

1985). Final positional parameters are given in Table 1, with selected bond distances and angles in Table 2.\* The atomic labelling scheme and molecular structure are shown in Fig. 1.

**Related literature.** For other Co/Sb complexes see Clegg, Compton, Errington, Hockless, Norman, Ramshaw & Webster (1990), and Norman, Webster & Farrugia (1992). Other related complexes containing Sb—Mn bonds include [SbCl{Mn(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)}{Mn(CO)<sub>5</sub>}<sub>2</sub>] (Lombard, Huttner & Zsolnai, 1988), [SbCl{Mn(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}{Mn<sub>2</sub>(CO)<sub>4</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] (von Seyerl, Wohlfahrt & Huttner, 1980), [SbBr{Mn(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)}{Fe(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] and [SbBr{Mn(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)}{Fe<sub>2</sub>(CO)<sub>4</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}] (Zsolnai, 1984). For other monohalo metallastibane or stibate(1-) species see Ferrer, Rossell, Seco & Braunstein (1989),

\* Lists of structure factors, anisotropic thermal parameters, H-atom positional parameters and complete bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55401 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1004]

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## Structure of 4-Piperidone Derivatives. III. 1,3,3-Trimethyl-2,6-diphenyl-4-piperidone and 2,6-Bis(*p*-chlorophenyl)-1,3,5-trimethyl-4-piperidone

BY K. SEKAR AND S. PARTHASARATHY\*

*Department of Crystallography and Biophysics,† University of Madras, Guindy Campus, Madras - 600 025, India*

AND T. R. RADHAKRISHNAN

*Drug Standardisation Research Unit [UNANI], Central Council for Research in Unani Medicine, Post Graduate Department of Chemistry, New College, Madras - 600 014, India*

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**Abstract.** C<sub>20</sub>H<sub>23</sub>NO (I), *M<sub>r</sub>* = 293.4, triclinic, *P* $\bar{1}$ , *a* = 6.486 (2), *b* = 10.921 (2), *c* = 12.542 (1) Å,  $\alpha$  = 79.90 (1),  $\beta$  = 88.87 (2),  $\gamma$  = 73.50 (2)°, *V* = 838.2 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.16 g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha)$  = 1.5418 Å,  $\mu$  = 5.15 cm<sup>-1</sup>, *F*(000) = 316, *T* = 295 K, *R* = 0.051, *wR* = 0.070 for 2641 unique observed reflections [*I* > 3 $\sigma$ (*I*)]. C<sub>20</sub>H<sub>21</sub>Cl<sub>2</sub>NO (II), *M<sub>r</sub>* = 362.3,

Trinh-Toan & Dahl (1971), Panster & Malisch (1976) and Malisch & Panster (1975, 1976).

### References

- CLEGG, W., COMPTON, N. A., ERRINGTON, R. J., HOCKLESS, D. C. R., NORMAN, N. C., RAMSHAW, M. & WEBSTER, P. M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 2375–2385.  
 FERRER, M., ROSSELL, O., SECO, M. & BRAUNSTEIN, P. (1989). *J. Organomet. Chem.* **364**, C5–C7.  
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.  
 LOMBARD, A., HUTTNER, G. & ZSOLNAI, L. (1988). *J. Organomet. Chem.* **352**, 295–302.  
 MALISCH, W. & PANSTER, P. (1975). *Z. Naturforsch. Teil B*, **30**, 229–234.  
 MALISCH, W. & PANSTER, P. (1976). *Angew. Chem. Int. Ed. Engl.* **15**, 618–619.  
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 NORMAN, N. C., WEBSTER, P. M. & FARRUGIA, L. J. (1992). *J. Organomet. Chem.* **430**, 205–219.  
 PANSTER, P. & MALISCH, W. (1976). *Chem. Ber.* **109**, 692–704, 2112–2120.  
 TRINH-TOAN, T. & DAHL, L. F. (1971). *J. Am. Chem. Soc.* **93**, 2654–2666.  
 SEYERL, J. VON, WOHLFAHRT, L. & HUTTNER, G. (1980). *Chem. Ber.* **113**, 2868–2875.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.  
 ZSOLNAI, L. (1984). PhD thesis. Univ. of Konstanz, Germany.

orthorhombic, *Pnma*, *a* = 7.420 (2), *b* = 23.118 (1), *c* = 10.624 (2) Å, *V* = 1822.4 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.32 g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha)$  = 1.5418 Å,  $\mu$  = 32.95 cm<sup>-1</sup>, *F*(000) = 760, *T* = 295 K, *R* = 0.042, *wR* = 0.048 for 1221 unique observed reflections [*I* > 3 $\sigma$ (*I*)]. The 4-piperidone ring has a slightly distorted chair conformation in both compounds and the mean torsion angles are 54.0 (2) and 52.7 (3)° for (I) and (II), respectively. In (I) the puckering is enhanced in the area of N1 and in (II) it is enhanced in the area of

\* Author for correspondence.

† Contribution No. 793.

C4. The phenyl rings are planar within six standard deviations and all molecular dimensions and van der Waals interactions are normal in both compounds.

**Experimental.** Crystals of the title compounds were grown from ethanol at room temperature. The intensities were collected with an Enraf-Nonius CAD-4 diffractometer using Ni-filtered Cu K $\alpha$  radiation. Unit-cell parameters were derived from a least-squares analysis of 25 reflections with  $25 \leq 2\theta \leq 35^\circ$ . Intensity data were collected with the  $\omega$ - $2\theta$  scan technique. The structures were solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined on *F* by weighted full-matrix least squares on a MicroVAX II computer with *SHELX76* (Sheldrick, 1976). Atomic scattering factors were those of *SHELX76* taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

(I): A crystal with dimensions  $0.25 \times 0.20 \times 0.20$  mm was used for data collection. 3031 unique reflections ( $h - 7$  to  $7$ ,  $k - 13$  to  $13$ ,  $l 0$  to  $15$ ) up to  $2\theta = 140^\circ$  were measured, of which 2641 had intensities greater than  $3\sigma(I)$ . During data collection three standard reflections, monitored after every 2 h of X-ray exposure, indicated no decay over the full 36 h period. The intensity data were corrected for Lorentz, polarization and absorption ( $\psi$ -scan method) effects (transmission-factor range 0.9603–0.9954). Using *STATC*, a Fortran program for conducting statistical tests for centrosymmetry (Parthasarathy, Ponnuswamy, Elango & Sekar, 1990), the space group of the crystal was found to be *P* $\bar{1}$ . H atoms were located from a difference Fourier map. All the H atoms were refined with isotropic atomic displacement parameters in the final cycles. Final maximum  $\Delta/\sigma = 0.05$  and maximum and minimum heights in final  $\Delta\rho$  maps were 0.204 and  $-0.224 \text{ e } \text{\AA}^{-3}$ , respectively. Refinement with weights given by  $w = [\sigma^2(F) + 0.006689(F_o^2)]^{-1}$  converged at  $R = 0.051$ ,  $wR = 0.070$  and  $S = 1.12$  for 291 parameters.

(II): A crystal with dimensions  $0.30 \times 0.20 \times 0.30$  mm was used for data collection. 1494 unique reflections ( $h 0$  to  $8$ ,  $k 0$  to  $27$ ,  $l 0$  to  $12$ ) up to  $2\theta = 130^\circ$  were measured, of which 1221 had their intensities greater than  $3\sigma(I)$ . During data collection three standard reflections, monitored after every 2 h of X-ray exposure, indicated no decay over the full 20 h period. The intensity data were corrected for Lorentz, polarization and absorption ( $\psi$ -scan method) effects (transmission-factor range 0.7631–0.9724). Systematic absences showed that the space group of the crystal could be either *Pna2*<sub>1</sub> or *Pnam*. The space group was tentatively chosen to be *Pna2*<sub>1</sub>. During refinement, an examination of the least-squares correlation matrix showed that the correlation coefficients of all pairs of atoms in the groups attached to

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
(I)				
N1	3041 (2)	1027 (1)	7623 (1)	45 (1)
C2	3213 (2)	1994 (1)	6671 (1)	44 (1)
C3	1785 (2)	1996 (1)	5679 (1)	49 (1)
C4	2210 (2)	611 (2)	5481 (1)	50 (1)
C5	2159 (3)	-379 (2)	6469 (1)	54 (1)
C6	3624 (2)	-299 (1)	7375 (1)	45 (1)
C7	4529 (4)	1050 (2)	8485 (1)	69 (1)
C8	2694 (2)	3329 (1)	6988 (1)	48 (1)
C9	978 (3)	3763 (2)	7641 (1)	59 (1)
C10	573 (4)	4963 (2)	7962 (2)	74 (1)
C11	1867 (4)	5754 (2)	7630 (2)	76 (1)
C12	3565 (4)	5345 (2)	6978 (2)	77 (1)
C13	3966 (3)	4149 (2)	6653 (2)	63 (1)
C14	-623 (3)	2494 (2)	5852 (2)	67 (1)
C15	2385 (4)	2831 (2)	4674 (1)	74 (1)
O16	2495 (2)	318 (1)	4591 (1)	65 (1)
C17	3465 (3)	-1274 (1)	8373 (1)	48 (1)
C18	1573 (3)	-1138 (2)	8935 (1)	63 (1)
C19	1436 (4)	-2028 (2)	9848 (2)	77 (1)
C20	3176 (4)	-3091 (2)	10192 (1)	74 (1)
C21	5035 (4)	-3244 (2)	9648 (2)	72 (1)
C22	5192 (3)	-2343 (1)	8729 (1)	58 (1)
(II)				
C11	1099 (1)	5080	1844 (1)	80 (1)
N1	143 (3)	2500	4627 (2)	40 (1)
C2	-499 (3)	3043 (1)	5208 (2)	41 (1)
C3	-2567 (3)	3047 (1)	5380 (2)	46 (1)
C4	-3144 (4)	2500	6044 (3)	49 (1)
C5	2115 (4)	2500	4625 (3)	57 (1)
C6	27 (3)	3546 (1)	4360 (2)	41 (1)
C7	794 (3)	4047 (1)	4845 (2)	48 (1)
C8	1140 (3)	4519 (1)	4079 (2)	54 (1)
C9	725 (3)	4486 (1)	2814 (2)	50 (1)
C10	-5 (3)	3988 (1)	2302 (2)	50 (1)
C11	-341 (3)	3522 (1)	3080 (2)	46 (1)
C12	-3236 (4)	3588 (1)	6063 (3)	70 (1)
O13	-3961 (4)	2500	7023 (2)	73 (1)

the 4-piperidone ring were large. Hence the space group *Pna2*<sub>1</sub> was discarded. Since the space group *Pnam* is not in the standard form, the equivalent space group *Pnma* was chosen and necessary transformations were made. H atoms were located from a difference Fourier map. All the H atoms were refined with isotropic atomic displacement parameters in the final cycles. Final maximum  $\Delta/\sigma = 0.05$  and maximum and minimum heights in final  $\Delta\rho$  maps were 0.13 and  $-0.33 \text{ e } \text{\AA}^{-3}$ , respectively. Refinement with weights given by  $w = [\sigma^2(F) + 0.006814(F_o^2)]^{-1}$  converged at  $R = 0.042$ ,  $wR = 0.048$  and  $S = 0.75$  for 158 parameters.

Final positional and thermal parameters are listed in Table 1\* with bond lengths and angles obtained using *PARST* (Nardelli, 1983) in Table 2. *PLUTO* (Motherwell & Clegg, 1978) drawings of each molecule showing the molecular geometry are presented in Figs. 1 and 2, respectively.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55383 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0270]

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°) for structures (I) and (II)

(I)			
N1—C2	1.474 (2)	C8—C13	1.391 (3)
C2—C3	1.565 (2)	C3—C14	1.526 (2)
C3—C4	1.522 (3)	C3—C15	1.533 (2)
C4—C5	1.501 (2)	C4—O16	1.211 (2)
C5—C6	1.525 (2)	C6—C17	1.517 (2)
C6—N1	1.476 (2)	C17—C18	1.387 (3)
N1—C7	1.472 (3)	C18—C19	1.385 (3)
C2—C8	1.522 (2)	C19—C20	1.381 (3)
C8—C9	1.391 (2)	C20—C21	1.357 (3)
C9—C10	1.391 (3)	C21—C22	1.401 (3)
C10—C11	1.377 (4)	C17—C22	1.382 (2)
C11—C12	1.376 (4)		
C12—C13	1.389 (3)		
N1—C2—C3	112.8 (1)	C14—C3—C15	109.3 (1)
C2—C3—C4	109.0 (1)	C4—C3—C14	106.7 (1)
C3—C4—C5	115.2 (1)	C4—C3—C15	109.2 (1)
C4—C5—C6	110.9 (1)	C3—C4—O16	123.3 (2)
C5—C6—N1	110.6 (1)	C5—C6—C17	109.4 (1)
C6—N1—C2	111.9 (1)	C6—C17—C18	121.1 (1)
C6—N1—C7	108.1 (1)	C17—C18—C19	120.9 (2)
C7—N1—C2	108.6 (1)	C18—C19—C20	120.1 (2)
C8—C9—C10	121.2 (2)	C19—C20—C21	119.8 (2)
N1—C2—C8	109.5 (1)	C20—C21—C22	120.5 (2)
C3—C2—C8	111.7 (1)	C21—C22—C17	120.5 (2)
C2—C8—C9	121.7 (1)	C22—C17—C6	120.7 (1)
N1—C6—C17	110.7 (1)	C22—C17—C18	118.2 (1)
O16—C4—C5	121.5 (2)	C13—C8—C2	120.7 (1)
C9—C10—C11	120.3 (2)	C2—C3—C14	113.4 (1)
C10—C11—C12	119.4 (2)	C2—C3—C15	109.1 (1)
C11—C12—C13	120.4 (2)		
C12—C13—C8	121.1 (2)		
C9—C8—C13	117.5 (2)		
N1—C2—C3—C4	-50.1 (2)	C4—C5—C6—N1	55.5 (2)
C2—C3—C4—C5	48.2 (2)	C5—C6—N1—C2	-59.4 (2)
C3—C4—C5—C6	-52.0 (2)	C6—N1—C2—C3	57.5 (2)
(II)			
N1—C2	1.478 (3)	C8—C9	1.381 (3)
C2—C3	1.545 (3)	C9—C10	1.384 (3)
C3—C4	1.510 (3)	C10—C11	1.381 (3)
N1—C5	1.463 (4)	C6—C11	1.388 (3)
C2—C6	1.522 (3)	C9—C11	1.739 (2)
C6—C7	1.390 (3)	C4—O13	1.204 (4)
C7—C8	1.385 (3)	C3—C12	1.529 (4)
N1—C2—C3	112.0 (2)	C6—C7—C8	121.0 (2)
C2—C3—C4	109.4 (2)	C7—C8—C9	119.1 (2)
C2—C3—C12	112.6 (2)	C8—C9—C10	121.1 (2)
C4—C3—C12	111.8 (2)	C8—C9—C11	119.8 (2)
C3—C4—O13	123.1 (1)	C11—C9—C10	119.1 (2)
C2—N1—C5	108.8 (1)	C9—C10—C11	119.0 (2)
C2—C6—C11	119.9 (2)	C10—C11—C6	121.3 (2)
C2—C6—C7	121.5 (2)	C7—C6—C11	118.5 (2)
C6—C2—N1	108.6 (2)	C6—C2—C3	108.7 (2)
C2—N1—C2'	116.3 (2)	C3—C4—C3'	113.8 (2)
N1—C2—C3—C4	51.1 (2)	C2'—N1—C2—C3	-50.3 (2)
C2—C3—C4—C3'	-56.6 (3)		

**Related literature.** The 4-piperidone rings in both compounds have a slightly distorted chair conformation. In the 4-piperidone ring, puckering is enhanced in the area of N1 and decreased in the area of C3 for compound (I); however, it is enhanced in the area of C4 and decreased in the area of N1 for compound (II). The puckering observed in the 4-piperidone rings of other structures, namely, (i) 3-methyl-2,6-diphenyl-4-piperidone (Sekar, Parthasarathy & Rajalingam, 1990), (ii) 2,6-bis(*p*-methoxyphenyl)-3,5-dimethyl-4-piperidone (Sekar, Parthasarathy & Radhakrishnan, 1990), (iii) 1,1'-di(4-pyridyl)-2,2',6,6'-bi(4-piperidone) dihydrochloride dihydrate (Cheer, Cosgrove & Vittimberga, 1984), (iv) 3,5-bis(4-dimethylaminobenzylidene)-1-methyl-4-piperidone (Jia, Quail, Arora & Dimmock, 1989a),

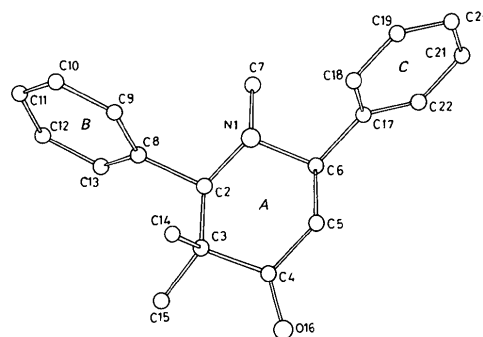


Fig. 1. A view of the molecular structure of compound (I) with atom numbering.

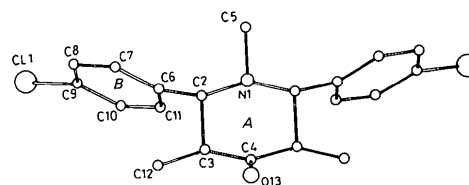


Fig. 2. A view of the molecular structure of compound (II) with atom numbering.

(v) 3,5-bis(benzylidene)-1-methyl-4-piperidone methobromide hemimethanol solvate (Jia, Quail, Arora & Dimmock, 1989b), (vi) 3,5-bis(4-dimethylaminobenzylidene)-1-methyl-4-piperidone methoiodide (Jia, Quail, Arora & Dimmock, 1989c) and (vii) 3,5-bis(benzylidene)-4-piperidone hydrochloride and its *N*-methyl analogue (Jia, Quail, Arora & Dimmock, 1988), is opposite to that observed in (II).

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#### References

- CHEER, C. J., COSGROVE, J. P. & VITTIMBERGA, B. M. (1984). *Acta Cryst.* **C40**, 1474–1475.
- JIA, Z., QUAIL, J. W., ARORA, V. K. & DIMMOCK, J. R. (1988). *Acta Cryst.* **C44**, 2114–2117.
- JIA, Z., QUAIL, J. W., ARORA, V. K. & DIMMOCK, J. R. (1989a). *Acta Cryst.* **C45**, 285–289.
- JIA, Z., QUAIL, J. W., ARORA, V. K. & DIMMOCK, J. R. (1989b). *Acta Cryst.* **C45**, 1117–1118.
- JIA, Z., QUAIL, J. W., ARORA, V. K. & DIMMOCK, J. R. (1989c). *Acta Cryst.* **C45**, 1119–1120.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- PARTHASARATHY, S., PONNUSWAMY, M. N., ELANGO, N. & SEKAR, K. (1990). *Acta Cryst.* **A46**, C-37.
- SEKAR, K., PARTHASARATHY, S. & RADHAKRISHNAN, T. R. (1990). *Acta Cryst.* **C46**, 1338–1340.
- SEKAR, K., PARTHASARATHY, S. & RAJALINGAM, P. (1990). *Acta Cryst.* **C46**, 1153–1155.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.