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# Structure of Dimethyl 8-Quinolyl Phosphate

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**Abstract.** $C_{11}H_{12}NO_4P$, $M_r = 253{\cdot}19$, monoclinic, $P2_1/c$, $a = 13{\cdot}604\,(4)$, $b = 7{\cdot}509\,(3)$, $c = 13{\cdot}093\,(5)$ Å, $\beta = 116{\cdot}56\,(3)°$, $V = 1196{\cdot}3\,(8)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}41$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}84$ cm$^{-1}$, $F(000) = 528$, final $R = 0{\cdot}040$, $wR = 0{\cdot}037$, $w = (\sigma^2F)^{-1}$, $S = 3{\cdot}16$ for 1337 reflections with $I > 2\sigma(I)$, number of parameters = 162. The structure of the title compound was determined in order to obtain information on the intra- and/or intermolecular interactions between the N atom and the ester methyl groups, as a model for the isomerization of the substrate into the zwitterionic product. The orientation of the $CH_3$ groups in the crystal gives no indication of the occurrence of methyl transfer in the solid state.

**Introduction.** The present study is part of a series of investigations concerning self-alkylating properties of phosphate esters containing a nucleophilic centre in one of the ester groups. Since it has been recently demonstrated (Cocks & Modro, 1985) that the O→N methyl transfer follows a bimolecular mechanism, the intermolecular N/$CH_3$ relationship in the title compound is of particular interest.

**Experimental.** Crystals were prepared by slow evaporation of concentrated aqueous solution, 0·16 × 0·38 × 0·50 mm; Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation at 294 K. Accurate cell constants from setting angles of 24 reflections ($14 \leq \theta \leq 15°$); $\omega$–$2\theta$ scans, scan width = $(0{\cdot}93 + 0{\cdot}35\tan\theta)°$, variable scan speed. 2374 reflections measured, of which 1337 considered observed [$I/\sigma(I) > 2{\cdot}0$]. $R_{\text{merge}} = 0{\cdot}0585$. Intensity checks every hour to monitor crystal decay (1·28%). Range of reflections $\theta = 1$–$25°$, $h$ −15,15; $k$ 0,8; $l$ 0,16. Data Lp processed. No absorption correction applied. Structure solved by direct methods using preliminary version of *SHELXS*84 (Sheldrick, 1983) and refined using full matrix on $F$ of *SHELX*76 (Sheldrick, 1978). H atoms observed in electron density map following anisotropic refinement of C, O, N and P. In the final refinement, all nonhydrogen atoms anisotropic, H atoms isotropic; methyl H atoms as rigid groups with a single temperature factor, ring-H placed in calculated positions with a single temperature factor. Max., min. residual electron density in the difference map 0·24, −0·27 e Å$^{-3}$. $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Complex neutral-atom scattering factors were taken from Cromer & Mann (1968) for the C, O, N, P atoms and from Stewart, Davidson & Simpson (1965) for H, with dispersion corrections from Cromer & Liberman (1970). The programs *PARST* (Nardelli, 1983) and *XANADU* (Roberts & Sheldrick, 1975) were used for calculations concerning molecular geometry and *PLUTO* (Motherwell, 1974) for a drawing of the molecule.

**Discussion.** The fractional atomic coordinates are given in Table 1,* and selected bond lengths, valence angles and N non-bonded distances are included in Table 2. A perspective view of the molecule is shown in Fig. 1. The geometry around P deviates from a regular tetrahedron according to the pattern typical for phosphate triesters, *i.e.* three O—P—O angles involving 'long' ester P—O bonds are smaller [101·3 (2)–103·8 (2)°] and three others involving the phosphoryl group are larger [115·5 (2)–116·7 (2)°] than the ideal value of 109·5°. The N···P non-bonded distance (3·79 Å) is considerably more than the sum of their van der Waals radii (3·44 Å) indicating that no N→P intramolecular interactions are present. This result contrasts with the short (3·02 Å) N···P distance observed in bis(4-nitrophenyl) 8-quinolyl phosphate (Bond, Modro & Nassimbeni, 1985), which was taken as evidence for an 'early stage' of the intramolecular displacement of a good leaving group (4-nitrophenoxy) by N.

In agreement with our recent kinetic observations, the crystal structure reveals that the N—C(methyl) distance is not only much greater than the corresponding sum of the van der Waals radii, but also that the orientations of the methyl ester groups with respect to the ring N are highly unfavourable for the intramolecular methyl-group transfer to occur. The bimolecular ($S_N2$) displacement of the *O*-methyl group by the ring N is, however, relatively fast in solution ($D_2O$, 333 K, $t_{1/2} = ca$ 13h). In the crystalline state the distance between the N atom and the methyl C of a

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* Lists of structure factors, all thermal parameters, bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42852 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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second molecule (symmetry translation $x, y-1, z$) is 3·66 Å, and the N(1)···C(31′)—O(3′) angle is 148°. These parameters are not much different from the analogous values (3·54 Å and 147°, respectively) obtained for methyl 4-dimethylaminobenzenesulfonate (Sukenik, Bonapace, Mandel, Lau, Wood & Bergman, 1977), for which intermolecular O→N methyl-transfer-rate enhancement was observed, and attributed to the proper orientation of the molecules in the crystal. However, the title phosphate shows no evidence for reaction in the solid state; while it isomerizes completely to the zwitterion in the solution or as a melt, its crystals show no indication of methyl-group transfer when heated to just below the m.p. (323 K). We believe that the major factor responsible for the dramatic difference in the chemical reactivity of the crystalline phosphate and sulfonate is the angular relationship within the nucleophile–electrophile system. In methyl 4-dimethylaminobenzenesulfonate the amino group is planar, with the non-bonding, 2*p* AO perpendicular to the plane determined by the ring and its substituents. The angle between the C(*ipso*)—N bond and the N···C′(methyl) line should therefore change during methyl transfer from 90° (substrate) to 109·5° (zwitterionic product). The value of this angle, calculated from the data reported for the sulfonate, is 105·6°, indicating considerable progress along the reaction coordinate, together with significant change in the hybridization ($sp^2 \rightarrow sp^3$) of the N atom (Fig. 2*a*). The title phosphate ester is very different. Here, the $sp^2$-hybridized AO is responsible for the nucleophilic character and is located in the plane of the quinoline ring. For methyl-group transfer to occur, the angle between the ring C(1)—N [and C(9)—N] and the N···C′(methyl) direction should be (and should remain) 120°. The crystal structure reveals that the methyl group of the second molecule is, in fact, located 3·31 Å above the plane of the ring, with corresponding C(arom.)—N···C(methyl) angles of 104·7 (4) and 65·0 (4)°, respectively (Fig. 2*b*). *N*-Methylation, involving retention of the trigonal geometry of N would therefore require considerable dislocation of one phosphate molecule with respect to its neighbour. The importance of the angular orientation of the orbitals involved in a solid-state reaction has frequently been noted. For example, in the methyl ester of *m*-bromocinnamic acid the centre-to-centre distance of C=C groups in glide-plane-related molecules is short (3·93 Å); however, the double bonds are not parallel. As a consequence, this material is essentially unchanged after irradiation over long periods, during which other cinnamic derivatives completely dimerize (Schmidt, 1971).

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* $U_{eq}$ ($\text{Å}^2 \times 10^3$) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized $U_{ij}$ matrix).

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| P(1) | 3370 (1) | 1474 (1) | 1082 (1) | 39 (1) |
| N(1) | 827 (2) | −1376 (4) | −462 (2) | 38 (1) |
| O(1) | 4370 (2) | 2006 (4) | 1038 (2) | 64 (2) |
| O(2) | 2992 (2) | −508 (3) | 752 (2) | 39 (1) |
| O(3) | 2314 (2) | 2508 (3) | 272 (2) | 53 (1) |
| O(4) | 3383 (2) | 1631 (4) | 2275 (2) | 59 (1) |
| C(1) | −201 (3) | −1823 (5) | −1053 (3) | 47 (2) |
| C(2) | −661 (3) | −2493 (5) | −2183 (3) | 51 (2) |
| C(3) | 1 (3) | −2697 (5) | −2689 (3) | 46 (2) |
| C(4) | 1116 (3) | −2261 (5) | −2101 (3) | 35 (2) |
| C(5) | 1872 (3) | −2468 (5) | −2560 (3) | 47 (2) |
| C(6) | 2940 (3) | −2033 (5) | −1945 (3) | 49 (2) |
| C(7) | 3329 (3) | −1331 (5) | −839 (3) | 43 (2) |
| C(8) | 2617 (3) | −1123 (4) | −379 (3) | 32 (2) |
| C(9) | 1502 (3) | −1586 (5) | −972 (3) | 31 (1) |
| C(31) | 2332 (5) | 4404 (6) | 163 (4) | 83 (3) |
| C(32) | 4373 (4) | 1561 (8) | 3316 (3) | 93 (3) |

Table 2. *Selected bond lengths* (Å), *angles* (°) *and non-bonded distances* (Å) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| P(1)—O(1) | 1·444 (3) | C(8)—O(2) | 1·411 (4) |
| P(1)—O(2) | 1·571 (3) | O(3)—C(31) | 1·432 (5) |
| P(1)—O(3) | 1·559 (3) | O(4)—C(32) | 1·426 (4) |
| P(1)—O(4) | 1·559 (3) | | |
| O(1)—P(1)—O(2) | 116·7 (2) | O(2)—P(1)—O(3) | 101·3 (2) |
| O(1)—P(1)—O(3) | 115·7 (2) | O(2)—P(1)—O(4) | 101·7 (2) |
| O(1)—P(1)—O(4) | 115·5 (2) | O(3)—P(1)—O(4) | 103·8 (2) |
| N(1)···P(1) | 3·792* | | |
| N(1)···O(3) | 3·433 (4) | | |
| N(1)···O(4) | 4·346* | | |
| N(1)···C(31′) | 3·661* | | |

* Only contacts less than 3·50 Å report e.s.d.'s.

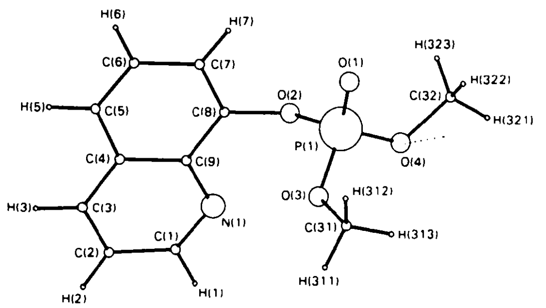

Fig. 1. Perspective view of the molecule, with the atomic numbering.

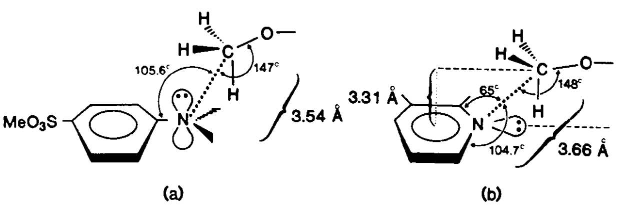

Fig. 2. Intermolecular nitrogen–methyl relations in: (*a*) methyl 4-dimethylaminobenzenesulfonate; and (*b*) dimethyl 8-quinolyl phosphate. A perspective view.

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# Structure du *N*-(*tert*-Butyl-2 hydroxy-6 cyclohexyl)-benzamide à 200 K

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**Abstract.** $C_{17}H_{25}NO_2$, $M_r = 275\cdot39$, rhombohedral, $R\overline{3}$, $a = 14\cdot385\,(4)$ Å, $\alpha = 65\cdot34\,(6)°$ (rhombohedral axes), $a = b = 15\cdot530\,(7)$, $c = 33\cdot747\,(14)$ Å, $V = 7048\cdot7$ Å$^3$, $Z = 18$, $D_m = 1\cdot15$, $D_x = 1\cdot167$ Mg m$^{-3}$, $F(000) = 900$ (hexagonal axes), $\lambda(\text{Mo } K\overline{\alpha}) = 0\cdot71069$ Å, $\mu = 0\cdot071$ mm$^{-1}$, $T = 200$ K, $R = 0\cdot044$ for 1242 observed reflections. The cyclohexane ring, which is in the chair conformation, is slightly affected by the presence of the *tert*-butyl substituent which is 2·3 (5)° from the perfectly staggered position. The plane of the amide group is tilted by 19 (1)° from that of the benzene ring. Two types of hydrogen bonds, $O(1)\cdots O(2') = 2\cdot707\,(4)$ and $O(1)\cdots N(1') = 3\cdot052\,(4)$ Å, link the molecules together. The molecules are associated in groups of three through the $O(1)\cdots N(1')$ hydrogen bonds. This 'trimer' is, in turn, H-bonded to others by the $O(1)\cdots O(2')$ bond. This results in a two-dimensional network parallel to the *ab* plane.

**Introduction.** Dans le cadre de nos travaux (Richer & Freppel, 1969, 1970, 1971) sur les dérivés 1,2-disubstitués du *tert*-butyl-3 cyclohexène et à la suite de nos observations antérieures sur les p*K* des divers isomères des amino-2 *tert*-butyl-3 (ou 6) cyclohexanol-1 (Richer, Freppel, Tchalpa & Welwart, 1973), nous avons voulu examiner la structure cristalline du *N*-(*tert*-butyl-2 hydroxy-6 cyclohexyl)-benzamide (Tapin, 1978) et en comparer la conformation à celles de molécules apparentées préparées tant dans nos laboratoires (Brisse, Beauchamp, Richer, Belluci & Ingrosso, 1976) que par Bellucci, Berti, Colapietro, Spagna & Zambonelli (1976). Une première étude à la température ambiante ayant révélé une forte agitation thermique, surtout au niveau du groupe *tert*-butyle, la détermination présentée ici a été conduite à 200 K (Pascard & Cesario, 1980).

**Partie expérimentale.** Synthèse décrite par Tapin (1978), recristallisation dans l'éther, PF = 460 K; dimensions du cristal 0,10 × 0,42 × 0,52 mm; maille à partir de 25 réflexions; $13 \leq 2\theta \leq 23°$; diffractomètre Nonius CAD-4; radiation du molybdène monochromatisée au graphite; densité par flottaison dans une solution aqueuse de $ZnCl_2$; balayage $\omega$–$2\theta$, largeur de balayage $\Delta\omega = (1{,}00 + 0{,}35\ \mathrm{tg}\theta)°$, durée maximum 50 s; $2\theta_{\max} = 45{,}0°$ ($0 \leq h \leq 16$, $0 \leq k \leq 16$, $-36 \leq l \leq 36$, avec $-h + k + l = 3n$); intensités de six réflexions de référence mesurées toutes les 2 h; orientation du cristal vérifiée après chaque 250 mesures, décroissance linéaire de l'intensité due à un début de sublimation (7% pendant la durée des mesures). 2325 réflexions mesurées 1242 réflexions (60%) répondant au critère $I \geq 1{,}96\sigma(I)$ ont servi à la détermination et à l'affinement de la structure, $\sigma(I)$ calculé à partir de la statistique de comptage. Correction Lp, pas de correction d'absorption; méthodes directes (*MULTAN*);* affinement par moindres carrés (approximation par blocs diagonaux); quantité minimisée $\sum w(|F_o| - |F_c|)^2$; les atomes

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* Les programmes utilisés dans ce travail sont listés dans Wyss, Brisse & Hanessian (1984).