conformation (Duax, Weeks & Rohrer, 1976), and the five-membered ring has the envelope conformation. C(7) is 0·587 (3) Å out of the plane [max. deviation 0·020 (3) Å] of the other five atoms in the six-membered ring, and C(14) is 0·629 (3) Å out of the plane [max. deviation = 0·043 (3) Å] of the other four atoms in the five-membered ring. Bond distances and angles are normal with a short C(5)—C(10) single bond [1·444 (3) Å] between the carbonyl group and the C(9)=C(10) double bond [1·346 (3) Å]. This situation is similar to that in (2). At the three sp^2 carbon atoms, the internal angles are near 120° with C(5)—C(10)—C(9) = 124·2 (2)°.

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Structure of 3,3′-Dichlorodibenzoyl Peroxide, $C_{14}H_8Cl_2O_4$

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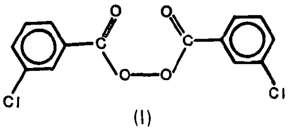
Abstract. $M_r = 311·12$, monoclinic, $C2/c$, $a = 14·655$ (2), $b = 9·318$ (3), $c = 10·373$ (2) Å, $\beta = 109·67$ (1)°, $V = 1333·96$ Å^3, $Z = 4$, $D_x = 1·549$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·494$ mm^{-1}, $T = 300$ K, $F(000) = 632$, final $R = 0·037$, $R_w = 0·054$ for 856 observed reflections with $F > 3\sigma(F)$. A twofold symmetry axis bisects the O—O peroxide bond. The peroxide bond distance is 1·453 (2) Å, and C—Cl is 1·734 (2) Å. The molecular structure shows an antiparallel arrangement of the C=O and C—Cl bonds yielding a *transoid* disposition. The molecules are held together by van der Waals forces, forming parallel chains.

Introduction. The structure elucidation of the title compound (I) was undertaken in conjunction with our interest in studying the nature of the peroxide (O—O) bond in various chemical and structural configurations. Of interest is the comparison of the O—O bond distance found in the present case to that recently observed in a strained environment in an ozonide molecule (Syed, Kirschenheuter, Jain, Griffin & Stevens, 1983).



(I)

Experimental. Crystals of the title compound were obtained by slow evaporation of a solution of the compound in ethanol. D_m not determined. Enraf–Nonius CAD-4 diffractometer. Approximate crystal dimensions 0·10 × 0·63 × 0·28 mm. Graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions from a least-squares analysis of 25 reflections with $20° \leq 2\theta \leq 36°$ accurately measured on diffractometer. Systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$; space group $C2/c$. ω:2θ scan mode to measure 1333 reflections with $2\theta \leq 50°$; $-17 \leq h \leq 17$, $0 \leq k \leq 11$, $0 \leq l \leq 12$; 1181 unique of which 856 treated as observed with $I > 3\sigma(I)$, where $\sigma(I)$ is the e.s.d. based on counting statistics, and included in the least-squares refinement. Three intensity-control standards measured every 2 h of exposure time (maximum decay 3·9%) and crystal-orientation check after every 200 reflections. Lorentz–polarization correction applied; absorption correction

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* On study leave from Tata Iron & Steel Co., Jamshedpur, India.

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ignored. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978; Frenz, 1982) based on 209 reflections; $3{\cdot}95 \geq E \geq 1{\cdot}32$. An E map calculated for the highest combined figure of merit (3·0) revealed positions of all the non-hydrogen atoms. H atoms located in subsequent difference Fourier synthesis. Full-matrix least-squares refinement, H atoms isotropic, others anisotropic, minimizing the function $\sum w(||F_o| - |F_c||)^2$ where $w = 1/\sigma^2(F)$ converged to $R = 0{\cdot}037$, $R_w = 0{\cdot}054$, $S = 2{\cdot}05$. $(\Delta/\sigma)_{\max} = 0{\cdot}03$. A final difference Fourier map showed no significant peaks, the largest being 0·21 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All computation using the *SDP* package on a PDP 11/34 computer (Frenz, 1982).

Table 1. *Positional parameters, isotropic thermal parameters and their estimated standard deviations*

	x	y	z	B(Å^2)
Cl	0·39848 (5)	0·12654 (9)	0·58623 (8)	6·47 (2)
O(1)	0·0485 (1)	0·0004 (2)	0·3004 (2)	5·44 (4)
O(2)	−0·0102 (1)	−0·1695 (3)	0·4028 (2)	6·38 (5)
C(1)	0·1529 (2)	−0·0899 (3)	0·5066 (2)	3·61 (5)
C(2)	0·2207 (2)	0·0080 (3)	0·4986 (2)	3·83 (5)
C(3)	0·3125 (2)	0·0040 (3)	0·5973 (2)	3·98 (5)
C(4)	0·3359 (2)	−0·0941 (3)	0·7015 (2)	4·36 (5)
C(5)	0·2673 (2)	−0·1911 (3)	0·7074 (2)	4·89 (6)
C(6)	0·1752 (2)	−0·1897 (3)	0·6108 (2)	4·51 (6)
C(7)	0·0537 (2)	−0·0950 (3)	0·4022 (2)	4·08 (5)
H(2)	0·295 (1)	0·426 (2)	0·569 (2)	3·3 (4)*
H(4)	0·400 (2)	−0·091 (3)	0·769 (3)	6·3 (7)*
H(5)	0·279 (2)	−0·259 (3)	0·766 (2)	5·4 (6)*
H(6)	0·632 (2)	0·247 (3)	0·616 (2)	5·4 (6)*

* Atoms refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $\frac{4}{3}[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos\gamma)\beta_{1,2} + ac(\cos\beta)\beta_{1,3} + bc(\cos\alpha)\beta_{2,3}]$.

Table 2. *Bond distances* (Å) *and angles* (°)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Cl–C(3)	1·734 (2)	C(1)–C(7)	1·493 (2)
O(1)–O(1′)	1·453 (2)	C(2)–C(3)	1·390 (2)
O(1)–C(7)	1·364 (2)	C(3)–C(4)	1·369 (3)
O(2)–C(7)	1·169 (2)	C(4)–C(5)	1·370 (3)
C(1)–C(2)	1·373 (2)	C(5)–C(6)	1·384 (3)
C(1)–C(6)	1·381 (3)		
O(1′)–O(1)–C(7)	110·1 (1)	C(2)–C(3)–C(4)	121·5 (2)
C(2)–C(1)–C(6)	120·7 (2)	C(3)–C(4)–C(5)	119·0 (2)
C(2)–C(1)–C(7)	121·7 (2)	C(4)–C(5)--C(6)	120·8 (2)
C(6)–C(1)–C(7)	117·6 (2)	C(1)–C(6)–C(5)	119·3 (2)
C(1)–C(2)–C(3)	118·6 (2)	O(1)–C(7)--O(2)	123·8 (2)
Cl–C(3)–C(2)	118·6 (2)	O(1)–C(7)–C(1)	109·2 (1)
Cl–C(3)–C(4)	119·9 (1)	O(2)–C(7)–C(1)	127·0 (2)

Discussion. The atomic fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1.* The bond lengths and angles are shown in Table 2. Respective e.s.d.'s have been provided in parentheses. The molecular conformation and the atom-labeling scheme are shown in an *ORTEP* (Johnson, 1976) plot in Fig. 1.

The crystal structure consists of individual molecules such that the C_6H_4ClO asymmetric unit is bonded to the other equivalent half by a twofold symmetry axis which bisects the O—O peroxide bond. The atom O(2) was easily identified as the carbonyl O from the difference in C—O bond lengths, the valence angle at C(7) (Ferguson & Sim, 1961) and the well defined peroxide distance, 1·453 (2) Å, involving the atom O(1). In contrast to 3-chloro-2′-iododibenzoyl peroxide (Gougoutas & Lessinger, 1975) the C=O and C—Cl bonds adopt an antiparallel arrangement about the C(1)—C(7) bond yielding, therefore, a *transoid* disposition which agrees well with that found in *m*-chlorobenzoic acid (Gougoutas & Lessinger, 1975). This, perhaps, is due to rotation of the phenyl ring about the C(1)—C(7) bond in order to minimize the nonbonded repulsions: torsion angles C(6)C(1)C(7)-O(1) and C(2)C(1)C(7)O(2) are −173·5 and −176·4° respectively.

The peroxide bond distance O(1)—O(1′) [1·453 (2) Å] is considerably shorter compared with the O—O distances, 1·469 (3)–1·484 (3) Å (Miura, Ikegami, Nojima, Kusabayashi, McCullough & Nagase, 1983; Syed *et al.*, 1983, and references therein), found in more strained environments such as the ozonides where the ring structure forces an eclipsed configuration about the O—O bond. The C—Cl length [1·734 (2) Å] compares well with the values for similar structures: 1·737 (Ferguson & Sim, 1961), and 1·740 (1) Å (Domenicano, Vaciago & Coulson, 1975; Bocelli & Grenier-Loustalot, 1983*a*,*b*,*c*).

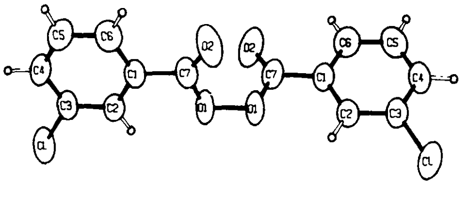

Fig. 1. *ORTEP* plot (Johnson, 1976) showing the atomic labeling scheme. The ellipsoids enclose 50% probability. H atoms are represented by spheres of arbitrary radius. A few torsion angles of interest are: C(2)C(1)C(7)O(2) −176·4, C(6)C(1)C(7)O(2) 5·0, C(2)C(1)C(7)O(1) 5·0, C(6)C(1)C(7)O(1) −173·5, C(1)-C(2)C(3)Cl 179·4, O(2)C(7)O(1)O(1′) 3·2, C(7)O(1)O(1′)-C(7′) 91·9° (e.s.d.'s ~0·4°).

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* Lists of structure factors, anisotropic thermal parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39415 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

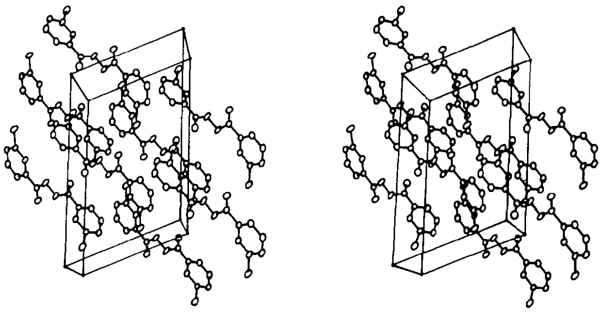

Fig. 2. Stereoview of the molecular packing in the unit cell along the *b* axis, with *c* axis approximately horizontal and *a* axis vertical.

Fig. 2 represents the stereopacking of the molecules. The shortest intermolecular contacts between non-hydrogen atoms are 3·279 (2) Å for Cl–O(2) and 3·285 (3) Å for O(2)–O(2). The molecules are held together by usual van der Waals forces to form parallel chains.

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Structure and Stereochemistry of 2-Methylthio-7-(*p*-bromophenyl)-8-phenoxy-4,5-benzo-3-aza-2-nonem,* $C_{24}H_{19}BrN_2O_2S$†

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Abstract. $M_r = 479{\cdot}4$, monoclinic, $P2_1/n$, $a = 16{\cdot}577\,(5)$, $b = 7{\cdot}838\,(1)$, $c = 16{\cdot}771\,(4)$ Å, $\beta = 95{\cdot}66\,(2)°$, $V = 2168\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 3{\cdot}66$ mm^{-1}, $F(000) = 976$, $T = 293$ K, final $R = 0{\cdot}043$ for 2451 reflections. The conformation of the molecule (RML-5) is governed by the steric and electrostatic interactions of the substituents. The diazepine ring adopts a boat conformation. The four-membered β-lactam ring is planar with phenyl substituents in the eclipsed conformation. Bond lengths and angles are normal.

Introduction. A great number of studies have been devoted to the search for structural analogues of cephalosporin and penicillin with specific activity (Guthikonda, Cama & Christensen, 1974; Bose, Ram, Hoffman, Hutchinson & Manhas, 1979; Itil, Saletu & Marasa, 1974). It appeared of interest to us to combine the two functionalities of cephalosporin and penicillin by preparing compounds in which the β-lactam moiety is integrated into the benzodiazepine system and to investigate their pharmacological profile. Synthesis of the title compound (1) was accomplished by cycloaddition of phenoxyacetyl chloride onto 2-*p*-bromophenyl)-4-methylthio-3*H*-1,5-benzodiazepine (Cortés & Martinez, 1983). The structure determination was undertaken to elucidate the stereochemistry of the product.

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* 2a-(*p*-Bromophenyl)-4-methylthio-2-phenoxy-1,2,2a,3-tetrahydroazeto[1,2-*a*][1,5]benzodiazepin-1-one.

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