

## Structure of 3,5-Bis(benzylidene)-1-methyl-4-piperidone Methobromide Hemioethanol Solvate

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**Abstract.**  $C_{21}H_{22}NO^+ \cdot Br^- \cdot \frac{1}{2}C_2H_6O$ ,  $M_r = 407.35$ , triclinic,  $P\bar{1}$ ,  $a = 11.330(1)$ ,  $b = 12.8159(7)$ ,  $c = 13.992(2)$  Å,  $\alpha = 79.230(8)$ ,  $\beta = 78.76(1)$ ,  $\gamma = 75.972(5)^\circ$ ,  $V = 1912.63$  Å<sup>3</sup>,  $Z = 4$  (two molecules per asymmetric unit),  $D_m$  (by flotation) = 1.37,  $D_x = 1.41$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 3.77$  cm<sup>-1</sup>,  $F(000) = 844$ ,  $T = 287$  K,  $R = 0.061$  ( $wR = 0.067$ ) for 3933 observed reflections. The two crystallographically independent molecules are almost identical. The central heterocyclic ring exhibits a boat conformation which is obviously flattened at the C(4) end due to the conjugated dienone system. The steric repulsions between H atoms attached to C(2)/C(6) and those on the phenyl rings cause increases in the bond angles at the C atoms joining the rings and rotations of the phenyl groups about the two C–Ph bonds at the expense of the conjugation energy of the system.

**Experimental.** Title compound prepared according to the literature procedure (Krapcho & Turk, 1979) in a yield of 87% with m.p. 488–490 K (found: C 65.76, H 6.08, N 3.75%;  $C_{21}H_{22}NO^+ \cdot Br^-$  requires C 65.63, H 5.77, N 3.65%). Crystallized from mixture of Et<sub>2</sub>O and 95% EtOH. Yellow crystal with dimensions 0.15 × 0.25 × 0.38 mm. Cell parameters by least squares using 25 reflections with  $9.63 < \theta < 25.20^\circ$ . Enraf–Nonius CAD-4 diffractometer used for data collection, 5043 unique reflections,  $-12 \leq h \leq 12$ ,  $-13 \leq k \leq 13$ ,  $0 \leq l \leq 14$ ,  $[(\sin\theta)/\lambda]_{\max} = 0.5313$  Å<sup>-1</sup>. 3933 reflections with  $I > 2\sigma(I)$  used in refinement. Three intensity and orientation monitor reflections, intensity fluctuation within 4.3%. No absorption or extinction correction applied. Merging  $R$  based on intensities of 0.0290 for 508 replicate reflections. Structure solved by direct methods using XTAL (Hall & Stewart, 1988), all non-H atoms found on  $E$  map and refined anisotropically; H atoms calculated and not refined.  $R = 0.061$ ,  $wR = 0.067$  [ $w = 1/\sigma^2(F)$ ],  $S = 3.978$  for 3933 observed reflections, 445 parameters refined.  $F$  magnitudes used in LS refinement. Final  $(\Delta/\sigma)_{av} = 0.012$ ,  $(\Delta/\sigma)_{\max} = 0.29$ .  $\Delta\rho$  in final difference

Table 1. Fractional coordinates and equivalent isotropic thermal parameters ( $\times 10^3$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*(\text{Å}^2)$
Br	0.22217 (7)	0.51683 (8)	0.01079 (6)	103
O(4)	0.3866 (3)	0.6199 (4)	0.4424 (3)	71
N(1)	0.4494 (4)	0.6272 (3)	0.1477 (3)	42
C(1A)	0.4695 (5)	0.6548 (5)	0.0369 (4)	53
C(1B)	0.4461 (5)	0.5098 (4)	0.1747 (4)	60
C(2)	0.5538 (4)	0.6497 (4)	0.1879 (3)	46
C(3)	0.5360 (4)	0.6226 (4)	0.2985 (4)	46
C(4)	0.4078 (5)	0.6415 (4)	0.3529 (4)	52
C(5)	0.3048 (4)	0.6905 (4)	0.2948 (3)	44
C(6)	0.3305 (4)	0.6977 (4)	0.1849 (4)	44
C(7)	0.1954 (5)	0.7283 (4)	0.3454 (4)	49
C(8)	0.6279 (5)	0.5837 (4)	0.3516 (4)	49
C(9)	0.7610 (5)	0.5637 (4)	0.3247 (4)	50
C(10)	0.8303 (5)	0.4961 (5)	0.3936 (4)	63
C(11)	0.9589 (5)	0.4754 (5)	0.3752 (4)	69
C(12)	1.0182 (5)	0.5204 (5)	0.2878 (5)	72
C(13)	0.9517 (5)	0.5864 (5)	0.2195 (4)	66
C(14)	0.8241 (5)	0.6100 (5)	0.2383 (4)	59
C(15)	0.0770 (5)	0.7850 (4)	0.3119 (4)	51
C(16)	-0.0297 (5)	0.7889 (5)	0.3820 (4)	61
C(17)	-0.1443 (5)	0.8388 (5)	0.3563 (5)	71
C(18)	-0.1530 (5)	0.8867 (5)	0.2614 (4)	66
C(19)	-0.0507 (5)	0.8860 (4)	0.1931 (4)	55
C(20)	0.0638 (5)	0.8343 (4)	0.2165 (4)	50
Br'	0.73240 (7)	0.05259 (6)	0.01567 (5)	80
O(4')	0.8929 (4)	0.1656 (5)	0.4481 (3)	112
N(1')	0.9589 (5)	0.2176 (3)	0.1532 (3)	63
C(1A')	0.9672 (6)	0.3278 (5)	0.1708 (5)	80
C(1B')	0.9798 (7)	0.2151 (5)	0.0446 (4)	80
C(2')	1.0556 (6)	0.1313 (4)	0.1980 (4)	61
C(3')	1.0325 (5)	0.1167 (5)	0.3079 (4)	59
C(4')	0.9072 (6)	0.1604 (6)	0.3607 (4)	74
C(5')	0.8048 (6)	0.1940 (5)	0.3043 (4)	68
C(6')	0.8318 (5)	0.1957 (4)	0.1951 (4)	60
C(7')	0.6906 (6)	0.2202 (5)	0.3556 (4)	73
C(8')	1.1181 (5)	0.0644 (5)	0.3636 (4)	62
C(9')	1.2477 (5)	0.0113 (4)	0.3411 (4)	60
C(10')	1.3142 (6)	-0.0176 (6)	0.4190 (5)	81
C(11')	1.4361 (6)	-0.0666 (6)	0.4061 (6)	97
C(12')	1.4930 (6)	-0.0882 (6)	0.3129 (6)	98
C(13')	1.4302 (6)	-0.0612 (5)	0.2358 (5)	83
C(14')	1.3087 (5)	-0.0128 (5)	0.2496 (4)	65
C(15')	0.5691 (5)	0.2435 (5)	0.3270 (4)	67
C(16')	0.4712 (6)	0.2951 (6)	0.3924 (4)	76
C(17')	0.3515 (6)	0.3150 (6)	0.3743 (5)	85
C(18')	0.3301 (6)	0.2836 (6)	0.2908 (5)	94
C(19')	0.4251 (6)	0.2327 (5)	0.2271 (5)	85
C(20')	0.5411 (6)	0.2116 (5)	0.2456 (4)	69
C(1S)	0.679 (2)	0.808 (2)	-0.004 (2)	294
C(2S)	0.774 (1)	0.727 (1)	-0.044 (1)	162
O(1S)	0.5740 (7)	0.8783 (6)	0.0063 (6)	134

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

map +0.38 and -0.42 e Å<sup>-3</sup> (other larger peaks +1.86 and +0.75 e Å<sup>-3</sup> within 0.91 Å from Br<sup>-</sup> and Br<sup>-'</sup>; larger holes -1.49, -1.28 and -0.78 e Å<sup>-3</sup>)

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

	Molecule (I)	Molecule (II)
O(4)—C(4)	1.221 (6)	1.214 (7)
N(1)—C(14)	1.510 (6)	1.506 (8)
N(1)—C(1B)	1.490 (7)	1.497 (7)
N(1)—C(2)	1.511 (7)	1.496 (6)
N(1)—C(6)	1.488 (5)	1.517 (7)
C(2)—C(3)	1.506 (6)	1.493 (7)
C(3)—C(4)	1.489 (6)	1.495 (7)
C(3)—C(8)	1.340 (7)	1.335 (8)
C(4)—C(5)	1.497 (7)	1.464 (9)
C(5)—C(6)	1.498 (6)	1.496 (7)
C(5)—C(7)	1.329 (6)	1.349 (8)
C(7)—C(15)	1.480 (7)	1.454 (9)
C(8)—C(9)	1.452 (7)	1.461 (7)
C(9)—C(10)	1.397 (7)	1.388 (9)
C(9)—C(14)	1.389 (7)	1.382 (8)
C(10)—C(11)	1.396 (7)	1.363 (9)
C(11)—C(12)	1.374 (8)	1.383 (9)
C(12)—C(13)	1.366 (8)	1.353 (9)
C(13)—C(14)	1.385 (7)	1.358 (8)
C(15)—C(16)	1.397 (6)	1.406 (8)
C(15)—C(20)	1.386 (7)	1.393 (9)
C(16)—C(17)	1.385 (7)	1.382 (9)
C(17)—C(18)	1.367 (8)	1.384 (9)
C(18)—C(19)	1.350 (7)	1.372 (9)
C(19)—C(20)	1.378 (7)	1.343 (9)
C(14)—N(1)—C(1B)	108.9 (4)	109.0 (4)
C(14)—N(1)—C(2)	109.6 (3)	110.2 (5)
C(14)—N(1)—C(6)	107.0 (3)	110.6 (4)
C(1B)—N(1)—C(2)	109.5 (3)	108.6 (4)
C(1B)—N(1)—C(6)	111.5 (3)	107.9 (5)
C(2)—N(1)—C(6)	110.3 (3)	110.4 (3)
N(1)—C(2)—C(3)	110.6 (4)	112.8 (4)
C(2)—C(3)—C(4)	117.9 (4)	119.6 (4)
C(2)—C(3)—C(8)	124.5 (4)	123.6 (4)
C(4)—C(3)—C(8)	117.6 (4)	116.9 (4)
O(4)—C(4)—C(3)	121.3 (4)	119.7 (5)
O(4)—C(4)—C(5)	120.6 (4)	122.2 (5)
C(3)—C(4)—C(5)	118.0 (4)	118.0 (5)
C(4)—C(5)—C(6)	119.3 (3)	118.9 (4)
C(4)—C(5)—C(7)	116.7 (4)	116.9 (5)
C(6)—C(5)—C(7)	124.0 (4)	124.2 (5)
N(1)—C(6)—C(5)	113.6 (3)	111.3 (5)
C(5)—C(6)—C(7)	130.9 (4)	131.9 (5)
C(3)—C(8)—C(9)	132.5 (4)	133.4 (5)
C(8)—C(9)—C(10)	117.0 (4)	116.6 (5)
C(8)—C(9)—C(14)	125.1 (4)	125.6 (5)
C(10)—C(9)—C(14)	117.8 (4)	117.8 (5)
C(9)—C(10)—C(11)	120.8 (4)	121.5 (6)
C(10)—C(11)—C(12)	119.8 (5)	118.4 (7)
C(11)—C(12)—C(13)	120.1 (5)	121.2 (5)
C(12)—C(13)—C(14)	120.5 (5)	119.8 (6)
C(9)—C(14)—C(13)	120.9 (4)	121.2 (6)
C(7)—C(15)—C(16)	117.4 (4)	116.2 (6)
C(7)—C(15)—C(20)	125.1 (4)	125.6 (5)
C(16)—C(15)—C(20)	117.5 (4)	118.0 (5)
C(15)—C(16)—C(17)	120.9 (5)	120.4 (6)
C(16)—C(17)—C(18)	119.6 (4)	118.8 (5)
C(17)—C(18)—C(19)	120.4 (5)	121.2 (6)
C(18)—C(19)—C(20)	121.0 (4)	120.0 (7)
C(15)—C(20)—C(19)	120.6 (4)	121.6 (5)

within 0.89 Å from Br<sup>-</sup> and Br<sup>+</sup>). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on a VAX8650 computer at the University of Saskatchewan.

The atomic parameters are summarized in Table 1.\* Bond distances and angles are listed in Table 2. Fig. 1 is

\*Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51757 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

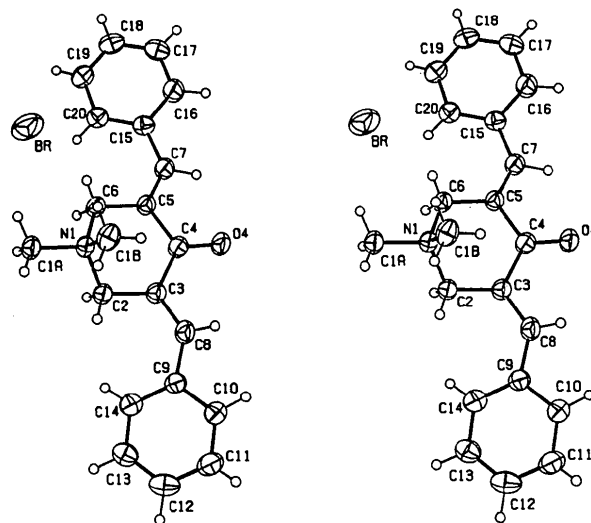


Fig. 1. Stereoscopic ORTEP view (Johnson, 1976) of molecule (I) with atomic numbering.

an ORTEP drawing (Johnson, 1976) of molecule (I) of the title compound.

**Related literature.** Other structures in this series of cyclic conjugated bis(benzylidene)ketones, which have various cytotoxicities to P388 leukemia cells (Warrington, Fang, Dimmock & Arora, 1988), have been previously reported (Jia, Quail, Arora & Dimmock, 1988, 1989). The title compound shows similar geometrical features to those of related molecules that mainly result from the steric repulsions (Tokuno, Matsui, Miyoshi, Asao, Ohashi & Kihara, 1986). There is a partially occupied and highly disordered ethanol solvent molecule in an asymmetric unit.

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