus should *lower* the calculated P–C overlap populations but a little reflection suggests how the P–C sacrifice can lead (and does lead in EHMO) to a C–F strengthening and an overall stabilization. This behavior might be referred to as an "altruistic covalent interaction" of the P–C bond, as described below.

Assume that a molecular species ABX_n of main group elements is describable in terms of perfectly coventional covalent bonds with A–B making use of valence s and p orbitals. Consider the effect of introducing a higher-lying orbital r on A into the bond description. If r lies low enough to avoid being excessively diffuse but high enough over a very low lying valence MO level (say one concentrated on the electronegative atoms X) that the matrix element $H_{rs} - ES_{rs}$ is positive for interaction $r_{A}s_{B}$, then the covalent overlap component $2C_rC_sS_{rs}$ is *negative*. In the associated molecular orbital, the addition of a small coefficient C_r allows C_s to be *increased* without spoiling normalization by virtue of the negative sign of $C_rC_sS_{rs}$. This increased C_s leads, in turn, to an enhancement of the BX covalent overlap that lowers the energy by more than is sacrificed in the AB overlap. While orbital r may be a d orbital there is nothing intrinsic in the symmetry requiring it to be a d orbital. Orbitals r and s can be σ or π.

The pattern found for $P(CF_3)_3$ in EHMO calculations was repeated for CF_3Cl where the C–Cl overlap populations were found to be 0.695 and 0.719 with and without d orbitals, while the comparable figures for CH_3Cl are 0.658 and 0.622. In the absence of d orbitals the calculated effect of fluorine substitution on C–P and C–Cl bonds is seen to be in the "normal" direction (popularly accounted for by Gillespie–Nyholm theory[32] or double-bond no-bond resonance[33]). Since the effect is weaker in the phosphines than in the chlorides, it is overridden by the "altruistic" effect, when d orbitals are introduced, in the case of $P(CF_3)_3$. The net atomic charges calculated may be of qualitative utility. With d orbitals included, they are: $P(CF_3)_3$, P +0.36, C +0.43, F −0.18; $P(CH_3)_3$, P +0.08, C −0.02, H 0.0; CF_3Cl, Cl +0.01, C +0.43, F −0.16; CH_3Cl, Cl −0.13, C +0.06, H +0.02. If d orbitals were neglected these results changed only slightly. It is worth noting that the electrostatic repulsion between P and C in $P(CF_3)_3$ implied by these figures is sufficient to lengthen the P–C bond (force constant 2.6 mdyn/Å) by roughly 0.04 Å, compared to $P(CH_3)_3$.

In view of the long P–C bonds found in this work and the apparent generality of the altruistic interaction concept discussed above, we searched the literature for further examples of long A–B bonds in species A–BX_n of the type defined earlier. While we do not claim that our search was comprehensive, in almost all the cases we discovered of the above type the A–B bond was longer than might be expected according to conventional rules of thumb (hybridization, Gillespie–Nyholm, covalent radius as a function of oxidation state, etc.). We mention a selection of examples drawn from neutral molecules, in which the bond lengthening seems to be particularly clearly established.

A microwave study of F_3Si–BF_2[34] yielded a value for the Si–B bond length of 2.04 (3) Å, whereas on the basis of the observed bond lengths in $Si(CH_3)_4$,[35] C_2H_6,[36] and $B(CH_3)_3$,[37] a value of about 1.92 Å is expected. The Si–B bond length reported in an electron diffraction study of F_3Si–SiF_2–BF_2[38] is similarly long at 2.009 (4) Å, and the Si–Si distance, at 2.363 (3) Å, is somewhat larger than that found in Si_2H_6,[39] 2.332 (3) Å. An x-ray study revealed that in S_8O,[40] the S–S(O) average bond length is 2.202 (4) Å, while the remaining six S–S bonds range in length from 2.000 (5) to 2.064 (4) Å. The average value in S_8[41] is 2.047. It should be noted that in general S–X bonds are shortened as oxygen atoms are bonded to S.[42] The P–P bond length in P_2F_4[27] was determined to be 2.281 (3) Å, appreciably longer than in other diphosphines such as P_2H_4,[43] 2.2191 (4), $P_2(CH_3)_4$,[28] 2.192 (9), or $P_2(CF_3)_4$,[27] 2.182 (8). The B–B bond length found for gaseous B_2Cl_4[44] is 1.70 (3) Å, in contrast to the expected value, based on the observed bond lengths in $B(CH_3)_3$[37] and C_2H_6[36] of 1.62 Å. One clear counterexample was found. In SiF_3PH_2,[45] the Si–P bond length of 2.207 (3) Å is distinctly shorter than that in SiH_3PH_2,[46] 2.249 (3) Å. In addition to the aforementioned factors applying to the analogous C–Cl shortening in CF_3Cl (1.751 Å) and CH_3Cl (1.784 Å),[23] it is natural in this case to invoke lone pair donation by phosphorus into d orbitals of silicon as facilitated by fluorine substitution. Such considerations confirm that it is not simple to foretell, reliably, when an altruistic effect will dominate.

The comparisons above are in some cases less definite than could be desired, due to the absence of experimental values of "normal" bond lengths between the pairs of atoms in question. Nevertheless, these examples suggest that the initially surprising result of the EHMO calculation, namely that empty orbitals on A can interact with bonding B–X orbitals, if X is very electronegative, in such a way as to weaken the A–B bond, may indeed be a common factor influencing bond lengths.

Note Added in Proof. Several developments since the above account was completed deserve mention. J. M. Howell has carried out ab initio calculations at the 4-31G level on CH_3PH_2 and CF_3PH_2 with and without d orbitals on phosphorus. No evidence for altruistic interactions involving d orbitals was found but neither did the derived structures or overlap populations account for the observed structure differences. Certain patterns of success and failure in ab initio calculations of structures employing similar basis sets have been discussed.[47] Several ab initio calculations on transition metal carbonyl complexes,[48] however, show net antibonding contributions between metal 4s and 4p orbitals and ligand orbitals entirely analogous to the "altruistic" 3d contributions in $P(CF_3)_3$. J. C. Thibeault, R. Hoffmann, and H. B. Bürgi, in unpublished research, suggest that such interactions occur quite generally under circumstances similar to those discussed in the foregoing text, although extended Hückel computations may exaggerate the antibonding. Hoffmann and Hoffmann[49] present a modified Wolfsberg–Helmholz formula to diminish the antibonding interactions approximately to ab initio levels. Fenske has applied his approximation of the Hartree–Fock–Roothaan molecular orbital procedure[50] to $P(CH_3)_3$ and $P(CF_3)_3$ excluding and including d orbitals. An altruistic result was obtained though its magnitude was smaller than that of the extended Hückel approach. We thank Professors Howell, Hoffmann, and Fenske for helpful conversations and for communicating results of their unpublished calculations.

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Registry No. $P(CF_3)_3$, 432-04-2.

Supplementary Material Available: Values of the leveled intensities $I_0(s)$ and the background function $I_B(s)$ for the 21 and 11 cm camera distances (8 pages). Ordering information is given on any current masthead page.

References and Notes

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