

Fig. 2. Stereoscopic view of the molecule with 50% probability thermal ellipsoids (Johnson, 1965).

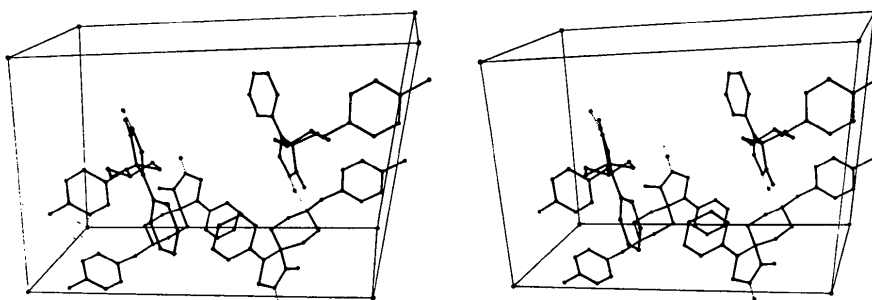


Fig. 3. Stereoscopic view of the molecular packing. The N(23)-H(23)···N(9) hydrogen bond is indicated by dotted lines.

Discussion. The atomic numbering scheme and the bond distances and angles are given in Fig. 1; Table 3 gives the bond distances and angles involving H atoms; Fig. 2 shows the conformation of the molecule. The five-membered and the 1-phenyl groups are nearly coplanar (17°) and perpendicular to the mean plane of the piperidine ring (93°).

Potential-energy calculations allowing rotation about C(5)-C(8) and C(8)-N(9) show that the structure corresponds to one of the energy minima of the isolated molecule.

Each molecule is hydrogen-bonded, N(9)···H(23)-N(23), to two neighbours as shown in Fig. 3; N(9)-N(23): 2.89 Å [N(23) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$].

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endo-7-Chloro-7-phenyl-2-oxabicyclo[4,1,0]heptane

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Abstract. C₁₂H₁₃OCl, F.W. 208.7; monoclinic, *P*2₁/*c*; *a* = 11.929 (1), *b* = 7.469 (1), *c* = 11.900 (2) Å, β = 96.25 (1)°; *D_x* = 1.315 g cm⁻³ for *Z* = 4, *D_o* = 1.317 g cm⁻³; *V* = 1054 Å³; μ = 28.9 cm⁻¹. The structure was solved by the heavy-atom method and refined to *R* = 0.074.

The tetrahydropyran ring is in an envelope conformation with only one atom being significantly out of the plane defined by the other five non-hydrogen atoms of that moiety. The phenyl ring is oriented parallel to the bridgehead bond of the bicyclic system.

Introduction. The effects of ring strain in fused-ring molecules are of interest to many chemists; however few molecular structures for fused 6:3 and 6:4 ring systems have been reported. Ledlie & Hearne (1969) have reported the synthesis and stereochemical assignment of the epimeric 7-chloro-7-phenyl-2-oxabicyclo-[4,1,0]heptanes. This structure investigation was initiated in order to allow an unequivocal stereochemical assignment for this compound and to determine the means by which the ring strain due to fusion is relieved.

Crystals of the title compound, hereinafter referred to as 2-OXA, were obtained by slow evaporation of a hexane solution. A platelet ($\sim 0.14 \times 0.20 \times 0.04$ mm) was selected for the X-ray study and was mounted on a glass fiber with [010] parallel to the ϕ axis of the diffractometer. The crystal and mount were then covered and sealed in one half of a gelatin capsule to retard sublimation. All diffraction measurements were made at room temperature ($\sim 21^\circ\text{C}$) on a Diano XRD-700 diffractometer using Cu $K\alpha$ radiation and a balanced nickel-cobalt filter pair. The Laue symmetry was $2/m$ with systematic absences ($0k0$ for k odd and $h0l$ for l odd) consistent with the space group $P2_1/c$. Lattice parameters were obtained by least-squares refinement of 40 independent 2θ measurements with $K\alpha_1$ (1.54050 Å) and $K\alpha_2$ (1.54433 Å) well resolved. The density was measured by flotation in AgNO_3 solution.

Measurements of ω scans for three reflections revealed peaks that were single, narrow ($< 0.5^\circ$ wide) and symmetrical, thus indicating suitable quality for data collection by the stationary-crystal stationary-counter technique. Of the 1895 reflections measured ($2\theta \leq 135^\circ$), 1207 possessed net intensities significantly above background (> 7 c.p.s.) and were used in the solution and refinement of the structure.

During the four days of data collection the intensities of five standard reflections declined by approximately 35%. The intensity data were broken into ten blocks according to the time at which they were collected and the decay correction factor appropriate to that block was applied to the net intensities. An empirical correction for absorption as a function of ϕ was applied (Silvers & Tulinsky, 1963) with the correction

factors ranging from 1.00 to 1.38. Corrections for Lorentz and polarization effects and α_1 - α_2 splitting (Tulinsky, Worthington & Pignataro, 1959) were also applied. Standard deviations in the structure factor magnitudes were calculated on the basis of counting statistics (Evans, 1961).

The structure was solved by the heavy-atom method. The phenyl group was treated as a rigid body in the least-squares calculations (120° bond angles, C-C distances 1.397, C-H distances 1.04 Å), with a variable isotropic temperature factor for each carbon atom. The isotropic temperature factor of each hydrogen atom was constrained to the same value as that of the carbon to which it is bonded. Full-matrix least-squares refinement of this model, including anisotropic temperature factors of the eight remaining non-hydrogen atoms, converged at $R=0.096$. A difference electron density map calculated at this point revealed positions for the remaining eight hydrogen atoms of the molecule. Three additional cycles of least-squares calculations varying the overall scale factor, the positional and anisotropic temperature factors of the eight non-hydrogen atoms of the bicyclic system, the positional and isotropic temperature factors for the hydrogen atoms of the bicyclic system, the positional and orientational parameters of the phenyl group and the isotropic temperature factors for the six carbon atoms of the phenyl group served to complete the refinement at $R=0.072$ [$R_w = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2} = 0.047$ with $w = \sigma^{-2}(|F_o|)$]. Final shifts in all parameters were less than 0.8σ . A final difference electron density map showed only a randomly fluctuating background below 0.25 e \AA^{-3} , except for three peaks (-0.35 , $+0.49$ and $+0.65 \text{ e \AA}^{-3}$) near the phenyl group and one other peak (-0.39 e \AA^{-3}) near the chlorine atom. Final atomic parameters are given in Tables 1 and 2.*

* A list of structure factors, complete tables of bond lengths and bond angles, and the final positional and isotropic thermal parameters for the atoms of the phenyl group have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31839 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional ($\times 10^4$) and anisotropic temperature factors ($\times 10^4$) for the non-group atoms

Estimated standard deviations are in parentheses. The temperature factor expression was

$$\exp [-2\pi^2(h^2a^{*2}U_{11} + h^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

The internal coordinate system of the phenyl ring was defined as follows: the ring lies in the xy plane with atom C(8) as the origin [0.3086 (3), 0.3379 (4), 0.3398 (3)] with $\phi = 34.98$, $\theta = -161.63$ and $\rho = 52.62^\circ$ (LaPlaca & Ibers, 1965), vector C(8)-C(11) coincident with the positive y axis and vector C(13)-C(9) coincident with the positive x axis.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	1231 (1)	4148 (2)	4420 (1)	442 (7)	466 (8)	1004 (14)	-64 (9)	279 (7)	44 (9)
C(7)	2383 (4)	4899 (7)	3726 (4)	293 (36)	371 (34)	476 (36)	-62 (27)	74 (30)	1 (26)
C(1)	2925 (5)	6632 (8)	4128 (5)	328 (36)	384 (34)	577 (43)	-38 (29)	69 (28)	-30 (30)
O	2534 (3)	7548 (5)	5034 (3)	594 (29)	446 (25)	521 (28)	70 (22)	34 (20)	-71 (22)
C(3)	1885 (6)	9107 (10)	4688 (6)	695 (57)	424 (42)	719 (50)	-9 (41)	122 (43)	-19 (43)
C(4)	854 (6)	8584 (10)	3921 (6)	438 (49)	474 (48)	1123 (71)	151 (40)	13 (39)	91 (46)
C(5)	1131 (7)	7598 (10)	2842 (6)	653 (57)	555 (51)	700 (57)	101 (44)	-163 (43)	99 (45)
C(6)	2218 (5)	6538 (8)	3006 (5)	547 (43)	437 (37)	386 (36)	37 (32)	24 (32)	33 (33)

Table 2. Final positional ($\times 10^3$) and isotropic thermal parameters for the hydrogen atoms

E.s.d.'s are in parentheses.

	x	y	z	B (\AA^2)
H(1)	374 (4)	662 (6)	422 (3)	3 (1)
H(31)	232 (4)	981 (7)	436 (4)	4 (1)
H(32)	172 (4)	970 (7)	557 (4)	6 (1)
H(41)	32 (4)	961 (7)	362 (4)	5 (1)
H(42)	37 (5)	777 (8)	421 (5)	7 (2)
H(51)	113 (4)	844 (7)	225 (4)	4 (1)
H(52)	56 (4)	665 (7)	262 (4)	5 (2)
H(6)	255 (3)	653 (6)	227 (3)	3 (1)

The atomic scattering factors for the chlorine, oxygen and carbon atoms were those of Cromer & Waber (1965). The atomic scattering factors for the hydrogen atoms were taken from Stewart, Davidson & Simpson (1965). The real and imaginary anomalous dispersion corrections for the chlorine atom were included (Cromer & Liberman, 1970).

All calculations were performed on a DEC-SYSTEM 10 computer. Structure factor and full-matrix least-squares calculations were performed with the program *NUCLS* (Davis, 1974). All Fourier computations were carried out with a program by Rao (1964).

Discussion. A stereoscopic drawing (Johnson, 1965) of 2-OXA is shown in Fig. 1 which also illustrates the

Table 3. Bond distances (\AA) not involving the hydrogen atoms

Estimated standard deviations are given in parentheses.

C(1)–C(6)	1.501 (8)	C(4)–C(5)	1.548 (11)
C(1)–C(7)	1.502 (8)	C(5)–C(6)	1.514 (10)
C(1)–O	1.400 (7)	C(6)–C(7)	1.495 (8)
C(3)–O	1.434 (8)	C(7)–C(8)	1.489 (6)
C(3)–C(4)	1.501 (11)	C(7)–Cl	1.770 (5)

Table 4. Bond angles ($^\circ$) not involving the hydrogen atoms

O—C(1)–C(6)	120.4 (5)	C(5)–C(6)–C(7)	124.0 (5)
O—C(1)–C(7)	119.9 (5)	C(1)–C(7)–C(6)	60.1 (4)
C(6)–C(1)–C(7)	59.7 (4)	C(1)–C(7)–C(8)	120.3 (4)
C(1)–O—C(3)	113.0 (5)	C(6)–C(7)–C(8)	121.3 (4)
O—C(3)–C(4)	110.2 (6)	C(1)–C(7)–Cl	117.0 (4)
C(3)–C(4)–C(5)	113.2 (6)	C(6)–C(7)–Cl	117.8 (4)
C(4)–C(5)–C(6)	113.5 (6)	C(8)–C(7)–Cl	111.7 (3)
C(1)–C(6)–C(5)	118.7 (5)	C(7)–C(8)–C(9)	120.3 (3)
C(1)–C(6)–C(7)	60.2 (4)	C(7)–C(8)–C(13)	119.6 (3)

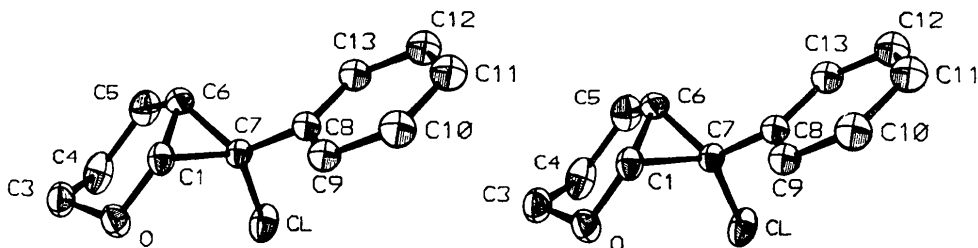


Fig. 1. Stereoscopic view of 2-OXA, with atoms represented by 30% equiprobability ellipsoids.

Table 5. Selected least-squares planes

The equations of the planes are of the form: $AX + BY + CZ - D = 0$, where X , Y and Z are Cartesian coordinates (\AA) relative to the directions a , b and c^* .

Plane	Atoms defining the planes	A	B	C	D
(I)	C(1), C(6), C(7) (cyclopropyl ring)	0.8654	-0.2351	-0.4425	-0.7685
(II)	C(7), C(8), C(11), M^\dagger	-0.4535	-0.0456	-0.8901	-5.1611
(III)	O, C(1), C(4), C(5), C(6)	0.5188	0.8101	-0.2730	4.1800

$\dagger M$ is the midpoint of the bond C(1)–C(6).

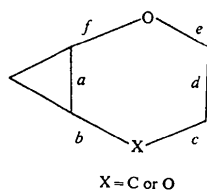
atom labeling scheme used. Bond lengths and bond angles are contained in Tables 3 and 4 respectively. Equations for selected planes are in Table 5.

The orientation of the phenyl ring relative to the cyclopropyl ring was unexpected. According to the model of Walsh (1949) a phenyl group should be oriented perpendicular to the plane of the cyclopropane moiety in order to maximize the overlap between the π cloud of the phenyl ring and the p orbital of the cyclopropyl carbon atom. This orientation has been inferred from the structures of several cyclopropane derivatives (Fritchie, 1966; Long, Maddox & Trueblood, 1969; Meester, Schenk & MacGillavry, 1971) but has not been conclusively demonstrated for phenylcyclopropanes (Lauher & Ibers, 1975).

In 2-OXA the plane of the cyclopropyl ring, plane (I), and plane (II) intersect to form an angle of 89.3° . In this orientation the electronic interaction between the two groups is minimized, as further evidenced by the fact that the three cyclopropyl C–C distances differ by less than one standard deviation from their average value, 1.499 (4) \AA . An explanation of the observed orientation can be made. In the 'bisecting' orientation the *ortho* hydrogen atom of the phenyl ring would be only 2.4 \AA from the chlorine atom. This distance would be 0.6 \AA shorter than the sum of the van der Waals radii (Pauling, 1960) for the two atoms. Thus it appears that any stabilization by the electronic interaction is less than the repulsive energy between the chlorine and hydrogen atoms.

A comparison of the conformation angles in the saturated six-membered rings of 2-OXA and *exo*-7-chloro-7-phenyl-2,5-dioxabicyclo[4,1,0]heptane, DOBH, (Oliver, Henslee & Rush, 1976) is shown in Table 6. The six-membered rings of both molecules are in nearly identical envelope conformations. The five atoms C(1), O, C(4), C(5) and C(6) are approximately coplanar (plane III) with the largest out-of-plane distance being 0.033 (6) Å. Atom C(3) is 0.668 (7) Å out of that same plane.

Table 6. Torsion angles ($^{\circ}$) of 2-OXA and DOBH
Bond labeling scheme



The convention followed in assigning torsion angles is that used in *Molecular Structures and Dimensions* (1972).

Bond	2-OXA	DOBH
<i>a</i>	6	1
<i>b</i>	-4	1
<i>c</i>	30	24
<i>d</i>	-59	-53
<i>e</i>	62	53
<i>f</i>	-35	-28

The two bonds adjacent to the cyclopropyl ring are slightly shorter than their normal values in non-fused ring systems. A similar behavior has been observed in DOBH and in norcaradiene structures (Fritchie, 1966; Maas, Fischer & Regitz, 1974).

The dihedral angle between planes (I) and (III), 67.7° , is normal, as are the bond angles at the bridgehead. The bond angle at the oxygen atom is virtually identical to the average C-O-C (dioxanyl) angle in DOBH. The remaining three bond angles in the saturated six-membered ring in 2-OXA average $112 (2)^{\circ}$ as compared to the average O-C-C angle in DOBH of $115 (1)^{\circ}$. Due to the effects of relatively high thermal motion this apparent difference is not significant.

No intermolecular contact distances shorter than the sum of the respective van der Waals radii of the atoms were observed.

In summary, the ring strain due to fusion of a six-membered ring to a three-membered ring is again accommodated in the more flexible ring. The fusion produces a significant shortening of the two bonds in the six-membered ring adjacent to the bridgehead atoms and results in the adoption of an unusual conformation for the six-membered ring. A general increase in the bond angles within the six-membered ring is a dual consequence of the effects of strain and the adoption of the envelope conformation for the six-membered ring.

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