

## Crystal and Molecular Structure of 1,4-Epoxy-4-(4-nitrophenylmethyl)-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one

By Donald F. Mullica, James D. Korp, W. O. Milligan,\* John S. Belew, James L. McAtee, Jr., and James Karban, Department of Chemistry, Baylor University, Waco, Texas 76703, U.S.A.

The title compound (I), an ozonide, crystallizes in a monoclinic unit cell, space group  $P2_1/c$ , with  $a = 8.205(9)$ ,  $b = 14.585(7)$ ,  $c = 15.925(5)$  Å,  $\beta = 100.05(8)^\circ$ , and  $Z = 4$ . The structure was determined by single crystal  $X$ -ray diffraction methods. The phase problem was solved by direct methods and refined by full-matrix least-squares techniques to  $R$  0.052 for 1 150 unique reflections. The five-membered ring is in an epoxide-oxygen pure envelope conformation with  $C_s$  symmetry and the six-membered ring of the bicyclic system also has an envelope or half-boat configuration.

MUCH attention has been given to the ozonolysis of the double bond since the early classical work of Harries<sup>1</sup> and Staudinger,<sup>2</sup> and many mechanisms of the ozonolysis of olefinic compounds have been suggested.<sup>3-8</sup> The refinement of Criegee's<sup>5</sup> mechanism by Bailey *et al.*<sup>9</sup> led to the conclusion that the conformation of the primary ozonide was crucial.

Renard and Fliszar<sup>10</sup> presented a quantum chemical conformational study in order to determine the preferential configuration of the 1,2,3-trioxolan ring. Their calculations indicated the half-chair conformation of the five-membered ozonide ring to be more stable than the envelope form. Microwave studies by Gilles and Kuczkowski<sup>11,12</sup> of ethylene ozonide substantiated this conformation, with  $C_2$  symmetry for the secondary ozonide. Later, a theoretical conformational analysis by Rouse<sup>13</sup> of a saturated-heterocycle substituted final ozonide (1,2,4-trioxolan, secondary) showed that the oxygen half-chair conformation was preferred, instead of the carbon-epoxide oxygen half-chair postulated by Bailey *et al.*<sup>9</sup>

A structural investigation of gaseous 1,2,4-trioxocyclopentane by electron diffraction methods<sup>14</sup> has shown that a  $C_2$  symmetry model yields very satisfactory agreement between experimental and theoretical intensity values. However, it was also possible to obtain very good agreement by assuming a  $C_s$  symmetry, the envelope conformation. Although the study favoured  $C_2$  symmetry, the conformational problem of the ozonide ring was not resolved. The only previous single-crystal structural analysis of an ozonide was carried out by Groth<sup>15</sup> for the ozonide 3-methoxycarbonyl-5-anisyl-1,2,4-trioxacyclopentane was achieved; however, the structure was disordered showing different conformations for the five-membered ring. The final conclusion was that the geometry for the ozonide ring was weighted, 35% corresponding to an envelope form while the

remainder (65%) was between an envelope and the conformation with  $C_2$  symmetry.

In order to acquire detailed structural information and present definite conformational assignment to the five-membered ozonide ring, a single-crystal  $X$ -ray analysis of the title compound (I) has been carried out. The choice of this particular *para*-substituted compound has been previously discussed.<sup>16</sup>

### EXPERIMENTAL

A solution of the indenone<sup>16</sup> in dry methylene chloride, cooled to 0 °C, was treated with oxygen-ozone to yield the ozonide 1,4-epoxy-4-(4-nitrophenylmethyl)-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one. The benzodioxepin was recrystallized several times from methanol to give clear colourless crystals which were suitable for single-crystal  $X$ -ray analysis.

**Crystallographic Measurements.**—A single crystal (0.100 × 0.125 × 0.450 mm) was selected for three-dimensional data collection on an Enraf-Nonius Cad 4 automatic diffractometer using Mo- $K_\alpha$  radiation. The orientation matrix used for data collection resulted from a least-squares refinement of 25 accurately centred reflections. Intensities were measured by  $\theta$ — $2\theta$  scan technique at a variable rate of 0.04—3.3° min<sup>-1</sup>, determined by a fast prescan of 3.3° min<sup>-1</sup>. All data were collected with a lithium-drifted silicon solid-state detector. During the prescan, all reflections having < 75 counts above background were considered unobserved. Data were collected in the range  $3 < 2\theta < 50^\circ$ . The intensities of two reflections monitored every two hours during data collection did not vary appreciably. The mean disagreement factor for each standard reflection from the averaged value was < 1.6%. Intensities having  $I > 3\sigma(I)$  were used in the structure refinement.<sup>17</sup> All unique diffraction data were corrected for Lorentz and polarization factors. An absorption correction was deemed unnecessary.

**Crystal Data and Statistical Summary.**— $C_{22}H_{15}NO_6$ ,  $M = 389.36$ . Monoclinic,  $a = 8.205(9)$ ,  $b = 14.585(7)$ ,  $c = 15.925(5)$  Å,  $\beta = 100.05(8)^\circ$ ,  $U = 1 876(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.36(1)$ ,  $D_c = 1.376(5)$  g cm<sup>-3</sup>. Space group  $P2_1/c$  ( $C_{2h}^6$ , No. 14). Unique refl., 1 150. Max.  $2\theta$ , 50°. Ext. Coeff.,  $g(10^5)$ , 1.80(4). Mo- $K_\alpha$ ,  $\lambda = 0.710 73$  Å;  $\mu(\text{Mo-}K_\alpha) = 1.098$  cm<sup>-1</sup>.

**Structural Analysis and Refinement.**—The structure factors were placed on an absolute scale by Wilson's method<sup>18</sup> ( $\beta$  5.013 Å<sup>2</sup> and the scale multiplier equals 3.642). By use of MULTAN,<sup>19</sup> normalized structure factors  $|E_{hkl}|$  were obtained by applying the overall temperature

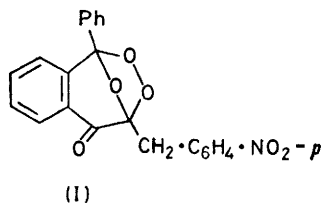


TABLE 1

Final atomic parameters ( $\times 10^4$ ), with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	1 323(9)	7 974(5)	2 266(5)
O(2)	8 421(6)	9 754(4)	2 299(4)
O(3)	7 527(8)	8 377(4)	1 756(4)
O(4)	6 577(7)	8 638(4)	2 411(4)
O(5)	6 193(8)	1 245(5)	809(5)
O(6)	4 712(8)	2 399(5)	1 013(6)
N	4 919(10)	1 583(7)	960(6)
C(1)	296(12)	8 445(7)	2 549(8)
C(2)	8 977(12)	8 987(7)	1 891(7)
C(3)	7 513(11)	9 371(6)	2 908(7)
C(4)	8 702(11)	8 975(6)	3 660(8)
C(5)	8 496(12)	9 029(7)	4 490(7)
C(6)	9 632(14)	8 644(8)	5 122(8)
C(7)	1 003(15)	8 209(8)	4 950(8)
C(8)	1 272(12)	8 132(7)	4 115(9)
C(9)	107(11)	8 516(6)	3 457(7)
C(10)	6 281(11)	61(7)	3 115(6)
C(11)	4 862(12)	9 720(6)	3 385(7)
C(12)	3 728(12)	357(8)	3 575(8)
C(13)	3 991(13)	1 295(8)	3 527(8)
C(14)	5 395(13)	1 630(7)	3 245(7)
C(15)	6 532(10)	990(7)	3 047(7)
C(16)	9 382(11)	9 201(6)	1 027(6)
C(17)	875(11)	9 853(7)	1 077(6)
C(18)	2 427(11)	9 466(6)	980(6)
C(19)	3 758(10)	45(7)	960(6)
C(20)	3 536(11)	968(7)	1 031(6)
C(21)	2 033(11)	1 350(6)	1 148(6)
C(22)	739(11)	770(7)	1 182(7)
H(1)	2 510	8 790	830
H(2)	4 860	9 830	800
H(3)	1 933	2 015	1 325
H(4)	9 600	1 020	1 250
H(5)	9 662	8 590	697
H(6)	8 355	9 525	653
H(7)	4 694	9 034	3 453
H(8)	2 680	115	3 753
H(9)	3 060	1 750	3 600
H(10)	5 535	2 320	3 170
H(11)	7 630	1 215	2 880
H(12)	7 480	9 320	4 640
H(13)	9 420	8 673	5 730
H(14)	1 646	7 800	5 400
H(15)	2 120	7 680	3 960

parameter. Phases of 400 strong reflections with  $|E| > 1.60$  were determined. The best solution from the summary of figures of merit was expanded to yield the positions for all 29 non-hydrogen atoms as well as tentative bond distances, bond angles, and an approximate structure. This solution by direct methods solved the phase problem and was the starting model. The atomic positional and isotropic thermal parameters were refined initially by block-diagonal least-squares methods. The first structure-factor calculation yielded a disagreement factor of  $R$  0.25. Several subsequent least-squares calculations gave an  $R$  value of 0.082. At this stage of refinement, a three-dimensional difference-Fourier synthesis was calculated in order to acquire the hydrogen-atom positions. Continued refinement of atomic parameters with anisotropic thermal factors for non-hydrogen atoms lowered  $R$  to 0.061. While holding the already refined hydrogen atom parameters constant, a final full-matrix least-square calculation with a refined secondary extinction correction, yielded final reliability factors of  $R$  0.052 and the weighted factor  $R'$  0.047 {where  $R'$  is defined as  $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  and  $w = \sigma^{-2}(|F_o|)$ }. The maximum value of abscission

\* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

TABLE 2

Interatomic distances ( $\text{\AA}$ ), with estimated standard deviations in parentheses

O(1)-C(1)	1.232(10)	C(10)-C(11)	1.401(11)
O(2)-C(2)	1.406(9)	C(10)-C(15)	1.377(11)
O(2)-C(3)	1.434(9)	C(11)-C(12)	1.385(12)
O(3)-O(4)	1.459(7)	C(11)-H(7)	1.018
O(3)-C(2)	1.473(9)	C(12)-C(13)	1.390(13)
O(4)-C(3)	1.466(9)	C(12)-H(8)	1.015
O(5)-N	1.217(8)	C(13)-C(14)	1.395(12)
O(6)-N	1.207(9)	C(13)-H(9)	1.034
N-C(20)	1.467(11)	C(14)-C(15)	1.394(12)
C(1)-C(2)	1.582(13)	C(14)-H(10)	1.023
C(1)-C(9)	1.484(13)	C(15)-H(11)	1.036
C(2)-C(16)	1.503(12)	C(16)-C(17)	1.542(11)
C(3)-C(4)	1.521(12)	C(16)-H(5)	1.079
C(3)-C(10)	1.504(11)	C(16)-H(6)	1.056
C(4)-C(5)	1.363(12)	C(17)-C(18)	1.426(11)
C(4)-C(9)	1.419(11)	C(17)-C(22)	1.355(11)
C(5)-C(6)	1.368(13)	C(18)-C(19)	1.386(11)
C(5)-H(12)	1.001	C(18)-H(1)	1.020
C(6)-C(7)	1.361(13)	C(19)-C(20)	1.365(11)
C(6)-H(13)	1.014	C(19)-H(2)	1.030
C(7)-C(8)	1.389(13)	C(20)-C(21)	1.395(11)
C(7)-H(14)	1.008	C(21)-C(22)	1.367(11)
C(8)-C(9)	1.406(12)	C(21)-H(3)	1.017
C(8)-H(15)	1.020	C(22)-H(4)	1.026

$[\Delta\xi_i/\sigma(\xi_i)]$ , where  $\xi_i$  values are varied parameters] of the 268 varied parameters was 0.08, mean  $3.7 \times 10^{-4}$ . The goodness-of-fit value,  $[\sum(w||F_o| - |F_c||)^2 / (N_o - N_v)]^{1/2}$  where  $N_o$  is the number of independent observations and  $N_v$  is the number of parameters varied in the refinement, was 1.64, which is quite reasonable and no abnormally large correlation coefficients resulted. The quantity minimized in the least-squares calculations was  $\sum w(|F_o| - |F_c|)^2$ . A final difference electron-density map was featureless  $[0.14(3) \text{ e}\text{\AA}^{-3}]$ . Scattering factors were obtained from ref. 20 and anomalous dispersion corrections applied to them were taken from ref. 21. Final atom parameters and their estimated standard deviations are listed in Table 1. Observed and calculated structure factors and anisotropic thermal parameters have been deposited as Supplementary Publication No. SUP 22591 (4 pp.).\*

## RESULTS AND DISCUSSION

A stereoscopic drawing<sup>22</sup> with the numbering scheme adopted throughout the structural analysis is shown in Figure 1.† Figure 2 is a packing diagram of the contents of the unit cell with 50% equiprobability ellipsoids represented. Bond distances and angles, with their estimated standard deviations, are listed in Tables 2 and 3, respectively. These show several unusual features, even after taking into account the fairly large standard deviations which were probably due to the low ratio (*ca.* 5 : 1) of observations to parameters involved in the least-squares refinement.

The most noticeable distortions are found in the bond angles of the two carbons of the ozonide ring. In each case, the interior O-C-O angle is compressed (102 and 103°), while the opposite C-C-C angle is quite enlarged (116 and 118°) relative to the ideal value of 109.4° for an  $sp^3$ -hybridized carbon. Naturally, the strain on the tetrahedral geometry by the five-membered ring leads

† The numbering scheme suggested by Experimental Services Division of the American Chemical Society in the naming of this compound is found in ref. 16.

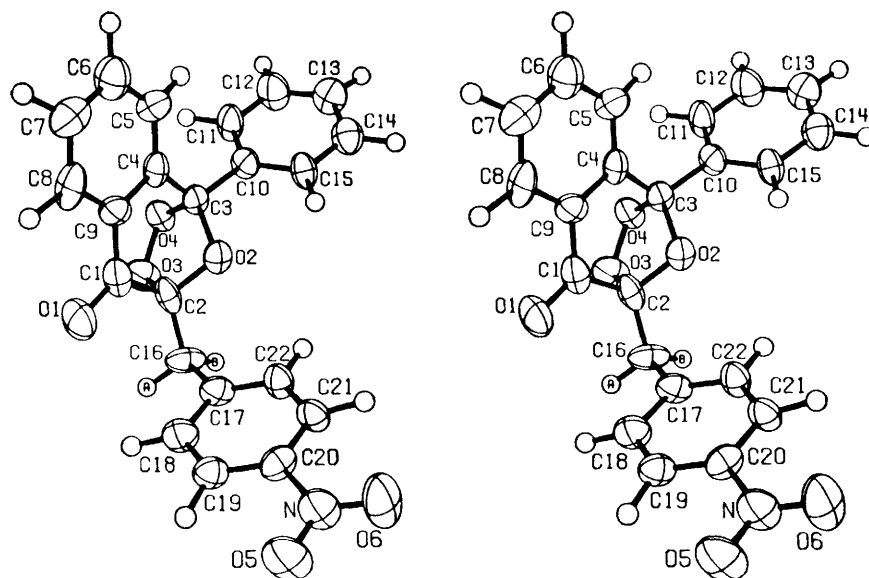


FIGURE 1 Stereoview with numbering scheme

to a normal situation of an interior angle compressed to *ca.* 106°, with the remaining angles apportioning the compensating expansion almost equally.<sup>11,12,23,24</sup> Unfortunately, in the ozonide determination by Groth<sup>15</sup> the disorder prevented a reliable measure of these angles, but in the microwave studies of ethylene and propylene ozonides by Gillies *et al.*<sup>11,12</sup> no such distortions are present. However, we found<sup>25,26</sup> two crystal structures involving non-ozonide five-membered rings, in which external tetrahedral distortions of 118 and 119° were reported, so the current observation is not unprecedented geometrically. The reason why the two C-C-C angles in the present investigation show such abnormal expansion is most likely due to steric considerations, with the phenyl  $\pi$ -cloud of C(10)-C(15) being repulsed by H(5), and the necessarily partially eclipsed methylene hydrogens of C(16) repelled by O(2) and O(3) lone-electron pairs.

The geometry of the five-membered ring itself is significantly different from those of the two microwave studies<sup>11,12</sup> only in the C(peroxide)-O distances and the angles at those oxygens. The present values (1.47 Å), however, are not unusual for a C(*sp*<sup>3</sup>)-O(*sp*<sup>3</sup>) single bond,

according to Sutton.<sup>27</sup> The C(epoxide)-O distances are in good agreement with previous results,<sup>23,28,29</sup> as is the O-O distance.<sup>11,12,30-33</sup>

There would appear to be resonance between the  $\pi$  system of C(4)-C(9) and the keto-group. Bond C(1)-C(9) is somewhat short for a pure C(*sp*<sup>2</sup>)-C(*sp*<sup>2</sup>) single bond, while C(1)-O(1) is a bit long. The pattern is not unusual as in, for example, tetralin-1-ones.<sup>34</sup> The external angles on the keto-carbon are again disparate (126 *vs.* 118°), perhaps owing to repulsion between an oxygen lone-pair and H(8).

The nitro-group parameters agree well with those of similar *para*-substituted nitrobenzenes as compiled elsewhere.<sup>35</sup> The characteristic widening of the O-N-O angle caused by oxygen repulsions is well observed. The remaining distances and angles of the structure also conform well to previously published values.

An electron-diffraction gaseous study of the unconstrained five-membered ozonide ring by Almenningen *et al.*,<sup>14</sup> demonstrated that a C<sub>2</sub> symmetry model was the preferred conformation, but the C<sub>s</sub> symmetry (envelope) could not be completely disregarded. The single-crystal analysis of an ozonide by Groth<sup>15</sup> pro-

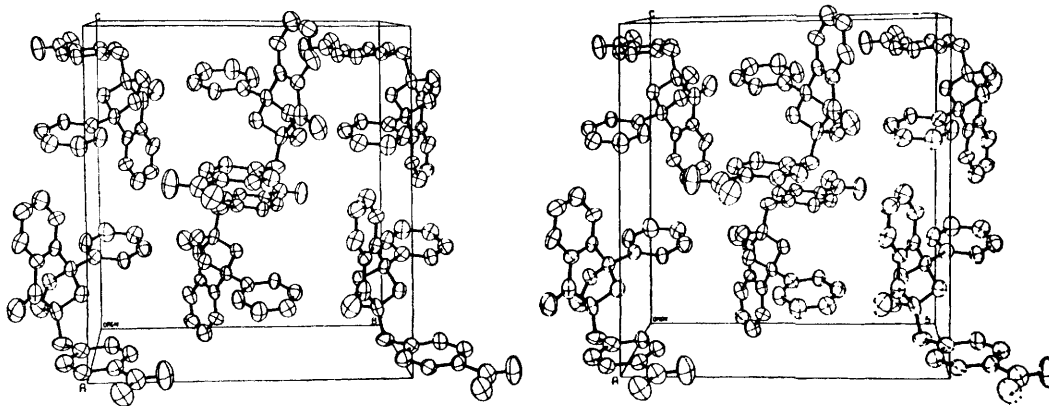


FIGURE 2 Stereoscopic packing diagram

TABLE 3

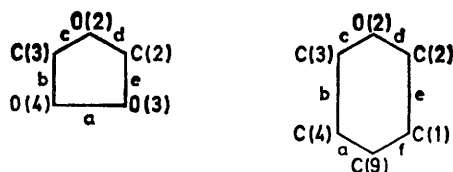
Bond angles ( $^{\circ}$ ), with estimated standard deviations in parentheses

C(2)-O(2)-C(3)	104.6(7)	C(11)-C(10)-C(15)	121.2(8)
O(4)-O(3)-C(2)	104.8(6)	C(10)-C(11)-C(12)	117.0(9)
O(3)-O(4)-C(3)	106.3(6)	C(10)-C(11)-H(7)	121.2
O(5)-N-O(6)	123.4(9)	C(12)-C(11)-H(7)	121.8
O(5)-N-C(20)	118.0(9)	C(11)-C(12)-C(13)	122.2(10)
O(6)-N-C(20)	118.5(9)	C(11)-C(12)-H(8)	117.5
O(1)-C(1)-C(2)	118.0(11)	C(13)-C(12)-H(8)	120.3
O(1)-C(1)-C(9)	126.1(11)	C(12)-C(13)-C(14)	120.4(10)
C(2)-C(1)-C(9)	115.8(9)	C(12)-C(13)-H(9)	120.0
O(2)-C(2)-O(3)	103.3(7)	C(14)-C(13)-H(9)	118.7
O(2)-C(2)-C(1)	109.4(9)	C(13)-C(14)-C(15)	117.5(10)
O(2)-C(2)-C(16)	113.7(9)	C(13)-C(14)-H(10)	119.8
O(3)-C(2)-C(1)	103.6(8)	C(15)-C(14)-H(10)	122.6
O(3)-C(2)-C(16)	107.0(8)	C(10)-C(15)-C(14)	121.7(9)
C(1)-C(2)-C(16)	118.3(9)	C(10)-C(15)-H(11)	118.7
O(2)-C(3)-O(4)	101.8(7)	C(14)-C(15)-H(11)	119.5
O(2)-C(3)-C(4)	110.1(7)	C(2)-C(16)-C(17)	112.3(8)
O(2)-C(3)-C(10)	109.6(8)	C(2)-C(16)-H(5)	112.1
O(4)-C(3)-C(4)	110.5(7)	C(2)-C(16)-H(6)	109.0
O(4)-C(3)-C(10)	107.3(8)	C(17)-C(16)-H(5)	107.4
C(4)-C(3)-C(10)	116.4(9)	C(17)-C(16)-H(6)	107.6
C(3)-C(4)-C(5)	124.8(10)	H(5)-C(16)-H(6)	108.2
C(3)-C(4)-C(9)	115.7(10)	C(16)-C(17)-C(18)	117.8(9)
C(5)-C(4)-C(9)	119.5(10)	C(16)-C(17)-C(22)	122.2(9)
C(4)-C(5)-C(6)	120.4(10)	C(18)-C(17)-C(22)	119.9(8)
C(4)-C(5)-H(12)	120.3	C(17)-C(18)-C(19)	119.0(9)
C(6)-C(5)-H(12)	119.2	C(17)-C(18)-H(1)	120.4
C(5)-C(6)-C(7)	121.6(11)	C(19)-C(18)-H(1)	120.0
C(5)-C(6)-H(13)	118.5	C(18)-C(19)-C(20)	118.8(9)
C(7)-C(6)-H(13)	119.9	C(18)-C(19)-H(2)	123.3
C(6)-C(7)-C(8)	120.4(11)	C(20)-C(19)-H(2)	117.2
C(6)-C(7)-H(14)	118.7	N-C(20)-C(19)	118.7(9)
C(8)-C(7)-H(14)	118.8	N-C(20)-C(21)	118.6(9)
C(7)-C(8)-C(9)	118.7(10)	C(19)-C(20)-C(21)	122.6(8)
C(7)-C(8)-H(15)	120.8	C(20)-C(21)-C(22)	117.9(8)
C(9)-C(8)-H(15)	118.7	C(20)-C(21)-H(3)	122.3
C(1)-C(9)-C(4)	118.8(10)	C(22)-C(21)-H(3)	118.6
C(1)-C(9)-C(8)	121.7(10)	C(17)-C(22)-C(21)	121.7(9)
C(4)-C(9)-C(8)	119.4(10)	C(14)-C(22)-H(4)	117.4
C(3)-C(10)-C(11)	117.1(9)	C(21)-C(22)-H(4)	120.8
C(3)-C(10)-C(15)	121.7(9)		

TABLE 4

Bond	Reference atoms	Angle
(a) Torsion angle ( $^{\circ}$ ) of five-membered ozonide ring *		
a O(3)-O(4)	C(2), O(3), O(4), C(3)	-1.0 (-sp)
b O(4)-C(3)	O(3), O(4), C(3), O(2)	25.9 (+sp)
c C(3)-O(2)	O(4), C(3), O(2), C(2)	-42.5 (-sc)
d O(2)-C(2)	C(3), O(2), C(2), O(3)	42.4 (+sc)
e C(2)-O(3)	O(2), C(2), O(3), O(4)	-24.9 (-sp)
(b) Torsion angle ( $^{\circ}$ ) of six-membered epoxide ring *		
a C(9)-C(4)	C(1), C(9), C(4), C(3)	-1.0 (-sp)
b C(4)-C(3)	C(9), C(4), C(3), O(2)	-38.9 (-sc)
c C(3)-O(2)	C(4), C(3), O(2), C(2)	74.7 (+sc)
d O(2)-C(2)	C(3), O(2), C(2), C(1)	-67.4 (-sc)
e C(2)-C(1)	O(2), C(2), C(1), C(9)	28.6 (+sp)
f C(1)-C(9)	C(2), C(1), C(9), C(4)	6.2 (+sp)

\* Labelling scheme



duced a disordered structure where an envelope conformation was observed approximately 1/3 of the time and a quasi-type conformation which was between an envelope and half-chair conformation for the remainder.

An important aspect of the structural study of the title compound reveals the configuration of the ozonide ring to be an epoxide-oxygen pure envelope.

The endocyclic torsion angles according to the convention ascribed in ref. 36 are listed in Table 4. As might be expected, these values are very nearly the same as those found in many furanose sugars and their derivatives<sup>23,37</sup> as listed according to the convention of Sundaralingam.<sup>38</sup> The least-squares planes defined by the non-hydrogen atoms of the two phenyl rings indicated that both rings are essentially flat. The planes of interest in the bicyclic arrangement are viewed in Figure 3 [planes (I), (Ia), (II), (III), and (IV)]. Table 5 presents selected molecular planes. Plane (II), owing to the slight distortion of the torsion angle [C(2)-C(1)-C(9)-C(4)] has poor planarity and is slightly non-coplanar with plane (I). The listed dihedral angle evidences this observation (1.9 $^{\circ}$ ). Plane (Ia), the shaded area of Figure 3(b), exhibits good planarity of the tested atoms. The least-squares planes program used

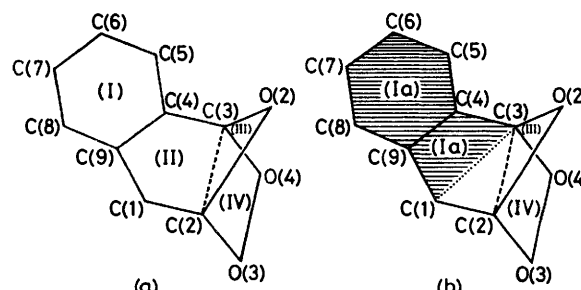


FIGURE 3 Planes of interest

in this structural analysis adapts the method developed by Schomaker *et al.*<sup>39</sup> A unique mean plane program which describes general monocyclic puckered rings was also employed, in which the geometry of the puckered

TABLE 5

Equation of least-squares mean plane in the form  $AX + BY + CZ - D = 0$  where  $X$ ,  $Y$ , and  $Z$  refer to crystallographic axes in Å units

(a) Planes

Plane (I): C(4)-(9)

$$[C(4) - 0.002, C(5) - 0.003, C(6) 0.006, C(7) - 0.004, C(8) - 0.002, C(9) 0.004]$$

Plane (Ia): C(1), C(3)-(9)

$$[C(1) 0.015, C(3) - 0.006, C(4) - 0.005, C(5) 0.002, C(6) 0.013, C(7) - 0.004, C(8) - 0.010, C(9) - 0.005]$$

Plane (II): C(1)-(4), C(9)

$$[C(1) 0.035, C(2) - 0.039, C(3) 0.031, C(4) - 0.017, C(9) - 0.020]$$

Plane (IV): O(3), O(4), C(2), C(3)

$$[O(3) - 0.006, O(4) 0.006, C(2) 0.004, C(3) - 0.004]$$

Mean standard deviation for atoms forming plane: (I) 0.009, (Ia) 0.010, (II) 0.018, (IV) 0.008.

(b) Angles between planes ( $^{\circ}$ )

(I)-(II)	1.9	(II)-(IV)	107.0	(Ia)-(IV)	108.7
(I)-(Ia)	0.3	(II)-(III)	63.9	(III)-(IV)	43.1
			(116.1)		(136.9)

TABLE 6  
Ring-puckering parameters

- (a) Five-membered ring  
 $q_2 = 0.399$ ,  $\phi_2 = 357.2^\circ$  ( $z_2 = -0.2$ ,  $z_5 = -0.2$ ;  $z_3 = 0.07$ ,  
 $z_4 = 0.09$ ),  $\phi = 0$  or  $180^\circ$  denotes pure envelope which has  
 $z_2 = z_5$  and  $z_3 = z_4$
- (b) Six-membered ring  
 $q_2 = 0.503$ ,  $q_3 = 0.324$ ,  $Q = 0.598$ ,  $\theta = 57.2^\circ$ ,  $\phi_2 = 353.1^\circ$   
( $z_2 = -0.25$ ,  $z_5 = 0.02$ ;  $z_3 = -0.04$ ,  $z_4 = 0.15$ )

The envelope or half-boat is considered the ring conformation when coplanarity of the base atoms is maintained. Such is the case for a small  $Q\theta$  value if  $\tan\theta = 2^{1/2}$  and  $\phi = 0$ . Here  $\phi = 353.1$  and  $\tan\phi = 1.55$ . Also, a half-boat is considered the proper conformation when  $\theta = 54.7^\circ$  and  $\phi = n\pi/3^\circ$  (where  $n = 1, 2 \dots 6$  and  $\pi$  is  $180^\circ$ ).\*

- (c) Seven-membered ring  
 $q_2 = 1.053$ ,  $q_3 = 0.392$ ,  $\phi_2 = 131.0^\circ$ ,  $\phi_3 = 93.6^\circ$

\* G. A. Jeffrey and J. H. Yates, *Carbohydrate Res.*, 1979, in the press.

plane is represented in terms of amplitude and phase co-ordinates. Ref. 40 fully discusses the general definition of ring-puckering co-ordinates; no mathematical approximations are involved as with treatments based on torsion angles. Table 6 presents the puckering parameters for the involved rings (five-, six-, and seven-membered).

This investigation of 1,4-epoxy-4-(4-nitrophenylmethyl)-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one by X-ray diffraction methods has explicitly elucidated the first unambiguous crystal structure of an ozonide. The conformational analyses have shown the five- and six-membered rings of the bicyclic arrangement to be pure envelope and half-boat configurations, respectively. Obviously, the constraint of the C(1)-C(9)-C(4) bridge must contribute highly towards formation of the less-favourable envelope by the ozonide ring, although physical models of the compound are found to have a certain degree of flexibility in this area. Structural studies of other stable ozonides have been initiated, and a preliminary analysis of another *para*-substituted epoxy-benzodioxepinone,<sup>41</sup> where bromine has replaced the nitro-group, has indicated a different configuration for the ozonide five-membered ring.

This investigation was supported by The Robert A. Welch Foundation.

[9/146 Received, 30th January, 1979]

#### REFERENCES

- <sup>1</sup> C. Harries, *Ann. Chem.*, 1910, **374**, 288.
- <sup>2</sup> H. Staudinger, *Chem. Ber.*, 1925, **58**, 925.

- <sup>3</sup> A. Rieche, R. Meister, and H. Sauthoff, *Annalen*, 1942, **553**, 187.
- <sup>4</sup> P. Criegee, *Annalen*, 1948, **560**, 131.
- <sup>5</sup> R. Criegee, *Rec. Chem. Progr.*, 1957, **18**, 111.
- <sup>6</sup> N. A. Milas, P. Davis, and J. T. Nolan, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 2536.
- <sup>7</sup> R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, 1966, **88**, 3143.
- <sup>8</sup> R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, 1967, **89**, 2429.
- <sup>9</sup> N. L. Bould, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, 1968, **90**, 1822.
- <sup>10</sup> J. Renard and S. Fliszar, *J. Amer. Chem. Soc.*, 1970, **92**, 2628.
- <sup>11</sup> C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 1972, **94**, 6337.
- <sup>12</sup> R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *J. Amer. Chem. Soc.*, 1974, **96**, 348.
- <sup>13</sup> R. A. Rouse, *Internat. J. Quantum Chem.*, 1973, Symp. No. 7, 289.
- <sup>14</sup> A. Almenningen, P. Kolsaker, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, 1969, **23**, 3398.
- <sup>15</sup> P. Groth, *Acta Chem. Scand.*, 1970, **24**, 2137.
- <sup>16</sup> J. Karban, J. L. McAtee, Jr., J. S. Belew, D. F. Mullica, W. O. Milligan, and J. Korp, *J.C.S. Chem. Comm.*, 1978, 729.
- <sup>17</sup> S. W. Peterson and H. A. Levy, *Acta Cryst.*, 1957, **10**, 70.
- <sup>18</sup> A. J. Wilson, *Nature*, 1942, **150**, 151.
- <sup>19</sup> G. Germain, P. Main, and M. M. Wolfson, *Acta Cryst.*, 1971, **A27**, 368.
- <sup>20</sup> D. T. Cromer and H. Mann, *Acta Cryst.*, 1968, **A24**, 321.
- <sup>21</sup> D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
- <sup>22</sup> C. K. Johnson, ORTEP II, Report ORNL 5138 (3rd revision of ORNL 3794), 1976, Oak Ridge National Laboratory, U.S.A.
- <sup>23</sup> A. Grand and J. Cadet, *Acta Cryst.*, 1978, **B34**, 1524.
- <sup>24</sup> J. Albertsson, B. Briggman, and Å. Oskarsson, *Cryst. Struct. Comm.*, 1978, **7**, 595.
- <sup>25</sup> A. C. Stergion, S. C. Kokkon, and P. J. Rentzeperis, *Acta Cryst.*, 1978, **B34**, 1662.
- <sup>26</sup> W. P. J. Gaykema and A. L. Spek, *Cryst. Struct. Comm.*, 1978, **7**, 649.
- <sup>27</sup> L. E. Sutton, *Chem. Soc. Special Publ.*, No. 18, 1965.
- <sup>28</sup> V. Buseti, M. Mammi, and G. Carazzolo, *Z. Krist.*, 1963, **119**, 310.
- <sup>29</sup> J. F. McConnell and J. D. Stevens, *Cryst. Struct. Comm.*, 1973, **2**, 619.
- <sup>30</sup> E. Price, S. F. Trevino, C. S. Choi, and M. K. Farr, *J. Chem. Phys.*, 1975, **63**, No. 6, 2620.
- <sup>31</sup> W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 1965, **42**, 3054.
- <sup>32</sup> M. J. Nolte and E. Singleton, *Acta Cryst.*, 1975, **B31**, 223.
- <sup>33</sup> U. Thewalt and G. Struckmeier, *Z. anorg. Chem.*, 1976, **419**, 163.
- <sup>34</sup> J. D. Korp and I. Bernal, unpublished results.
- <sup>35</sup> A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 221.
- <sup>36</sup> W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.
- <sup>37</sup> E. Shefter, *J. Pharm. Sci.*, 1968, **57**, 1157.
- <sup>38</sup> M. Sundaralingam, *Biopolymers*, 1969, **7**, 821.
- <sup>39</sup> V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.
- <sup>40</sup> D. Cremer and J. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 1354.
- <sup>41</sup> J. D. Oliver, D. F. Mullica, W. O. Milligan, J. Karban, J. L. McAtee, Jr., and J. S. Belew, *Acta Cryst.*, in the press.