# Bond Length and Reactivity: 1-Arylethyl Ethers and Esters. 5.* Structure of 1-(4-Nitrophenyl)ethyl Diphenyl Phosphate

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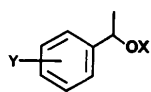
And Martin R. Edwards and Anthony J. Kirby

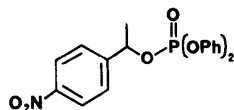*University Chemical Laboratory, Cambridge CB2 1EW, England*

**Abstract.** $C_{20}H_{18}NO_6P$, $M_r = 399.34$, triclinic, $P\bar{1}$, $a = 8.441$ (2), $b = 10.177$ (2), $c = 11.638$ (3) Å, $\alpha = 72.30$ (2), $\beta = 87.76$ (2), $\gamma = 86.79$ (2)°, $U = 950.7$ Å$^3$, $Z = 2$, $D_x = 1.39$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.18$ mm$^{-1}$, $F(000) = 416$, $T = 293$ K, $R = 0.047$ for 3583 reflections. The benzylic C—O bond length, 1.466 (3) Å, is longer than in most other compounds in this series apart from the 3,5-dinitrobenzoate esters. The —NO$_2$ group in the title compound restricts the C—O bond lengthening. The phosphate ester crystallizes in the usual conformation for this type of compound with the C—methyl bond perpendicular to the 4-nitrophenyl ring.

**Introduction.** As part of our broader investigation of bond length–reactivity correlations (Jones & Kirby, 1984), we have measured crystal structures for nine derivatives (1) of 1-arylethanols (Jones, Sheldrick, Edwards & Kirby, 1986; Jones, Edwards & Kirby, 1986*a,b,c*). The choice of substituent groups $X$ and $Y$, designed primarily to allow a wide spread of compound reactivity, has had to be modified on the one hand by the requirements of crystal quality, and is limited on the other by the stability of the compounds. Compounds (1) that combine very good leaving groups ($XO^-$) and electron-donating substituents $Y$, such as methoxy, could not be prepared.

We were able to prepare the diphenyl phosphate of 1-phenylethanol itself, but not to produce suitable crystals. We report here the crystal structure of the stable diphenyl phosphate (2) of 1-(4-nitrophenyl)-ethanol.



(1)                    (2)

**Experimental.** Phosphate ester (2) was prepared from the alcohol and diphenyl phosphorochloridate, using pyridine as the base, in dichloromethane. Pale yellow prisms and tablets, m.p. 339–340 K, were grown by diffusion of petrol into a solution in diisopropyl ether.

Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation. $2\theta_{max}$ 55°, $-h\pm k\pm l$; 4345 profile-fitted reflections (Clegg, 1981), *ca* 8% decay for 3 check reflections, appropriate correction. No absorption correction. Crystal size 0.7 × 0.4 × 0.35 mm. 4341 unique reflections, 3583 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Index range $|h| \le 10$, $|k| \le 13$, $|l| \le 15$. Cell constants refined from $\pm 2\theta$ values of 30 reflections in the range 20–23°. Structure solution by routine direct methods. Refinement on $F$ to $R$ 0.047, $wR$ 0.059; all non-H atoms anisotropic, H atoms included using a riding model [C—H 0.96 Å, H—C—H 109.5°, $U(H) = 1.2U_{eq}(C)$]. 256 parameters; weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$, $S$ 2.48; max. $\Delta/\sigma$ 0.14; max. and min. features in final $\Delta\rho$ map <0.3 e Å$^{-3}$. Atomic scattering factors as incorporated in *SHELXTL*.

**Discussion.** Final atom coordinates and derived parameters are presented in Tables 1 and 2, and a thermal-ellipsoid plot of (2) is shown in Fig. 1: the atom-numbering scheme in the benzylic system is the same as for previous compounds in this series.†

The phosphate ester (2) crystallizes in the usual conformation for derivatives (1), with the C—methyl bond close to perpendicular to the 4-nitrophenyl ring [torsion angles C(4)—C(3)—C(11)—C(12,16) −97.8 (3), 79.2 (3)°]. The C(3)—O bond is the longest we have observed so far in this series, 1.466 (3) Å,

apart from the 3,5-dinitrobenzoate esters [(1), $Y = H$ and $OCH_3$]. Diphenyl phosphate is a better leaving group (the parent acid is stronger) than 3,5-dinitrobenzoate, but the 4-nitro group of (2) evidently restricts C—O bond lengthening. These questions will be discussed in more detail when the full set of structures is available (Edwards, Jones & Kirby, 1986).

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$

|  | x | y | z | U* |
|---|---|---|---|---|
| P | 3064 (1) | 3611 (1) | 3206 (1) | 47 (1) |
| O(1) | 2683 (2) | 2370 (1) | 4153 (1) | 65 (1) |
| O(2) | 4692 (1) | 3540 (1) | 2531 (1) | 50 (1) |
| O(3) | 3094 (1) | 4896 (1) | 3676 (1) | 53 (1) |
| O(4) | 1838 (2) | 4132 (1) | 2158 (1) | 59 (1) |
| C(3) | 5678 (2) | 2255 (2) | 2803 (2) | 49 (1) |
| C(4) | 6453 (3) | 2200 (2) | 1632 (2) | 66 (1) |
| C(11) | 6867 (2) | 2236 (2) | 3743 (2) | 44 (1) |
| C(12) | 7265 (2) | 1000 (2) | 4610 (2) | 52 (1) |
| C(13) | 8398 (2) | 939 (2) | 5444 (2) | 53 (1) |
| C(14) | 9124 (2) | 2136 (2) | 5400 (2) | 48 (1) |
| C(15) | 8754 (2) | 3378 (2) | 4561 (2) | 51 (1) |
| C(16) | 7625 (2) | 3413 (2) | 3728 (2) | 51 (1) |
| N | 10328 (2) | 2072 (2) | 6303 (1) | 57 (1) |
| O(41) | 10772 (2) | 935 (2) | 6963 (1) | 74 (1) |
| O(42) | 10816 (2) | 3161 (2) | 6355 (1) | 74 (1) |
| C(31) | 3542 (2) | 6231 (2) | 2999 (2) | 47 (1) |
| C(32) | 2675 (2) | 7014 (2) | 2032 (2) | 57 (1) |
| C(33) | 3104 (3) | 8330 (2) | 1454 (2) | 72 (1) |
| C(34) | 4361 (3) | 8874 (2) | 1844 (2) | 80 (1) |
| C(35) | 5197 (3) | 8084 (2) | 2830 (2) | 76 (1) |
| C(36) | 4796 (2) | 6751 (2) | 3412 (2) | 59 (1) |
| C(41) | 1710 (2) | 3427 (2) | 1297 (2) | 53 (1) |
| C(42) | 823 (2) | 2299 (2) | 1554 (2) | 60 (1) |
| C(43) | 680 (3) | 1643 (2) | 685 (2) | 73 (1) |
| C(44) | 1396 (3) | 2102 (3) | −404 (2) | 83 (1) |
| C(45) | 2337 (4) | 3219 (3) | −652 (2) | 105 (1) |
| C(46) | 2499 (4) | 3908 (3) | 200 (2) | 90 (1) |

* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
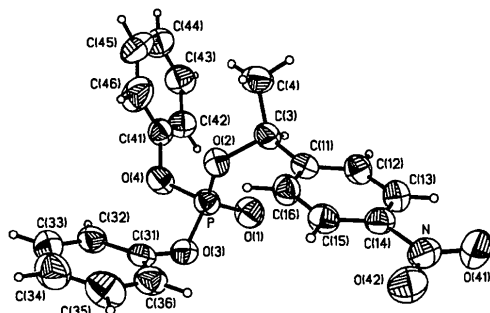
Table 2. *Bond lengths* (Å), *bond angles and torsion angles* (°)

| O(1)—P | 1·444 (2) | O(2)—P | 1·565 (2) |
|---|---|---|---|
| O(3)—P | 1·565 (2) | O(4)—P | 1·576 (2) |
| C(3)—O(2) | 1·466 (3) | C(3)—C(4) | 1·504 (4) |
| C(11)—C(3) | 1·508 (4) | C(11)—C(12) | 1·385 (3) |
| C(11)—C(16) | 1·384 (4) | C(12)—C(13) | 1·375 (4) |
| C(13)—C(14) | 1·380 (4) | C(14)—C(15) | 1·370 (3) |
| C(14)—N | 1·475 (3) | C(15)—C(16) | 1·377 (4) |
| N—O(41) | 1·226 (3) | N—O(42) | 1·222 (3) |
| C(31)—O(3) | 1·412 (3) | C(31)—C(32) | 1·375 (3) |
| C(31)—C(36) | 1·374 (4) | C(32)—C(33) | 1·366 (4) |
| C(33)—C(34) | 1·376 (5) | C(34)—C(35) | 1·379 (4) |
| C(35)—C(36) | 1·374 (4) | C(41)—O(4) | 1·409 (4) |
| C(41)—C(42) | 1·357 (4) | C(41)—C(46) | 1·379 (4) |
| C(42)—C(43) | 1·382 (5) | C(43)—C(44) | 1·343 (4) |
| C(44)—C(45) | 1·374 (5) | C(45)—C(46) | 1·392 (5) |

| O(1)—P—O(2) | 115·3 (2) | O(1)—P—O(3) | 112·4 (2) |
|---|---|---|---|
| O(2)—P—O(3) | 106·3 (2) | O(1)—P—O(4) | 116·1 (2) |
| O(2)—P—O(4) | 103·8 (2) | O(3)—P—O(4) | 101·6 (2) |
| P—O(2)—C(3) | 121·0 (2) | P—O(3)—C(31) | 126·2 (2) |
| P—O(4)—C(41) | 121·0 (2) | O(2)—C(3)—C(4) | 106·7 (2) |
| O(2)—C(3)—C(11) | 109·6 (3) | C(4)—C(3)—C(11) | 112·6 (2) |
| C(3)—C(11)—C(12) | 119·3 (3) | C(3)—C(11)—C(16) | 121·5 (2) |
| C(12)—C(11)—C(16) | 119·1 (3) | C(11)—C(12)—C(13) | 120·6 (3) |
| C(12)—C(13)—C(14) | 118·5 (2) | C(13)—C(14)—C(15) | 122·5 (3) |
| C(13)—C(14)—N | 118·5 (2) | C(15)—C(14)—N | 119·0 (3) |
| C(14)—C(15)—C(16) | 118·0 (3) | C(11)—C(16)—C(15) | 121·3 (2) |
| C(14)—N—O(41) | 118·3 (2) | C(14)—N—O(42) | 117·9 (2) |
| O(41)—N—O(42) | 123·8 (3) | O(3)—C(31)—C(32) | 121·1 (3) |
| O(3)—C(31)—C(36) | 116·9 (2) | C(32)—C(31)—C(36) | 121·8 (3) |
| C(31)—C(32)—C(33) | 118·7 (3) | C(32)—C(33)—C(34) | 120·8 (3) |
| C(33)—C(34)—C(35) | 119·7 (3) | C(34)—C(35)—C(36) | 120·3 (3) |
| C(31)—C(36)—C(35) | 118·8 (3) | O(4)—C(41)—C(42) | 120·0 (3) |
| O(4)—C(41)—C(46) | 118·8 (3) | C(42)—C(41)—C(46) | 121·2 (3) |
| C(41)—C(42)—C(43) | 119·0 (3) | C(42)—C(43)—C(44) | 121·4 (3) |
| C(43)—C(44)—C(45) | 119·5 (4) | C(44)—C(45)—C(46) | 120·5 (3) |
| C(41)—C(46)—C(45) | 118·2 (3) | | |

| O(1)—P—O(2)—C(3) | 4·3 (3) | O(3)—P—O(2)—C(3) | 129·4 (2) |
|---|---|---|---|
| O(4)—P—O(2)—C(3) | −123·9 (2) | O(1)—P—O(3)—C(31) | 174·9 (2) |
| O(2)—P—O(3)—C(31) | 47·9 (2) | O(4)—P—O(3)—C(31) | −60·4 (2) |
| O(1)—P—O(4)—C(41) | −72·5 (2) | O(2)—P—O(4)—C(41) | 55·1 (2) |
| O(3)—P—O(4)—C(41) | 165·3 (2) | P—O(2)—C(3)—C(4) | 144·2 (2) |
| P—O(2)—C(3)—C(11) | −93·5 (2) | P—O(3)—C(31)—C(32) | 64·8 (3) |
| P—O(3)—C(31)—C(36) | −120·5 (3) | P—O(4)—C(41)—C(42) | 82·5 (3) |
| P—O(4)—C(41)—C(46) | −97·5 (3) | O(2)—C(3)—C(11)—C(12) | 143·5 (3) |
| O(2)—C(3)—C(11)—C(16) | −39·5 (3) | C(4)—C(3)—C(11)—C(12) | −97·8 (3) |
| C(4)—C(3)—C(11)—C(16) | 79·2 (3) | C(13)—C(14)—N—O(41) | 8·5 (3) |
| C(13)—C(14)—N—O(42) | −170·9 (3) | C(15)—C(14)—N—O(41) | −172·2 (3) |
| C(15)—C(14)—N—O(42) | 8·4 (3) | | |

Sign convention as defined by Klyne & Prelog (1960).



Fig. 1. Thermal-ellipsoid plot of (2), showing the atom-numbering scheme.

### References

CLEGG, W. (1981). *Acta Cryst.* A37, 22–28.

EDWARDS, M. R., JONES, P. G. & KIRBY, A. J. (1986). *J. Am. Chem. Soc.* Submitted.

JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1986a). *Acta Cryst.* C42, 1355–1358.

JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1986b). *Acta Cryst.* C42, 1359–1360.

JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1986c). *Acta Cryst.* C42, 1365–1367.

JONES, P. G. & KIRBY, A. J. (1984). *J. Am. Chem. Soc.* 106, 6207–6212.

JONES, P. G., SHELDRICK, G. M., EDWARDS, M. R. & KIRBY, A. J. (1986). *Acta Cryst.* C42, 1361–1364.

KLYNE, W. & PRELOG, V. (1960). *Experientia,* 16, 521–523.

SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.