C(37*B*)‡	0.159 (3)	0.0121 (6)	0.069 (2)	0.135 (11)
C(38)	0.5579 (10)	0.1475 (3)	0.4615 (10)	0.089 (3)
C(39)	0.4214 (11)	0.0847 (2)	0.6292 (10)	0.058 (3)
C(40)	0.2982 (12)	0.0418 (2)	0.6987 (9)	0.095 (4)
C(41)	0.5331 (10)	0.0504 (3)	0.4272 (10)	0.058 (3)
C(42)	0.7396 (9)	0.0219 (2)	0.5823 (9)	0.076 (3)
O(1)	0.4543 (6)	0.30249 (15)	0.3731 (5)	0.064 (2)
O(2)	0.2340 (6)	0.14577 (14)	0.4986 (5)	0.053 (2)
O(3)	0.3158 (8)	0.0602 (2)	0.5968 (6)	0.072 (2)
O(4)	0.4993 (8)	0.0916 (2)	0.7361 (6)	0.088 (2)
O(5)	0.6337 (7)	0.05010 (14)	0.5474 (6)	0.066 (2)
O(6)	0.5385 (7)	0.0303 (2)	0.3482 (6)	0.090 (2)
O(7)	0.1720 (8)	0.0343 (2)	0.1731 (6)	0.081 (2)
O(8)	0.3209 (7)	0.0666 (2)	0.1123 (7)	0.087 (2)
O(9)	0.5421 (6)	0.1264 (2)	0.5572 (6)	0.065 (2)

† Occupancy 0.453 (15). ‡ Occupancy 0.547 (15).

Table 2. *Selected geometric parameters (Å, °)*

P(1)—N(7)	1.643 (6)	C(32)—C(33)	1.575 (10)
P(1)—N(6)	1.655 (6)	C(33)—O(9)	1.415 (9)
P(1)—N(2)	1.667 (6)	C(33)—C(34)	1.509 (10)
P(1)—C(31)	1.731 (8)	C(33)—C(39)	1.514 (11)
N(2)—C(3)	1.415 (9)	C(34)—C(35)	1.351 (10)
N(2)—C(14)	1.516 (9)	C(34)—C(41)	1.453 (11)
C(3)—C(4)	1.371 (10)	C(35)—C(36)	1.494 (11)
C(3)—C(20)	1.471 (10)	C(36)—O(8)	1.233 (11)
C(4)—C(5)	1.448 (10)	C(36)—O(7)	1.272 (11)
C(4)—H(4*A*)	0.93	C(37*A*)—O(8)	1.56 (2)
C(5)—N(6)	1.288 (9)	C(37*B*)—O(7)	1.43 (2)
C(5)—C(27)	1.542 (10)	C(41)—O(6)	1.201 (9)
C(31)—C(32)	1.435 (10)	C(41)—O(5)	1.340 (10)
C(31)—C(35)	1.450 (10)	C(42)—O(5)	1.443 (9)
C(32)—O(2)	1.232 (8)		
N(7)—P(1)—N(6)	105.8 (3)	O(9)—C(33)—C(34)	117.1 (7)
N(7)—P(1)—N(2)	111.7 (3)	O(9)—C(33)—C(39)	104.9 (7)
N(6)—P(1)—N(2)	105.2 (3)	C(34)—C(33)—C(39)	113.9 (7)
C(3)—N(2)—C(14)	120.7 (6)	O(9)—C(33)—C(32)	110.9 (6)
C(3)—N(2)—P(1)	113.1 (5)	C(34)—C(33)—C(32)	102.2 (7)
C(14)—N(2)—P(1)	124.0 (5)	C(39)—C(33)—C(32)	107.6 (7)
C(4)—C(3)—N(2)	120.1 (7)	C(35)—C(34)—C(41)	125.3 (8)
C(4)—C(3)—C(20)	118.6 (7)	C(35)—C(34)—C(33)	110.2 (7)
N(2)—C(3)—C(20)	121.3 (7)	C(41)—C(34)—C(33)	124.2 (8)
C(3)—C(4)—C(5)	122.4 (8)	C(34)—C(35)—C(31)	112.5 (7)
C(3)—C(4)—H(4*A*)	118.8 (5)	C(34)—C(35)—C(36)	122.6 (8)
C(5)—C(4)—H(4*A*)	118.8 (5)	C(31)—C(35)—C(36)	124.9 (8)
N(6)—C(5)—C(4)	121.6 (7)	O(8)—C(36)—O(7)	125.3 (9)
N(6)—C(5)—C(27)	119.5 (8)	O(8)—C(36)—C(35)	119.1 (10)
C(4)—C(5)—C(27)	118.7 (8)	O(7)—C(36)—C(35)	115.6 (10)
C(5)—N(6)—P(1)	119.0 (6)	O(6)—C(41)—O(5)	122.1 (9)
C(32)—C(31)—C(35)	107.4 (7)	O(6)—C(41)—C(34)	126.6 (9)
C(32)—C(31)—P(1)	124.8 (6)	O(5)—C(41)—C(34)	111.3 (8)
C(35)—C(31)—P(1)	127.6 (6)	C(41)—O(5)—C(42)	116.9 (7)
O(2)—C(32)—C(31)	130.8 (7)	C(36)—O(7)—C(37*B*)	112.1 (12)
O(2)—C(32)—C(33)	121.6 (7)	C(36)—O(8)—C(37*A*)	107.8 (10)
C(31)—C(32)—C(33)	107.5 (7)		
N(2)—P(1)—N(6)—C(5)	32.5 (8)	N(2)—C(3)—C(4)—C(5)	8 (1)
N(6)—P(1)—N(2)—C(3)	−45.6 (7)	C(3)—C(4)—C(5)—N(6)	−25 (1)
P(1)—N(2)—C(3)—C(4)	29 (1)	C(4)—C(5)—N(6)—P(1)	0 (1)

Data were collected by profile analysis over all reflections (Lehman & Larsen, 1974; Grant & Gabe, 1978). The structure was solved by Patterson methods and the automatic phase expansion procedure using *DIRDIF* (Beurskens *et al.*, 1992). The structure was refined anisotropically by least-squares methods using *SHELXL*93 (Sheldrick, 1993). Geometrical calculations were made using *PARST* (Nardelli, 1983). All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray group VAX computers.

Data collection: *Diffractometer Control Software* (Enraf–Nonius, 1993). Cell refinement: *CRYSDA* (Beurskens *et al.*, 1992). Data reduction: *REFLEX* (local program). Program(s) used to solve structure: *DIRDIF*. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *EUCLID* (Spek, 1982). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, spectroscopy data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl Triphenylphosphoranylideneacetate: a Redetermination

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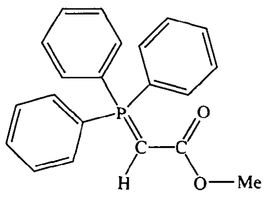
Abstract

The structure of the title compound, $C_{21}H_{19}O_2P$, has been redetermined to provide a more precise molecular geometry. Close C—H···O contacts, not remarked upon in the original paper, are discussed briefly.

Comment

The original structure determination of the title compound (MTPPA) (Cherepinskii-Malov, Aleksandrov, Gusev & Struchkov, 1972) reported an unusually long carbonyl bond length. It was not clear whether this feature of the molecular geometry was indicative of a sizable contribution of an enolate-like resonance structure in the bonding of the ylide or a limitation in the accuracy of the structure determination. The present work was undertaken to confirm the molecular geometry of MTPPA. The atomic numbering scheme and non-standard space-group setting were chosen for this work in order to conform with the originally published structure.



MTPPA

The present study shows the gross structural features of the original structure determination to be essentially correct. The bond-length e.s.d.'s for this work are about an order of magnitude smaller than the original work, as would be expected when comparing results from a diffractometer to work in which the intensities were estimated visually. Table 2 contains selected bond distances and angles for the MTPPA molecule. Comparing the relevant distances listed in Table 2 to the analogous quantities reported previously (Cherepinskii-Malov, Aleksandrov, Gusev & Struchkov, 1972) shows that the values for the P—C19 and C19—C20 bond lengths agree to within 1σ (using the 1972 e.s.d. values). The C20—O1 bonds differ by 5σ.

The Cambridge Structural Database (CSD; Allen & Kennard, 1993) was searched for carbonyl-stabilized ylides in order to establish an average carbonyl bond length for this class of compounds. A search on the C_3P—Csp^2—CO_2—C fragment yielded 27 fragments with 25 refcodes. The mean C═O bond length is 1.219 Å. The length of C20—O1 in the present work falls within one standard deviation (0.032 Å) of the mean for the sample population. Given this agreement of the present work with values of C═O distances obtained for similar structures, it is reasonable to conclude that the C═O bond length reported in the original structure determination is erroneous and is not reflective of a contribution to the bonding of any enolate-like resonance structure.

The other molecular geometric parameters fall within expected ranges. The average P—C(phenyl) bond length is 1.8111 (9) Å, with minimum and maximum values of 1.8029 (16) and 1.8207 (16) Å, respectively. The average C—C phenyl distance is 1.3804 (7) Å with minimum and maximum values of 1.364 (4) and 1.395 (3) Å, respectively. The averaging of the phenyl distances was performed with regard to neither the effect of the P substitution on the ring distances nor account of the systematic shortening of the distances owing to libration.

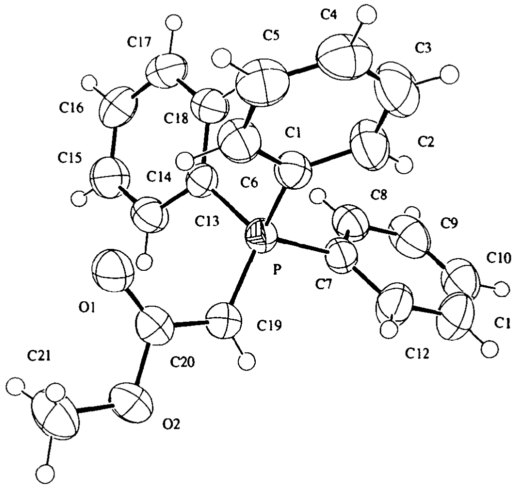


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of MTPPA showing displacement ellipsoids at the 50% probability level. For clarity, H atoms are drawn with arbitrary radii.

The intra- and intermolecular geometries were analysed using *PLATON* (Spek, 1990). This analysis indicates that O1 forms two close contacts which could be construed as C—H···O hydrogen bonds. One of these is an intramolecular hydrogen bond to H6, a phenyl H atom and the other is an intermolecular bond to H21*B*, a methyl H atom at a site ($\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$) relative to the asymmetric unit. The metric parameters for the intramolecular C—H···O hydrogen bond are C6···O1 = 3.147 (2), C6—H6 = 0.98 (2), H6···O1 = 2.30 (2) Å, and the C6—H6···O1 angle is 144 (2)°. The intermolecular C—H···O contact has the following geometry: C21···O1^{i} = 3.453 (3), C21—H21*B* = 0.98 (3), H21*B*···O1^{i} = 2.48 (3) Å, C21—H21*B*···O1^{i} = 170 (2)° [(i) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$].

Experimental

A powdered sample was obtained from Dr M. M. Kayser of the University of New Brunswick, Saint John. Crystals were grown by layering a CH_2Cl_2 solution of MTPPA with diethyl ether.

Crystal data

$C_{21}H_{19}O_2P$
M_r = 334.35

Mo $K\alpha$ radiation
λ = 0.71069 Å

Monoclinic
$P2_1/a$
$a = 19.0500\,(20)$ Å
$b = 8.9927\,(8)$ Å
$c = 10.4180\,(20)$ Å
$\beta = 101.05\,(1)^\circ$
$V = 1751.6\,(4)$ Å^3
$Z = 4$
$D_x = 1.268$ Mg m^{-3}
D_m not measured

Cell parameters from 24 reflections
$\theta = 15.00$–17.00°
$\mu = 0.16$ mm^{-1}
$T = 295$ K
Prism
0.68 × 0.45 × 0.28 mm
Colorless

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.96$, $T_{\max} = 1.00$
6111 measured reflections
3069 independent reflections

2999 observed reflections $[I_{\rm net} > 0.5\sigma(I_{\rm net})]$
$R_{\rm int} = 0.027$
$\theta_{\max} = 24.96^\circ$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 80 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.051$
$S = 1.61$
3069 reflections
294 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.055 (6)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2*B*)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
P	0.07733 (2)	0.29722 (4)	0.79115 (4)	0.0391 (2)
C1	0.04881 (8)	0.47891 (17)	0.72347 (15)	0.0435 (8)
C2	−0.02056 (11)	0.5299 (2)	0.7182 (2)	0.0665 (12)
C3	−0.04068 (14)	0.6696 (3)	0.6677 (3)	0.0802 (15)
C4	0.00764 (13)	0.7588 (2)	0.6238 (2)	0.0682 (12)
C5	0.07689 (13)	0.7111 (2)	0.6300 (2)	0.0653 (12)
C6	0.09726 (10)	0.5713 (2)	0.67855 (18)	0.0551 (10)
C7	−0.00045 (8)	0.21395 (17)	0.83669 (17)	0.0445 (9)
C8	−0.00976 (10)	0.20718 (19)	0.96524 (19)	0.0507 (10)
C9	−0.07245 (12)	0.1499 (2)	0.9941 (3)	0.0675 (12)
C10	−0.12554 (12)	0.1006 (2)	0.8960 (3)	0.0743 (15)
C11	−0.11663 (12)	0.1032 (3)	0.7688 (3)	0.0775 (15)
C12	−0.05431 (10)	0.1591 (2)	0.7381 (2)	0.0628 (11)
C13	0.14069 (8)	0.33761 (16)	0.93994 (15)	0.0404 (8)
C14	0.19365 (9)	0.2351 (2)	0.98456 (18)	0.0512 (9)
C15	0.24101 (11)	0.2587 (2)	1.1007 (2)	0.0647 (11)
C16	0.23629 (10)	0.3855 (2)	1.17257 (19)	0.0604 (10)
C17	0.18430 (10)	0.4886 (2)	1.12821 (18)	0.0582 (10)
C18	0.13644 (9)	0.46599 (19)	1.01226 (17)	0.0513 (9)
C19	0.10854 (9)	0.17500 (19)	0.69037 (16)	0.0458 (9)
C20	0.17005 (9)	0.20613 (18)	0.64121 (15)	0.0457 (8)
C21	0.24951 (15)	0.1215 (3)	0.5060 (3)	0.0769 (15)
O1	0.20862 (7)	0.31590 (14)	0.66532 (14)	0.0628 (8)
O2	0.18650 (7)	0.09685 (14)	0.55961 (12)	0.0605 (7)

Table 2. *Selected geometric parameters (Å, °)*

P—C1	1.8207 (16)	C19—C20	1.394 (2)
P—C7	1.8029 (16)	C20—O1	1.227 (2)
P—C13	1.8097 (16)	C20—O2	1.3743 (19)
P—C19	1.7039 (17)	C21—O2	1.435 (3)
C1—P—C19	116.98 (8)	C19—C20—O1	126.76 (15)
C7—P—C19	107.20 (8)	C19—C20—O2	113.02 (15)
C13—P—C19	113.77 (8)	O1—C20—O2	120.21 (15)
P—C19—C20	120.93 (13)		

During data reduction, the intensity data were corrected for Lorentz and polarization effects. The literature coordinates were used as the starting point for the structure refinement. All non-H atoms were allowed to refine with anisotropic displacement parameters. H-atom positional and isotropic displacement parameters were allowed to refine. The range of C—H distances varied from 0.862 (21) to 1.017 (25) Å and the range of isotropic displacement parameters varied from 0.048 (5) to 0.119 (11) Å^2. The calculated structure factors included corrections for anomalous dispersion (Cromer, 1974). The final cycles of refinement included an extinction correction (Larson, 1970). Except for calculations using *PLATON*, all crystallographic calculations were performed using the *NRCVAX* program package (Gabe, Le Page, Charland, Lee & White, 1989).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES* (Jan 94 Version).

Dr M. M. Kayser of the University of New Brunswick, St. John, Canada is acknowledged for kindly supplying the powdered sample of MTPPA.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1237). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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