Structure of 5,6,11,12-Tetrahydro-2,5,8,11-tetramethylphenomazine

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Abstract. 2,5,8,11-Tetramethyl-5,6,11,12-tetrahydro-dibenzo[*b*,*f*][1,5]diazocine, $C_{18}H_{22}N_2$, $M_r = 266$, monoclinic, $P2_1/c$, $a = 10.130$ (2), $b = 7.390$ (8), $c = 20.770$ (3) Å, $\beta = 105.42$ (1)°, $V = 1498.9$ Å^3, $Z = 4$, $D_x = 1.17$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.37$ cm^{-1}, $F(000) = 576$, final $R = 0.077$ for 1962 reflections with $I > 3\sigma(I)$ out of 2105 unique reflections measured. The molecule has a twisted boat configuration with the planes of the two phenyl rings at an angle of 49.2° to each other.

Introduction. Cooper & Partrige (1957) reported the preparation of a series of 17 different 5,11-*endo*-substituted 5,6,11,12-tetrahydro-2,8-dimethylpheno-mazines with the eight-membered phenomazine ring common to all of them. The present work reports the structure of one of the members of this series, with methyl as the 5 and 11 *endo* substituents, and forms part of a larger program to study the conformational aspects of the eight-membered phenomazine ring in various members and the structure–reactivity relationship among them.

Experimental. Compound (I) obtained as a reaction product of benzoyl peroxide with *N,N*-dimethyl-*p*-toluidine in chloroform (Roy & Swan, 1966). Color-

(I)
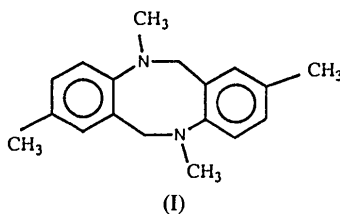
less crystals from aqueous ethanol. 0.3 × 0.3 × 0.015 mm crystal. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ with graphite monochromator. Cell parameters from 25 reflections automatically centered in the range $1.5(1.0 + 0.34\tan\theta)$°. Six standard reflections measured every 2 h of X-ray exposure. 3123 reflections measured, $\theta_{max} = 25°$, 2105 unique reflections, 1962 with $I > 3.0\sigma(I)$, $R_{int} = 0.029$ for 72 common reflections, index range for *h, k, l*: 0 to 11, 0 to 8, −20 to 20. Absorption ignored. Structure

solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement with *SHELX*76 (Sheldrick, 1976), atomic-scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); anisotropic temperature factors for C and N atoms; individual isotropic terms for H atoms; $\Sigma w(F_o - F_c)^2$ minimized, $w = 1/\sigma^2(F_o)$; reflections with $I < 3\sigma(I)$ excluded from refinement; max. $\Delta/\sigma = 0.378$ in the final least-squares cycle. Final $R = 0.077$, $wR = 0.089$ and $S = 4.8$ for the 1962 reflections with $I > 3\sigma(I)$. Atomic coordinates are listed in Table 1.* The *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display and label the *ORTEP* (Johnson, 1965) drawings.

Discussion. Bond lengths, bond angles and torsion angles are given in Table 2 and their values are normal. Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the molecule and Fig. 2 a packing view of the molecules in the unit cell. The atoms linked covalently to the two benzene rings are coplanar with the respective benzene planes; these planes are inclined at an angle of 49.2° to each other and the molecule assumes a twisted boat configuration. The entire molecule may be considered as made up of two chemically identical parts – one consisting of atoms from C1 to N10 and the other from C11 to N20 – which have similar geometry as evident from the similar bond lengths, bond angles and torsion angles of the respective pairs. In the phenomazine ring, both N—CH$_3$ groups are on one side and both the —CH$_2$— groups on the other side of the mean plane through the ring giving a *cis* isomer, although a more symmetrical *trans* isomer would have been energetically more favorable. The structures of other members of the series should be investigated to give a better understanding of this aspect. The only intermolecular interactions in the structure are of the van der Waals type with distances all greater than 3.5 Å.

Table 1. Atomic fractional coordinates and equivalent isotropic temperature factors (Å^2) with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

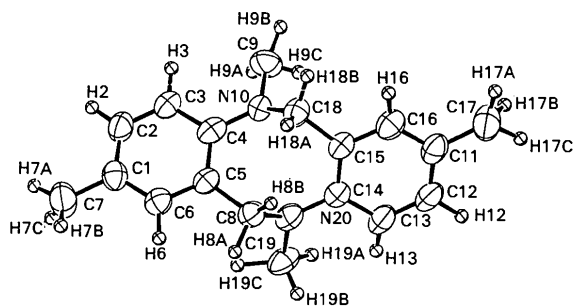|	x	y	z	B_{eq}
C1	0.1903 (5)	0.2816 (7)	0.0640 (2)	4.5 (2)
C2	0.2760 (5)	0.1430 (8)	0.0558 (3)	4.8 (2)
C3	0.4154 (4)	0.1699 (7)	0.0685 (2)	4.3 (2)
C4	0.4764 (5)	0.3367 (6)	0.0902 (2)	3.8 (2)
C5	0.3892 (4)	0.4787 (6)	0.1002 (2)	3.7 (2)
C6	0.2494 (5)	0.4464 (7)	0.0863 (2)	4.3 (2)
C7	0.0370 (6)	0.254 (1)	0.0498 (4)	6.5 (3)
C8	0.4444 (5)	0.6616 (7)	0.1284 (2)	4.3 (2)
C9	0.7081 (6)	0.2101 (9)	0.1123 (3)	5.6 (3)
N10	0.6171 (4)	0.3618 (5)	0.1031 (2)	4.1 (2)
C11	0.9582 (5)	0.8058 (7)	0.1903 (2)	4.8 (2)
C12	0.9031 (5)	0.8500 (7)	0.2425 (3)	4.9 (2)
C13	0.7709 (5)	0.7996 (7)	0.2428 (3)	4.4 (2)
C14	0.6877 (4)	0.7020 (6)	0.1894 (2)	3.7 (2)
C15	0.7430 (5)	0.6519 (6)	0.1364 (2)	3.8 (2)
C16	0.8752 (5)	0.7066 (7)	0.1384 (3)	4.4 (2)
C17	1.1027 (6)	0.855 (1)	0.1901 (4)	6.5 (3)
C18	0.6696 (6)	0.5276 (7)	0.0804 (2)	4.1 (2)
C19	0.5141 (7)	0.6566 (8)	0.2517 (3)	5.1 (3)
N20	0.5559 (4)	0.6496 (5)	0.1900 (2)	4.3 (2)

Fig. 1. An ORTEP diagram of the title compound showing the atomic numbering scheme. The C and N atoms are shown as 50% boundary ellipsoids; H atoms are drawn as spheres with $B = 1.5\,\text{Å}^2$.

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) with e.s.d.'s in parentheses

C1—C6	1.382 (7)	N10—C18	1.463 (6)	
C1—C2	1.383 (7)	C11—C12	1.384 (7)	
C1—C7	1.515 (7)	C11—C16	1.388 (7)	
C2—C3	1.381 (7)	C11—C17	1.509 (8)	
C3—C4	1.398 (6)	C12—C13	1.391 (7)	
C4—N10	1.391 (6)	C13—C14	1.401 (6)	
C4—C5	1.422 (6)	C14—N20	1.393 (6)	
C5—C6	1.389 (6)	C14—C15	1.411 (6)	
C5—C8	1.520 (6)	C15—C16	1.389 (7)	
C8—N20	1.467 (6)	C15—C18	1.513 (6)	
C9—N10	1.431 (6)	C19—N20	1.455 (6)	

C6—C1—C2	117.7 (4)	C12—C11—C16	116.5 (5)	
C6—C1—C7	120.8 (5)	C12—C11—C17	122.7 (5)	
C2—C1—C7	121.5 (5)	C16—C11—C17	120.8 (5)	
C3—C2—C1	120.9 (5)	C11—C12—C13	122.0 (5)	
C2—C3—C4	122.0 (5)	C12—C13—C14	120.8 (5)	
N10—C4—C3	121.5 (4)	N20—C14—C13	120.9 (4)	
N10—C4—C5	121.2 (4)	N20—C14—C15	120.9 (4)	
C3—C4—C5	117.3 (4)	C13—C14—C15	118.2 (4)	
C6—C5—C4	118.8 (4)	C16—C15—C14	118.7 (4)	
C6—C5—C8	118.9 (4)	C16—C15—C18	118.2 (4)	
C4—C5—C8	122.2 (4)	C14—C15—C18	122.9 (4)	
C1—C6—C5	123.2 (5)	C11—C16—C15	123.9 (5)	
N20—C8—C5	113.7 (4)	N10—C18—C15	114.0 (4)	
C4—N10—C9	120.8 (4)	C14—N20—C19	120.1 (4)	
C4—N10—C18	119.4 (4)	C14—N20—C8	119.5 (4)	
C9—N10—C18	115.0 (4)	C19—N20—C8	115.4 (4)	

C1—C6—C5—C4	0.9 (7)	C8—N20—C14—C13	139.5 (5)	
C1—C6—C5—C8	-176.4 (4)	C8—N20—C14—C15	-43.2 (6)	
C1—C2—C3—C4	0 (1)	C8—C5—C4—N10	-3.0 (6)	
C2—C3—C4—N10	179.7 (5)	C9—N10—C18—C15	-92.4 (6)	
C2—C3—C4—C5	1.3 (7)	N10—C18—C15—C16	125.9 (5)	
C2—C1—C6—C5	0.6 (7)	N10—C18—C15—C14	-48.6 (7)	
C3—C2—C1—C6	-1.0 (8)	C11—C12—C13—C14	-0.4 (8)	
C3—C2—C1—C7	179.6 (6)	C11—C16—C15—C14	1.2 (7)	
C3—C4—N10—C9	-16.9 (6)	C11—C16—C15—C18	-173.6 (5)	
C3—C4—N10—C18	137.2 (4)	C12—C11—C16—C15	0.2 (9)	
C3—C4—C5—C6	-1.7 (6)	C12—C13—C14—N20	179.2 (5)	
C3—C4—C5—C8	175.4 (4)	C12—C13—C14—C15	1.8 (7)	
C4—N10—C18—C15	112.0 (5)	C13—C12—C11—C16	-0.6 (8)	
C4—C5—C8—N20	-50.2 (6)	C13—C12—C11—C17	-178.2 (5)	
C5—C6—C1—C7	179.9 (7)	C13—C14—N20—C19	-14.6 (7)	
C5—C4—N10—C9	161.4 (4)	C13—C14—C15—C16	-2.1 (6)	
C5—C4—N10—C18	-44.4 (4)	C13—C14—C15—C18	172.3 (4)	
C5—C8—N20—C14	112.2 (5)	C15—C16—C11—C17	177.9 (5)	
C5—C8—N20—C19	-92.5 (5)	C15—C14—N20—C19	162.7 (4)	
C6—C5—C4—N10	180 (1)	C16—C15—C14—N20	-179.6 (4)	
C6—C5—C8—N20	127.0 (4)	C18—C15—C14—N20	-5.1 (7)	
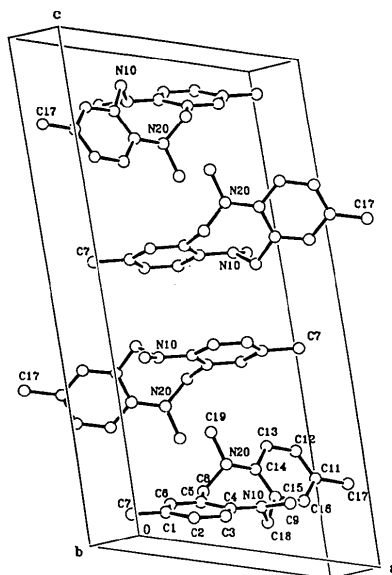
Fig. 2. An ORTEP diagram illustrating the packing of the molecules in the unit cell.

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Dimanganese Octacarbonyl Complexes with Bridging Phosphanido Ligands

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Abstract. Octacarbonyl-$1\kappa^4C,2\kappa^4C$-bis-μ-(dicyclohexylphosphanido-$1:2\kappa^2P$)-dimanganese, [Mn$_2$-(C$_{12}$H$_{22}$P)$_2$(CO)$_8$], (I), $M_r = 728.5$, triclinic, $P\bar{1}$, $a = 8.945\,(2)$, $b = 10.098\,(2)$, $c = 11.376\,(3)$ Å, $\alpha = 109.76\,(2)$, $\beta = 93.30\,(2)$, $\gamma = 114.32\,(1)°$, $V = 857.7$ Å^3, $Z = 1$, $D_x = 1.410$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.84$ mm^{-1}, $F(000) = 380$, $T = 296\,(1)$ K, $R = 0.046$, $wR = 0.041$ for 2221 unique intensities. Octacarbonyl-$1\kappa^4C,2\kappa^4C$-bis-μ-(phenylphosphanido-$1:2\kappa^2P$)-dimanganese, [Mn$_2$(C$_6$H$_6$P)$_2$(CO)$_8$], (II), $M_r = 552.1$, triclinic, $P\bar{1}$, $a = 6.848\,(1)$, $b = 8.720\,(2)$, $c = 10.805\,(2)$ Å, $\alpha = 100.16\,(1)$, $\beta = 99.43\,(1)$, $\gamma = 106.22\,(1)°$, $V = 594.1$ Å^3, $Z = 1$, $D_x = 1.543$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.20$ mm^{-1}, $F(000) = 276$, $T = 298\,(1)$ K, final $R = 0.055$, $wR = 0.053$ for 2003 unique intensities. Both compounds consist of two edge-sharing coordination octahedra with planar Mn$_2$P$_2$ rings. Of the two possible isomers of (II), the one with *anti* position of the P ligands is realized. The average Mn—P bond lengths are 2.411 (2) Å for (I) and 2.358 (1) Å for (II).

Experimental. Compound (I) was prepared by reaction of Mn$_2$(CO)$_{10}$ with HP(C$_6$H$_{11}$)$_2$ dissolved in xylene in a glass tube at 433 K for 10 h; for (II), Mn$_2$(CO)$_{10}$ and H$_2$P(C$_6$H$_5$) were treated at 453 K under the same conditions. Both substances were recrystallized from CH$_2$Cl$_2$/pentane.

For (I), a yellow crystal of size 0.08 × 0.20 × 0.24 mm was used for data collection on a Siemens *R3m/V* diffractometer with graphite-monochromated

Mo $K\alpha$ radiation. Lattice parameters were refined from 25 reflections ($15 \le 2\theta \le 25°$). ω–2θ scans were used to collect 4166 intensities for $3 \le 2\theta \le 55°$, $-11 \le h \le 11$, $-13 \le k \le 13$, $0 \le l \le 14$. Three standards, monitored every 400 reflections, showed only random deviations. Lp corrections were applied, as well as an empirical absorption correction (lamina) *via* ψ scans; minimum/maximum transmission 0.812/0.999. 3968 unique intensities were obtained after merging ($R_{int} = 0.032$), of which 2278 had $F > 4\sigma(F)$. The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement (based on F) of 199 parameters, with anisotropic refinement for all but H atoms, H atoms fixed at idealized positions with common isotropic displacement parameters $U_{iso} = 0.08$ Å^2, converged to $R = 0.046$, $wR = 0.041$ [$1/w = \sigma^2(F) + 0.0001F^2$], $S = 1.321$. Maximum $(\Delta/\sigma) = 0.001$, minimum/maximum height in the final ΔF map $-0.33/0.29$ e Å^{-3}.

For (II), a yellow crystal of size 0.15 × 0.19 × 0.57 mm was used with a diffractometer as above. Lattice parameters were refined from 25 reflections ($10 \le 2\theta \le 27°$). Data collection was as above for 2845 intensities with $-8 \le h \le 8$, $-11 \le k \le 11$, $0 \le l \le 14$. Three standards, monitored every 400 reflections, showed decay of 4%; intensities were scaled on the standards. Other corrections were as above, with minimum/maximum transmission for absorption 0.430/0.464, 2703 unique intensities were obtained after merging ($R_{int} = 0.013$), of which 2067 had $F > 4\sigma(F)$. Structure solution and refinement was as above for 133 parameters, with phenyl groups