

C4—N4—C7'		120.9 (2)
N4—C7'—O7'		124.9 (2)
N4—C7'—O8'		110.0 (2)
O7'—C7'—O8'	124.7 (2)	125.1 (2)
C7'—O8'—C9'	122.0 (3)	121.2 (2)
O8'—C9'—C10'	109.9 (3)	110.5 (2)
O8'—C9'—C11'	110.1 (3)	109.7 (2)
O8'—C9'—C12'	102.5 (3)	102.5 (2)
C10'—C9'—C11'	112.2 (3)	112.4 (2)
C10'—C9'—C12'	111.3 (3)	110.1 (2)
C11'—C9'—C12'	110.4 (3)	111.2 (2)
C1—C6—C5—C4	-56.7 (6)	56.8 (3)
C6—C5—C4—C3	60.9 (5)	-55.4 (3)
C5—C4—C3—C2	-58.5 (4)	55.8 (3)
C4—C3—C2—C1	53.1 (5)	-55.8 (3)
C3—C2—C1—C6	-47.7 (6)	55.1 (3)
C2—C1—C6—C5	48.9 (6)	-55.8 (3)
C6—C1—C1'—O1'	1.4 (9)	-176.2 (3)
C1—C1'—O2'—C2'	169.4 (5)	-176.1 (2)
O4—C4—C3—N3	56.8 (4)	
C4—C3—N3—C7'	-147.7 (3)	
C2—C3—N3—C7'	90.2 (4)	
C3—N3—C7'—O8'	-169.3 (3)	
N3—C7'—O8'—C9'	-175.2 (3)	
O3—C3—C4—N4		54.9 (3)
C3—C4—N4—C7'		-163.1 (2)
C5—C4—N4—C7'		74.7 (3)
C4—N4—C7'—O8'		179.2 (2)
N4—C7'—O8'—C9'		-178.1 (2)
C7'—O8'—C9'—C12'	179.2 (3)	175.5 (2)

The structures were solved by direct methods and refined by full-matrix least squares. The methyl H-atom coordinates were calculated and the atoms given a common isotropic temperature factor. The coordinates of the other H atoms were refined and the atoms were given individual isotropic temperature factors. Calculations were performed on a VAX 8800 computer.

For both compounds, data collection: Rigaku AFC software; cell refinement: Rigaku AFC software; data reduction: Rigaku AFC software; program(s) used to solve structures: *SHELX76* (Sheldrick, 1976); program(s) used to refine structures: *SHELX76*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *Xtal3.0* (Hall & Stewart, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Ball, J. B., Wong, M. G., Capuano, B., Gulbis, J. M., Mackay, M. F. & Alewood, P. F. (1990). *J. Heterocycl. Chem.* **26**, 161–169.
- Bendetti, E., Pedone, C., Toniolo, C., Némethy, G., Pottle, M. S. & Scheraga, H. A. (1980). *Int. J. Pept. Protein Res.* **16**, 156–17.
- Campbell, M. & McLeish, M. J. (1993). *J. Chem Res. (S)*, pp. 148–149.
- Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structures*, Vol. 1, pp. 18–19. New York: Plenum.
- Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal3.0 Reference Manual*. Univ. of Western Australia, Australia, and Maryland, USA.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

*Acta Cryst.* (1994). **C50**, 1738–1741

## Benzoylmethylenetriphenylphosphorane, C<sub>26</sub>H<sub>21</sub>OP

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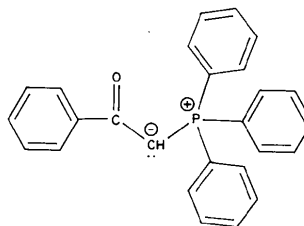
(Received 18 August 1993; accepted 28 January 1994)

## Abstract

The air-stable phosphorane (2-oxo-2-phenyltri-phenylphosphoniummethylide) is shown to be a resonance hybrid of an ylene, ylidic and enolate canonical assembly. The geometry around the P atom is nearly tetrahedral. The O atom is oriented *cis* to the P atom. The phenyl ring of the benzoyl group is twisted with respect to the plane containing the carbonyl group.

## Comment

Phosphoranes of the type  $R_3PCHCOC_6H_5$  ( $R = \text{aryl}$ ) can coordinate to metals through either C or O atoms. We have recently prepared metal derivatives of the title ylide. The crystal and molecular structure of the benzene solvate (Shao, Jin, Tang, Huang & Huang, 1982) of the title compound, which crystallized in space group  $P2_1/c$ , was reported without e.s.d.'s for the bond parameters. This structural investigation has been undertaken to obtain more accurate metrical parameters for the title compound, (I), and to see how they vary with a change in delocalization in the metal derivatives as well as in other resonance-stabilized ylides.



(I)

The crystal structure analysis reveals that there are two independent molecules in the asymmetric unit of the  $P2/n$  cell. The crystallographic numbering scheme is given in Fig. 1. The  $P1-C1-C2-O1-C26$  and  $P1'-C1'-C2'-O1'-C26'$  moieties of the two independent molecules can be superimposed with a maximum distance between topologically equivalent atoms of 0.14 Å. The bond lengths and bond angles of both molecules are listed in Table 2. The bond lengths of the two molecules are identical to within the limits of standard deviations, but there are significant differences in the analogous bond angles. We

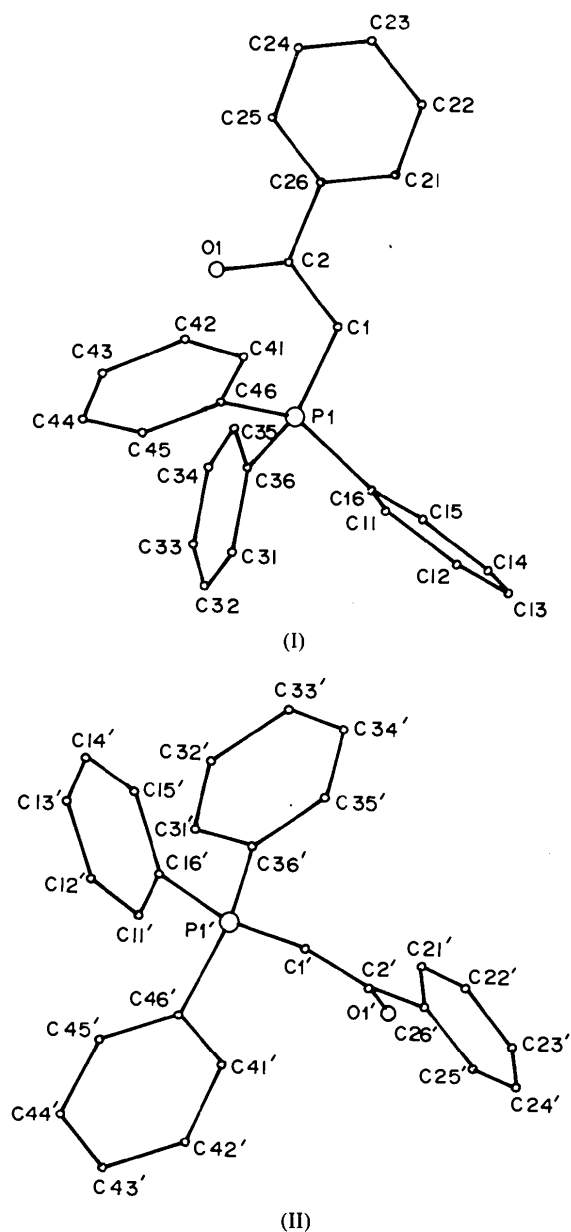


Fig. 1. Crystallographic atom-labelling schemes for molecules 1 and 2 (primed).

ascribe these differences to crystal-packing effects. The  $P1-C1$  and  $P1'-C1'$  bond lengths of 1.716 (5) and 1.725 (4) Å, respectively, are shorter than the other  $P-C$  bonds [1.816 (5), 1.815 (4), 1.803 (4) Å in molecule 1; 1.811 (4), 1.810 (4), 1.802 (5) in molecule 2] observed in the title compound (Fig. 1), and longer than the equivalent bond length of 1.66 Å reported for methylenetriphenylphosphorane (Bart, 1969), which shows partial double-bond character for these two bonds.  $C2-O1$  [1.265 (7) Å] and  $C2'-O1'$  [1.247 (7) Å] are longer than the  $C=O$  bond lengths in ketones (1.210 Å; Allen *et al.*, 1987). The  $C1-C2$  [1.407 (8) Å] and  $C1'-C2'$  [1.399 (8) Å] bonds are also longer than the typical  $C=C$  distance (1.331 Å; Allen *et al.*, 1987). These bond distances suggest resonance delocalization in the molecule (Fig. 3).

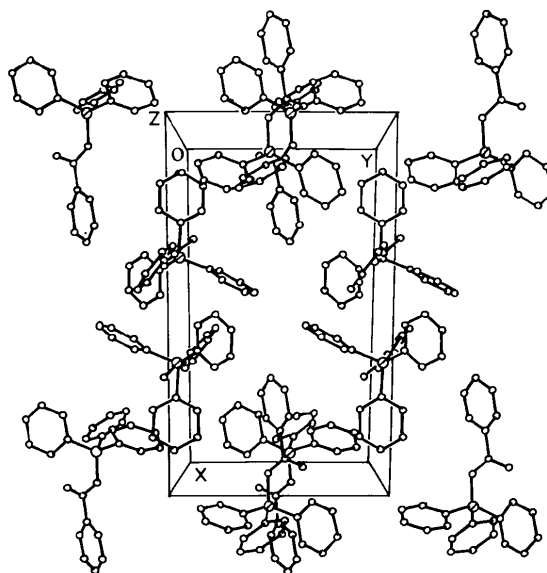


Fig. 2. Crystal structure of benzoylmethylenetriphenylphosphorane.

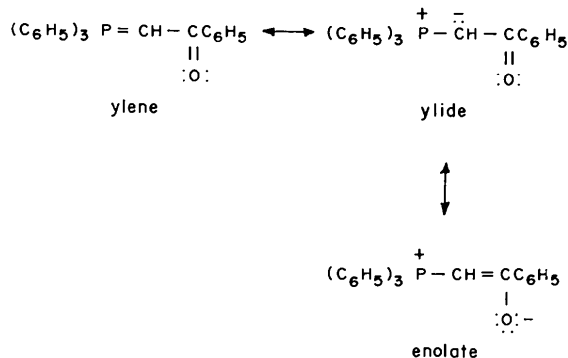


Fig. 3. Resonance in the title compound.

The resonance formulation is supported by the near planarity of P1, C1, O1, C2 and C26 (molecule 1) and P1', C1', O1', C2' and C26' (molecule 2). The torsion angles O1—C2—C1—P1 and O1'—C2'—C1'—P1' of 0.9 (8) and -2.2 (9)°, respectively, also indicate resonance. The phenyl ring of the benzoyl group is twisted with respect to the plane containing the carbonyl group through angles of 13.8 (2) and 21.7 (2)° for molecules 1 and 2, respectively.

Bond angles of 115.3 (4) and 123.0 (4)° for P1—C1—C2 and P1'—C1'—C2', respectively, indicate a distorted trigonal arrangement about C1 and C1'. The non-bonded distances P1...O1 and P1'...O1' of 2.868 (5) (molecule 1) and 3.091 (5) Å (molecule 2), respectively, are significantly shorter than the sum of the van der Waals radii of P and O (3.3 Å; Dunitz, 1979), indicating a strong intramolecular interaction between P<sup>+</sup> and O<sup>-</sup> charge centres, which leads to the *cis* orientation. The replacement of the H atom by a halogen on the ylidic C atom has no significant effect on the bond lengths and hence on the conjugation of the P=C—CX—C=O linkage (Table 3).

The bond lengths within the molecules of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCHCOC<sub>6</sub>H<sub>5</sub>, as shown in Table 2, are an order of magnitude more accurate than those of its benzene solvate (Shao, Jin, Tang, Huang & Huang, 1982). The bond angle of 121.1° around the ylidic C atom (P—C—C) reported for the benzene solvate, lies between the values of 115.3 (4) and 123.0 (4)° observed for the corresponding angle in the unsolvated molecules 1 and 2, respectively, in the present investigation.

## Experimental

The title compound was prepared according to the reported procedure of Ramirez & Dershowitz (1957). The phosphonium salt (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>CH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>Br<sup>-</sup>, formed by the action of phenacyl bromide on triphenylphosphine, was treated with an aqueous solution of sodium carbonate. The resulting solid was recrystallized from a benzene-petroleum mixture (m.p. 451–452 K). Density *D<sub>m</sub>* was measured by flotation in heptane and CCl<sub>4</sub>.

### Crystal data

C<sub>26</sub>H<sub>21</sub>OP  
*M<sub>r</sub>* = 380.4  
 Monoclinic  
*P*2/*n*  
*a* = 18.978 (7) Å  
*b* = 10.921 (5) Å  
*c* = 19.620 (11) Å  
 $\beta$  = 105.02 (4)°  
*V* = 3927 (3) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.287 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.28 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 5–31°  
 $\mu$  = 0.15 mm<sup>-1</sup>  
*T* = 148 K  
 Plate  
 0.42 × 0.18 × 0.1 mm  
 White

### Data collection

Nicolet R3m diffractometer  
 $\omega$  scans  
 Absorption correction: empirical  
 $T_{\min}$  = 0.775,  $T_{\max}$  = 0.785  
 8058 measured reflections  
 7758 independent reflections  
 3140 observed reflections  
 $[I > 3\sigma(I)]$

$R_{\text{int}}$  = 0.022  
 $\theta_{\text{max}}$  = 26°  
 $h = 0 \rightarrow 24$   
 $k = 0 \rightarrow 14$   
 $l = -25 \rightarrow 25$   
 3 standard reflections monitored every 100 reflections  
 intensity variation: none

### Refinement

Refinement on *F*  
 $R = 0.0625$   
 $wR = 0.0476$   
 $S = 1.5726$   
 3140 reflections  
 410 parameters  
 Only coordinates of H atoms refined

$w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0.103$   
 $\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$   
 Atomic scattering factors from SHELX76 (Sheldrick, 1976)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
P1	0.1535 (1)	-0.0031 (2)	0.0775 (1)	0.019 (1)
P1'	0.5679 (1)	0.5514 (1)	0.1474 (1)	0.018 (1)
O1	0.2005 (2)	0.0818 (4)	-0.0419 (2)	0.028 (2)
O1'	0.4508 (2)	0.3905 (4)	0.1875 (2)	0.026 (2)
C1	0.1272 (3)	-0.0647 (5)	-0.0057 (2)	0.018 (2)
C2	0.1568 (3)	-0.0076 (5)	-0.0563 (3)	0.021 (2)
C1'	0.4739 (2)	0.5583 (5)	0.1213 (3)	0.017 (2)
C2'	0.4291 (3)	0.4774 (5)	0.1462 (3)	0.021 (2)
C11	0.0434 (2)	-0.1047 (3)	0.1269 (2)	0.034 (3)
C12	0.0130 (2)	-0.1878 (3)	0.1651 (2)	0.039 (3)
C13	0.0577 (2)	-0.2697 (3)	0.2114 (2)	0.036 (3)
C14	0.1329 (2)	-0.2684 (3)	0.2195 (2)	0.036 (3)
C15	0.1634 (2)	-0.1852 (3)	0.1813 (2)	0.032 (3)
C16	0.1186 (2)	-0.1034 (3)	0.1350 (2)	0.022 (3)
C21	0.0764 (2)	-0.1302 (3)	-0.1571 (2)	0.028 (3)
C22	0.0566 (2)	-0.1648 (3)	-0.2280 (2)	0.026 (2)
C23	0.0963 (2)	-0.1222 (3)	-0.2738 (2)	0.026 (2)
C24	0.1560 (2)	-0.0449 (3)	-0.2487 (2)	0.029 (2)
C25	0.1758 (2)	-0.0103 (3)	-0.1778 (2)	0.022 (2)
C26	0.1360 (2)	-0.0529 (3)	-0.1321 (2)	0.018 (2)
C21'	0.3171 (2)	0.5699 (3)	0.0609 (2)	0.022 (2)
C22'	0.2423 (2)	0.5936 (3)	0.0419 (2)	0.029 (3)
C23'	0.1983 (2)	0.5477 (3)	0.0830 (2)	0.031 (2)
C24'	0.2291 (2)	0.4782 (3)	0.1430 (2)	0.034 (3)
C25'	0.3039 (2)	0.4545 (3)	0.1619 (2)	0.030 (2)
C26'	0.3479 (2)	0.5003 (3)	0.1208 (2)	0.018 (2)
C45'	0.6492 (2)	0.6723 (3)	0.2687 (2)	0.035 (3)
C44'	0.6772 (2)	0.6844 (3)	0.3415 (2)	0.045 (3)
C43'	0.6646 (2)	0.5932 (3)	0.3867 (2)	0.034 (3)
C42'	0.6239 (2)	0.4899 (3)	0.3591 (2)	0.043 (3)
C41'	0.5959 (2)	0.4778 (3)	0.2863 (2)	0.038 (3)
C46'	0.6086 (2)	0.5690 (3)	0.2411 (2)	0.019 (2)
C11'	0.5710 (2)	0.7937 (4)	0.1100 (2)	0.024 (3)
C12'	0.5885 (2)	0.8920 (4)	0.0720 (2)	0.030 (2)
C13'	0.6322 (2)	0.8733 (4)	0.0257 (2)	0.028 (3)
C14'	0.6583 (2)	0.7564 (4)	0.0173 (2)	0.029 (3)
C15'	0.6407 (2)	0.6581 (4)	0.0552 (2)	0.027 (3)
C16'	0.5970 (2)	0.6767 (4)	0.1015 (2)	0.016 (2)
C35'	0.5654 (1)	0.3355 (3)	0.0713 (2)	0.021 (2)
C34'	0.5973 (1)	0.2332 (3)	0.0489 (2)	0.022 (2)
C33'	0.6711 (1)	0.2082 (3)	0.0778 (2)	0.028 (3)
C32'	0.7130 (1)	0.2854 (3)	0.1292 (2)	0.028 (2)
C31'	0.6811 (1)	0.3877 (3)	0.1517 (2)	0.024 (2)

C36'	0.6074 (1)	0.4127 (3)	0.1227 (2)	0.017 (2)
C31	0.1126 (2)	0.1893 (3)	0.1538 (2)	0.026 (2)
C32	0.0782 (2)	0.3002 (3)	0.1595 (2)	0.027 (3)
C33	0.0476 (2)	0.3690 (3)	0.0992 (2)	0.032 (3)
C34	0.0514 (2)	0.3267 (3)	0.0331 (2)	0.032 (3)
C35	0.0858 (2)	0.2158 (3)	0.0274 (2)	0.027 (2)
C36	0.1165 (2)	0.1470 (3)	0.0877 (2)	0.021 (2)
C41	0.2912 (2)	-0.1000 (3)	0.1047 (2)	0.024 (2)
C42	0.3672 (2)	-0.0985 (3)	0.1279 (2)	0.025 (3)
C43	0.4033 (2)	0.0085 (3)	0.1561 (2)	0.029 (2)
C44	0.3636 (2)	0.1141 (3)	0.1610 (2)	0.025 (2)
C45	0.2876 (2)	0.1126 (3)	0.1378 (2)	0.021 (2)
C46	0.2514 (2)	0.0056 (3)	0.1096 (2)	0.021 (2)

Table 2. Selected geometric parameters (Å, °)

For molecule 2, each atom label should be appended by a prime.

	Molecule 1	Molecule 2
P1—C1	1.716 (5)	1.725 (4)
C1—C2	1.407 (8)	1.399 (8)
O1—C2	1.265 (7)	1.247 (7)
P1—C16	1.816 (5)	1.802 (5)
P1—C36	1.815 (4)	1.811 (4)
P1—C46	1.803 (4)	1.810 (4)
C2—C26	1.519 (7)	1.513 (7)
C36—P1—C46	107.9 (2)	105.3 (2)
C16—P1—C46	108.9 (2)	108.8 (2)
C16—P1—C36	105.2 (2)	107.4 (2)
C1—P1—C46	111.9 (3)	115.7 (3)
C1—P1—C36	115.7 (3)	115.2 (3)
C1—P1—C16	107.0 (3)	104.2 (3)
P1—C1—C2	115.3 (4)	123.0 (4)
O1—C2—C1	122.9 (5)	125.4 (5)
C1—C2—C26	119.8 (5)	116.1 (5)
O1—C2—C26	117.3 (5)	118.5 (5)

Table 3. Comparison of some structural features (Å, °) of  $(C_6H_5)_3PC(X)COC_6H_5$  ( $X = H, Cl$  and  $I$ ) compounds

	P—C	C=O	C—CO
$(C_6H_5)_3PCHCOC_6H_5$ (1)	1.716 (5)	1.265 (7)	1.407 (8)
$(C_6H_5)_3PCHCOC_6H_5$ (2)	1.725 (4)	1.247 (7)	1.399 (8)
$(C_6H_5)_3PC(Cl)COC_6H_5^a$	1.736 (14)	1.301 (19)	1.361 (20)
$(C_6H_5)_3PC(I)COC_6H_5^b$	1.71 (5)	1.28 (6)	1.35 (7)

References: (a) Stephens (1965b); (b) Stephens (1965a).

Initial data reduction was carried out using *SHELXTL* (Sheldrick, 1984). All the H atoms were included in the final cycle of refinement riding at distances of 1.08 Å with displacement parameters equal to  $1.2U_{eq}$  of the parent non-ring atoms. The displacement parameters for ring H atoms were fixed at  $0.05 \text{ \AA}^2$ . All phenyl rings were refined as rigid groups. The final refinement and the table of  $F_o$  and  $F_c$  were obtained using *SHELX76* (Sheldrick, 1976). Bond parameters and equations of planes were obtained by the use of *PARST* (Nardelli, 1983).

The financial support of University Grants Commission, New Delhi, for the Minor Research Project to MK is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Bart, J. C. J. (1969). *J. Chem. Soc. B*, pp. 350–365.
- Dunitz, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, p. 339. Ithaca: Cornell Univ. Press.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Ramirez, F. & Dershowitz, S. (1957). *J. Org. Chem.* **22**, 41–45.
- Shao, M., Jin, X., Tang, Q., Huang, Q. & Huang, Y. (1982). *Tetrahedron Lett.* **23**, 5343–5346.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1984). *SHELXTL User's Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- Stephens, F. S. (1965a). *J. Chem. Soc.* pp. 5640–5650.
- Stephens, F. S. (1965b). *J. Chem. Soc.* pp. 5658–5678.

*Acta Cryst.* (1994). **C50**, 1741–1745

## Hexamethylenediammonium Bis( $\beta$ -phenylacrylate) Dihydrate and Hexamethylenediammonium 3,3'-(1,4-Phenylene)diacrylate Monohydrate

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(Received 8 August 1993; accepted 20 December 1993)

## Abstract

The crystal structures of hexamethylenediammonium bis( $\beta$ -phenylacrylate) dihydrate,  $C_6H_{18}N_2^{2+} \cdot 2C_9H_7O_2^- \cdot 2H_2O$ , (I), and hexamethylenediammonium phenylene-1,4-diacrylate monohydrate,  $C_6H_{18}N_2^{2+} \cdot C_{12}H_8O_4^- \cdot H_2O$ , (II), have been studied. In (I) the anions related by  $\bar{1}$  symmetry overlap each other, but the distance between the C=C double bonds, 5.165 (3) Å, is too long for photodimerization to occur. In (II) the anions and cations are stacked alternately, so no short contact is observed between the C=C double bonds of the anions.

## Comment

As part of a study to design photoreactive crystals (Iwamoto & Kashino, 1990), the crystal structures of

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