CRYSTAL STRUCTURE AND NMR SPECTRA OF 3-CARBOETHOXY-3-TRIPHENYLPHOSPHORANYLIDENE-2-OXOPROPANE TRIPHENYL PHOSPHONIUM BROMIDE CHLOROFORM SOLVATE

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SUMMARY

The crystal structure of $C_{42}H_{37}O_3P_2Br$ has been determined by single crystal X-ray diffraction. The title compound is monoclinic, space group $P2_1/n$ (Nr. 14), with unit cell parameters a = 11.220(6), b = 14.345(10), c = 25.616(17) A, β = 97.21(5)° and Z = 4. The compound crystallizes with solvent molecules of chloroform, and has triphenylphosphonium ylide and triphenyl phosphonium salt moieties linked by the carbon chain of 3-carboethoxy-2-oxopropane. The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra are discussed and related to the crystal structure.

Key Words: Phosphorus ylide, triphenyl phosphonium salt, NMR spectra, X-ray structure.

RESUMEN

Se informa la estructura cristalina del compuesto de fórmula molecular $C_{42}H_{37}O_3P_2Br$, la cual ha sido determinada por difracción de rayos X. El compuesto cristaliza con moléculas de solvente en el grupo espacial $P2_1/n$ (Nr 14), con parámetros reticulares de a = 11.220(6), b = 14.345(10), c = 25.616(17) Å, β = 97.21(5)° y Z = 4. La estructura se puede describir como un iluro de trifenilfósforo y una sal de trifenilfosfonio unidas por una cadena de 3-carboetoxi-2-oxopropano. Se discuten los espectros de ^{1}H-, ^{13}C- y ^{31}P-RMN y se relacionan con la estructura cristalina del compuesto.

Palabras Claves: Iluro de fósforo, sal de trifenilfosfonio, espectros de RMN, estructura de rayos-X.

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INTRODUCTION

There has been a long-standing controversy regarding the nature of the bonding in phosphonium ylides specially about the hybridization of the P and C atoms[1]. For this reason we are interested in the structure of 3-carboethoxy-3-triphenylphosphoranylidene-2-oxopropane-triphenylphosphonium bromide in order to obtain information about the effect of the ester- and keto-groups on the extent of delocalization in the P=C ylidic bond. We relate here the X-ray structure to the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of this compound, since these techniques prove the nature of the P=C bond, and the evidence can be useful for comparisons with other ylides which are not readily crystallized.

EXPERIMENTAL

Synthesis

An equimolar mixture of carboethoxymethylenetriphenyl phosphorane and its conjugated acid (the phosphonium salt) was heated and stirred at reflux in dry benzene, the solid which formed was separated by filtration, washed with benzene, and dried. The compound was recrystallized from chloroform-ethyl acetate[2].

X-ray structure determination

The intensity data were collected with a Siemens R3m/V diffractometer using graphite monochromated MoKα radiation and the 2θ/θ scan mode. Cell parameters were obtained by least squares adjustment of the setting angles of 25 reflections in the range $18 < 2\theta < 40°$. Three standard reflections monitored every 47 reflections showed no significant decay. The program used for data collection and cell refinement was P3/P4-PC Diffractometer Program[3].

The structure was solved by direct methods and refined on F^2 by full-matrix lest-squares methods. The positions of the H atoms were calculated geometrically and they were allowed to ride on their parent C atoms with fixed isotropic U values. The programs used to solve and refine the structure were SHELXS-86[4] and SHELXTL-93[5], respectively. Atomic scattering factors were taken from the International Tables for Crystallography[6].

NMR spectra

Proton and carbon NMR spectra were recorded on a Bruker AVANCE DRX 300 spectrometer operating at 300.13 and 75.47 MHz respectively, in deuterochloroform as solvent and withTMS (tetramethylsilane) as internal standard. ^{31}P-NMR spectra (^{1}H decoupled) were obtained at 121.44 MHz; H_3PO_4 (85%) was used as external reference.

DISCUSSION AND RESULTS

Crystal structure

The crystal data are summarized in Table I. The final positions and equivalent isotropic thermal parameters of all non-hydrogen atoms are reproduced in Table II. Selected interatomic distances and bond angles with their estimated standard deviation (esd's) are given in Table III.

TABLE I. Data collection and structure refinement parameters.

Crystal Data

Compound	$C_{42}H_{37}O_3P_2Br \cdot CHCl_3$
F weight	850.93
Temp. °K	293
Space group	$P2_1/n$
Cell constants	
a[Å]	11.220(6)
b[Å]	14.345(10)
c[Å]	25.616(17)
β[deg]	97.21(5)
V[A^3]	4090(5)
Z	4
D_x [Mg·m^{-3}]	1.382
μ calc, [mm^{-1}]	1.317

Data Collection

Diffractometer	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Monochromator	graphite
Crystal size [mm]	0.30x0.34x0.40
Data collection mode	2theta-theta-scan
2-theta range [deg]	3.2 to 45.0
Range of h	0 h 12
Range of k	0 k 15
Range of l	-27 l 27
Measured reflections	5675
Independent reflections	5352
Observed reflections I > 2σ (I)	1871
Absorption correction	none

Refinement

Solution by	Direct methods
Refinement on F^2	Full-Matrix Least-Squares
Final R	0.0475
wR	0.1026
Parameters	469
GOF	0.676
Weighting scheme	$w=1/[s^2F_o^2 + (0.0363P)^2, P=(F_o^2 + 2F_c^2)/3$
Largest difference peak eÅ^{-3}	0.259
Largest difference hole eÅ^{-3}	-0.361

TABLE II. Final atomic coordinated (x 10⁴) and equivalent isotropic thermal parameters (Å x 10³).

| Atom	x	y	z	U_{eq}*
Br	0.1010(1)	0.6041(1)	0.2130(1)	0.073(1)
Cl(1)	0.7259(2)	0.6656(1)	0.0459(1)	0.040(1)
Cl(2)	0.7567(2)	0.6818(1)	0.2573(1)	0.039(1)
Cl(3)	0.7348(4)	0.7378(3)	0.1469(2)	0.044(1)
P(1)	0.7410(5)	0.4474(3)	0.1425(2)	0.088(2)
P(2)	0.7237(6)	0.4560(4)	0.0587(2)	0.105(2)
O(1)	0.7756(5)	0.6081(4)	0.2023(2)	0.034(2)
O(2)	0.7443(6)	0.6525(5)	0.1489(3)	0.035(2)
O(3)	0.7291(5)	0.5957(5)	0.1024(2)	0.030(2)
C(1)	0.7334(6)	0.4979(6)	0.1050(3)	0.051(2)
C(2)	0.7267(9)	0.3572(5)	0.0551(3)	0.086(3)
C(3)	0.8455(8)	0.3232(6)	0.0538(4)	0.128(4)
C(4)	0.2426(6)	0.1014(6)	0.1584(3)	0.087(3)
C(5)	0.3416(2)	0.0654(2)	0.1162(1)	0.118(1)
C(6)	0.1676(3)	0.2014(2)	0.1322(1)	0.159(1)
C(7)	0.1416(3)	0.0159(3)	0.1662(1)	0.199(2)
C(11)	0.7672(6)	0.6024(5)	0.3124(2)	0.039(2)
C(12)	0.6855(6)	0.6054(6)	0.3490(3)	0.059(2)
C(13)	0.6944(7)	0.5387(6)	0.3885(3)	0.069(3)
C(14)	0.7791(8)	0.4709(6)	0.3921(3)	0.076(3)
C(15)	0.8608(7)	0.4692(6)	0.3563(3)	0.073(3)
C(16)	0.8543(7)	0.5343(5)	0.3164(3)	0.058(2)
C(21)	0.8686(6)	0.7706(5)	0.2697(2)	0.036(2)
C(22)	0.8738(6)	0.8440(5)	0.2361(3)	0.057(2)
C(23)	0.9626(8)	0.9096(6)	0.2459(3)	0.080(3)
C(24)	1.0475(7)	0.9025(7)	0.2885(3)	0.073(2)
C(25)	1.0401(7)	0.8305(6)	0.3225(3)	0.078(3)
C(26)	0.9529(7)	0.7642(5)	0.3139(3)	0.065(2)
C(31)	0.6091(6)	0.7320(5)	0.2488(2)	0.035(2)
C(32)	0.5148(8)	0.6790(6)	0.2226(2)	0.062(2)
C(33)	0.3989(8)	0.7144(7)	0.2179(3)	0.074(3)
C(34)	0.3801(8)	0.8006(8)	0.2381(4)	0.082(3)
C(35)	0.4690(9)	0.8522(6)	0.2634(3)	0.078(3)
C(36)	0.5864(7)	0.8172(5)	0.2697(3)	0.055(2)
C(41)	0.7292(6)	0.5967(5)	-0.0126(2)	0.037(2)
C(42)	0.6255(7)	0.5577(5)	-0.0375(3)	0.055(2)
C(43)	0.6287(8)	0.4999(6)	-0.0807(3)	0.075(3)
C(44)	0.7390(1)	0.4811(6)	-0.0981(3)	0.083(3)
C(45)	0.8385(8)	0.5208(6)	-0.0751(3)	0.080(3)
C(46)	0.8362(6)	0.5795(5)	-0.0315(3)	0.059(2)
C(51)	0.8552(6)	0.7391(5)	0.0500(2)	0.035(2)
C(52)	0.8620(7)	0.8120(6)	0.0148(3)	0.059(2)
C(53)	0.9620(9)	0.8689(6)	0.0167(3)	0.080(3)
C(54)	1.0572(8)	0.8531(6)	0.0537(4)	0.082(3)
C(55)	1.0538(7)	0.7826(7)	0.0891(3)	0.078(3)
C(56)	0.9529(7)	0.7235(5)	0.0865(3)	0.060(2)
C(61)	0.5924(5)	0.7380(4)	0.0343(2)	0.035(2)
C(62)	0.5641(7)	0.7840(5)	-0.0137(3)	0.057(2)
C(63)	0.4672(8)	0.8440(5)	-0.0220(3)	0.075(3)
C(64)	0.3960(7)	0.8553(5)	0.0161(4)	0.067(3)
C(65)	0.4165(6)	0.8066(6)	0.0617(3)	0.062(2)
C(66)	0.5145(6)	0.7465(5)	0.0720(2)	0.044(2)

*Equivalent isotropic U defined as one third of the trace of orthogonalized U_{ij} tensor

TABLE III. Selected bond lengths (Å) and angles (°).

Distances

P(1)	C(3)	1.758(6)	O(3)	C(4)	1.324(7)
P(1)	C(51)	1.787(7)	O(3)	C(5)	1.421(8)
P(1)	C(41)	1.800(6)	C(1)	C(2)	1.510(7)
P(1)	C(61)	1.815(6)	C(2)	C(3)	1.436(8)
P(2)	C(21)	1.790(6)	C(3)	C(4)	1.405(9)
P(2)	C(31)	1.794(6)	C(5)	C(6)	1.424(9)
P(2)	C(1)	1.794(5)	Cl(1)	C(7)	1.724(7)
P(2)	C(11)	1.806(6)	Cl(2)	C(7)	1.753(8)
O(1)	C(2)	1.229(6)	Cl(3)	C(7)	1.699(8)
O(2)	C(4)	1.197(7)			

Angles

C(3)	P(1)	C(51)	110.8(3)	O(1)	C(2)	C(3)	122.0(6)
C(3)	P(1)	C(41)	111.9(3)	O(1)	C(2)	C(1)	117.9(6)
C(51)	P(1)	C(41)	105.8(3)	C(3)	C(2)	C(1)	120.1(5)
C(3)	P(1)	C(61)	113.1(3)	C(4)	C(3)	C(2)	121.8(6)
C(51)	P(1)	C(61)	108.6(3)	C(4)	C(3)	P(1)	127.3(5)
C(41)	P(1)	C(61)	106.3(3)	C(2)	C(3)	P(1)	110.4(5)
C(21)	P(2)	C(31)	110.6(3)	O(2)	C(4)	O(3)	115.8(7)
C(21)	P(2)	C(1)	114.2(3)	O(2)	C(4)	C(3)	129.9(7)
C(31)	P(2)	C(1)	109.8(3)	O(3)	C(4)	C(3)	114.3(7)
C(21)	P(2)	C(11)	109.5(3)	O(3)	C(5)	C(6)	112.0(8)
C(31)	P(2)	C(11)	108.4(3)	Cl(3)	C(7)	Cl(1)	110.4(5)
C(1)	P(2)	C(11)	103.9(3)	Cl(3)	C(7)	Cl(2)	109.9(4)
C(4)	O(3)	C(5)	120.7(6)	Cl(1)	C(7)	Cl(2)	108.8(4)
C(2)	C(1)	P(2)	115.2(5)				

The crystal structure of the title compound consists of triphenylphosphonium ylide and triphenyl phosphonium ion units linked by the 3-carboethoxy-2-oxopropane chain. A drawing of the molecule is shown in Figure 1, with the labeling of the atoms.
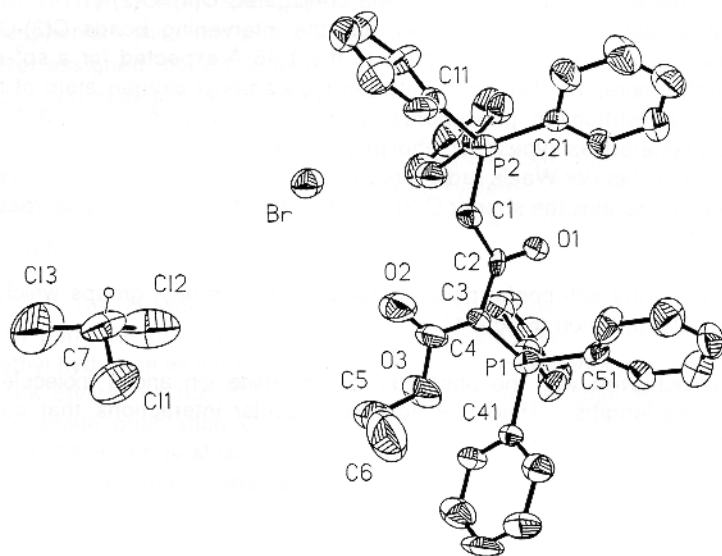
FIG. 1. Drawing of the molecule with the atoms labeled according to the tables.

The phosphorus atoms in the structure are of different types, P(1) corresponds to the phosphonium ylide and P(2) to the phosphonium ion. Both ylide and phosphonium salt have, as expected, a slightly distorted tetrahedral arrangement[7]. The mean bond angles C(phenyl)-P-C(phenyl) are 106.9(1.5) and 109.5(1.1)° and the C(phenyl)-P-C are 111.9(1.2) and 109.3(5.2)° for P(1) and P(2) respectively. The molecule adopts a near-eclipsed conformation referred to the phosphorus atoms as shown in Figure 2, with torsion angles C(11)-P(2)-P(1)-C(41), C(21)-P(2)-P(1)-C(51) and C(31)-P(2)-P(1)-C(61) equal to 6.8, 9.5 and 11.5°, respectively.
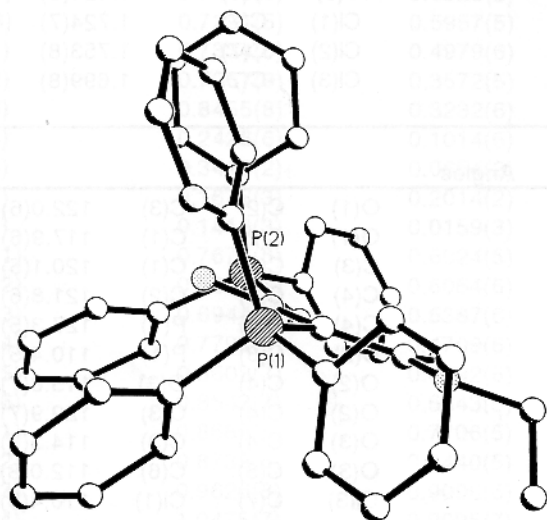
FIG. 2. View down the P(1)→P(2) directions showing the near-eclipsed conformation.

The most interesting feature of the structure is the bond between the ylidic carbon C(3) and the phosphorus atom P(1). It is known that stabilized ylides have a longer P=C bond due to the reduction of the negative charge at the ylidic carbon by the stabilizing groups[8]. The bond length P(1)-C(3) is 1.758(6)Å, a value between these for a P-C single bond (1.80-1.83 Å) and a P=C double bond (1.665 Å). It is considerably longer than the corresponding bond of 1.70(2)Å in the related compound N-p-bromophenylimino-triphenylphosphorane[9], but clearly indicates a considerable double bond character. The hybridization of C(3) is sp², where the sum of the bond angles is 359.5°. In the conjugatively stabilized ylides, the bond of the conjugated C(4)=O(2) (1.197 Å) is also shortened compared to a typical C=O bond (1.22 Å), and the intervening bonds C(3)-C(2) (1.436 Å) and C(3)-C(4) (1.405 Å) also are shortened relative to the 1.46 Å expected for a sp²-sp² bond between sp² carbons. Furthermore, the distances between the carbonyl oxygen atom of the keto group and the ylidic and phosphonium phosphorus atoms are 2.777 Å and 2.921 Å, respectively, which can be considered as typical of phosphorus oxygen interactions. These distances are lower than the sum of Van der Waals radii. Another attractive interaction is observed between P(1)-O(3) (3.025 Å) which explains the shorter C(3)-C(4) bond probably due to a decreased mesomeric effect in the ester group.

Another important result is the anti conformation between both carbonyl groups which is adopted to reduce the dipole-dipole repulsion (Figure 1).

The crystal packing is achieved with the uncoordinated bromide ion and a molecule of chloroform which has normal bond lengths. There are no intermolecular interactions that could correspond to hydrogen bonds.

NMR assignment

In Figure 3 are the ^{13}C chemical shifts (ppm) and in parentheses are the phosphorus-carbon coupling constants (J_{P-C} in Hz) for this phosphorane-phosphonium compound.
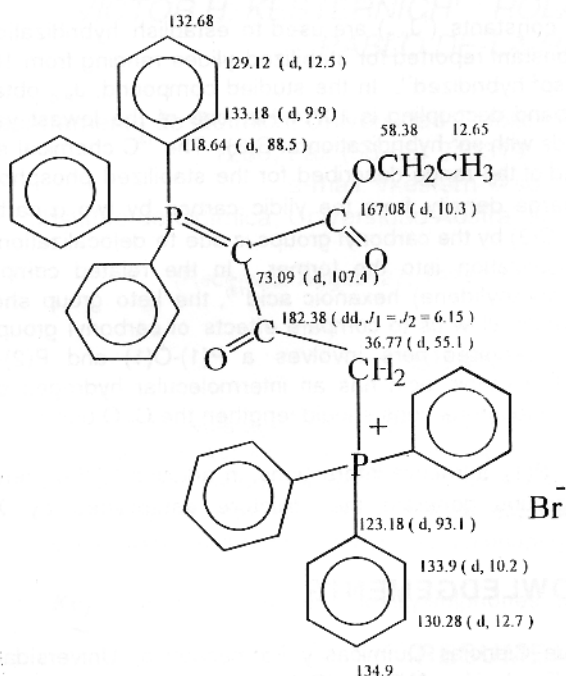

FIG. 3. [13]C Chemical shifts and phosphorus-carbon coupling constants in parenthesis.

The ^{31}P-NMR spectrum showed two signals corresponding to the phosphorus atoms of phosphonium ylide and phosphonium ion at δ 18.40 and 21.90 ppm, respectively. These signals were assigned by comparison with the ^{31}P-NMR signal of ethanoylcarboethoxymethylene-triphenylphosphorane (δ 17.73 ppm).

The ^{13}C shifts for the methylenic carbon atom in the phosphonium ion moiety and J_{P-C} 55.1 Hz are in agreement with values for similar systems[7,10,11]. These signals were assigned by a DEPT 135 spectrum. The ^{13}C shifts for the aromatic carbon atoms were assigned by using data for phosphonium salts[10].

The ^{1}H-NMR spectrum of the compound under study shows an unexpected high field shift (0.57 ppm) due to an anisotropic shielding by one phenyl group in the propeller conformation on the methyl hydrogen which requires that there is an important contribution of the conformer established in the crystal on the total conformer population in solution. This conformer clearly has the appropriate orientation of one of the phenyl groups and a methyl hydrogen at a distance of 3.667(2)Å which is shielding by this phenyl group. The high population of this conformer can be explained by virtue of delocalization of the ylidic double bond through both carbonyl groups which

499

adopt an anti conformation in order to limit the mutual electrostatic repulsion. Similar changes in chemical shifts has also been observed in some other acylethoxycarbonylalkyliden triphenylphosphoranes.

CONCLUSIONS

The pristine phosphonium salt contains a tetrahedrally hybridized phosphorus atom[12] whose geometry is maintained in the conversion into the phosphonium ylide reported here.

The phosphorus-carbon coupling constants ($^1J_{P-C}$) are used to establish hybridization at the ylidic carbon. The high value of this constant reported for stabilized ylides ranging from 108 to 131 Hz, indicates that the ylidic carbon is sp^2 hybridized[1]. In the studied compound, J_{P-C} obtained directly from ^{13}C spectrum with ^1H broad-band decoupling is 107.4 Hz, one of the lowest values reported for a stabilized ylide, which accords with sp^2 hybridization at C(3). The ^{13}C chemical shifts for the ylidic carbon fall in the downfield end of the range described for the stabilized phosphonium ylides[1] which reflects the removal of charge density from the ylidic carbon by two α-carbonyl groups. The stabilization of carbanion-like C(3) by the carbonyl groups is due to delocalization into ester and keto groups, with major delocalization into the former. In the related compound 6-ethoxycarbonyl-5-oxo-6-(triphenylphosphoranylidene) hexanoic acid[13], the keto group showed the more pronounced effect. Both compounds allow us to compare effects of carbonyl groups on ylidic carbons. However, the compound reported here involves a P(1)-O(1) and P(2)-O(1) intramolecular interaction, and the related hexanoic acid has an intermolecular hydrogen bond, which complicates this analysis because these interactions should lengthen the C=O bond.

Finally, O(1)-P(1), O(1)-P(2), O(3)-P(1), attractive interactions, in addition to the preferred anti conformation of both β-carbonyl groups generate the structure established by X-ray crystallography of the title compound.

ACKNOWLEDGEMENTS

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