Experimental Section

Some data on preparation, melting point, and elemental analysis of the compounds studied are given in the microfilm edition[10] of this volume of the journal.

Dissociation Constants. The thermodynamic pK_a^* values were determined using the method described by van Veen, *et al.*[43] Part III of this series[1] provides some details as to calculation and precision, and also a discussion of the correction of the "overall" pK_a^* values of the amino acids for the presence of ammoniocarboxylic acid and/or zwitterion.

Methyl 4-aminophenylacetate hydrochloride was obtained by treating a solution of the amino ester in ether with dry hydrochloric acid gas: mp 189–191° (C, H, and N analyses were correct); pK_a^* in 50% ethanol, 3.89.

Acknowledgments. The authors thank: A. G. N. Boers for allowing them to use and quote some of his unpublished data; R. O. C. Norman and D. J. Byron for the determination of several rate constants; R. W. Taft and S. Ehrenson for pleasant contacts and for permission to quote from an unpublished paper; H. van Bekkum and J. G. Watkinson for some samples; M. van Leeuwen for carrying out the elemental analyses; and M. A. Hoefnagel for the preparation of some compounds.

This paper and parts II and III of this series were composed at the University of California at Santa Cruz while B. M. W. was on sabbatical leave. Thanks are due to J. F. Bunnett for kind hospitality and thoughtful discussions.

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[43] A. van Veen, A. J. Hoefnagel, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **90**, 289 (1971).

Crystal Structure of 2,2,3,3,4,4-Hexafluoro(triphenylphosphoranylidene)cyclobutane

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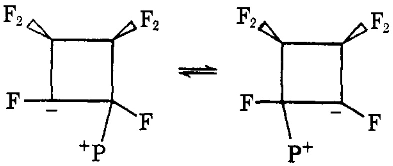
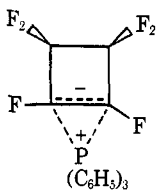
Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242. *Received November 3, 1972*

Abstract: 2,2,3,3,4,4-Hexafluoro(triphenylphosphoranylidene)cyclobutane ($(C_6H_5)_3PC_4F_6$) crystallizes in the triclinic space group, $P\bar{1}$, with cell parameters $a = 9.571$ (13) Å, $b = 10.478$ (5) Å, $c = 11.189$ (5) Å, $\alpha = 116.85$ (3)°, $\beta = 93.46$ (18)°, $\gamma = 96.40$ (18)°, $Z = 2$. The observed and calculated densities are 1.46 (3) and 1.432 g/cm³. Intensity measurements were made on a Picker four-circle automatic diffractometer. A total of 2558 independent reflections were fitted by least-squares methods to a molecular model with $R_2 = 0.046$. The molecular configuration of the compound was found to be that of the ylide structure. The phosphorus atom has four neighbors at essentially tetrahedral angles. The phosphorus–ylide carbon bond length is 1.713 (3) Å (compared with C=P of 1.665 Å and C—P of 1.828 Å). The phosphorus atom is coplanar with the cyclobutane ring. The carbon–fluorine bond lengths are slightly longer than those in perfluorocyclobutane with the exception of the carbon(3)–fluorine(3) bond.

Stockel, Megson, and Beachem reported isolation of a 1:1 adduct when triphenylphosphine and perfluorocyclobutene were allowed to react in anhydrous ether solvent.[1] The structure postulated was either a 1,3-dipolar species (I) which underwent rapid equilibration in solution or a nonclassical structure (Ia).



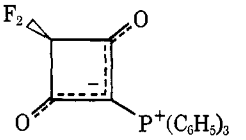
I



Ia

Rapid equilibration accounted for the ^{19}F nmr spectrum which showed a symmetrical multiplet due to four chemically equivalent fluorines at ϕ 86.1 and a symmetrical multiplet at ϕ 124.2 due to two equivalent fluorines.

The 1,3-dipolar structure seemed unlikely due to the ease of carbanions to eliminate a β-fluoride ion. Also, mechanistic consideration of the hydrolysis reaction of this 1:1 adduct leading to the ketobetaine type ylide (II) indicated that nucleophilic attack by water occurred on the cyclobutane ring. This would be unlikely on the basis of the proposed structure.



II

Repetition of the reaction of triphenylphosphine with perfluorocyclobutene in our laboratories resulted in the isolation of a compound with identical properties with those reported previously.[1] Although the possibility of a 1,3-dipolar structure was readily eliminated, the structures III, IV, and V are possible.

All these structures would be expected to belong to the same nuclear spin system, $A_2A_2'MM'X$. Due to the unique nature of IV and V, it was thought that a computer programmed analysis of the ^{19}F nmr spectrum would not comprise conclusive proof of the identity of this compound. Therefore, a complete

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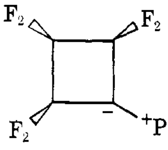
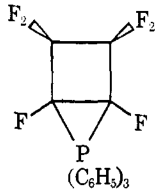
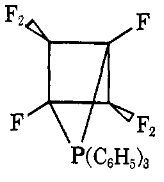
[1] R. F. Stockel, F. Megson, and M. T. Beachem, *J. Org. Chem.*, 33, 4395 (1968).



III



IV

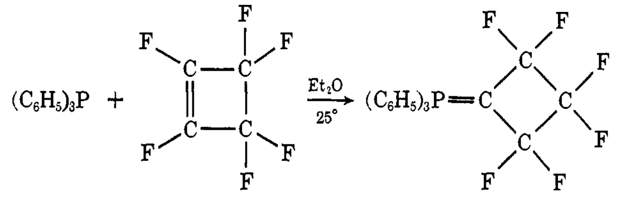


V

X-ray crystal structure determination was done. The results proved the ylide structure III for the 1:1 adduct in the solid state.

Experimental Section

Crystal Data. The 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane used in the X-ray study was prepared by the reaction



The product precipitated as a white powder which was isolated by filtration under dry nitrogen. Crystals for X-ray analysis were obtained by recrystallization of the powder from a 1:2 mixture of tetrahydrofuran and diethyl ether under a dry nitrogen atmosphere. The molecular formula was established by a combination of nmr and mass spectrometric data. Crystals formed clear colorless octahedra elongated along the *b* axis. The bounding faces and the perpendicular distances between them are ($001,00\bar{1}$; 0.175 mm), ($100,\bar{1}00$; 0.075 mm), ($010,0\bar{1}0$; 0.27 mm), and ($0\bar{3}2,03\bar{2}$; 0.23 mm).

Preliminary Weissenberg and precession photographs of the crystals indicated a triclinic crystal system (($P1$ or $P\bar{1}$). The cell dimensions (b, c, and α) were determined from back-reflection Weissenberg photographs (18 resolved α_1–α_2 pairs) using Cu K radiation ($\alpha_1 = 1.54051$ and $\alpha_2 = 1.54433$ Å) using an extrapolation method to correct for systematic errors.[2] Precession films (Mo Kα = 0.7107 Å) were used to determine the remaining angles and the a cell dimensions. The cell dimensions are $a = 9.571\ (13)$ Å, $b = 10.478\ (5)$ Å, $c = 11.189\ (5)$ Å, $\alpha = 116.85\ (3)°$, $\beta = 93.46\ (18)°$, $\gamma = 96.40\ (18)°$. The data were collected at 24°. The calculated density is 1.432 g/cm^3 (molecular weight = 424.23 g/mol, $Z = 2$). The observed density obtained by flotation is 1.46 (3) g/cm^3.

Three-dimensional intensity data were obtained by mounting a crystal in a sealed capillary with the b^* axis coincident with the ϕ axis of the four-circle diffractometer. Intensity data were collected using the θ–2θ scan mode to a $2\theta = 69.4°$. The scan rate was 1°/min and the scan range was 1°. Background intensity was determined by making 10-sec counts at each limit of the scan range. The number of reflections measured was 5586, of which 2558 were independent. Three reflections were measured at 60 reflection intervals to monitor the crystal and equipment stability. The standard deviation of these standards over the entire data collection period was 3, 4, and 5%; as a result, no adjustments for crystal or instrument instability were made.

The integrated intensity for each reflection was determined as $I_n = I - Bt_s/t_b$. The estimate of the standard deviation of the intensity of a reflection was determined from the larger of the two quantities

$$s_{(I)}{}^2 = \sum_{i=1}^{N}[I_i + B_i(t_s/t_b)_i]/N \text{ or } s_{(I)}{}^2 = \sum_{i=1}^{N}[I_n - \bar{I}_n]_i{}^2/(N-1) \text{ if } N > 2$$

B is the sum of the two background counts; t_s is the scan time; t_b is the sum of the background counting times; $\bar{I}_n$ is the average I_n value; and N is the number of equivalent reflections measured. A reflection was considered absent if I_n was less than $3s_B$, where

$$s_B{}^2 = \sum_{i=1} B_i/N$$

Table I. Positional Parameters for 2,2,3,3,4,4-Hexafluoro(triphenylphosphoranylidene)cyclobutane[b]

Atom[a]	x	y	z
P	3639 (1)	6639 (1)	2974 (1)
F(2)	527 (2)	4461 (2)	885 (3)
F(2′)	583 (2)	4248 (2)	2663 (2)
F(3)	1583 (3)	1981 (3)	9650 (2)
F(3′)	1482 (2)	1771 (2)	1447 (2)
F(4)	4250 (2)	3281 (2)	459 (2)
F(4′)	4181 (2)	3139 (2)	2289 (2)
C(1)	2867 (3)	4865 (3)	2059 (3)
C(2)	1419 (3)	4162 (3)	1671 (3)
C(3)	1911 (3)	2711 (3)	970 (3)
C(4)	3420 (3)	3521 (3)	1466 (3)
C(5)	2781 (3)	7498 (3)	4467 (3)
C(6)	2341 (3)	8840 (3)	4852 (3)
C(7)	1679 (4)	9439 (3)	6015 (3)
C(8)	1473 (4)	8740 (4)	6787 (3)
C(9)	1899 (4)	7416 (4)	6404 (3)
C(10)	2557 (3)	6796 (3)	5251 (3)
C(11)	3575 (3)	7686 (3)	2074 (3)
C(12)	2531 (3)	7275 (3)	996 (3)
C(13)	2476 (4)	8110 (4)	322 (3)
C(14)	3443 (3)	9314 (3)	689 (3)
C(15)	4473 (3)	9725 (3)	1747 (3)
C(16)	4534 (3)	8925 (3)	2441 (3)
C(17)	5483 (3)	6688 (3)	3429 (3)
C(18)	6049 (3)	7170 (3)	4752 (3)
C(19)	7487 (3)	7160 (4)	5026 (3)
C(20)	8318 (3)	6679 (4)	4014 (4)
C(21)	7756 (3)	6216 (4)	2701 (3)
C(22)	6341 (3)	6234 (4)	2419 (3)
H(6)	2510 (30)	9322 (30)	4292 (27)
H(7)	1369 (33)	374 (32)	6220 (29)
H(8)	926 (33)	9122 (33)	7590 (29)
H(9)	1624 (35)	6922 (34)	6952 (31)
H(10)	2824 (32)	5866 (32)	4993 (29)
H(12)	1893 (31)	6403 (31)	762 (27)
H(13)	1742 (33)	7766 (33)	9582 (31)
H(14)	3404 (34)	9879 (34)	162 (31)
H(15)	5166 (33)	540 (33)	1912 (30)
H(16)	5239 (31)	9175 (31)	3177 (28)
H(18)	5429 (29)	7511 (30)	5448 (27)
H(19)	7809 (32)	7448 (31)	5917 (28)
H(20)	9298 (30)	6595 (30)	4173 (27)
H(21)	8361 (29)	5858 (29)	1904 (26)
H(22)	5987 (30)	5962 (29)	1558 (26)

[a] Atom symbols refer to those assigned in Figure 1, and the hydrogen atom is assigned on the basis of the carbon atom to which it is attached. [b] All positions and standard deviations are expressed as fractions of the unit cell edges and are multiplied by 10^4.

The data were corrected for Lorentz and polarization effects, but not for absorption since for $\mu = 1.88$ cm^{-1} for Mo Kα radiation the absorption correction would vary only from 0.94 to 0.99. The atom scattering factors used are those for the neutral species.[3]

Structure Solution and Refinement. The observed structure amplitudes were scaled by means of a Wilson plot, and normalized structure amplitudes (E) were calculated utilizing the FAME[4] program. Statistical tests based on the distribution of normalized structure amplitudes suggested space group $P\bar{1}$. An initial set of eight phase-determining symbolic signs, three of which determined an origin, were used by the MAGIC[4] and LINK[4] programs to determine the phases of 217 E's ranging from 3.5 to 1.7 from a set of the largest 800 E values. An E map based on these phases clearly

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(2) The minimum value of $\Sigma(D_m - D_c)^2$ was sought by varying the cell parameters and the coefficient (E) of a systematic error function. D_m are the measured distances between equivalent reflections in the back reflection region, $D_c = 4R[\pi/2 + \arcsin(\lambda^2/4d^2 + \mathrm{Ef}(\theta))^{1/2}]$, and $\mathrm{f}(\theta) = \sin^2\theta\cos^2\theta\,[1/\sin\theta - 1/\theta]$.

(3) "International Tables of X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202.

(4) R. B. K. Dewar and A. Stone, private communication.

Howells, et al. / 2,2,3,3,4,4-Hexfluoro(triphenylphosphoranylidene)cyclobutane

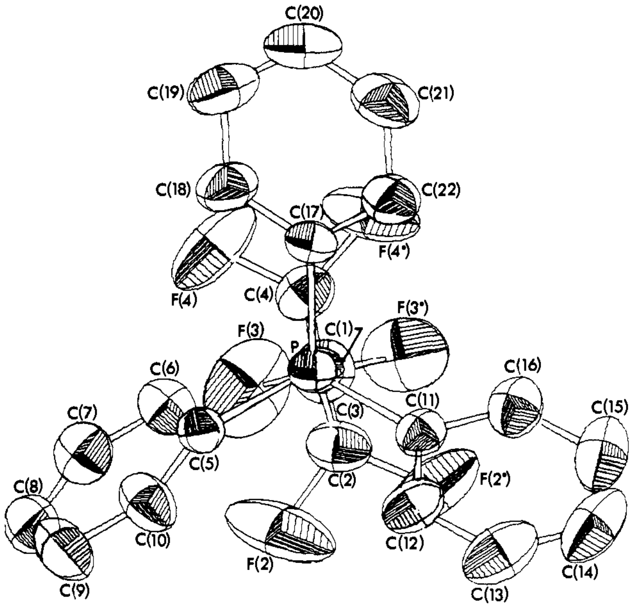

Figure 1. The molecular configuration of 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane. The view is chosen approximately along the phosphorus–carbon(1) bond.

showed the majority of nonhydrogen atoms. Initially the phosphorus, three fluorine, and 14 carbon atoms were used to calculate structure factors which were used to phase an electron density map. Upon comparison of the two maps, the remainder of the molecule was apparent in the E map.

The progress of refinement was followed by monitoring

$$R_1 = \sum\Delta F/\sum F_o \text{ and } R_2 = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$$

where $\Delta F = |F_o| - |F_c|$ (F_o = scaled observed structure factor, F_c = calculated structure factor). The function minimized was $\Sigma w(\Delta F)^2$. Any reflection below the minimum observable intensity was assigned $w = 0.0$ unless $F_o < F_c$ in which case it was assigned $w = 1.0$.

Refinement for six cycles with a full matrix least-squares program varying the coordinates and individual isotropic temperature factors for all nonhydrogen atoms (116 parameters) brought R_2 to 0.16 with unit weights assumed. At this point of refinement a change to a block-diagonal (9 × 9 blocks) was made, and a weighting scheme[5] based on the experimentally measured estimates of the standard deviation was used. Each reflection was weighted by $w = 1/[s_{(F)}^2 + c^2F_o^2]$. Anisotropic temperature factors were calculated for all nonhydrogen atoms (261 parameters) bringing R_2 to 0.07. An electron density difference map was generated in which all the hydrogen atoms were located. The hydrogen atom coordinates were allowed to refine with fixed isotropic temperature factors (306 parameters). Refinement on the temperature factors for the hydrogen atoms was unsuccessful. The final temperature factors for the hydrogen atoms were assigned on the basis of the carbon atoms to which they were attached.

In the last cycle of refinement the average shift of the parameters was 0.3% of the estimated standard deviation and $R_1 = 0.052$ and $R_2 = 0.046$. The constant (c) in the weighting function was 0.009; the function $[\Sigma w(\Delta F)^2/(m - n)]^{1/2} = 1.34$ (n = number of parameters, m = number of independent reflections). A final electron density difference map shows no additional peaks greater than $^1/_3$ the value of a hydrogen peak. The calculated and observed structure factors and weights for the last cycle of refinement are listed in the microfilm edition of this paper.[6] All computations were made using an IBM 360/65 and locally written programs unless otherwise noted.

Discussion

The results of the structure determination of 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane are recorded in the following tables. The final positional parameters are listed in Table I.[7] The most relevant bond distances and angles are given in Table II.[8] The numerical designations for the atoms in all tables are based on those assigned in Figure 1 (drawn by ORTEP)[9] with the hydrogen atom number based on the carbon atom to which it is attached. For the sake of clarity, the hydrogen atoms are deleted from Figure 1.

Table II. Intramolecular Distances and Bond Angles (deg) in 2,2,3,3,4,4-Hexafluoro(triphenylphosphoranylidene)cyclobutane

P–C (1)[a]	1.713 (3)[b]		
		C(2)–F(2)	1.348 (4)
P–C(5)	1.802 (3)	C(2)–F(2′)	1.383 (4)
P–C(11)	1.796 (3)	C(4)–F(4)	1.364 (4)
P–C(17)	1.796 (3)	C(4)–F(4′)	1.362 (4)
	Av 1.798		Av 1.364
C(1)–C(2)	1.436 (4)	C(3)–F(3)	1.317 (4)
C(1)–C(4)	1.438 (4)	C(3)–F(3′)	1.355 (4)
C(2)–C(3)	1.508 (4)	F(2)–F(2′)	2.098 (3)
C(3)–C(4)	1.523 (4)	F(3)–F(3′)	2.126 (3)
		F(4)–F(4′)	2.123 (3)
C(1)–C(3)	2.082 (4)		
C(2)–C(4)	2.091 (4)		
Average C–C distance in the phenyl rings = 1.379 (max distance = 1.395; min distance = 1.357)			
C(1)–P–C(5)	109.5 (1)	C(2)–C(1)–C(4)	93.4 (2)
C(1)–P–C(11)	114.4 (1)	C(2)–C(3)–C(4)	87.2 (2)
C(1)–P–C(17)	108.3 (1)	C(1)–C(4)–C(3)	89.3 (2)
C(5)–P–C(11)	108.0 (1)	C(1)–C(2)–C(3)	90.0 (2)
C(5)–P–C(17)	110.3 (1)		Sum 359.9
C(11)–P–C(17)	106.2 (1)		
		F(2)–C(2)–F(2′)	100.3 (2)
		F(4)–C(4)–F(4′)	102.3 (2)
		F(3)–C(3)–F(3′)	105.4 (2)
Phenyl ring angles average 120.0° (the max angle = 121.1°; the min angle = 118.2°)			

[a] Atom symbols refer to those assigned in Figure 1. [b] Bond distances are reported in ångströms with estimated standard deviations in parentheses.

One of the interesting features of the structure is the P–C(1) bond length, 1.713 (3) Å, for the bond is one of the shortest reported for a stabilized ylide structure (see the stabilized ylide compounds **1–8** in Table III). The bond length can be compared with the phosphorus–ylide carbon length of 1.709 (19) found in *p*-tolyl (triphenylphosphoranylidene)methyl sulfone (compound **1**, Table III). The two compounds are similar in the respect that neither has a carbonyl group in conjugation with the ylide carbon atom to provide for delocalization of charge. However, whereas the ylide carbanion in the sulfone could be stabilized through d-orbital participation of the sulfur atom, the

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[5] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, 25, 374 (1969).

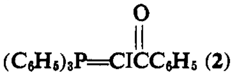
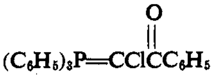
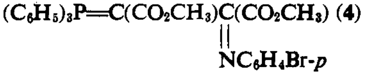
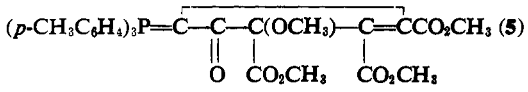
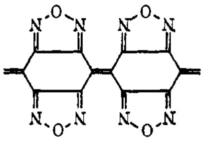
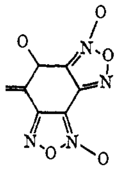
[6] The table (IV) of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journal Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-5366. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

[7] A listing of the thermal parameters appears in the microfilm edition of this paper as Table V.

[8] A listing of additional intramolecular distances, some significant intermolecular distances, and a more complete listing of bond angles is given in the microfilm edition of this paper as Table VI.

[9] C. K. Johnson, "A FORTRAN Thermal Ellipsoid Plot Program for Crystal Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table III. Comparison of Some Structural Features in Compounds of the Formula $(C_6H_5)_3P{=}CXY$

Molecule	P=C	P—C	Mean	Ref
	Section A. Bond Lengths[a]			
$(C_6H_5)_3P{=}CHSO_2C_6H_4CH_3\text{-}p$ (**1**)	1.709 (19)[b]	1.777–1.832 (17)[c]	1.808	*d*
 $(C_6H_5)_3P{=}CI\overset{O}{\overset{\|}{C}}C_6H_5$ (**2**)	1.71 (5)	1.77–1.82 (6)	1.79	*e*
 $(C_6H_5)_3P{=}CCl\overset{O}{\overset{\|}{C}}C_6H_5$ (**3**)	1.736 (14)	1.798–1.822 (14)	1.807	*f*
 $(C_6H_5)_3P{=}C(CO_2CH_3)\underset{NC_6H_4Br\text{-}p}{\underset{\|}{C}}(CO_2CH_3)$ (**4**)	1.70 (3)	1.81–1.87 (3)	1.83	*g*
 $(p\text{-}CH_3C_6H_4)_3P{=}\underset{O}{\underset{\|}{C}}{-}\underset{CO_2CH_3}{\underset{\|}{C}}{-}C(OCH_3){-}\underset{CO_2CH_3}{\underset{\|}{C}}{=}CCO_2CH_3$ (**5**)	1.728 (8)	1.805–1.828 (8)	1.819	*h*
$(C_6H_5)_3P{=}CC(CF_3)_2OP(C_6H_5)_3$ (**6**)	1.745 (20) 1.760 (20)	1.793–1.902 (21)	1.848	*i*
$(C_6H_5)_3P{=}R{=}P(C_6H_5)$ (**7**) R = 	1.708 (14) 1.767 (12)	1.804–1.832 (14)	1.816	*j*
$(C_6H_5)_3P{=}R$ (**8**) R = 	1.77 (2)	1.79–1.82	1.81	*k*
$(C_6H_5)_3P{=}C{=}C{=}O$ (**9**)	1.648 (7)	1.793–1.815 (6)	1.805	*l*
$(C_6H_5)_3P{=}C{=}C{=}S$ (**10**)	1.677 (8)	1.783–1.803 (7)	1.795	*m*
$(C_6H_5)_3P{=}C{=}P(C_6H_5)_3$[c] (**11**)	1.629 (3)	1.823–1.845 (6)	1.837	*n*
	1.633 (4)	1.827–1.835 (6)	1.823	
$(C_6H_5)_3P{=}CH_2$ (**12**)	1.661 (8)	1.811–1.839 (5)	1.823	*o*
$(C_6H_5)_3P{=}CCF_2CF_2CF_2$ (**13**)	1.713	1.796–1.802	1.798	This work

Molecule[q]	C—P—C	Mean	C—P=C	Mean
		Section B. Bond Angles[p]		
1	106.1–107.2 (8)[c]	106.8	105.2–118.2 (8)	112.0
2	106–107 (2)	106.7	110–115 (2)	112.3
3	105.4–108.9 (6)	106.9	110.2–113.2 (6)	111.9
4	106.1–110.0	107.4	108.4–113.7	111.3
5	106.1–108.4 (4)	107.3	109.2–112.9 (4)	111.3
6	101.4–107.4 (9)	104.4	112.5–116.3 (9)	114.1
7	105–109	108	106–115	111
	108–110	109	108–112	110
8	108–109	108	108–114	110
9	106.1–108.7 (3)	107.3	110.6–113.0 (4)	111.5
10	105.9–110.3 (3)	108.1	110.3–111.6 (4)	110.8
11	102.6–105.1 (3)	104.0	109.9–116.1 (3)	114.5
	103.1–104.0 (3)	103.5	109.2–117.8 (3)	114.9
12	102.8–107.4 (2)	105.0	111.4–115.0 (3)	113.5
13	106.2–110.3 (1)	108.2	108.3–114.4 (1)	110.7

[a] Ångströms. [b] Standard deviations. [c] Two unique molecular configurations were reported. [d] P. J. Wheatley, *J Chem. Soc.*, 5785 (1965). [e] F. S. Stephens, *ibid.*, 5640 (1965). [f] *ibid.*, 5658 (1965). [g] T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **18**, 81 (1965). [h] O. Kennard, W. D. S. Motherwell, and J. C. Coppola, *J. Chem. Soc. C*, 2461 (1971). [i] G. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 568 (1968). [j] T. S. Cameron and C. K. Prout, *J. Chem. Soc. C*, 2292 (1969). [k] A. S. Bailey, J. M. Peach, T. S. Cameron, and C. K. Prout, *ibid.*, 2295 (1969). [l] J. J. Daly and P. J. Wheatley, *J. Chem. Soc. A*, 1703 (1966). [m] J. J. Daly, *ibid.*, 1913 (1967). [n] A. T. Vincent and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, **1**, 617 (1972). [o] J. C. J. Bart, *J. Chem. Soc. B*, 350 (1969). [p] Degrees. [q] See section A.

ylide carbanion in 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane would be stabilized by the strong inductive effect of the adjacent highly electronegative fluorine atoms.

In the compounds **2**–**5** of Table III, there is a possibility of conjugation with a carbonyl group which would decrease the double bond character of the P=C and C=O bonds and consequently lengthen these bonds. At the same time, the π-bond character of the intermediate C–C bond is increased and thus the bond is shortened. For example, in compound **3**, the C–O bond length (1.301 Å) is longer than the nonconjugated carbonyl distance of 1.23 Å.[10] The P–C distance is 1.736 (14) Å which is longer than a double

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(10) L. E. Sutton, *Chem. Soc., Spec. Publ.*, **No. 11**, S13, S14, S17 (1958).

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bond distance of 1.665 Å.[11] The intermediate C–C distance is shortened to 1.36 Å from an expected 1.46 Å[10] for an sp^2–sp^2 single bond.

The phosphorus–ylide carbon bond length (1.713 Å) in 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)-cyclobutane is closer to a phosphorus–carbon double bond length (1.665 Å) than a phosphorus–carbon single bond length (1.828 Å in triphenylphosphine),[12] indicative of a considerable amount of double bond character formed by the overlap of the phosphorus d orbitals with the ylide carbon p orbitals.

The cyclobutane ring distances show a marked similarity in the C(1)–C(2) and C(1)–C(4) bond lengths. These bond lengths, 1.436 (4) and 1.438 (4) Å, agree within one standard deviation with the average (1.440 Å) of the standard carbon single (sp^3–sp^3) bond length (1.543 Å) and the carbon double (sp^2–sp^2) bond length (1.337 Å).[10] The carbon–fluorine bond lengths on the α-ring positions (C(2) and C(4)) appear to be slightly elongated, since the average carbon–fluorine bond length in perfluorocyclobutane is 1.333 Å.[13]

The phosphorus and the carbon skeleton of the cyclobutane ring lie in a plane, the deviations being P, −0.001 Å; C(1), 0.015 Å; C(2), −0.013 Å; C(3), 0.012 Å; C(4), −0.013 Å. The fluorine atoms form parallel planes above and below the phosphorus–cyclobutane ring plane. The lack of puckering in the four-membered ring also lends some support to the partial double bond character in the C(1)–C(2) and C(1)–C(4) bonds. Thus, the shortened C(1)–C(2) and C(1)–C(4) bond distance average (1.437 Å) compared with the C(2)–C(3) and C(4)–C(3) bond distance average (1.515 Å), the lengthened fluorine bonds to C(2) and C(4), and the shortened P–C bond length support a delocalized version of the ylide structure.

A conclusive statement cannot be made about bond distances in the phenyl rings since none of the atom positions were corrected for thermal motion. The average aromatic carbon–carbon bond length is 1.379 Å, and the average carbon–hydrogen bond length is 0.98 Å.

The bond angles associated with the cyclobutane ring (Table II) are similar to those found in perfluorocyclobutane,[13] while the bond angles about phosphorus are essentially tetrahedral as in the other triphenylphosphonium ylides listed in Table III. The F(2)–C(2)–F(2′) and F(4)–C(4)–F(4′) bond angles are significantly smaller than the F(3)–C(3)–F(3′) bond angle, again indicating the occurrence of delocalized bonding.

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(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(12) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(13) C. H. Chang, R. F. Porter, and S. H. Bauer, private communication.

Structures of Analogs of Nicotinamide–Adenine Dinucleotide. I. Crystal Structure of *N*-(3-(Aden-9-yl)propyl)-3-carbamoylpyridinium Bromide Trihydrate, (Ade-C$_3$-Nic$^+$)Br$^-$·3H$_2$O[1]

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Received December 29, 1972

Abstract: The crystal structure of *N*-(3-(aden-9-yl)propyl)-3-carbamoylpyridinium bromide trihydrate, (Ade-C$_3$-Nic$^+$)Br$^-$, a molecule containing the bases of NAD$^+$ with a trimethylene bridge linking the adenine and pyridinium moieties, has been determined. The crystals of $(C_{14}H_{16}N_7O)^+Br^- \cdot 3H_2O$ are triclinic with a = 10.258 (2), b = 16.423 (2), and c = 5.664 (1) Å; α = 88.48 (2), β = 91.63 (2), and γ = 103.98 (2)°, and there are two molecules in the unit cell; the space group is $P\bar{1}$. The structure has been refined to an R factor of 0.058 on the 2932 nonzero reflections collected on an automatic diffractometer (Cu Kα radiation). The trimethylene chain is extended as the N–C–C–C torsion angles in the chain are completely staggered. The amide group is twisted out of the plane of the pyridinium ring by 38°48′. The adenine ring is linked to another centrosymmetrically related adenine ring by two N(6)–H···N(7) hydrogen bonds and is overlapped by another centrosymmetrically related and hence parallel adenine ring (related to the first by a translation in c) at a distance of 3.35 Å. The >C(6)–NH$_2$ group of one adenine ring overlaps the five-membered portion of the other ring. There is extensive hydrogen bonding in the crystal involving the pyridinium and adenine rings, the bromide anion, and the three water molecules. Rather surprisingly, the amide oxygen atom is not involved in hydrogen bonding.

The nicotinamide–adenine dinucleotide coenzymes NAD$^+$ (I) and NADH (II) have been detected in many living systems and play an important role in enzymatic oxidation–reduction reactions.[3] While the constitution and stereochemistry are well established,[4]

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(1) This work was supported by USPH Grants GM 12470 and GM 19336 and Training Grant GM 722.

(2) Alfred P. Sloan Research Fellow, 1968–1970.

(3) N. O. Kaplan, *Enzymes, 2nd Ed.*, 3, 105 (1960).

(4) L. J. Haynes, N. A. Hughes, G. W. Kenner, and S. A. Todd, *J. Chem. Soc.*, 3727 (1957); N. A. Hughes, G. W. Kenner, and S. A. Todd, *ibid.*, 3733 (1957).