

were placed in idealized positions and that bonded to O(3) located on a difference Fourier map and its coordinates refined; all H atoms had fixed thermal parameters $U = 0.06 \text{ \AA}^2$. In the final cycle, $R = 0.049$, $wR = 0.064$ for 1697 observed reflections, $S = 1.30$. The function minimized was $\sum w(\Delta F)^2$, where $w = [\sigma(F_o)^2 + 0.0028(F_o)^2]^{-1}$. Maximum $\Delta/\sigma = 0.291$. Minimum and maximum residuals in the final $\Delta\rho$ synthesis were -0.20 and 0.19 e \AA^{-3} . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a NOVA 4S computer using *SHELXTL* (Sheldrick, 1983).

Discussion. Final atomic coordinates are given in Table 1.* Fig. 1 shows a view of the molecule and the atom-numbering scheme. Bond lengths and angles are listed in Table 2. The structure of wigandol determined by X-ray analysis is characterized by the *cis,trans* geometry of the cyclodeca-1,5-diene system, the *anti* arrangement of methyl groups at C(6) and C(10), and by the crossed orientation [angle between planes $29.5(1)^\circ$] of the C(6)=C(7) and C(10)=C(11) double bonds. The conformation of the ten-membered ring can be described as a chair-half-chair and closely resembles that found in NMR studies of neolinderolactone (Tori, Horibe, Kuriyama & Takeda, 1970). Comparison of the inner torsion angles of the ten-membered ring in wigandol (Table 3) with those of the schkuriolid (Rychlewska, 1982) shows that they differ mainly by

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55287 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0594]

distortions at the ring fusion. Significant departures from the ideal torsion angles of the *cis* (6°) and *trans* (-168°) double bonds reflect strain from transannular non-bonded interactions [C(7)⋯C(10) $3.075(5)$ and C(6)⋯C(11) $3.064(5) \text{ \AA}$]. The dihydrobenzoquinone moiety is essentially planar and the acetate group lies nearly perpendicular [angle between planes $81.2(2)^\circ$] to the phenyl ring. In the crystal the molecules are held together by hydrogen bonds [$D-H$ $0.855(31)$, $H\cdots A$ $1.928(27)$, $D\cdots A$ $2.719(3) \text{ \AA}$; $D-H\cdots A$ $153(3)^\circ$] involving the phenolic group O(3)—H(3a) and the carbonyl atom O(2) in the acetate group of a symmetry-related molecule ($0.5 - x, 0.5 + y, 0.5 - z$), forming endless zigzag chains along the *b* axis. Fig. 2 shows the crystal packing.

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Triphenylphosphine Oxide Hydrogen Bromide

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Abstract. $C_{18}H_{16}OP^+Br^-$, $M_r = 359.20$, monoclinic, $P2_1/n$, $a = 9.540(3)$, $b = 17.763(5)$, $c = 10.390(6) \text{ \AA}$,

$\beta = 106.91(4)^\circ$, $V = 1685(1) \text{ \AA}^3$, $Z = 4$, $D_x = 1.416 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 2.504 \text{ mm}^{-1}$, $F(000) = 728$, $T = 298 \text{ K}$, $R = 0.042$ for 1122 observed reflections [$I > 2\sigma(I)$]. The structure

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consists of unique $C_{18}H_{15}POH^+.Br^-$ ion pairs; no extensive hydrogen-bonding scheme is formed. The proton is bonded to the phosphine oxide O atom, O—H 0.98 (9) Å, and directed towards a Br atom, O—H...Br⁻ 162 (4)°, at a distance of 2.0 (1) Å.

Introduction. Although rare, some compounds of stoichiometry $aryl_3PO.HX$ have previously been studied by X-ray diffraction (Thierbach & Huber, 1979*a,b*; Haupt, Huber, Kruger, Preut & Thierbach, 1977), and by infrared spectroscopy (Hadzi, 1962). Thierbach and co-workers have determined the single-crystal X-ray structures of $Ph_3PO.HF$ (Thierbach & Huber, 1979*a*) and $Ph_3PO.HCl$ (Haupt, Huber, Kruger, Preut & Thierbach, 1977). However, attempts to form crystals of $Ph_3PO.HBr$ yielded instead the hydrated complex $(Ph_3PO)_2.H_2O.HBr$ (Thierbach & Huber, 1979*b*).

We have been able to obtain anhydrous $Ph_3PO.HBr$ by an adventitious route; by reaction of Ph_3PBr_2 with $Mn_2(CO)_{10}$ in a 1:1 ratio in dry diethyl ether, the $Ph_3PO.HBr$ crystallized from the filtrate after removal of the bulk solid product.

Experimental. A pale yellow crystal, $0.3 \times 0.2 \times 0.2$ mm, was examined on a Rigaku AFC-6S diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions were determined from the setting angles of 20 accurately centred reflections ($14.6 < 2\theta < 25.7^\circ$). A total of 3276 reflections were scanned using ω - 2θ scan mode and ω -scan speed of 8° min^{-1} with up to two additional scans of weak reflections [$I < 10\sigma(I)$] and ω -scan width of $(1.15 + 0.30 \tan \theta)^\circ$. Intensity standards (331, 303, 421) measured every 150 reflections showed a 4% decline. Lp, decomposition and absorption (azimuthal scan technique, maximum and minimum transmission factors 1.21, 0.81) corrections were applied. *MITHRIL* (Gilmore, 1984) was used to solve the phase problem, all non-H atoms were found in Fourier maps, and H atoms from ΔF syntheses. Full-matrix least-squares refinement of 254 variables with 1122 reflections [$I > 2\sigma(I)$] and based on F using *TEXAN* crystallographic software (Molecular Structure Corporation, 1985) led to a final $R = 0.042$, $wR = 0.043$, $w = 1/[\sigma^2(F_o) + 0.03F_o^2]$ with anisotropic thermal parameters for heavier atoms and isotropic for H atoms. Maximum shift/e.s.d. in final cycle 0.14 and maximum fluctuations in final difference Fourier map in the range -0.28 to $0.33 \text{ e } \text{Å}^{-3}$. Scattering factors from Cromer & Waber (1974), computations carried out on a Digital VAX station 2530. Literature survey performed via the Cambridge Structural Database using the *Crystal Structure Search and Retrieval* interactive system (CSSR, 1984). Fractional atomic coordinates and vibrational parameters for non-H atoms are pre-

Table 1. Fractional coordinates and B_{eq} values (Å^2) for non-H atoms

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq} |
|-------|--------------|-------------|--------------|----------|
| Br(1) | 0.23832 (11) | 0.45541 (7) | 0.74453 (14) | 6.98 (6) |
| P(1) | 0.4472 (2) | 0.3492 (1) | 0.5081 (2) | 3.5 (1) |
| O(1) | 0.4676 (6) | 0.4024 (4) | 0.6304 (6) | 4.8 (3) |
| C(1) | 0.3503 (8) | 0.2659 (5) | 0.5238 (9) | 3.2 (4) |
| C(2) | 0.3546 (9) | 0.2394 (6) | 0.6502 (10) | 4.3 (5) |
| C(3) | 0.2863 (10) | 0.1729 (6) | 0.6653 (11) | 5.3 (5) |
| C(4) | 0.2144 (9) | 0.1317 (5) | 0.5555 (12) | 4.8 (5) |
| C(5) | 0.2078 (11) | 0.1584 (6) | 0.4325 (11) | 5.1 (5) |
| C(6) | 0.2756 (10) | 0.2254 (6) | 0.4133 (10) | 4.8 (5) |
| C(7) | 0.3517 (8) | 0.3939 (4) | 0.3562 (8) | 3.4 (4) |
| C(8) | 0.4181 (9) | 0.4113 (5) | 0.2594 (9) | 4.4 (4) |
| C(9) | 0.3427 (10) | 0.4464 (7) | 0.1413 (10) | 5.7 (5) |
| C(10) | 0.1969 (10) | 0.4614 (6) | 0.1172 (12) | 6.1 (5) |
| C(11) | 0.1298 (10) | 0.4464 (7) | 0.2152 (12) | 6.3 (5) |
| C(12) | 0.2056 (10) | 0.4115 (6) | 0.3339 (11) | 5.1 (5) |
| C(13) | 0.6291 (8) | 0.3259 (5) | 0.5519 (8) | 3.6 (4) |
| C(14) | 0.7392 (10) | 0.3761 (6) | 0.5591 (11) | 5.4 (5) |
| C(15) | 0.8840 (10) | 0.3612 (9) | 0.5705 (13) | 8.1 (7) |
| C(16) | 0.9181 (12) | 0.2921 (10) | 0.5367 (12) | 7.6 (7) |
| C(17) | 0.8126 (15) | 0.2390 (7) | 0.4895 (13) | 6.8 (7) |
| C(18) | 0.6654 (11) | 0.2557 (6) | 0.4761 (11) | 5.3 (5) |

Table 2. Selected bond lengths (Å) and angles (°)

| | | | |
|-----------------|-----------|-----------------|-----------|
| P(1)—O(1) | 1.550 (6) | O(1)—H(1) | 0.98 (9) |
| O(1)—P(1)—C(1) | 112.1 (4) | C(1)—P(1)—C(13) | 109.6 (4) |
| O(1)—P(1)—C(7) | 111.6 (4) | C(7)—P(1)—C(13) | 111.9 (4) |
| O(1)—P(1)—C(13) | 103.6 (3) | P(1)—O(1)—H(1) | 126 (6) |
| C(1)—P(1)—C(7) | 108.1 (4) | | |

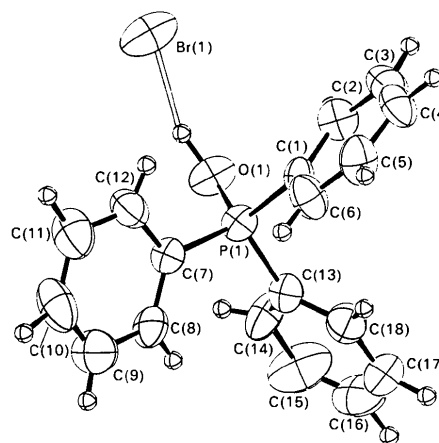


Fig. 1. The title molecule drawn using *ORTEP*II (Johnson, 1976).

sented in Table 1* and selected bond lengths and angles in Table 2. The title molecule, including atomic labels, is displayed in Fig. 1.

Discussion. The structure of the title compound consists of $C_{18}H_{15}POH^+.Br^-$ ion pairs, as evidenced

* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55239 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0534]

Table 3. *Triphenylphosphine oxide and its HX adducts* ($X = \text{F}, \text{Cl}, \text{Br}$)

| | P—O (Å) | O—H (Å) | H—X (Å) | O—X (Å) |
|---|--|------------|---------|-----------|
| Ph ₃ PO | 1.491 (2) ^a 1.494 (4) ^b | — | — | — |
| Ph ₃ PO.HBr | 1.550 (6) | 0.98 (9) | 2.0 (1) | 2.930 (6) |
| Ph ₃ PO.HCl | 1.517 (2) | 1.116 (40) | — | 2.747 (2) |
| Ph ₃ PO.HF | 1.495 (4) | 1.423 | 0.998 | 2.384 (5) |
| (Ph ₃ PO) ₂ .H ₂ O.HBr | 1.492 (6) ^c | — | — | — |

Notes: (a) orthorhombic form, (b) monoclinic form, (c) mean value.

by the short O—H bond [0.98 (9) Å] and long H—Br distance [2.0 (1) Å]. Following on from this work, a comparison can be made between the structures of Ph₃PO.HX, where $X = \text{F}, \text{Cl}, \text{Br}$ (Table 3). The structure of Ph₃PO.HF comprises molecular triphenylphosphine oxide, hydrogen bonded to hydrogen fluoride. The P—O bond length [1.495 (4) Å] is comparable to that of free triphenylphosphine oxide [1.491 (2) Å, orthorhombic form; 1.494 (4) Å, monoclinic form] (Brock, Dunitz & Schweizer, 1985). On the other hand, the structure of the hydrogen chloride adduct has been shown to be that of the ionic Ph₃P⁺OH⁻·Cl⁻, having a much longer P—O distance (1.517 Å) and a short O—H bond (1.116 Å).

The lengthening of the P—O bond is more pronounced in the hydrogen bromide adduct now reported, showing the increasing trend to ionicity with the heavier halogens.

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Structure of *N*-(2-Dimethylaminoethyl)phenothiazine-1-carboxamide Hydrochloride

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Abstract. C₁₇H₂₀N₃OS⁺.Cl⁻, $M_r = 349.88$, orthorhombic, $Pna2_1$, $a = 7.983$ (3), $b = 18.028$ (2), $c = 11.668$ (1) Å, $V = 1679.1$ (9) Å³, $Z = 4$, $D_m = 1.39$ (1), $D_x = 1.419$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 4.3$ cm⁻¹, $F(000) = 736$, $T = 293$ (1) K, $R = 0.044$ for 741 [$I > 2.5\sigma(I)$] reflections. The phenothiazine cation adopts a butterfly shape by bending approximately along the S(9)–N(10) direction. The dihedral angle between the individually planar aromatic rings is 160.4°. The amide group is oriented to form an intramolecular hydrogen bond between N(10) and the amide O atom. There are 12 close intermolecular contact distances (non-H) shorter

than 3.49 Å. The non-planar structure of this compound is consistent with its observed lack of intercalative binding to DNA.

Introduction. Tricyclic carboxamides of general structure (1) with a coplanar chromophore intercalate DNA and show *in vivo* antitumour activity, whereas analogues with non-planar chromophores do not bind in this manner, and show no activity (Palmer, Newcastle, Atwell, Baguley & Denny, 1988). The only apparent exception to this was the phenothiazine-1-carboxamide (2), which did not appear to unwind closed circular supercoiled DNA [a typical indicator of intercalation (Atwell, Cain, Baguley, Finlay & Denny, 1984)] but did show significant *in*

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