

Crystal Structure and Stereochemistry of a Derivative of a Lactam: *N*-(*p*-Chlorophenyl)- α -isopropyl- β -phenyl- β -lactam

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Crystals of *N*-(*p*-Chlorophenyl)- α -isopropyl- β -phenyl- β -lactam (C₁₈H₁₈ONCl) are monoclinic, space group *P*2₁/*c* with four molecules in the unit cell. The cell parameters at 22 ± 3 °C are: *a* = 5.918 ± 0.003, *b* = 17.240 ± 0.002, *c* = 15.480 ± 0.003 Å, β = 94.11 ± 0.02° (Cu *K* α ₁ = 1.5405 Å). Three-dimensional intensity data of 3006 reflections were obtained by the stationary-crystal stationary-counter method, to the limit 2 θ = 145° for Cu *K* α . The structure has been refined by Fourier and least-squares methods to a final *R* index of 0.040. The thermal motion is analyzed in terms of rigid-body vibrations and is shown to involve rigid-body librations of the two phenyl groups. The four-membered β -lactam ring is planar. A relatively long C–C bond of 1.575 ± 0.004 Å occurs in the four-membered ring. The arrangement of the bonds around the nitrogen atom is a very flat pyramid. The normals to the least-squares planes through the phenyl rings ϕ_1 and ϕ_2 , which are attached respectively to the carbon and nitrogen atoms in the lactam ring, are at angles of 79.1 and 7.9° with respect to the normal to the least-squares plane through the β -lactam ring. The isopropyl group and the phenyl ring ϕ_1 are *cis* to one another.

Introduction

Many compounds containing the β -lactam ring possess various interesting biological properties (Testa, Fontanella & Cristiani, 1960). These compounds have been studied by different physical methods. Previous X-ray studies have been carried out on benzyl penicillin (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949) and cephalosporin C2 (Hodgkin & Maslen, 1961). A series of β -lactams was prepared and thorough chemical and nuclear magnetic resonance studies on these compounds were carried out by Kagan and his co-workers (Kagan, Basselier & Luche, 1964; Audier, Fetizon, Kagan & Luche, 1967). Some stereochemical problems arose in the interpretation of the n.m.r. spectra and the present investigation was undertaken to shed more light on these problems. The details of the n.m.r. and the chemical work on these β -lactams, as well as some preliminary results of the X-ray analysis of *N*-(*p*-Chlorophenyl)- α -isopropyl- β -phenyl- β -lactam and its bromine homolog, have been published (Luche, Kagen, Parthasarathy, Tsoucaris, Rango & Zelwer, 1967). This paper presents the results of the structure analysis and the full three-dimensional refinement of the structural parameters of *N*-(*p*-Chlorophenyl)- α -isopropyl- β -phenyl- β -lactam (hereinafter referred to as PIPL).

Experimental

Excellent crystals of PIPL were provided by Dr H. B. Kagan of the Laboratoire de Chimie Organique des Hormones, Paris, France. The chemical formula for this compound is as in Fig. 1. The crystals are fine

needles elongated along the *a* axis. They are monoclinic, and the systematically absent reflections (*h*0*l* absent for *l* = 2*n* + 1, 0*k*0 absent for *k* = 2*n* + 1) are consistent with the space group *P*2₁/*c*. The cell constants are, at a temperature of 22 ± 3 °C, *a* = 5.918 ± 0.003, *b* = 17.240 ± 0.002, *c* = 15.480 ± 0.003 Å, β = 94.11 ± 0.02° (Cu *K* α ₁ = 1.5405 Å). The density calculated on the basis of four molecules in the unit cell is 1.30 g.cm⁻³. The observed density is 1.28 g.cm⁻³.

The intensities were measured by the stationary-crystal stationary-counter method (Furnas & Harker, 1955). Ni–Co balanced Ross filters were used for monochromatization. A total of 3006 reflections was measured (to the limit 2 θ = 145° for Cu *K* α ₁) of which 698 were considered unobservable. The crystal used for the data collection had the dimensions 0.30 × 0.12 × 0.12 mm. Lorentz–polarization factors were applied and the data were processed in the usual way. No correction for absorption was applied (μ = 21.4 cm⁻¹).

Determination and refinement of the structure

The chlorine atom was located with the aid of the Harker section (*v* = $\frac{1}{2}$) and Harker line (0, *v*, $\frac{1}{2}$) of the three-dimensional Patterson maps. The heavy-atom phases were used to calculate a three-dimensional Fourier synthesis of the electron density. The positions of 6 peaks from this synthesis were used for the next cycle of structure factor–electron density map calculations. Four such iterative cycles showed the location of all the 21 non-hydrogen atoms. The *R* index at this stage was 0.28. The structure was refined by a series of least-squares analyses employing a block-diagonal approximation. Blocks of (9 × 9) and (4 × 4) were employed

for atoms with anisotropic and isotropic thermal parameters respectively. Six cycles of least-squares refinement with individual isotropic temperature factors were carried out on an IBM 7040 computer. Another five cycles of refinement with individual anisotropic temperature factors reduced the R index to 0.107. An electron density difference map at this stage clearly revealed all 18 hydrogen atoms and inclusion of these hydrogen atoms in the structure factor calculations reduced the R index to 0.07. Another six cycles of least-squares refinements in which the positional and isotropic thermal parameters of the hydrogen atoms were also allowed to vary brought the R index to 0.04. None of the shifts in the final stages was greater than one-tenth the corresponding standard deviation for the non-hydrogen atoms and one-fifth the standard deviation for the hydrogen atoms.

The observations were weighted according to the scheme of Evans (1961), and the refinement was carried out by minimizing $\sum[w(|F_{\text{obs}}| - 1/K|F_{\text{calc}}|)^2]$. Reflections too weak to be observed were given zero weight during the refinement and for the R index calculation. Atomic scattering factors and the corrections $\Delta f'$ and $\Delta f''$ for anomalous dispersion for Cl were those presented in *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters and their standard deviations are listed in Table 1. These standard deviations were obtained from the inverse of the block-diagonal matrix. The final observed and calculated structure factors are given in Table 2. The final value of the 'goodness of fit' - $[\sum(|F_o| - |F_c|)^2/m - n]^{1/2} - 2.4$.

Analysis of thermal motion in terms of rigid-body vibrations

The thermal motions of three groups of atoms were analyzed to check whether the individual anisotropic thermal motions of the atoms in each group could be explained in terms of rigid-body librations. The three groups of atoms are:

- (i) The molecule as a whole except the isopropyl group.
- (ii) The first phenyl ring, ϕ_1 , consisting of atoms C(13) through C(18), and the atom C(1).
- (iii) The second phenyl ring, ϕ_2 , consisting of atoms C(4) through C(9), and Cl.

The method used was that developed by Schomaker & Trueblood (1968) and the program was made available to us through Professor Trueblood, to whom our thanks are due. In this method, the rigid-body motion of molecules in crystals is analyzed in terms of three tensors: one for libration, one for translation and an additional tensor needed to account for correlations of libration and translation. These tensors are denoted respectively by L, T and S. The tensor L is independent of origin, whereas T and S depend on it. For removing

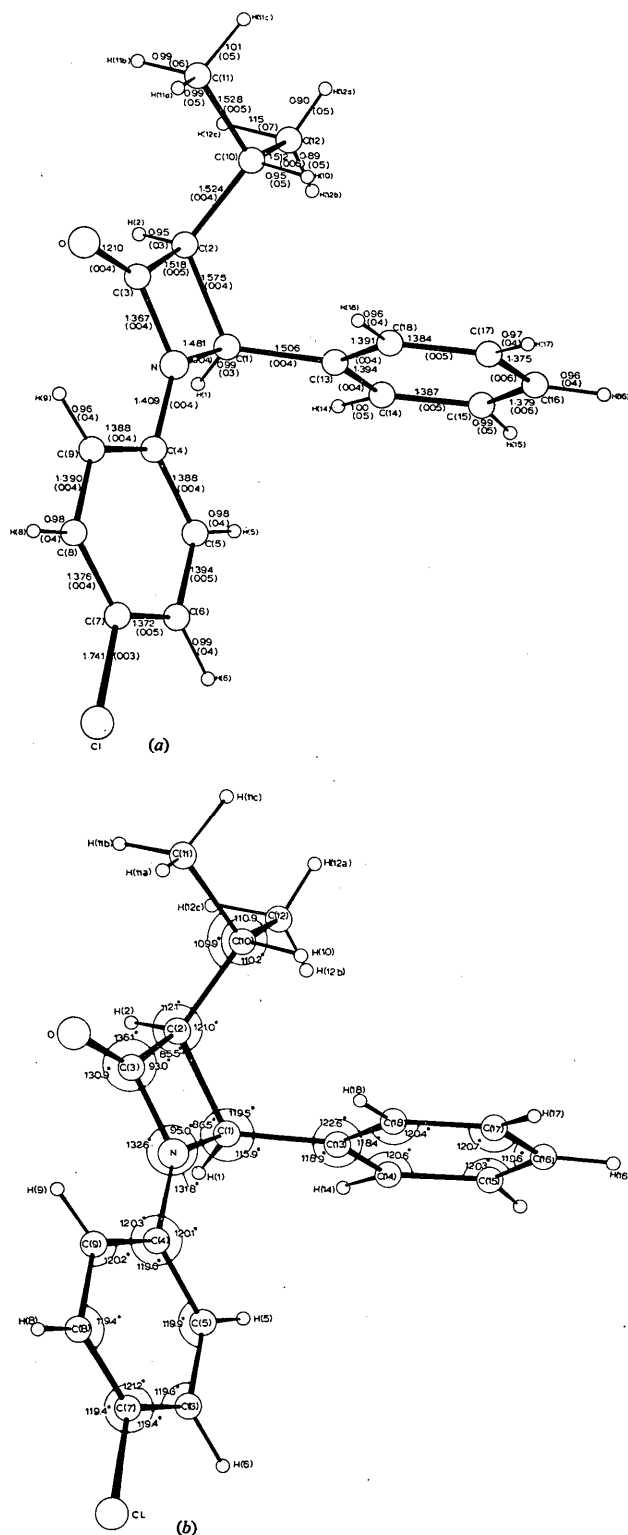


Fig. 1. Bond distances and angles in PIPL. The quantities in parentheses are the e.s.d. values of the bond distances and angles. The e.s.d.'s for the bond angles involving hydrogen atoms are 5° and non-hydrogen atoms, 0.3° . (a) Bond distances, (b) bond angles.

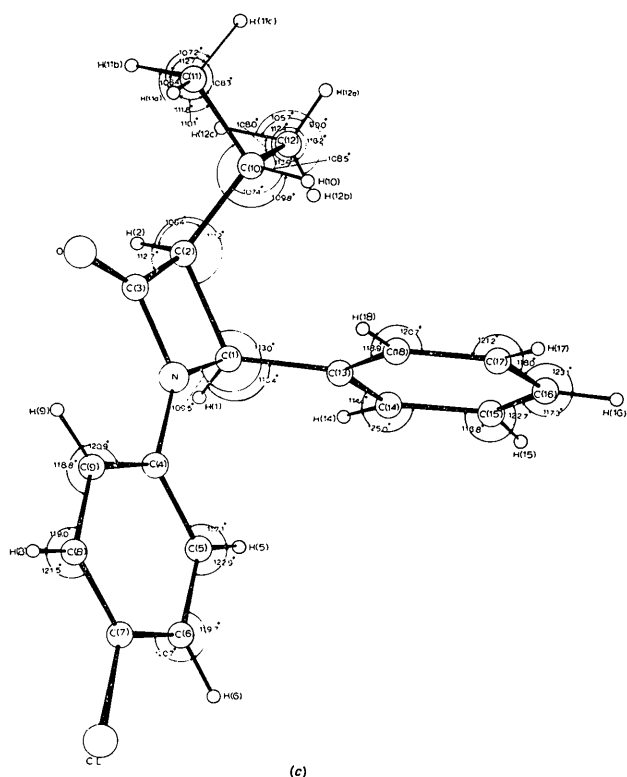


Fig. 1. (cont.) (c) bond angles involving hydrogen atoms.

the ambiguity in the origin, a unique origin is derived which symmetrizes S.

The r.m.s. differences between the observed and calculated U_{ij} values were, respectively, 0.0052, 0.0017 and 0.0015 \AA^2 for the three groups of atoms. The U_{ij} values observed and those derived from rigid-body libration for the first group of atoms do not fit as well as the corresponding quantities for groups (ii) and (iii). The rigid-body tensors for groups (ii) and (iii) are given in Table 3. The maximum amplitude of libration associated with the first phenyl ring is 5.1° and the corresponding principal axis of libration makes an angle of 24.5° with the normal to the least-square plane of φ_1 . The maximum amplitude of libration for the second phenyl ring is 7.7° and the corresponding principal axis makes an angle of 7.7° with C1-C(7) direction. The minimum amplitude is nearly in the plane of the φ_2 ring.

Geometry of the molecule

The bond distances and angles as calculated from the parameters of Table 1 are shown in Fig. 1. The quantities in parentheses are the estimated standard deviations. A list of bond distances that have been corrected for libration is given in Table 4. The average correction to the bond distances within the two rings φ_1 and φ_2 due to thermal libration is 0.006 and 0.008 \AA respectively, nearly the same order of magnitude as the standard deviations for the bonds.

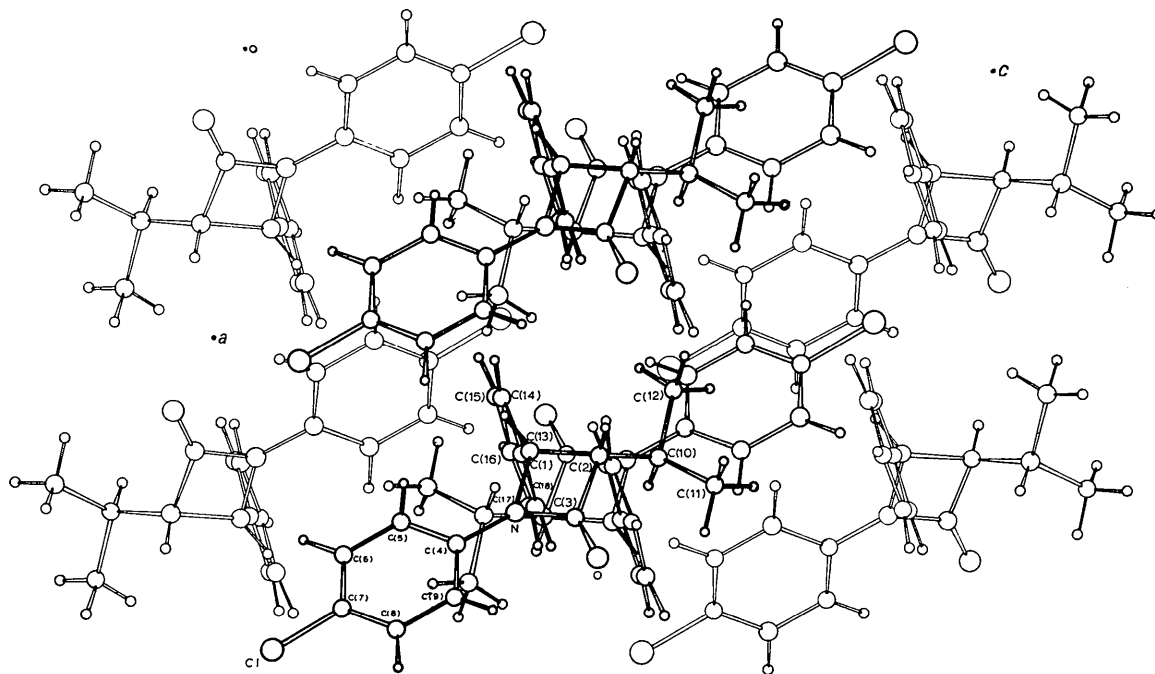


Fig. 2. A view along *b* of the packing of the PIPL molecule. The ring φ_2 and the four membered ring are nearly planar, whereas φ_1 is nearly normal to them.

The C—C bonds in the phenyl rings average to 1.385 and C(16)—C(17) bonds which show an apparent ± 0.007 Å. The C—C bonds in the phenyl rings are shortening. The correction for thermal libration does not remove this disparity in the bond lengths.

Table 1. *Fractional coordinates, thermal parameters and their estimated standard deviations*

T.F. = exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.						
	<i>x</i>	<i>y</i>	<i>z</i>			
Cl	1.08391 (20)	0.07015 (10)	0.11429 (10)			
O	0.7488 (5)	0.0485 (2)	0.5430 (2)			
N	0.5907 (5)	0.1236 (1)	0.4278 (2)			
C(1)	0.3769 (5)	0.1654 (2)	0.4402 (2)			
C(2)	0.3904 (6)	0.1292 (2)	0.5338 (2)			
C(3)	0.6089 (6)	0.0920 (2)	0.5089 (2)			
C(4)	0.7046 (6)	0.1092 (2)	0.3526 (2)			
C(5)	0.6311 (6)	0.1441 (2)	0.2749 (2)			
C(6)	0.7477 (7)	0.1312 (2)	0.2011 (2)			
C(7)	0.9342 (6)	0.0838 (2)	0.2059 (2)			
C(8)	1.0058 (6)	0.0471 (2)	0.2819 (2)			
C(9)	0.8902 (5)	0.0598 (2)	0.3556 (2)			
C(10)	0.3952 (6)	0.1807 (2)	0.6139 (2)			
C(11)	0.4919 (8)	0.1356 (2)	0.6930 (2)			
C(12)	0.1599 (8)	0.2103 (3)	0.6273 (3)			
C(13)	0.3847 (5)	0.2521 (2)	0.4297 (2)			
C(14)	0.1911 (6)	0.2907 (2)	0.3958 (2)			
C(15)	0.1883 (7)	0.3709 (2)	0.3892 (2)			
C(16)	0.3788 (8)	0.4134 (2)	0.4147 (2)			
C(17)	0.5712 (7)	0.3758 (2)	0.4473 (2)			
C(18)	0.5758 (6)	0.2958 (2)	0.4545 (2)			
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.0473 (4)	0.0045 (1)	0.0047 (1)	0.0012 (2)	0.0112 (2)	-0.0009 (1)
O	0.0561 (10)	0.0044 (1)	0.0042 (1)	0.0120 (6)	0.0017 (6)	0.0010 (2)
N	0.0335 (9)	0.0029 (1)	0.0036 (1)	0.0040 (5)	0.0017 (5)	-0.0002 (2)
C(1)	0.0283 (11)	0.0030 (1)	0.0039 (1)	-0.0001 (6)	0.0012 (7)	-0.0004 (2)
C(2)	0.0361 (14)	0.0026 (1)	0.0041 (2)	-0.0021 (7)	0.0047 (7)	-0.0002 (2)
C(3)	0.0410 (13)	0.0026 (1)	0.0036 (2)	0.0018 (7)	0.0022 (7)	-0.0003 (2)
C(4)	0.0314 (10)	0.0024 (1)	0.0038 (1)	-0.0001 (5)	0.0006 (6)	-0.0004 (2)
C(5)	0.0408 (10)	0.0040 (1)	0.0039 (1)	0.0089 (5)	0.0030 (6)	0.0003 (2)
C(6)	0.0484 (10)	0.0041 (1)	0.0036 (2)	0.0065 (6)	0.0039 (6)	0.0007 (2)
C(7)	0.0357 (10)	0.0029 (1)	0.0040 (1)	-0.0094 (5)	0.0054 (6)	-0.0006 (2)
C(8)	0.0312 (11)	0.0029 (1)	0.0047 (1)	0.0010 (6)	0.0025 (6)	-0.0007 (2)
C(9)	0.0321 (12)	0.0027 (1)	0.0040 (1)	0.0001 (6)	0.0037 (7)	0.0005 (2)
C(10)	0.0414 (13)	0.0031 (1)	0.0040 (2)	-0.0016 (6)	0.0056 (7)	0.0002 (2)
C(11)	0.0593 (17)	0.0048 (2)	0.0038 (2)	0.0035 (10)	0.0062 (10)	0.0004 (3)
C(12)	0.0509 (18)	0.0061 (2)	0.0062 (2)	0.0099 (9)	0.0080 (9)	-0.0016 (3)
C(13)	0.0273 (10)	0.0032 (1)	0.0034 (1)	0.0019 (5)	0.0027 (6)	0.0001 (2)
C(14)	0.0294 (11)	0.0042 (1)	0.0045 (2)	0.0035 (6)	0.0049 (7)	0.0007 (2)
C(15)	0.0432 (14)	0.0043 (2)	0.0054 (2)	0.0107 (8)	0.0087 (8)	0.0023 (3)
C(16)	0.0547 (16)	0.0031 (1)	0.0052 (2)	0.0052 (7)	0.0098 (9)	0.0009 (2)
C(17)	0.0466 (16)	0.0034 (1)	0.0045 (2)	-0.0048 (7)	0.0062 (9)	0.0004 (2)
C(18)	0.0307 (10)	0.0033 (1)	0.0039 (1)	0.0002 (6)	0.0019 (6)	0.0001 (2)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		
H(1)	0.253 (6)	0.143 (2)	0.401 (2)	2.0 Å ²		
H(2)	0.272 (6)	0.092 (2)	0.539 (2)	2.0		
H(5)	0.493 (9)	0.175 (3)	0.274 (3)	4.1		
H(6)	0.698 (7)	0.158 (2)	0.148 (3)	3.1		
H(8)	1.142 (7)	0.014 (3)	0.286 (3)	3.7		
H(9)	0.936 (6)	0.032 (2)	0.407 (2)	2.7		
H(10)	0.495 (9)	0.226 (3)	0.603 (4)	2.7		
H(11 <i>a</i>)	0.651 (8)	0.120 (3)	0.685 (3)	4.4		
H(11 <i>b</i>)	0.407 (9)	0.087 (3)	0.702 (4)	6.0		
H(11 <i>c</i>)	0.495 (9)	0.171 (3)	0.745 (4)	4.1		
H(12 <i>a</i>)	0.156 (9)	0.238 (3)	0.675 (3)	5.9		
H(12 <i>b</i>)	0.086 (8)	0.230 (3)	0.579 (3)	4.7		
H(12 <i>c</i>)	0.039 (8)	0.157 (3)	0.637 (3)	8.2		
H(14)	0.058 (8)	0.256 (3)	0.380 (3)	4.7		
H(15)	0.050 (8)	0.395 (3)	0.361 (3)	4.9		
H(16)	0.370 (7)	0.469 (2)	0.408 (3)	3.6		
H(17)	0.707 (7)	0.407 (3)	0.461 (3)	3.8		
H(18)	0.709 (6)	0.270 (2)	0.478 (3)	2.9		

Table 2. Final observed and calculated structure factors

FOBS = 10.0 x |Fo|, FCAL = 10.0 x |Fc|.

Reflections too weak to be observed were given zero weight in the refinement and were omitted in the R index calculation. The unobserved reflections are given half the minimum value in that range, and are listed separately.

Table with 16 columns: H, K, L, F OBS FCAL, H, K, L, F OBS FCAL, H, K, L, F OBS FCAL, H, K, L, F OBS FCAL, H, K, L, F OBS FCAL, H, K, L, F OBS FCAL, H, K, L, F OBS FCAL, H, K, L, F OBS FCAL. The table contains a dense grid of numerical data representing structure factors for various reflections.

Table 3. Results of rigid-body analysis of thermal parameters

	Eigenvalues	Eigenvectors*		
		(Direction cosines $\times 10^4$)		
Librational tensor L	25.7 ($^\circ$) ²	-3452	-3331	8774
	7.7	-1370	9428	3039
	2.5	-9285	-0153	-3711
Translational tensor T*	0.0524 \AA^2	-7959	-5080	-3292
	0.0447	3084	-8082	5017
	0.0396	-5209	2978	8000
Symmetrized Screw tensor S*		$\begin{pmatrix} 17 & 14 & -105 \\ & -63 & -84 \\ & & -47 \end{pmatrix} \times 10^5 \text{ rad. } \text{\AA}$		

The unique origin is 1.62 \AA away from the unweighted center of gravity displaced along the a , b , c^* axes by -0.34, 1.09 and 0.58 \AA respectively.

II. Atoms C1, C(4), C(5), C(6), C(7), C(8), C(9)

Librational tensor L	59.2 ($^\circ$) ²	-4936	2389	8362
	9.4	-5459	6634	-5118
	8.1	-6770	-7091	-1970
Translational tensor T*	0.0526 \AA^2	-9880	1531	0215
	0.0452	0056	1744	9847
	0.0326	1545	9729	1737
Symmetrized Screw tensor S*		$\begin{pmatrix} 110 & 13 & 164 \\ & -54 & -37 \\ & & -56 \end{pmatrix} \times 10^5 \text{ rad. } \text{\AA}$		

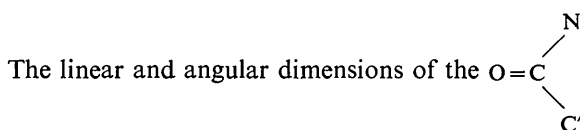
The unique origin is 1.11 \AA away from the center of gravity displaced along the a , b , c^* axes by 0.41, 0.09 and -1.03 \AA respectively.

* Direction cosines are relative to the orthogonal axes a , b , c^* . S is expressed relative to the principal axes of L and to the unique origin.

Table 4. Bond distances in rings ϕ_1 and ϕ_2 before and after the correction for thermal libration

	Uncorrected	Corrected
C(4)-C(5)	1.388 \AA	1.398 \AA
C(5)-C(6)	1.394	1.398
C(6)-C(7)	1.372	1.382
C(7)-C(8)	1.376	1.386
C(8)-C(9)	1.390	1.394
C(9)-C(4)	1.388	1.398
C(13)-C(14)	1.394	1.401
C(14)-C(15)	1.387	1.392
C(15)-C(16)	1.379	1.385
C(16)-C(17)	1.375	1.381
C(17)-C(18)	1.384	1.389
C(18)-C(13)	1.391	1.397

Okaya & Bednowitz (1967) found that in chlorosulfonate of a novel cage chlorocarbon the C-C bonds in the four-membered ring ranged from 1.53 to 1.59 \AA . Electron diffraction values for the C-C bond lengths in cyclobutane are $1.548 \pm 0.003 \text{\AA}$ reported by Almenningen, Bastiansen & Skancke (1961). An explanation for the lengthening of these C-C bonds in terms of the non-bonded interaction has been offered by Dunitz & Schomaker (1952). In cyclobutane, the nonbonded C-C distance across the diagonals is 2.18 \AA . The C(1)-C(3) and C(2)-N contact distances in PIPL respectively are 2.100 ± 0.004 and $2.094 \pm 0.004 \text{\AA}$. These short nonbonded interactions may be the reason for the lengthening of the C(1)-C(2) bond.



group in PIPL are similar to those occurring in peptides (see, e.g. Marsh & Donohue, 1967). In PIPL, the central carbon atom C is out of the least-squares plane through O, C, C(1) and N by 0.012 \AA .

The C(1)-C(2) bond in the four membered ring is considerably stretched ($1.575 \pm 0.004 \text{\AA}$). Such long bonds in cyclobutane and its derivatives are known. A few cases where such long C-C bonds have been observed are listed below: $1.566 \pm 0.015 \text{\AA}$ tetraphenylcyclobutane (Dunitz, 1949; Margulis, 1965); $1.573 \pm 0.015 \text{\AA}$ in octachlorocyclobutane (Margulis, 1965).

Stereochemistry of the molecule

Three important stereochemical problems pertaining to this molecule are discussed in this section: (i) the planarity of the four-membered ring and the stereochemistry of the nitrogen atom; (ii) the angles between the four-membered ring and the two phenyl rings ϕ_1 and ϕ_2 , (iii) the conformation of the isopropyl group with respect to the lactam ring and the phenyl ring ϕ_1 .

(i) Planarity of the four membered ring and the stereochemistry of the nitrogen atom

The atoms N, C(1), C(2) and C(3) are planar. The least-squares plane through these atoms and their individual deviations from this plane are given in Tables 5 and 6.

Table 5. *Least-squares planes in PIPL**

No.	Equation to the plane†	Atoms determining the plane
1	$0.4944X + 0.7972Y + 0.3465Z = 5.454$	N, C(1), C(2), C(3)
2	$0.5790X + 0.7796Y + 0.2387Z = 4.942$	C(4), C(5), C(6), C(7), C(8), C(9)
3	$-0.3800X + 0.0720Y + 0.9222Z = 5.740$	C(13), C(14), C(15), C(16), C(17), C(18)

* See Table 6 also.

† *X*, *Y* and *Z* are cartesian coordinates in Ångstrom units along the *a*, *b* and *c** axes, and the coefficients of *X*, *Y*, *Z* are the direction cosines with respect to these axes.

Table 6. *Deviations of atoms from least-squares planes* ($\text{Å} \times 10^3$)*

See also Table 5. Bold face deviations indicate the atoms used to define the least-squares plane.

	Plane 1	Plane 2	Plane 3
N	-5	C(4) 12	C(13) 8
C(1)	5	C(5) -7	C(14) -7
C(2)	4	C(6) -5	C(15) 2
C(3)	4	C(7) 11	C(16) 1
O	-20	C(8) -5	C(17) 0
		C(9) -7	C(18) -4
		Cl 63	H(14) 2*
		N 44	H(15) -8*
		H(5) -6*	H(16) -1*
		H(6) 1*	H(17) -6*
		H(7) -7*	H(18) 0*
		H(8) 3*	

* The deviations for the hydrogen atoms are in $\text{Å} \times 10^2$.

It is generally accepted that the four-membered ring in cyclobutane is puckered (Lambert & Roberts, 1965; Dows & Rich, 1967). In PIPL, the four-membered ring is quite planar and this seems to be due to an increase in conjugation in the four-membered ring due to the N-C=O system as well as to the phenyl ring φ_2 .

The arrangement of bonds around the N is approximately planar. The angle between the N-C(4) bond and the mean β -lactam ring is 9.2° . Similar results have been obtained in *p*-bromophenylsuccinimide and the dimer of phenylisocyanate (see Luche *et al.*, 1967). The corresponding angles in these cases are 9.0° and 10.0° respectively. In *p*-bromophenylsuccinimide, the angle between the normals to the ring containing N and the phenyl group is 65° (Barassin, Tsoucaris & Lumbroso, 1961), in contrast to a value of 7.9° in

PIPL. It has been shown in *p*-bromophenylsuccinimide (Barassin, Tsoucaris & Lumbroso, 1961) that coplanarity of the phenyl ring and the ring containing N would involve a severe short contact from the oxygen atoms to the hydrogen atoms *ortho* to the nitrogen atom. Such a short contact is not present in PIPL and the O---H(9) distance is 2.66 Å , just larger than the sum of van der Waals radii of 2.6 Å (Pauling, 1960) for O and H.

(ii) *Angles between the four-membered ring and the two phenyl rings φ_1 and φ_2*

The least-squares planes through the two phenyl rings φ_1 and φ_2 are given in Table 5 and the individual deviations of the atoms from the least-squares planes are in Table 6. The angle between the normals to the phenyl ring 2 and the four-membered ring is 7.9° . The corresponding angle for phenyl ring 1 is 79.1° . The two phenyl groups are at an angle of 86.8° .

(iii) *Conformation of the isopropyl group*

The isopropyl group and the first phenyl ring are *cis* to one another, and the angle between the normals to the planes defined by C(10), C(2), C(1) and C(2), C(1) and C(13) respectively is 0.1° . For a *trans* configuration, this angle would have been around 120° . Between the isopropyl group and the ring φ_1 , which are eclipsed, the shortest contact is $3.103 \pm 0.004 \text{ Å}$, between the atoms C(10) and C(13).

Packing of the molecule

Packing of the molecules is shown in Figs. 2, 3 and 4. The structure is stabilized by van der Waals and di-

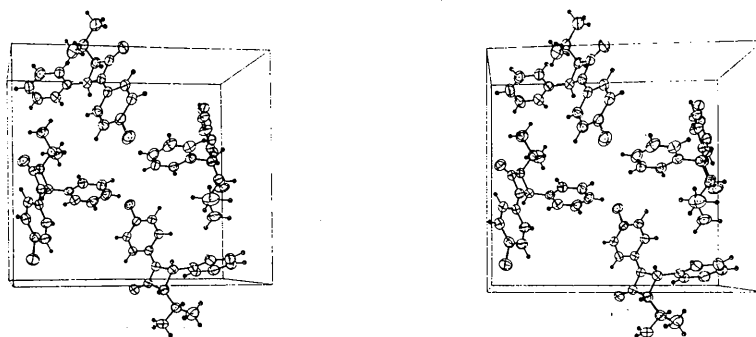


Fig. 3. A stereoscopic pair illustrating the packing of the molecules and the thermal ellipsoids. The view is nearly along the *a* axis.

polar forces. The intermolecular contact distances shorter than 3.6 Å for nonhydrogen atoms are given in Table 7. There appears to be no intermolecular contact involving a hydrogen atom and any other atom which is shorter than 3 Å. The shortest contacts of 3.161 and 3.163 Å occur for Cl and the two hydrogen atoms H(15) and H(17), respectively, of neighboring molecules.

Table 7. Contact distances shorter than 3.6 Å between non-hydrogen atoms

Unprimed Primed	x $1-x$	y $-y$	z $1-z$	d	d
O---O'	3.561 Å	O---C(3')	3.279 Å		
O---C(2')	3.367	C(3)-C(3')	3.428		

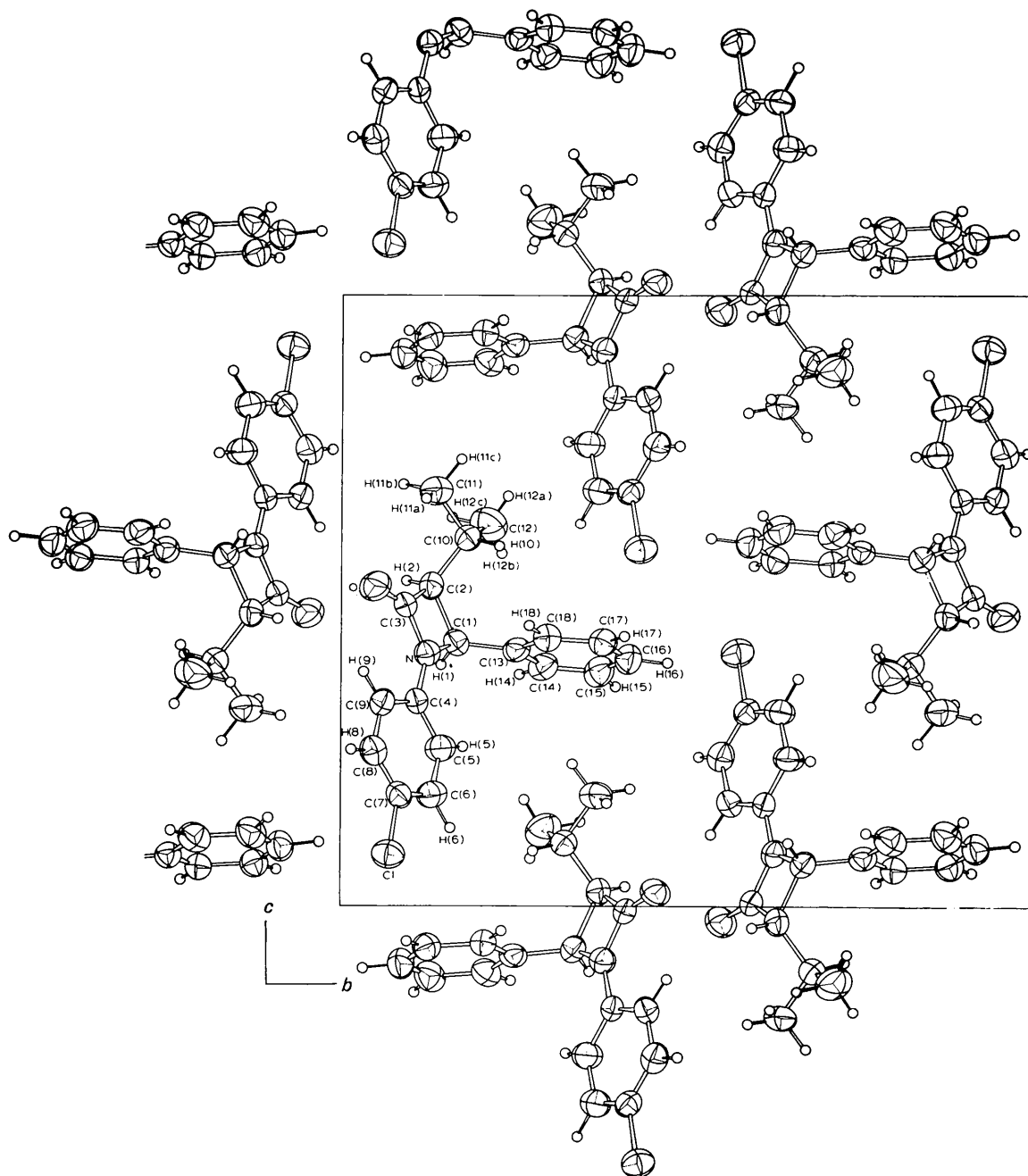


Fig. 4. Packing of the molecule and illustration of the thermal ellipsoids.

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Les Dérivés Chlorés de la Benzoquinone-1,4.

I. Structure Cristalline de la Chlorobenzoquinone-1,4

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(Reçu le 17 décembre 1969)

The crystal structure of chloro-*p*-benzoquinone has been determined from diffractometer measurements using Mo K α radiation. The final *R* value was 0.031. A detailed analysis of the thermal motion was carried out. Some evidence was found for a slight deformation of the molecular plane. Short distances between oxygen and hydrogen atoms of neighbouring molecules were observed.

Introduction

La structure cristalline de la benzoquinone-1,4 a été publiée par Trotter (1960), celle de la tétrachlorobenzoquinone-1,4 par Chu, Jeffrey & Sakurai (1962). Nous avons entrepris une étude systématique des benzoquinones partiellement chlorées.

Dans la suite, nous désignerons la chlorobenzoquinone-1,4 par *A*.

* Equipe de recherche associée au C.N.R.S.

Partie expérimentale

Préparation – données cristallographiques

A a été préparé suivant la méthode de Levy & Schultz (1881) et purifié par recristallisations répétées dans l'alcool dilué. Le composé a été caractérisé par son point de fusion et son spectre d'absorption dans l'infrarouge (Yates, Ardao & Fieser, 1956). Les cristaux, obtenus par recristallisation dans l'éther de pétrole, ont la forme décrite par Groth (1917).

Les cristaux appartiennent au système orthorhombique.