Towards a Configurationally Stable Hydroxyphosphorane

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I. X-ray Experimental for $C_{18}H_9O_5F_{12}P$ (**2B**):

Crystals grew as large, colorless prisms by slow evaporation of methylene chloride. The data crystal was a long lathe that had approximate dimensions; 0.30x0.27x0.25 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 352 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 132 seconds per frame. The data were collected at –120 °C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR92[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atom positions were observed in a ΔF map and refined with isotropic displacement parameters. The fluorine atoms on two of the trifluoromethyl groups, carbon atoms C29 and C33, were found to be disordered by rotation about the C27-Cmethyl bond. The disordered was modeled by refining the site occupancy factors for the affected F atoms while refining a common isotropic displacement parameter for each trifluoromethyl group. At the same time, the geometry of the CF_3 groups were restrained to be equivalent. The site occupancy for the major component refined to 67(2)% for F30, F31 and F32 and 62(2)% for F33, F34 and F35. In the final refinement, anisotropic displacement parameters for the F atoms were refined while restraining the parameters to be approximately isotropic. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0325*P)^2 + (1.0491*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0792, with R(F) equal to 0.0314 and a goodness of fit, S, = 1.13. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[4] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (6.8(12)x10^{-6})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor.

Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in tables 1 through 6.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. 26, 343-350.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

II. Table 1. Crystal data and structure refinement for 1.

Empirical formula	C18 H9 F12 O5 P	
Formula weight	564.22	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 11.2604(1) Å	α= 90°.
	b = 15.5456(2) Å	β= 113.165(1)°.
	c = 12.5778(2) Å	γ = 90°.
Volume	2024.23(5) $Å^3$	
Z	4	
Density (calculated)	1.851 Mg/m^3	
Absorption coefficient	0.277 mm^{-1}	
F(000)	1120	
Crystal size	.30 x .27 x .25 mm	
Theta range for data collection	3.16 to 27.48°.	
Index ranges	-14<=h<=14, -20<=k<=20, -16<=l<=16	
Reflections collected	8214	
Independent reflections	4609 [R(int) = 0.0134]	
Completeness to theta = 27.48°	99.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4609 / 204 / 420	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0761	
R indices (all data)	R1 = 0.0371, wR2 = 0.0792	
Extinction coefficient	$6.8(12)x10^{-6}$	
Largest diff. peak and hole 0.53 and -0.36 e.$Å^{-3}$		

III. Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P1	3595(1)	5520(1)	3024(1)	18(1)
O2	3412(1)	5146(1)	4106(1)	22(1)
C3	2140(1)	4936(1)	3966(1)	21(1)
C4	1105(1)	5441(1)	3273(1)	20(1)
C5	-132(2)	5191(1)	3161(1)	27(1)
C6	-303(2)	4463(1)	3717(2)	32(1)
C7	750(2)	3979(1)	4405(2)	31(1)
C8	1985(2)	4213(1)	4533(1)	28(1)
C9	1334(1)	6252(1)	2705(1)	19(1)
O10	2546(1)	6261(1)	2580(1)	21(1)
C11	1382(2)	7042(1)	3466(1)	26(1)
F12	2382(1)	6971(1)	4472(1)	43(1)
F13	1506(1)	7775(1)	2979(1)	39(1)
F14	321(1)	7098(1)	3681(1)	41(1)
C15	326(2)	6381(1)	1453(1)	28(1)
F16	153(1)	5652(1)	864(1)	43(1)
F17	721(1)	6970(1)	896(1)	37(1)
F18	-809(1)	6638(1)	1432(1)	44(1)
O19	4872(1)	5849(1)	3220(1)	25(1)
O20	3094(1)	4758(1)	2136(1)	20(1)
C21	3298(1)	4691(1)	1107(1)	18(1)
C22	3734(1)	3909(1)	854(1)	17(1)
C23	3874(1)	3852(1)	-201(1)	21(1)
C24	3582(2)	4542(1)	-964(1)	24(1)
C25	3144(2)	5307(1)	-688(1)	25(1)
C26	2997(2)	5383(1)	351(1)	23(1)
C27	4032(1)	3101(1)	1625(1)	19(1)
O28	4235(1)	2433(1)	979(1)	29(1)
C29	2890(2)	2839(1)	1963(1)	26(1)
F30	1762(3)	3120(2)	1206(3)	33(1)

F31	2788(7)	1990(2)	2056(6)	31(1)
F32	3042(4)	3166(3)	3007(2)	27(1)
F30A	1806(8)	2908(5)	1004(6)	63(3)
F31A	3036(13)	1993(4)	2201(11)	27(2)
F32A	2719(8)	3217(7)	2814(6)	54(2)
C33	5285(2)	3203(1)	2729(1)	26(1)
F34	5330(4)	3875(2)	3389(4)	31(1)
F35	6289(4)	3258(3)	2419(4)	33(1)
F36	5484(12)	2504(4)	3396(9)	28(1)
F34A	5174(9)	3805(5)	3426(8)	89(3)
F35A	6288(8)	3412(6)	2479(9)	83(3)
F36A	5580(20)	2471(6)	3328(16)	32(2)

IV. Table 3. Bond lengths [Å] and angles [°] for 1.

P1-O19	1.4526(11)
P1-O2	1.5662(11)
P1-O20	1.5722(11)
P1-O10	1.5860(10)
O2-C3	1.4117(18)
C3-C8	1.380(2)
C3-C4	1.391(2)
C4-C5	1.399(2)
C4-C9	1.520(2)
C5-C6	1.383(2)
C5-H5	0.95(2)
C6-C7	1.384(3)
C6-H6	0.92(2)
C7-C8	1.383(2)
C7-H7	0.99(2)
C8-H8	0.94(2)
C9-O10	1.4334(17)
C9-C11	1.545(2)
C9-C15	1.550(2)
C11-F12	1.327(2)
C11-F14	1.3270(19)
C11-F13	1.3275(19)
C15-F16	1.327(2)
C15-F18	1.329(2)
C15-F17	1.3311(19)
O20-C21	1.4051(17)
C21-C26	1.386(2)
C21-C22	1.394(2)
C22-C23	1.399(2)
C22-C27	1.5405(19)
C23-C24	1.389(2)
C23-H23	0.948(18)
C24-C25	1.384(2)
C24-H24	0.944(18)

C25-C26	1.385(2)
C25-H25	0.97(2)
C26-H26	0.95(2)
C27-O28	1.3917(17)
C27-C33	1.550(2)
C27-C29	1.560(2)
O28-H28	0.81(2)
C29-F32A	1.300(6)
C29-F30	1.326(3)
C29-F31	1.334(4)
C29-F30A	1.341(5)
C29-F31A	1.344(6)
C29-F32	1.354(3)
C33-F34A	1.321(6)
C33-F34	1.322(3)
C33-F35A	1.327(6)
C33-F36A	1.333(6)
C33-F36	1.337(4)
C33-F35	1.337(3)
O19-P1-O2	116.24(6)
O19-P1-O20	116.18(6)
O2-P1-O20	101.80(6)
O19-P1-O10	110.74(6)
O2-P1-O10	103.95(6)
O20-P1-O10	106.73(6)
C3-O2-P1	116.82(9)
C8-C3-C4	122.62(14)
C8-C3-O2	116.92(14)
C4-C3-O2	120.45(13)
C3-C4-C5	117.45(14)
C3-C4-C9	120.46(13)
C5-C4-C9	122.05(14)
C6-C5-C4	120.57(16)
C6-C5-H5	119.5(12)
C4-C5-H5	119.9(12)
C5-C6-C7	120.33(16)

C5-C6-H6	119.1(13)
C7-C6-H6	120.5(13)
C8-C7-C6	120.36(16)
C8-C7-H7	120.5(12)
C6-C7-H7	119.2(12)
C3-C8-C7	118.65(16)
C3-C8-H8	118.5(13)
C7-C8-H8	122.8(13)
O10-C9-C4	113.88(11)
O10-C9-C11	104.96(11)
C4-C9-C11	109.75(12)
O10-C9-C15	103.65(11)
C4-C9-C15	113.12(12)
C11-C9-C15	111.08(12)
C9-O10-P1	124.31(9)
F12-C11-F14	107.80(14)
F12-C11-F13	107.87(13)
F14-C11-F13	107.71(13)
F12-C11-C9	109.56(12)
F14-C11-C9	111.38(13)
F13-C11-C9	112.35(13)
F16-C15-F18	108.49(14)
F16-C15-F17	107.46(14)
F18-C15-F17	107.49(13)
F16-C15-C9	110.16(13)
F18-C15-C9	111.94(13)
F17-C15-C9	111.13(13)
C21-O20-P1	124.51(9)
C26-C21-C22	122.27(13)
C26-C21-O20	119.33(13)
C22-C21-O20	118.30(12)
C21-C22-C23	116.85(13)
C21-C22-C27	125.23(12)
C23-C22-C27	117.90(13)
C24-C23-C22	121.54(14)
C24-C23-H23	121.0(11)

C22-C23-H23	117.5(11)
C25-C24-C23	119.99(14)
C25-C24-H24	119.9(10)
C23-C24-H24	120.0(10)
C24-C25-C26	119.83(14)
C24-C25-H25	120.9(11)
C26-C25-H25	119.3(12)
C25-C26-C21	119.51(14)
C25-C26-H26	122.1(11)
C21-C26-H26	118.4(11)
O28-C27-C22	106.63(11)
O28-C27-C33	107.40(12)
C22-C27-C33	112.14(11)
O28-C27-C29	107.84(12)
C22-C27-C29	112.69(11)
C33-C27-C29	109.86(12)
C27-O28-H28	112.4(17)
F30-C29-F31	107.4(3)
F32A-C29-F30A	109.1(5)
F32A-C29-F31A	107.7(6)
F30A-C29-F31A	105.5(5)
F30-C29-F32	107.0(2)
F31-C29-F32	105.6(3)
F32A-C29-C27	120.8(5)
F30-C29-C27	112.2(2)
F31-C29-C27	113.0(4)
F30A-C29-C27	106.9(5)
F31A-C29-C27	105.9(7)
F32-C29-C27	111.3(2)
F34A-C33-F35A	107.2(5)
F34A-C33-F36A	107.4(6)
F34-C33-F36A	112.4(9)
F35A-C33-F36A	107.1(6)
F34A-C33-F36	101.3(7)
F34-C33-F36	107.0(4)
F35A-C33-F36	113.6(8)

F34A-C33-F35	117.4(5)
F34-C33-F35	107.7(3)
F36-C33-F35	106.4(4)
F34A-C33-C27	112.1(4)
F34-C33-C27	116.1(2)
F35A-C33-C27	111.8(5)
F36A-C33-C27	111.0(10)
F36-C33-C27	110.4(6)
F35-C33-C27	108.7(3)

V. Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

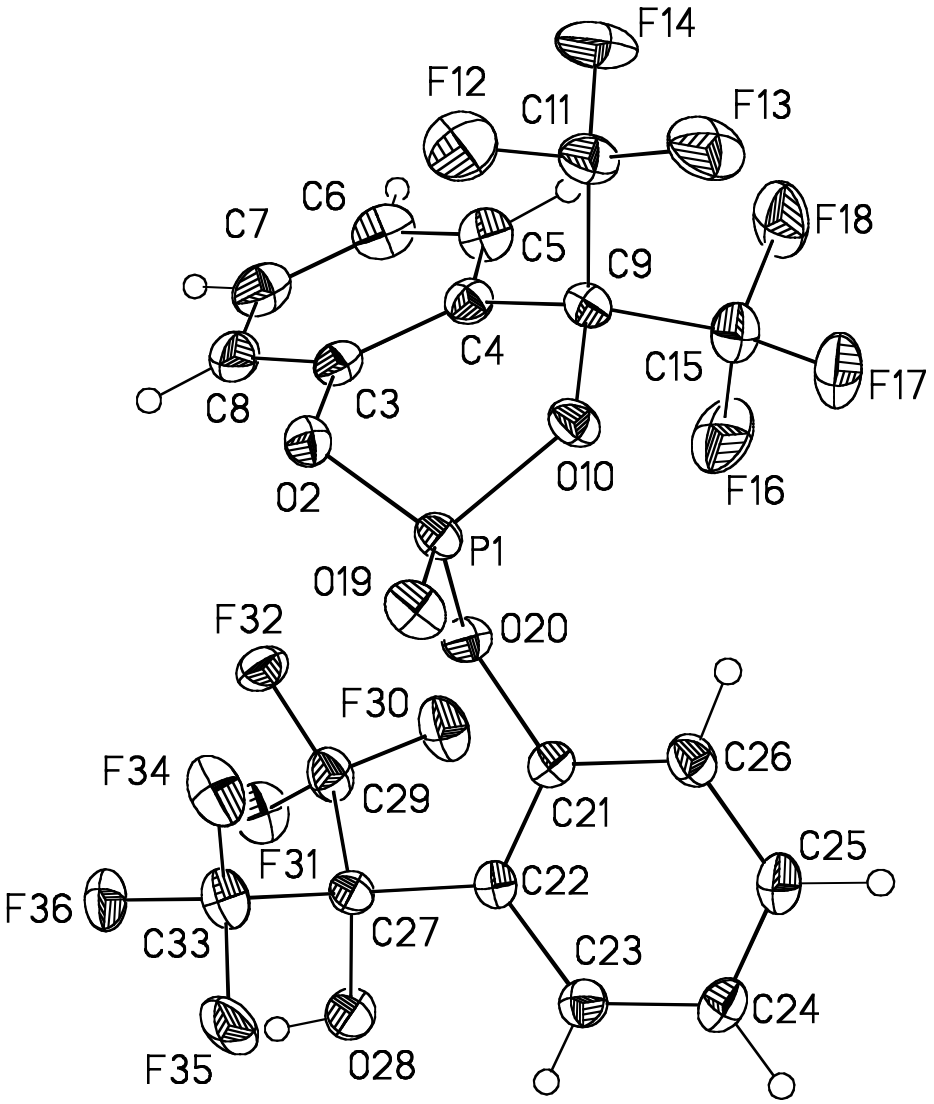
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P1	18(1)	15(1)	21(1)	0(1)	7(1)	0(1)
O2	20(1)	24(1)	20(1)	2(1)	7(1)	2(1)
C3	24(1)	21(1)	18(1)	-3(1)	10(1)	-2(1)
C4	23(1)	18(1)	19(1)	-3(1)	8(1)	-2(1)
C5	23(1)	29(1)	28(1)	-2(1)	9(1)	-3(1)
C6	31(1)	32(1)	35(1)	-6(1)	17(1)	-11(1)
C7	45(1)	24(1)	32(1)	0(1)	23(1)	-7(1)
C8	37(1)	24(1)	25(1)	3(1)	15(1)	3(1)
C9	18(1)	19(1)	21(1)	-1(1)	7(1)	2(1)
O10	21(1)	16(1)	28(1)	3(1)	13(1)	2(1)
C11	29(1)	21(1)	31(1)	-3(1)	14(1)	1(1)
F12	47(1)	40(1)	31(1)	-16(1)	2(1)	1(1)
F13	52(1)	17(1)	56(1)	-2(1)	30(1)	-1(1)
F14	45(1)	34(1)	58(1)	-8(1)	36(1)	4(1)
C15	26(1)	31(1)	24(1)	4(1)	6(1)	0(1)
F16	55(1)	43(1)	23(1)	-8(1)	5(1)	-11(1)
F17	36(1)	41(1)	31(1)	16(1)	10(1)	3(1)
F18	22(1)	62(1)	41(1)	17(1)	6(1)	9(1)
O19	21(1)	21(1)	33(1)	-1(1)	10(1)	-2(1)
O20	25(1)	16(1)	23(1)	-1(1)	13(1)	-1(1)
C21	18(1)	20(1)	18(1)	-1(1)	7(1)	-3(1)
C22	16(1)	17(1)	18(1)	1(1)	5(1)	-2(1)
C23	20(1)	23(1)	19(1)	-2(1)	7(1)	-1(1)
C24	23(1)	29(1)	18(1)	1(1)	7(1)	-4(1)
C25	24(1)	24(1)	23(1)	7(1)	6(1)	-1(1)
C26	23(1)	18(1)	27(1)	3(1)	10(1)	2(1)
C27	22(1)	15(1)	20(1)	-1(1)	9(1)	1(1)
O28	47(1)	17(1)	27(1)	1(1)	17(1)	8(1)
C29	26(1)	21(1)	30(1)	6(1)	11(1)	0(1)
F30	18(1)	34(1)	45(1)	13(1)	10(1)	-1(1)
F31	33(3)	19(1)	39(2)	3(1)	13(2)	-8(1)

F32	36(1)	25(1)	28(1)	4(1)	21(1)	5(1)
F30A	31(3)	73(5)	67(4)	42(3)	0(3)	-12(3)
F31A	25(4)	20(2)	33(3)	4(2)	9(2)	-4(2)
F32A	61(5)	36(3)	92(5)	-3(3)	59(4)	0(3)
C33	24(1)	21(1)	29(1)	4(1)	5(1)	1(1)
F34	26(1)	19(1)	33(2)	-7(1)	-3(1)	-3(1)
F35	16(1)	42(1)	44(2)	13(1)	14(1)	7(1)
F36	32(2)	25(2)	23(2)	7(2)	6(2)	4(2)
F34A	95(6)	57(4)	52(4)	-30(3)	-39(3)	43(4)
F35A	40(4)	108(6)	75(5)	50(4)	-7(3)	-28(3)
F36A	36(4)	26(4)	27(4)	3(2)	5(3)	12(3)

VI. Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1.

	x	y	z	U(eq)
H5	-860(19)	5532(12)	2720(17)	29(5)
H6	-1120(20)	4317(13)	3645(17)	34(5)
H7	610(20)	3457(14)	4788(18)	39(5)
H8	2720(20)	3895(14)	4984(18)	38(5)
H23	4164(17)	3322(12)	-383(15)	21(4)
H24	3654(16)	4482(11)	-1684(16)	19(4)
H25	2951(18)	5795(13)	-1205(17)	30(5)
H26	2700(17)	5899(13)	569(16)	27(5)
H28	4490(20)	1997(16)	1360(20)	45(6)

VII. Figure 1. View of **1** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size. The minor occupancy F atoms were omitted for clarity.



VIII. Figure 2. Unit cell packing diagram for **1**. Molecules form H-bound columns parallel to the **b** axis. The geometry of this H-bonding interaction is: O28-H28···O19 (related by 1-x, -_+y, _-z), O···O 2.700(2)Å, H···O 1.92(3)Å, O-H···O 161(2)°.