C2—O2 111.3 (3) and O2—C2—C7 113.7 (3)°, of 2-hydroxy-4,4-dimethyl-2-(4-tolyl)morpholinium bromide are similar to those of 2-(4-cyanophenyl)-2-hydroxy-4,4-dimethylmorpholinium bromide [C2—O1 1.425 (5), C2—O2 1.391 (6), C2—C7 1.516 (6) Å; C2—O1—C3 112.3 (3), O1—C2—O2 111.7 (3), O2—C2—C7 114.0 (4)° (Altbach *et al.*, 1988)]. Bond lengths and bond angles are also in agreement with those of 4,4-dimethyl-2-oxomorpholinium bromide (Garcia-Guajardo, Fronczek & Gandour, 1986). The torsion angle O1—C2—C1—N −49.6 (4)° of the title molecule is in agreement with that of 2-(4-cyanophenyl)-2-hydroxy-4,4-dimethylmorpholinium bromide [−50.3 (5)° (Altbach *et al.*, 1988)]. Pharmacological activity of related compounds is reported by Anderson *et al.* (1966) and Lee *et al.* (1992).

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Structure of 1,4-Bis(dibenzylamino)benzene

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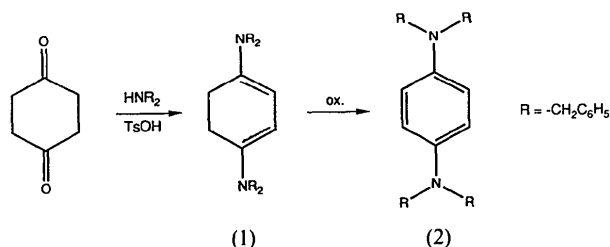
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Abstract. N,N,N',N'-Tetrabenzyl-p-phenylenediamine, $C_{34}H_{32}N_2$, $M_r = 468.68$, monoclinic, $P2_1/n$, $a = 14.766$ (3), $b = 5.604$ (2), $c = 15.897$ (3) Å, $\beta = 97.34$ (2)°, $V = 1304.6$ (6) Å^3, $Z = 2$, $D_x = 1.19$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.064$ mm^{-1}, $F(000) = 500$, room temperature, $R = 0.040$ for 1372 unique reflections having $|F| > 4\sigma(|F|)$. The N atoms of the title compound show sp^2 hybridization. Conjugation with the aromatic ring system is not complete. The torsion angle C(11)—N(1)—C(2)—C(3) is 156.78°.

Experimental. Condensation of 1,4-cyclohexanedione with two equivalents of dibenzylamine in the presence of a catalytic amount of toluene-4-sulfonic acid gave 1,4-bis(dibenzylamino)-1,3-cyclohexadiene (1). 1,4-Bis(dibenzylamino)benzene (2) was prepared by oxidation of compound (1). This system was selected as a model for the preparation of substituted p-phenylenediamine derivatives. The crystals of (2) were grown in acetone. A yellowish crystal of about $0.2 \times 0.2 \times 0.1$ mm, cut from a needle, was chosen for structure analysis. Determination of structure and intensity measurements were carried out at room temperature with a Syntex $P2_1$ automated single-crystal diffractometer using graphite-monochromated Mo $K\alpha$ radiation.

(1)   (2)

R = -CH₂C₆H₅

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic displacement parameters* $(Å^2 \times 10^3)$

Equivalent isotorpic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	4504 (1)	2542 (3)	1402 (1)	54 (1)
C(1)	4203 (1)	1297 (3)	−77 (1)	49 (1)
C(2)	4754 (1)	1290 (3)	708 (1)	44 (1)
C(3)	5556 (1)	−25 (3)	760 (1)	49 (1)
C(11)	3884 (1)	4546 (3)	1279 (1)	54 (1)
C(12)	2874 (1)	3975 (3)	1195 (1)	49 (1)
C(13)	2254 (1)	5559 (4)	782 (1)	62 (1)
C(14)	1327 (2)	5129 (4)	708 (2)	77 (1)
C(15)	1000 (2)	3099 (5)	1044 (1)	76 (1)
C(16)	1609 (2)	1502 (4)	1449 (1)	73 (1)
C(17)	2538 (1)	1919 (4)	1520 (1)	62 (1)
C(21)	4866 (1)	1906 (3)	2263 (1)	53 (1)
C(22)	5629 (1)	3471 (3)	2688 (1)	47 (1)
C(23)	5911 (1)	3212 (4)	3549 (1)	65 (1)
C(24)	6581 (1)	4655 (5)	3964 (1)	75 (1)
C(25)	6980 (1)	6385 (4)	3525 (1)	70 (1)
C(26)	6722 (1)	6638 (4)	2672 (1)	70 (1)
C(27)	6049 (1)	5187 (4)	2253 (1)	59 (1)

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

N(1)—C(2)	1.397 (2)	N(1)—C(11)	1.446 (2)
N(1)—C(21)	1.449 (2)	C(1)—C(2)	1.400 (2)
C(1)—C(3ⁱ)	1.383 (3)	C(2)—C(3)	1.388 (2)
C(3)—C(1ⁱ)	1.383 (3)	C(11)—C(12)	1.515 (3)
C(12)—C(13)	1.380 (3)	C(12)—C(17)	1.381 (3)
C(13)—C(14)	1.380 (3)	C(14)—C(15)	1.370 (4)
C(15)—C(16)	1.370 (3)	C(16)—C(17)	1.381 (3)
C(21)—C(22)	1.516 (2)	C(22)—C(23)	1.387 (2)
C(22)—C(27)	1.378 (3)	C(23)—C(24)	1.379 (3)
C(24)—C(25)	1.372 (3)	C(25)—C(26)	1.367 (3)
C(26)—C(27)	1.387 (3)		

C(2)—N(1)—C(11)	120.6 (1)	C(2)—N(1)—C(21)	121.3 (1)
C(11)—N(1)—C(21)	118.0 (1)	C(2)—C(1)—C(3ⁱ)	121.3 (2)
N(1)—C(2)—C(1)	121.4 (2)	N(1)—C(2)—C(3)	122.0 (1)
C(1)—C(2)—C(3)	116.7 (2)	C(2)—C(3)—C(1ⁱ)	122.0 (1)
N(1)—C(11)—C(12)	116.5 (2)	C(11)—C(12)—C(13)	119.5 (2)
C(11)—C(12)—C(17)	122.7 (2)	C(13)—C(12)—C(17)	117.8 (2)
C(12)—C(13)—C(14)	121.2 (2)	C(13)—C(14)—C(15)	120.5 (2)
C(14)—C(15)—C(16)	118.9 (2)	C(15)—C(16)—C(17)	120.8 (2)
C(12)—C(17)—C(16)	120.8 (2)	N(1)—C(21)—C(22)	116.2 (2)
C(21)—C(22)—C(23)	119.4 (2)	C(21)—C(22)—C(27)	122.5 (2)
C(23)—C(22)—C(27)	118.1 (2)	C(22)—C(23)—C(24)	121.2 (2)
C(23)—C(24)—C(25)	120.0 (2)	C(24)—C(25)—C(26)	119.6 (2)
C(25)—C(26)—C(27)	120.5 (2)	C(22)—C(27)—C(26)	120.6 (2)

Symmetry code: (i) $1 - x$, $-y$, $-z$.

Unit-cell constants were calculated from 25 reflections with $20 < 2\theta < 26°$. Of 2003 reflections collected, intensity data were measured for 1697 unique reflections ($R_{int} = 1.96\%$) with ($+h$, $+k$, $+l$) and ($+h$, $+k$, $-l$) indices in the 2θ range $2 < 2\theta < 45°$ ($|h_{max}| = 15$, $|k_{max}| = 6$, $|l_{max}| = 17$), applying a $2\theta/\omega$ scan (scan speed 3–15° min⁻¹ in ω, range 1.20° plus $K\alpha$ separation) and no absorption correction.

Profile fitting was carried out by a learnt-profile method (Clegg, 1981). After every 69 reflections, three standard reflections (501̄, 031 and 008) were measured; no decay of intensities was observed.

Using 1372 observed reflections with $|F| > 4\sigma(|F|)$, the crystal structure was solved with direct-

methods programs of the *XTAL*2.6 system (Hall & Stewart, 1989). Full-matrix least-squares refinement minimized $\sum w(F_o - F_c)^2$. H atoms were included using a riding model with fixed isotropic U values. Final refinement on $|F|$ with anisotropic atomic displacement parameters for all non-H atoms (1372 reflections, 228 parameters) resulted in $R = 0.040$, $wR = 0.049$, $S = 1.35$. (For all data $R = 0.050$ and $wR = 0.052$.) Weights were assigned as $w^{-1} = \sigma^2(F) + 0.0007F^2$. The maximum least-squares shift to e.s.d. in the final refinement cycle was $(\Delta/\sigma)_{max} = 0.02$. Maximal electron density found in the difference synthesis was $(\Delta\rho)_{max} = 0.11$ and $(\Delta\rho)_{min} = -0.18$ e Å⁻³. Neutral complex scattering factors used were those of Cromer & Mann (1968).

The final values of the atomic coordinates and equivalent isotropic displacement parameters and their e.s.d.'s are given in Table 1.* Bond lengths and angles are listed in Table 2. Fig. 1, showing the atomic numbering scheme, was prepared, and final calculations were performed, with the *SHELXTL-Plus*88 structure-determination programs (Sheldrick, 1988).

Related literature. The N(1)—C(2) bond length in the diamine (2) is between that of *N,N*-dimethylaniline in its hexafluorobenzene complex measured at 120 K [1.39 Å (Dahl, 1985)] and that measured at room temperature [1.47 Å (Dahl, 1977)]. The N(1) atom shows good planarity indicating that it is a π donor, although the torsion angle to the aromatic ring is 156.78°. There is no significant steric influence of the very bulky benzyl moieties. The three bond angles of N(1) are all very close to 120°.
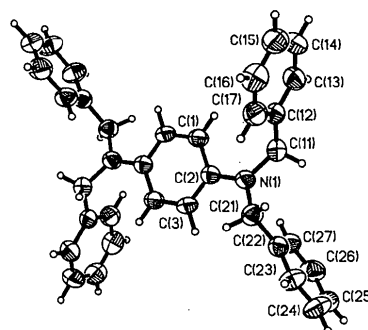
Fig. 1. Projection of the molecule approximately on the least-squares plane of the centrosymmetric benzene ring. The thermal ellipsoids for non-H atoms are drawn at the 50% probability level.

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Structures of 2-(3,5-Dibromo-4-butoxy-1-hydroxy-4-methoxy-2,5-cyclohexadien-1-yl)ethanamide (I) and 2-(3,5-Dibromo-1-hydroxy-4,4-dimethoxy-2,5-cyclohexadien-1-yl)ethanamide (II). Two Marine Compounds

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Abstract. (I) $C_{13}H_{19}Br_2NO_4$, $M_r = 413.15$, monoclinic, $P2_1/c$, $a = 8.235\,(4)$, $b = 12.649\,(6)$, $c = 15.896\,(8)$ Å, $\beta = 93.60\,(4)°$, $V = 1652\,(1)$ Å^3, $Z = 4$, $D_x = 1.66$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0.71073$ Å, $\mu = 48.68$ cm^{-1}, $F(000) = 824$, $T = 293$ K, $R = 0.059$ for 1501 unique observed reflections. (II) $C_{10}H_{13}Br_2NO_4$, $M_r = 371.03$, monoclinic, $P2_1/n$, $a = 9.057\,(2)$, $b = 12.720\,(3)$, $c = 11.678\,(4)$ Å, $\beta = 101.66\,(2)°$, $V = 1318\,(1)$ Å^3, $Z = 4$, $D_x = 1.87$ g cm^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1.54178$ Å, $\mu = 79.38$ cm^{-1}, $F(000) = 728$, $T = 293$ K, $R = 0.045$ for 1639 unique observed reflections. For both molecules the cyclohexadiene rings are planar, the acetal groups show an *anti–anti* conformation and the conformation of the acetamide group is governed by an O—H⋯O intramolecular hydrogen bond. In compound (I) the butyl group is fully extended and *anti*-related to the acetamide. Molecules are held together in the crystal by N—H⋯O hydrogen bonds.

Experimental. The title compounds were isolated from the marine sponges *Aplysina* (*Verongia*) *thiona* (I) and *Aplysina* sp. (II). Suitable single crystals were obtained from acetone solutions by slow evaporation.

For compound (I), a cube-like yellow crystal, 0.38 × 0.38 × 0.4 mm, was used for data collection on a Nicolet *R*3*m* diffractometer with incident-beam graphite monochromator. 25 centered reflections

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with $4.12 \le 2\theta \le 17.13°$ were used for determining cell parameters. Data were collected using ω scans of width 1.2° and rate a function of count rate (4° min^{-1} minimum, 30° min^{-1} maximum), to maximum $(\sin\theta)/\lambda$ of 0.5946 Å^{-1}, and over range of hkl of $0 \le h \le 8$, $0 \le k \le 13$, $-16 \le l \le 16$. Two standards ($1\bar{1}3$ and $00\bar{2}$) monitored every 50 reflections showed random variation of ±3%, no decay correction was applied. 2463 reflections were measured, of which 2155 were unique ($R_{int} = 0.035$) and 654 were unobserved $[F_o \le 3\sigma(F_o)]$. Data were corrected for Lorentz and polarization effects but not for absorption. Space group was determined from absences: $h0l$ with l odd, $0k0$ with k odd and $00l$ with l odd.

Direct methods were applied to solve the phase problem. Block-matrix least-squares refinement was based on F magnitudes, with $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = [\sigma^2(F) + 0.001F_o^2]^{-1}$. Refinement included an isotropic extinction correction according to $F_c^* = F_c/[1 + 0.002\chi(F_c^2)/\sin2\theta]^{0.25}$, with $\chi = 0.0006$. H atoms on heteroatoms (N or O) were located by difference Fourier method, those on C atoms were fixed (C—H = 0.96 Å). 191 parameters were refined: atom coordinates and anisotropic temperature factors for all non-H atoms, coordinates of H atoms on O(1) and N(1), scale factor, and one extinction parameter. All H-atom thermal parameters were fixed at $U = 0.06$ Å^2. Refinement converged to give $R = 0.059$, $wR = 0.055$ for 1501 unique observed reflections ($R = 0.095$, $wR = 0.068$ for all data), $S = 1.211$, $(\Delta/\sigma)_{max} = 0.035$, $\Delta\rho_{min}$ and $\Delta\rho_{max}$ in final difference map -0.58 and $+0.58$ e Å^{-3} respectively. Complex atomic scattering factors were taken from *International Tables for*