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[1-(Ethoxycarbonyl)-1-cyclopentyl]triphenylphosphonium Bromide, $[(C_6H_5)_3PC(C_4H_8)(COOC_2H_5)]Br$

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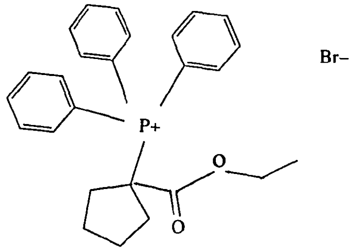
Abstract

The crystal structure of the title phosphonium salt consists of a tetrahedral $(C_6H_5)P^+C(C_4H_8)(COOCH_2CH_3)$ cation and a Br^- anion. The triphenylphosphonium group has P—C(phenyl) distances which are equal within experimental error [mean 1.802 (9) Å] and is attached directly to an endocyclic tertiary C atom with a larger P—C distance of 1.857 (8) Å. The tetrahedral C—P—C angles range from 104.9 (4) to 114.4 (4)°. The carbonyl O atom of the ethoxycarbonyl group is located on the opposite side of the positively charged P atom.

Comment

The title compound (I) was synthesized by a cyclization reaction between ethoxycarbonylmethylidenetriphenylphosphorane and 1,4-dibromobutane. The alkaline hydrolysis of this salt yielded triphenylphosphine oxide, cyclopentanecarboxylic acid and ethylcyclopentanecarboxylate (Araya-Maturana & Castañeda, 1993).



(I)

The homologous R_1-triphenylphosphonium salts (R_1 = 1-ethoxycarbonylcyclopropyl and 1-ethoxycarbonylcyclobutyl), synthesized by reaction of cycloalkylidenetriphenylphosphorane with chloroformate, have been known for some yeras (Bestmann, Denzel, Kuntsmann & Lengyel, 1968; Fuchs, 1974). In addition, the related 1-carboxycycloalkyltriphenylphosphonium salt has been synthesized by the reaction between cycloalkylidenetriphenylphosphorane and carbon dioxide (Bestmann, Denzel & Salbaum, 1974). This homologous series includes the cyclic compounds with three to seven C atoms, with the exception of the cyclopentane derivative.

The present compound contains discrete $(C_6H_5)_3P^+(C_4H_8)(COOCH_2CH_3)$ and Br^- ions. The cation exhibits the usual tetrahedral coordination at P (Table 2). The equal P—C(phenyl) distances compare well with those reported previously for other triphenylphosphonium salts (Ferguson, McCrindle, McAlees & Rice, 1988; Bélanger & Beauchamp, 1993). The phenyl rings are essentially planar (mean deviation from plane = 0.006, maximum deviation = 0.014 Å) with normal bond distances and angles.

The orientation of the carbonyl C=O bond can be compared with that in the related ethoxycarbonylmethyltriphenylphosphonium cation. The carbonyl bond in the latter can adopt orientations towards and away from the P ion, as was observed in the related phosphonium counter ions of some polymolybdate salts reported by Arzoumanian *et al.* (1985). In the present compound, the carbonyl C(6)=O(2) bond is rotated away from the P ion, with a relative orientation almost identical to that present in the phosphonium counter ion of one of the

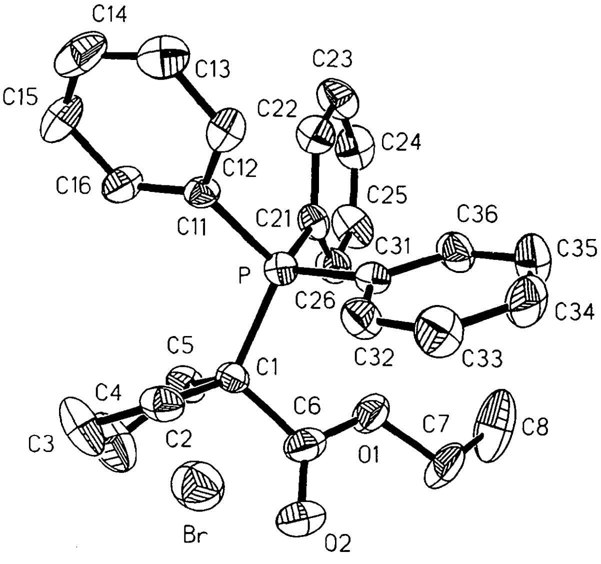


Fig. 1. View of the molecular structure with labelling of non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

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reported polymolybdate salts, $[(C_6H_5)_3PCH_2COOCH_2CH_3]_2^+[Mo_6O_{19}]^{2-}$.

Short interionic contacts involve the Br anion and C atoms of the phenyl rings of symmetrically related cations, the shortest of these being Br···C(15) = 3.710 (9) Å.

Experimental

Crystal data

$C_{26}H_{28}O_2P^+.Br^-$
$M_r = 483.4$
Orthorhombic
$P2_12_12_1$
$a = 8.875$ (2) Å
$b = 9.826$ (2) Å
$c = 26.468$ (5) Å
$V = 2308.2$ (8) Å^3
$Z = 4$
$D_x = 1.391$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2$–15°
$\mu = 1.870$ mm^{-1}
$T = 293$ K
Parallelepiped
0.34 × 0.14 × 0.10 mm
Colourless

Data collection

Siemens $R3m/V$ diffractometer
ω scans
Absorption correction: none
3051 measured reflections
2325 independent reflections
1271 observed reflections [$F > 4.0\sigma(F)$]

$R_{\rm int} = 0.022$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -25 \rightarrow 31$
2 standard reflections monitored every 98 reflections intensity variation: <2%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.031$
$S = 1.006$
1271 reflections
272 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0002F^2]$

$(\Delta/\sigma)_{\rm max} = 0.012$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

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	$U_{\rm eq}$
Br	0.6786 (1)	1.0262 (1)	0.1381 (1)	0.047 (1)
P	0.3540 (2)	0.5374 (2)	0.1345 (1)	0.028 (1)
O(1)	0.6081 (6)	0.4206 (5)	0.0869 (2)	0.043 (2)
O(2)	0.7822 (7)	0.5594 (8)	0.1191 (2)	0.068 (3)
C(1)	0.5446 (8)	0.5301 (8)	0.1634 (3)	0.028 (3)
C(2)	0.5833 (10)	0.6640 (7)	0.1927 (3)	0.037 (3)
C(3)	0.6293 (12)	0.6169 (9)	0.2450 (3)	0.065 (4)
C(4)	0.6673 (13)	0.4748 (9)	0.2429 (3)	0.068 (4)
C(5)	0.5645 (10)	0.4122 (7)	0.2027 (3)	0.037 (3)
C(6)	0.6598 (11)	0.5061 (9)	0.1208 (3)	0.040 (4)
C(7)	0.6998 (11)	0.3922 (9)	0.0424 (3)	0.060 (4)
C(8)	0.6349 (14)	0.2728 (10)	0.0168 (3)	0.090 (6)
C(11)	0.2269 (9)	0.6331 (8)	0.1740 (3)	0.027 (3)
C(12)	0.1319 (10)	0.7308 (8)	0.1520 (3)	0.037 (3)
C(13)	0.0202 (11)	0.7948 (9)	0.1817 (3)	0.044 (4)
C(14)	0.0102 (12)	0.7627 (9)	0.2318 (3)	0.053 (4)
C(15)	0.1050 (11)	0.6669 (9)	0.2540 (4)	0.047 (4)
C(16)	0.2123 (10)	0.6018 (8)	0.2246 (3)	0.036 (3)
C(21)	0.2651 (10)	0.3742 (8)	0.1267 (3)	0.029 (3)
C(22)	0.1068 (11)	0.3712 (10)	0.1264 (3)	0.039 (4)
C(23)	0.0285 (11)	0.2507 (10)	0.1209 (3)	0.047 (4)
C(24)	0.1098 (14)	0.1303 (11)	0.1165 (3)	0.050 (4)
C(25)	0.2638 (13)	0.1310 (10)	0.1174 (3)	0.046 (4)
C(26)	0.3428 (10)	0.2517 (8)	0.1221 (3)	0.037 (3)
C(31)	0.3689 (8)	0.6253 (8)	0.0750 (3)	0.028 (3)
C(32)	0.4350 (10)	0.7541 (8)	0.0733 (3)	0.037 (3)
C(33)	0.4525 (11)	0.8217 (9)	0.0282 (3)	0.047 (4)
C(34)	0.4034 (11)	0.7603 (11)	−0.0154 (3)	0.054 (4)
C(35)	0.3360 (13)	0.6324 (10)	−0.0150 (3)	0.056 (4)
C(36)	0.3226 (10)	0.5652 (8)	0.0302 (3)	0.039 (3)

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

P—C(1)	1.857 (8)	C(1)—C(2)	1.565 (11)
P—C(11)	1.803 (8)	C(1)—C(5)	1.569 (11)
P—C(21)	1.800 (9)	C(2)—C(3)	1.517 (12)
P—C(31)	1.802 (8)	C(3)—C(4)	1.438 (13)
O(1)—C(6)	1.313 (10)	C(4)—C(5)	1.529 (13)
O(1)—C(7)	1.458 (10)	C(1)—C(6)	1.539 (11)
O(2)—C(6)	1.206 (11)	C(7)—C(8)	1.472 (13)
C(1)—P—C(11)	110.6 (3)	C(2)—C(1)—C(5)	105.5 (6)
C(1)—P—C(21)	114.4 (4)	C(1)—C(2)—C(3)	104.8 (6)
C(11)—P—C(21)	104.9 (4)	C(2)—C(3)—C(4)	108.8 (7)
C(1)—P—C(31)	108.1 (3)	C(3)—C(4)—C(5)	106.1 (8)
C(11)—P—C(31)	107.6 (4)	C(1)—C(5)—C(4)	103.4 (6)
C(21)—P—C(31)	111.0 (4)	P—C(1)—C(2)	111.8 (5)
P—C(1)—C(6)	108.1 (5)	P—C(1)—C(5)	113.8 (5)
C(2)—C(1)—C(6)	110.2 (7)	C(6)—O(1)—C(7)	118.7 (7)
C(5)—C(1)—C(6)	107.3 (6)	O(1)—C(6)—O(2)	124.5 (8)
O(1)—C(6)—C(1)	111.5 (7)	O(2)—C(6)—C(1)	124.0 (7)
O(1)—C(7)—C(8)	107.8 (8)		

The structure was solved by direct methods and refined by full-matrix least-squares calculations using *SHELXTL-Plus* (Sheldrick, 1992). H atoms were placed at geometrically idealized positions with C—H = 0.96 Å and were allowed to ride over their parent C atoms with their corresponding equivalent isotropic displacement parameters. The absolute structure was determined using the *SHELXTL* routine to refine the η parameter, which converged to +1.07 (5) (Rogers, 1981).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Araya-Maturana, R. & Castañeda, F. (1993). *Phosphorus Sulfur Silicon*, **81**, 165–172.

Arzoumanian, H., Baldy, A., Lai, R., Odreman, A., Metzger, J. & Pierrot, M. (1985). *J. Organomet. Chem.* **295**, 343–352.

Bélanger, S. & Beauchamp, A. L. (1993). *Acta Cryst.* C**49**, 388–391.

Bestmann, H. J., Denzel, Th., Kunstmann, R. & Lengyel, J. (1968). *Tetrahedron Lett.* pp. 2895–2898.

Bestmann, H. J., Denzel, Th. & Salbaum, H. (1974). *Tetrahedron Lett.* pp. 1275–1276.

Ferguson, G., McCrindle, R., McAlees, A. J. & Rice, R. E. (1988). *Acta Cryst.* C**44**, 53–56.

Fuchs, P. L. (1974). *J. Am. Chem. Soc.* **96**, 1607–1609.
Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.
Sheldrick, G. M. (1992). *SHELXTL-Plus*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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7-Dimethylaminocyclopenta[*c*]coumarin, in Two Polymorphic Forms

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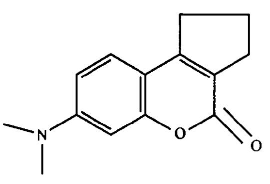
Abstract

Polymorphism in aminocoumarins has been observed in only one other instance [Jasinski & Paight (1994). *Acta Cryst.* C**50**, 1928–1930]. This structure, $C_{14}H_{15}NO_2$, represents the first reported observation of a non-centrosymmetric moiety in an aminocoumarin laser-dye compound. These differences, as well as those observed in luminescence changes, may result from the crystallization of C13 in an out-of-plane position in the cyclopenta[*c*] ring of polymorph (II). The crystal structures of both polymorphs [(I) and (II)] are stabilized by van der Waals forces.

Comment

The title compound is also known as Coumarin 138 (Kodak, USA). Aminocoumarin laser dyes, such as the title compound, are used in bicyclic dye laser-stability studies (Fletcher, 1977; Fletcher & Bliss, 1978), as fluorescent brightners and photographic sensitizers (Baczynski, Targowski, Sietek & Radomska, 1990), and as analytical fluorescent probes in micelles (Abdel-Mottalaeb, Antonious, Ali, Ismail, El-Sayed & Sherief, 1992). Both polymorphs were obtained from the same crystal crop in a fashion similar to that for (±)-β-promedol alcohol (De Camp & Ahmed, 1972). Under a black light, the centrosymmetric polymorph crystals, (I), produce a green luminescence and the non-centrosymmetric polymorph crystals, (II), give a purple luminescence.



Bond lengths and angles in the coumarin moiety are normal (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985; Murthy, Ramamurthy & Venkatesan, 1988). The dihedral angles between the least-squares planes of the planar pyrone [χ^2 = 19.4 (I), 24.4 (II)] and benzene [χ^2 = 15.1 (I), 5.6 (II)] moieties are 1.21 (3)° in (I), and 1.53 (2)° in (II). The dihedral angles between the least-squares planes of the cyclopenta[*c*] ring [χ^2 = 15.6 (I), 346.9 (II)] are tilted slightly more with respect to the benzene-ring plane, 3.72 (3) and 2.47 (2)° in (I) and (II), respectively. The torsion angles C2—C3—C4—C10 [−0.48 (4) (I), −0.9 (5)° (II)], C2—C3—C4—C14 [178.6 (3) (I), 179.6 (3)° (II)] and C10—C4—C3—C12 [−177.5 (2) (I), −179.5 (3)° (II)] indicate planar relationships that are almost identical for both polymorphs. However, the torsion angles C3—C12—C13—C14 [−0.66 (45) (I), 9.6 (5)° (II)] and C4—C14—C13—C12 [1.5 (5) (I), −9.4 (5)° (II)] indicate a deviation from planarity in polymorph (II) resulting from the displacement of C13 from the least-squares plane of the cyclopenta[*c*] ring. Therefore, the difference in luminescence behavior, along with the observed polymorphism of the two structures, may be associated with the crystallization of C13 in an out-of-plane position in (II).

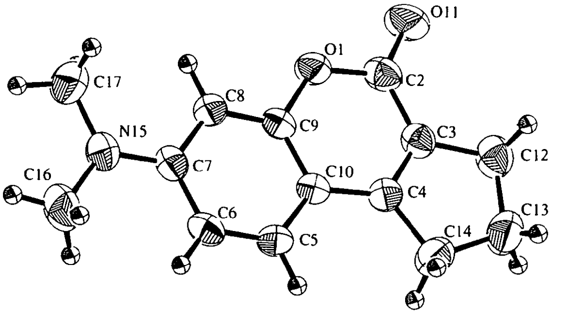


Fig. 1. *ORTEP* (Johnson, 1965) drawing and atom-numbering scheme for 7-dimethylaminocyclopenta[*c*]coumarin in two polymorphic modifications. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystals of both modifications of the title compound (Sigma, USA) were grown from acetonitrile in the same beaker by slow evaporation.

Compound (I)

Crystal data

$C_{14}H_{15}NO_2$
M_r = 229.28
Orthorhombic
Pbca
a = 21.937 (8) Å
b = 15.327 (3) Å
c = 6.924 (1) Å

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 10.6–16.9°
μ = 0.082 mm^{-1}
T = 296 K