C—C length in the *tert*-butyl group, 1.530 (5) Å, is in excellent agreement with that in (III), 1.527 (5) Å.

Bond distances associated with the P atom reflect the steric bulk of its substituents. Thus the P—C(2) length in (I) of 1.844 (6) Å, from P to the backbone phenylene ring, falls directly between the P—C distances in (II) and (III) of 1.821 (4) and 1.864 (7) Å respectively. Similarly, the P—phenyl-C(11) distance of 1.840 (6) Å in (I) is significantly longer than that of 1.818 (5) Å in (IV), and the mean value of 1.827 (3) Å in (II). The bond length P—*tert*-butyl-C(17) of 1.888 (6) Å in (I) is considerably shorter than the mean value of 1.917 (6) Å in the di-*tert*-butyl complex (III), while the P—*n*-butyl-C(17) distance in (IV) is only 1.817 (5) Å.

The six-membered chelate ring adopts a twist-boat conformation of absolute configuration λ, in which atoms C(2), C(1) and C(7) are displaced by 0.149 (5), −0.250 (6) and −0.789 (6) Å respectively from the Pt—P—N plane. The C(8) methyl group is axially disposed, as is the C(10) *N*-methyl group, while C(9) is equatorial. The sterically uncrowded position of C(10) is consistent with the twofold disorder observed in a difference Fourier synthesis. The *tert*-butyl and phenyl substituents on the P atom bracket the plane of the chelate ring almost equally, showing no tendency to occupy pseudo-axial and pseudo-equatorial positions.

In conclusion, the absolute configuration of the less-soluble diastereomer of *cis*-$PtCl_2$(terphenphos) crystallized from methylene chloride–diethyl ether mixtures has been shown to be (*S*,1*S*); that of the free ligand is therefore (*R*,1*S*). Studies of the efficacy of complexes of this and related ligands in asymmetric synthesis are in progress.

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References

Ball, R. G., Bowman, N. J. & Payne, N. C. (1976). *Inorg. Chem.* **15**, 1704–1707.

Busing, W. R. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.

Cahen, D. & Ibers, J. A. (1972). *J. Appl. Cryst.* **5**, 298–299.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cullen, W. S., Evans, S. V., Han, N. F. & Trotter, J. (1987). *Inorg. Chem.* **26**, 514–519.

Enraf–Nonius (1983). *Enraf–Nonius Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1984). *Enraf–Nonius CAD-4 Operators Manual.* Enraf–Nonius, Delft, The Netherlands.

Larsen, A. C. (1967). *Acta Cryst.* **23**, 664–665.

McKay, I. D. (1986). PhD thesis, Univ. of Western Ontario, Canada.

McKay, I. D. & Payne, N. C. (1986*a*). *Can. J. Chem.* **64**, 1930–1935.

McKay, I. D. & Payne, N. C. (1986*b*). *Acta Cryst.* C**42**, 304–306.

Payne, N. C. & Stephan, D. W. (1982). *Inorg. Chem.* **21**, 182–188.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Takenaka, A., Sasada, Y., Yamamoto, K. & Tsuji, J. (1977). *Bull. Chem. Soc. Jpn*, **50**, 3177–3181.

Tobin, G. R. & Payne, N. C. (1992). In preparation.

Acta Cryst. (1992). C**48**, 48–50

Structure of Sodium 4-(4-Hydroxyphenylazo)benzoate Tetrahydrate

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Abstract. $Na^+.C_{13}H_9N_2O_3^-.4H_2O$, $M_r = 336.28$, $P\bar{1}$, $Z = 2$, $a = 7.297$ (1), $b = 17.704$ (2), $c = 6.343$ (1) Å, $\alpha = 94.03$ (1), $\beta = 107.71$ (1), $\gamma = 83.40$ (1)°, $V = 774.9$ Å^3, $D_x = 1.441$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, graphite monochromator, $\mu = 0.132$ mm^{-1}, $F(000) = 352$, $T = 173$ K, $R = 0.037$,

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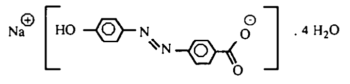
$wR = 0.036$ for 2106 reflections. The crystal structure consists of hydrophilic and hydrophobic layers stacked along the *b* axis. The hydrophilic layer contains the Na ions, the water molecules, and the hydroxyl and carboxylate groups of the azobenzene anion. The hydrophobic layer consists of the azobenzene moieties which pack in an anti-parallel fashion along the *a* axis. The azobenzene moiety itself is found to be quite planar.

Introduction. The changes in absorbance of 2-(4′-hydroxyphenylazo)benzoic acid (HABA) when bound to the biotin-binding protein avidin are routinely used to quantify avidin concentration (Baxter, 1964; Green, 1970). Several structural analogs of HABA were synthesized as part of a program to understand the structural basis of the interaction of HABA in the biotin-binding site of streptavidin, an avidin-like protein secreted from *Streptomyces avidinii* (Chaiet & Wolf, 1964). An accurate crystal structure of one analog was determined when no reliable structures of simple azobenzene derivatives were found in the literature. Here we report the crystal structure of the sodium salt of 4-(4′-hydroxyphenylazo)benzoic acid (I) synthesized by coupling diazotized 4-aminobenzoic acid to phenol.



(I)

Experimental. Intensity data were collected on a light-orange plate with dimensions 0.06 × 0.35 × 0.35 mm on a Syntex *P*3 diffractometer equipped with a graphite monochromator and a Syntex LT1 low-temperature apparatus which kept the crystal cooled to 173 K. Unit-cell parameters were obtained from the least-squares refinement of the computer-centered positions of 70 reflections in the range $20 < 2\theta < 30°$. The ω-scan method was used with a scan width of 1.0° and the scan speed varied from 2.9 to $11.7° \text{min}^{-1}$. A total of 3885 reflections were collected with $4.0 < 2\theta < 55.0°$ and within the range $-9 \leq h \leq 9$, $-22 \leq k \leq 22$, $-9 \leq l \leq 0$. With the averaging of 320 redundant reflections, $R_{\text{int}} = 0.026$, the total number of unique reflections was 3565. Of these, 2106 reflections were found to be non-zero with $I > 3\sigma(I)$. Three standard reflections ($2\bar{2}\bar{2}$, $42\bar{1}$, 080) were measured every 97 reflections and showed less than 2% variation. No absorption correction was applied (a ψ scan showed a 2.9% variation). The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971) and full-matrix least-squares refinement was performed on F_o using a package of local programs (Calabrese, 1990). The Na, O, N and C atoms were refined with anisotropic thermal parameters; the H atoms, located by difference Fourier techniques, were refined with isotropic thermal parameters. Refinement converged at $R = 0.037$ and $wR = 0.036$, error of fit = 1.22, $\Delta/\sigma_{\text{max}} = 0.05$, 279 parameters, data/parameter ratio = 7.55, with weights assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$.* The maximum peak in the final difference Fourier map was 0.23 e Å^{-3} and was located near C(4); the minimum was -0.25 e Å^{-3}. The scattering factors, including anomalous terms for Na, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102).

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

Refinement with anisotropic thermal parameters, $B_{\text{eq}} = \frac{4}{3}\sum_{i=j}^{3}\sum_{j=1}^{3}\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$, where $\mathbf{a}_i$ and $\mathbf{a}_j$ refer to the real lattice vector.

	x	*y*	*z*	B_{eq}
Na(1)	0.0	0.0	0.0	2.20 (3)
Na(2)	0.5	0.0	0.0	1.99 (3)
O(1)	0.0691 (2)	0.1273 (1)	0.1513 (2)	2.60 (5)
O(2)	−0.0303 (2)	0.1180 (1)	0.4464 (2)	2.17 (4)
O(3)	0.4260 (2)	0.7680 (1)	1.1018 (3)	2.61 (5)
O(4)	0.3284 (2)	−0.0270 (1)	0.2619 (3)	2.68 (5)
O(5)	0.1873 (2)	0.0105 (1)	−0.2517 (2)	2.23 (4)
O(6)	0.5721 (2)	−0.1309 (1)	−0.1054 (3)	2.41 (5)
O(7)	−0.3622 (3)	0.1641 (1)	0.5362 (3)	2.60 (5)
N(1)	0.2298 (2)	0.4560 (1)	0.6230 (3)	2.08 (5)
N(2)	0.2227 (2)	0.4773 (1)	0.8138 (3)	2.07 (5)
C(1)	0.1769 (3)	0.3807 (1)	0.5578 (3)	1.9 (1)
C(2)	0.1748 (3)	0.3558 (1)	0.3454 (4)	2.1 (1)
C(3)	0.1305 (3)	0.2829 (1)	0.2697 (3)	2.0 (1)
C(4)	0.0854 (3)	0.2340 (1)	0.4063 (3)	1.7 (1)
C(5)	0.0863 (3)	0.2599 (1)	0.6189 (3)	2.1 (1)
C(6)	0.1314 (3)	0.3324 (1)	0.6956 (3)	2.1 (1)
C(7)	0.0399 (3)	0.1545 (1)	0.3258 (3)	1.8 (1)
C(8)	0.2796 (3)	0.5513 (1)	0.8814 (3)	1.9 (1)
C(9)	0.2612 (3)	0.5795 (1)	1.0840 (4)	2.1 (1)
C(10)	0.3111 (3)	0.6515 (1)	1.1634 (3)	2.1 (1)
C(11)	0.3781 (3)	0.6957 (1)	1.0366 (3)	2.0 (1)
C(12)	0.3980 (3)	0.6679 (1)	0.8332 (4)	2.3 (1)
C(13)	0.3511 (3)	0.5959 (1)	0.7568 (4)	2.2 (1)

Discussion. Atomic positions and equivalent isotropic temperature factors for the non-H atoms are listed in Table 1. The bond distances and angles are given in Table 2. The atomic numbering scheme is shown in Fig. 1. No unusual bond distances were found. The difference in the chemically equivalent C(7)—O(1) and C(7)—O(2) bonds is related to the different environments of the two O atoms: O(1) has more sp^2 character because it bonds to three atoms [C(7), Na(1), H(O6)] in a distorted trigonal conformation, while O(2) has more sp^3 character because it bonds to four atoms [C(7), H(O5) H(O5′), H(O7)] in a distorted tetrahedral arrangement. The azobenzene moiety is essentially planar: the ring containing atoms C(1) through C(6) is planar to within

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54154 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å), angles (°) and hydrogen-bond geometries (Å, °) with e.s.d.'s in parentheses*

Na(1)—O(1)	2.433 (1)	C(1)—C(2)	1.384 (3)
Na(1)—O(4)	2.482 (2)	C(1)—C(6)	1.397 (3)
Na(1)—O(5)	2.425 (2)	C(2)—C(3)	1.386 (3)
Na(2)—O(4)	2.464 (2)	C(3)—C(4)	1.397 (3)
Na(2)—O(5)	2.349 (2)	C(4)—C(5)	1.392 (3)
Na(2)—O(6)	2.411 (2)	C(4)—C(7)	1.502 (3)
O(1)—C(7)	1.243 (2)	C(5)—C(6)	1.380 (3)
O(2)—C(7)	1.284 (2)	C(8)—C(9)	1.384 (3)
O(3)—C(11)	1.368 (2)	C(8)—C(13)	1.398 (3)
N(1)—N(2)	1.257 (2)	C(9)—C(10)	1.384 (3)
N(1)—C(1)	1.428 (2)	C(10)—C(11)	1.384 (3)
N(2)—C(8)	1.418 (3)	C(11)—C(12)	1.391 (3)
		C(12)—C(13)	1.374 (3)

O(1)—Na(1)—O(4)	79.18 (6)	O(1)—C(7)—C(4)	120.6 (2)
O(1)—Na(1)—O(4^{a})	100.82 (6)	O(2)—C(7)—C(4)	116.0 (2)
O(1)—Na(1)—O(5)	89.74 (5)	O(3)—C(11)—C(10)	122.5 (2)
O(1)—Na(1)—O(5^{a})	90.26 (5)	O(3)—C(11)—C(12)	117.0 (2)
O(4)—Na(1)—O(5)	81.33 (5)	N(1)—C(1)—C(2)	116.2 (2)
O(4)—Na(1)—O(5^{a})	98.67 (5)	N(1)—C(1)—C(6)	123.9 (2)
O(4)—Na(2)—O(5)	83.22 (6)	N(2)—C(8)—C(9)	116.5 (2)
O(4)—Na(2)—O(5^{b})	96.78 (6)	N(2)—C(8)—C(13)	124.0 (2)
O(4)—Na(2)—O(6)	96.08 (6)	C(2)—C(1)—C(6)	119.9 (2)
O(4)—Na(2)—O(6^{b})	83.92 (6)	C(1)—C(2)—C(3)	120.3 (2)
O(5)—Na(2)—O(6)	94.10 (6)	C(2)—C(3)—C(4)	120.3 (2)
O(5)—Na(2)—O(6^{b})	85.90 (6)	C(3)—C(4)—C(5)	118.9 (2)
Na(1)—O(4)—Na(2)	95.08 (6)	C(3)—C(4)—C(7)	120.4 (2)
Na(1)—O(5)—Na(2)	99.67 (6)	C(5)—C(4)—C(7)	120.7 (2)
Na(1)—O(1)—C(7)	124.1 (1)	C(4)—C(5)—C(6)	121.0 (2)
N(2)—N(1)—C(1)	114.1 (2)	C(1)—C(6)—C(5)	119.6 (2)
N(1)—N(2)—C(8)	114.4 (2)	C(9)—C(8)—C(13)	119.5 (2)
O(1)—C(7)—O(2)	123.4 (2)	C(8)—C(9)—C(10)	120.8 (2)
		C(9)—C(10)—C(11)	119.1 (2)
		C(10)—C(11)—C(12)	120.6 (2)
		C(11)—C(12)—C(13)	120.0 (2)
		C(8)—C(13)—C(12)	119.9 (2)

D—H$\cdots A$	$D\cdots$H	$D\cdots A$	H$\cdots A$	D—H$\cdots A$
O(3)—H(O3)$\cdots$O(7^{c})	0.87 (3)	2.659 (2)	1.80 (3)	166 (2)
O(4)—H(O4)$\cdots$O(7^{d})	0.86 (3)	2.776 (2)	1.92 (3)	172 (3)
O(5)—H(O5)$\cdots$O(2^{e})	0.88 (3)	2.788 (2)	1.92 (3)	171 (2)
O(5)—H(O5')$\cdots$O(2^{a})	0.82 (3)	2.712 (2)	1.89 (3)	175 (2)
O(6)—H(O6)$\cdots$O(1^{b})	0.88 (3)	2.730 (2)	1.89 (3)	159 (3)
O(6)—H(O6')$\cdots$O(3^{f})	0.78 (3)	2.773 (2)	2.00 (3)	168 (3)
O(7)—H(O7)$\cdots$O(2)	0.93 (3)	2.679 (2)	1.78 (3)	162 (3)
O(7)—H(O7')$\cdots$O(6^{a})	0.82 (3)	2.755 (2)	1.95 (3)	168 (2)

Symmetry codes: (*a*) $-x, -y, -z$; (*b*) $1-x, -y, -z$; (*c*) $-x, 1-y, 2-z$; (*d*) $-x, -y, 1-z$; (*e*) $x, y, -1+z$; (*f*) $x, -1+y, -1+z$.

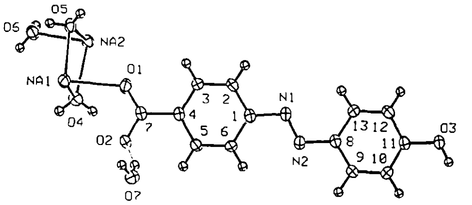

Fig. 1. Asymmetric unit of sodium 4-(4'-hydroxyphenylazo)-benzoate tetrahydrate.

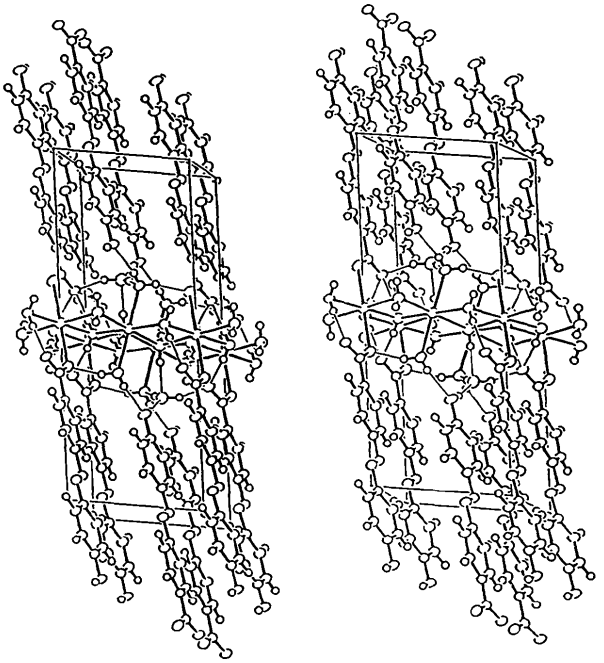

Fig. 2. Packing diagram. The unit cell as shown has the *a* axis horizontal and the *b* axis, from $-b/2$ to $b/2$, vertical.

±0.004 (2) Å with atoms N(1), N(2) and C(7) deviating by −0.037 (2), 0.008 (2) and −0.027 (2) Å, respectively; the ring containing C(8) through C(13) is planar to within ±0.009 (2) Å with atoms N(1), N(2) and O(3) deviating by 0.122 (2), 0.030 (2) and 0.028 (2) Å, respectively; the dihedral angle between the two rings is 7.8 (4)°. The plane of the carboxylate group is twisted 11.5 (3)° out of the plane of the C(1)–C(6) ring. The two crystallographically independent Na cations sit on inversion centers in octahedral sites. Na(1) and Na(2) are bridged by two independent water molecules, O(4) and O(5), and their symmetry equivalents, to form an infinite chain along the *a* axis. The coordination sphere of the Na(1) is completed by bonding to two carboxylate O atoms; two water molecules complete the Na(2) sphere. All of the O—H protons, except H(O4'), participate in forming strong hydrogen bonds, some details of which are given in Table 2. The arrangement of the various ions and water molecules, along with the complete hydrogen-bonding pattern, is shown in Fig. 2, which also shows the segregation into hydrophobic and hydrophilic layers along the *b* axis. While the parallel packing of the azobenzene moieties suggests some π-type interaction between neighbouring rings, there are no particularly short contacts: the shortest C—C and N—N contacts are 3.456 (2) and 3.474 (2) Å, respectively.

References

Baxter, J. M. (1964). *Arch. Biochem. Biophys.* **108**, 375–383.

Calabrese, J. C. (1990). Central Research & Development, E. I. Du Pont de Nemours & Co., Inc., PO Box 80228, Wilmington, DE 19880-0228, USA.

Chaiet, L. & Wolf, F. J. (1964). *Arch. Biochem. Biophys.* **106**, 1–5.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Green, N. M. (1970). *Methods in Enzymology*, Vol. 18A, edited by D. B. McCormick & L. D. Wright, pp. 418–424. New York: Academic Press.