

Crystal Structure of 2,4-Bis(4-chlorophenyl)-3-azabicyclo[3.3.1]nonan-9-one

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The crystal structure of the title compound, C₂₀H₁₉NOCl₂, confirms that the bicyclic ring system adopts the *chair-chair* conformation. The phenyl rings are equatorially disposed with respect to the bicyclic ring. There is a slight deviation from the chair conformation in the case of the cyclohexane ring.

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Azabicyclononane and their derivatives are studied intensively because of their pharmaceutical use and their application as an important structure in the field of molecular recognition. The 3-azabicyclo[3.3.1]nonane skeletal system, which is easily constructed¹ *via* a double Mannich reaction, has been known for some time. The bicyclo[3.3.1]nonane carbon framework is frequently encountered in natural products, particularly in alkaloids and terpenoids, *e.g.* clovene,² upial,³ and trifarienols.⁴

Cyclohexanone (0.02 mol), 4-chlorobenzaldehyde (0.04 mol), dry ammonium acetate (0.02 mol) and ethanol (10 mL) were taken and heated until ammonium acetate dissolved. The mixture was allowed to stand until no more solid gets separated. When the turbidity appeared to be sufficient, ether was added to keep the mixture clear. The separated solid was filtered off and recrystallized from a chloroform-benzene mixture. The purity of the compound was checked by TLC, and the melting point was recorded. Yield: 25%, M.P.154°C.

The crystal and experimental details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final reliability value of 0.0368. H atoms were placed at calculated positions and allowed to ride on their carrier atoms with C-H = 0.93 - 0.97 Å, N-H = 0.86 Å and $U_{iso} = 1.2U_{eq}(C,N)$ for the CH₂, CH and NH groups. The atomic coordinates and temperature factors for the non-hydrogen atoms are presented in Table 2.

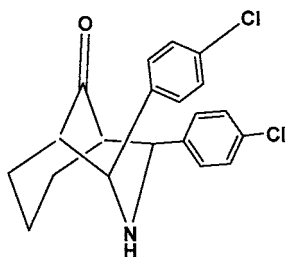


Fig. 1 Chemical diagram.

Figure 1 shows a chemical diagram and Fig. 2 a thermal ellipsoid plot of the complex. The bicyclo[3.3.1]nonane ring can exist in *chair-chair*, *chair-boat* and *boat-boat* conformations. Among these, the *chair-chair* conformation is the most favorable one. From the present study of the title compound, it is found that the bicyclic ring system adopts the *chair-chair* conformation, as in related structures previously studied.^{5,6} In the cyclohexane ring of the compound, atoms C11 and C13 deviate from the C10/C12/C14/C15 plane by -0.707 (3) and 0.556(3)Å, respectively, indicating a departure from the ideal chair conformation. These values are found to be

Table 1 Crystal and experimental data

Empirical formula	C ₂₀ H ₁₉ NO Cl ₂
Formula weight	362.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	$a = 8.284(8)$ Å $b = 10.665(10)$ Å $c = 11.131(11)$ Å $\alpha = 72.94(17)^\circ$ $\beta = 71.88(15)^\circ$ $\gamma = 88.07(20)^\circ$
Volume	891.67(15) Å ³
Z, Calculated density	2, 1.342 Mg/m ³
Absorption coefficient	0.370 mm ⁻¹
θ_{max}	25
Reflections collected/unique	3840/3127
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.029
Final R indices	$R1 = 0.0368$, $wR2 = 0.0964$
$[I > 2\sigma(I)]$	
R indices (all data)	$R1 = 0.0493$, $wR2 = 0.1046$
Largest diff. peak and hole	0.549 and -0.524 e.Å ⁻³
Measurement	Enraf Nonius-CAD4
Structure determination	SHELXS97
Refinement	SHELXL97
Structure drawing	ORTEP

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Table 2 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U(eq)
C(1)	2961(3)	1847(2)	5598(2)	44(1)
C(10)	3706(3)	1284(2)	823(2)	48(1)
C(11)	3844(3)	326(2)	2079(2)	53(1)
C(12)	2699(3)	634(2)	3282(2)	45(1)
C(13)	545(3)	1329(2)	1984(2)	56(1)
C(14)	838(3)	581(2)	3291(2)	52(1)
C(15)	1898(3)	1106(2)	793(2)	58(1)
C(16)	3930(2)	3707(2)	-391(2)	39(1)
C(17)	4858(3)	3699(2)	-1670(2)	47(1)
C(18)	4559(3)	4560(2)	-2768(2)	51(1)
C(19)	3325(3)	5450(2)	-2587(2)	48(1)
C(2)	2065(3)	2072(2)	6781(2)	47(1)
C(20)	2403(3)	5493(2)	-1337(2)	50(1)
C(21)	2714(3)	4616(2)	-248(2)	45(1)
C(3)	661(3)	2803(2)	6833(2)	44(1)
C(4)	161(3)	3327(2)	5727(2)	48(1)
C(5)	1080(3)	3100(2)	4547(2)	45(1)
C(6)	2479(2)	2348(2)	4466(2)	38(1)
C(7)	3418(2)	1983(2)	3225(2)	40(1)
C(9)	4229(2)	2686(2)	784(2)	41(1)
Cl(1)	-517(1)	3071(1)	8327(1)	70(1)
Cl(2)	2916(1)	6521(1)	-3965(1)	73(1)
N(1)	3329(2)	2974(2)	2025(1)	40(1)
O(1)	4776(3)	-571(2)	2119(2)	84(1)

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

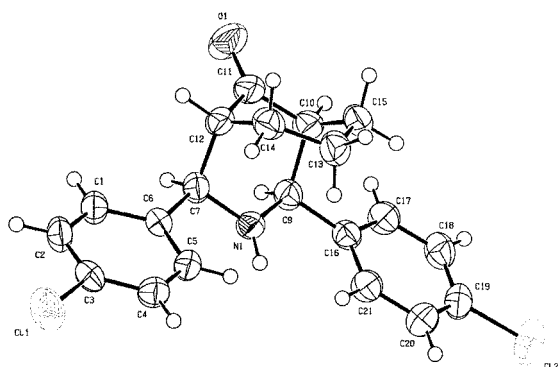
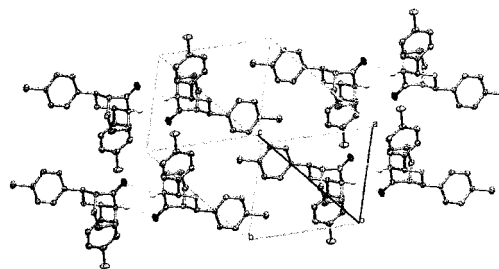


Fig. 2 ORTEP of the molecule at 50% probability.

$-0.732(2)$ and $0.540(3)\text{\AA}$ and 0.720 and $-0.537(4)\text{\AA}$ in the cyclohexanes of the related compounds.^{5,6} The piperidine ring has near ideal chair conformation. The planar phenyl rings are oriented at an angle of $16.8(1)^\circ$ to each other, and are equatorially disposed with respect to the piperidine ring, with the torsion angles being $C11-C10-C9-C16 = -173.9(2)^\circ$ and

Fig. 3 Packing diagram showing the $R_2^2(8)$ motif.Table 3 Hydrogen bonding geometry (\AA , $^\circ$)

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(10)-H(10)...O(1) ⁱ	0.98	2.53	3.423(2)	152
C(14)-H(14A)...Cg(1) ⁱⁱ	0.97	2.72	3.662(2)	163

(i) $1-x, -y, -z$ (ii) $-x, -y, 1-z$ Cg(1) is C1-C6 centroid

$C11-C12-C7-C6 = -174.2(2)^\circ$. The corresponding values in a related compound⁶ are $179.2(2)^\circ$ and $177.9(2)^\circ$. These differences in the values are possibly due to differences in the substituent atoms.

There is a C-H...O hydrogen bond between the molecules related through a center of inversion, leading to the formation of centrosymmetric dimers generating a graph set motif, $R_2^2(8)$ (Table 3, Fig. 3). In addition, there is a C-H... π interaction (Table 3).

Acknowledgements

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