Crystal and Molecular Structure of *endo,endo*-2,6-Bis(phenylcarbamoyloxy)-*cis*-bicyclo[3.3.0]octane

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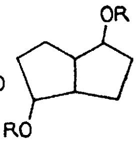
The crystal and molecular structure of the title compound (II) has been determined by a three-dimensional *X*-ray analysis. Crystals are orthorhombic, space group *F2dd*, with $a = 5{\cdot}289(7)$, $b = 12{\cdot}948(9)$, and $c = 55{\cdot}15(4)$ Å, $Z = 8$, molecular symmetry 2. The structure was solved by a combination of Patterson and Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal parameters to R 0·033 for 583 reflections measured by diffractometer. Discrete molecules are linked in the c direction by N–H ··· O hydrogen bonds [3·084(7) Å]. The oxygen substituents on the *cis*-bicyclo[3.3.0]octane nucleus are *endo*, and the system itself is skewed to relieve intramolecular O ··· H interactions which would otherwise be severe; as a consequence there is a marked puckering of the unique five-membered ring which adopts a half-chair conformation with approximately C_2 symmetry. Bond lengths have expected values.

WHEREAS mono-olefins are oxidized by palladium(II) salts in acetic acid to yield vinyl or allylic acetates,[1] it has been shown [2] that addition of certain oxidants to the reaction mixture changes the products to saturated diacetates. Thus, a mixture of $PdCl_2$ and $Pb(OAc)_4$ in HOAc will convert cyclo-octa-1,5-diene into a diacetoxybicyclo[3.3.0]octane of m.p. 36 °C in 70% yield.[3] The product could be one of a number of isomers of (I). To determine unambiguously the structure and stereochemistry of the ring system in (I) we examined crystals of (I) and of (II).

(I) R=Ac
(II) R=PhNHCO



EXPERIMENTAL

The relatively low melting point (37 °C) of (I), and the consequent large thermal motion of its atoms resulted in very poor quality *X*-ray data and precluded it from being analysed in detail. However, the phenylurethane derivative (II), m.p. 188 °C, yielded satisfactory plate-like crystals, elongated along a with {001} prominent, on recrystallization from 1 : 1 methanol–water. These crystals were used for a complete three-dimensional *X*-ray analysis.

Crystal Data.—$C_{22}H_{24}N_2O_4$, $M = 380$, Orthorhombic, $a = 5{\cdot}289(7)$, $b = 12{\cdot}948(9)$, $c = 55{\cdot}15(4)$ Å, $U = 3777$ Å^3, $D_m = 1{\cdot}34(1)$, $Z = 8$, $D_c = 1{\cdot}338$, $F(000) = 1616$. Space group *F2dd* (C_{2v}^{19}, No. 43) (a nonstandard setting of *Fdd*2 with equivalent positions: $\langle 0,0,0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0\rangle + \langle x,y,z;\ x,\bar{y},\bar{z};\ \frac{1}{4}+x,\frac{1}{4}+y,\frac{1}{4}-z;\ \frac{1}{4}+x,\frac{1}{4}-y,\frac{1}{4}+z\rangle$) from systematic absences: hkl for $h+k$, $k+l$, $h+l$ odd; $hk0$ for $(h+k) \neq 4n$; $h0l$ for $h+l \neq 4n$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 7·7 cm^{-1}. Molecular symmetry 2.

Crystallographic Measurements.—The space-group symmetry and preliminary unit-cell dimensions were obtained from rotation, Weissenberg, and precession photographs taken with Cu-K_α radiation and a crystal with dimensions $0{\cdot}33 \times 0{\cdot}15 \times 0{\cdot}05$ mm^3 mounted along a.

Accurate cell parameters were obtained by a least-squares treatment of the setting angles of 12 reflections measured on a Hilger and Watts Y 290 computer-controlled diffractometer. Three-dimensional intensity data were only collected to a maximum Bragg angle (Cu-K_α) of 57° as preliminary photographic investigation had shown that intensities fell off fairly rapidly with increasing θ. The θ—2θ scan technique was used with Ni-filtered Cu-radiation and a symmetric scan of 80 steps of 0·01° with a 3 s count at each step. Stationary-crystal–stationary-counter background counts of 60 s were measured at each end of the integrated scan. The intensities of 3 standard reflections, monitored at 5 hour intervals throughout data collection, had maximum variation of <2·6%.

Each intensity was corrected for background and of 699 accessible independent reflections 583 having $I > 3\sigma(I)$ were labelled observed. Data were corrected for Lorentz and polarization factors but not for absorption which is negligible. All calculations were carried out on an IBM 370/55 computer with locally modified programs for data-handling and also by use of the '*X*-Ray '72' system.[4]

Structure Determination.—With 8 molecules in the unit cell of space group *F2dd*, molecular symmetry 2 is demanded. A detailed analysis of the three-dimensional Patterson function revealed that the bicyclo-octane substituents were *endo* and yielded co-ordinates for the bicyclo[3.3.0]octane system. A three-dimensional Fourier synthesis phased with the contributions from these atoms showed clearly the phenylurethane group. Positional and isotropic thermal parameters were refined by full-matrix least-square calculations. In three cycles, with unit weights assigned to all observed data fell from 0·46 to 0·09. A difference synthesis computed at this stage confirmed the correctness of the structure by its general flat topography, indicated some anisotropic motion associated with the phenylurethane group, and revealed the positions of all the hydrogen atoms as small peaks 0·2—0·3 eÅ^{-3} in height. Accordingly, in subsequent cycles, the hydrogen contributions were allowed for (in their calculated positions with an overall isotropic thermal parameter U 0·05 Å^2) but were not refined. Three more cycles of refinement with the carbon, nitrogen, and oxygen atoms allowed anisotropic motion reduced R to its final value of 0·033. During the course of the anisotropic refinement, a weighting scheme based on counting statistics, in the form $\sqrt{w} = 1/(\sigma^2 F +$

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[1] P. M. Maitlis, 'The Organic Chemistry of Palladium,' vol. II, Academic Press, New York, 1971, pp. 93—105.

[2] P. M. Henry, *J. Org. Chem.*, 1967, **32**, 2575; 1973, **38**, 1681.

[3] P. M. Henry, M. Davies, G. Ferguson, S. Phillips, and R. Restivo, *J.C.S. Chem. Comm.*, 1974, 112.

[4] '*X*-Ray '72' System of Computing Programs, Computing Science, Center, University of Maryland, College Park, Maryland, U.S.A., Report TR 192.

$pF^2)^{\frac{1}{2}}$ was applied. The final weighted $R' \{= \sqrt{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^2\}}$ was 0·041. Adjustment of the p parameter (final p 8 × 10^{-4}) produced a satisfactory weighting scheme as evidenced by the analysis of $\Sigma w\Delta^2$ as a function of ranges of F_o. The standard deviation of an observation of unit weight is 1·37. In all structure-factor calculations, atomic scattering factors for non-hydrogen atoms were taken from ref. 5, and for hydrogen atoms from ref. 6. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21175 (9 pp.).*

TABLE 1

Atomic parameters

(*a*) Final fractional co-ordinates (× 10^4), with standard deviations in parentheses

Atom	x	y	z
C(1)	0 *	−442(3)	96·0(7)
C(2)	1648(10)	−17(3)	307·6(6)
C(3)	2970(11)	955(3)	214·0(7)
C(4)	1021(11)	1388(3)	37·1(7)
C(5)	2789(12)	−1501(3)	537·2(7)
C(6)	4724(11)	−2894(3)	777·2(6)
C(7)	6707(11)	−3039(3)	939·8(7)
C(8)	6724(12)	−3896(4)	1088·4(7)
C(9)	4824(12)	−4616(4)	1078·0(8)
C(10)	2886(12)	−4480(3)	915·6(8)
C(11)	2819(11)	−3626(3)	764·9(6)
O(1)	3599(9)	−720(2)	392·3(5)
O(2)	602(9)	−1698(2)	576·1(5)
N	4844(10)	−2018(3)	622·9(6)

(*b*) Final anisotropic thermal parameters † (Å² × 10^3); estimated standard deviations range from 2 to 3 × 10^{-3}

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	29	46	54	1	0	12
C(2)	39	50	44	9	0	6
C(3)	54	39	52	−4	−4	−1
C(4)	53	41	58	8	2	6
C(5)	45	47	43	6	5	8
C(6)	37	50	39	10	5	2
C(7)	39	54	47	4	2	9
C(8)	49	72	55	6	−3	17
C(9)	60	54	65	9	6	24
C(10)	61	45	68	−1	6	0
C(11)	47	49	50	2	0	1
O(1)	36	54	51	6	3	16
O(2)	32	65	69	2	9	20
N	35	52	51	5	−2	12

* Held constant to fix origin of unit cell.

† Values of U_{ij} in the expression: $\exp[-2\pi^2(U_{11}h^2a^* + U_{22}k^2b^{*2} + U_{33}l^2c^* + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$.

TABLE 2

Fractional co-ordinates (× 10^3) of the hydrogen atoms; the atom to which each is attached is given in square brackets

Atom	x	y	z
H(01)[N]	668	−175	57
H(11)[C(1)]	−185	−61	16
H(21)[C(2)]	51	17	46
H(31)[C(3)]	340	149	35
H(32)[C(3)]	466	77	12
H(41)[C(4)]	−42	176	14
H(42)[C(4)]	186	192	−8
H(71)[C(7)]	820	−247	95
H(81)[C(8)]	823	−400	123
H(91)[C(9)]	489	−531	118
H(101)[C(10)]	143	−503	90
H(111)[C(11)]	135	−352	64

Table 1 gives the final co-ordinates of the atoms together with their thermal parameters and standard deviations derived from the final least-squares matrix. Figure 1 is an ORTEP [7] view of the molecule showing the crystallographic numbering scheme, bond lengths, valency angles, and torsion angles in the bicyclo[3.3.0]octane moiety. Table 2 gives the calculated co-ordinates of the hydrogen atoms. Table 3 shows selected intramolecular distances and all intermolecular contacts <3·5 Å, and Table 4 details of least-squares planes calculated through portions of the molecule.

TABLE 3

Non-bonded contacts

(*a*) Intermolecular contacts <3·5 Å

C(7) $\cdots$ O($2^{\rm I}$)	3·359(6)	C(7) $\cdots$ C($11^{\rm I}$)	3·458(8)
N(1) $\cdots$ O($2^{\rm I}$)	3·084(8)	C(8) $\cdots$ C($10^{\rm I}$)	3·479(9)

(*b*) Selected intramolecular non-bonded contacts (Å)

C(2) $\cdots$ C($2^{\rm II}$)	3·392(5)	O(1) $\cdots$ H($42^{\rm II}$)	2·49
C(4) $\cdots$ C($4^{\rm II}$)	3·617(6)	H(32) $\cdots$ H($32^{\rm II}$)	2·38
O(1) $\cdots$ H($32^{\rm II}$)	2·87		

Roman numeral superscripts refer to the following transformations, relative to the reference molecule at x, y, z:

I $1 + x, y, z$ II $x, -y, -z$

TABLE 4

Equations of least-squares planes in the form $pX + qY + rZ + d = 0$ where p, q, and r are direction cosines of the plane normal, d is the distance from the plane to the origin, and X, Y, and Z are orthogonal co-ordinates in Å (related to x, y, and z by $X = ax$, $Y = by$, and $Z = cz$). Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (1): C(1)—(4), C(1′)

$$-0{\cdot}7761X + 0{\cdot}3499Y + 0{\cdot}5247Z - 0{\cdot}0705 = 0$$

[C(1) 0·007, C(2) 0·14, C(3) −0·24, C(4) 0·25, C(1′) −0·15]

Plane (2): N, C(5), O(1), O(2)

$$0{\cdot}0216X + 0{\cdot}6087Y + 0{\cdot}7931Z - 1{\cdot}1914 = 0$$

[N −0·002, C(5) 0·007, O(1) −0·002, O(2) −0·003, C(2) 0·16, H(21) 0·96]

Plane (3): C(6)—(11)

$$-0{\cdot}5131X + 0{\cdot}5050Y + 0{\cdot}6941Z + 0{\cdot}2055 = 0$$

[C(6) 0·006, C(7) −0·004, C(8) −0·001, C(9) 0·004, C(10) −0·003, C(11) −0·003]

DISCUSSION

It is established by this *X*-ray analysis of (II) that the molecule (I), the main product obtained on oxidation of cyclo-octa-1,5-diene by palladium(II) chloride–lead tetra-acetate in acetic acid, has *endo*-substitution and a *cis*-bicyclo-octane skeleton.

An idealized bicyclo[3.3.0]octane skeleton would contain two planar five-membered rings making a dihedral angle of 120°. The carbon framework found here is twisted somewhat to relieve intramolecular overcrowding which would be most severe between *endo*-oxygen atom O(1) and the hydrogen atom on C(4′) (Figure 1). In the idealized model this O $\cdots$ H distance would be 1·85 Å, whereas the distance found is 2·49 Å. A measure of the distortion of the bicyclo[3.3.0]octane skeleton is provided by the non-equivalence of the C(2) $\cdots$ C(2′) and C(4) $\cdots$ C(4′) transannular distances

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[5] D. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[6] R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] C. K. Johnson, ORTEP, 1965, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[3·392(5) and 3·617(6) Å]. As a consequence of these distortions to provide relief from steric strain, the unique five-membered ring adopts a half-chair conformation (Table 4) with only small deviations from C_2 symmetry; from the torsion angles in the five-membered ring (Figure 1) it may be deduced that an approximate two-fold axis passes through C(1) and the mid-point of the C(3)–C(4) bond. As well as increasing the O · · · H separation, the half-chair conformation also serves to minimize intramolecular H · · · H interactions by rotating CH_2 groups away from fully eclipsed conformations.

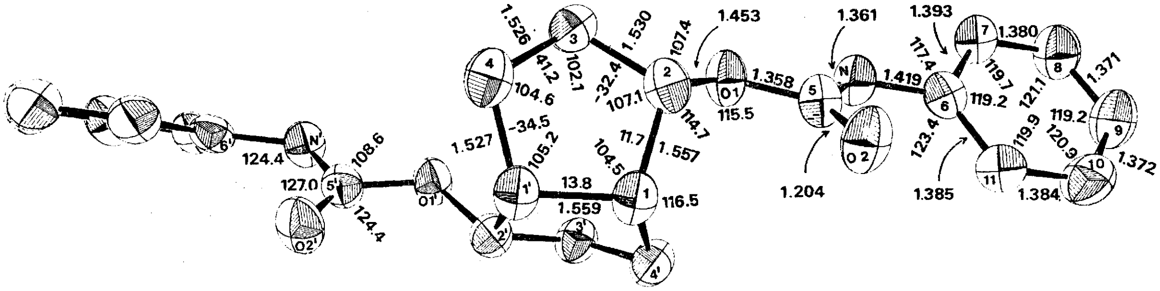

FIGURE 1 A view of (II). The crystallographic two-fold symmetry axis passes through the centre of the C(1)–C(1′) bond. Bond lengths (mean σ 0·006 Å) and bond angles (mean σ 0·2°) are shown as well as torsion angles (°) within the unique five-membered ring. The termal ellipsoids are at the 50% probability level

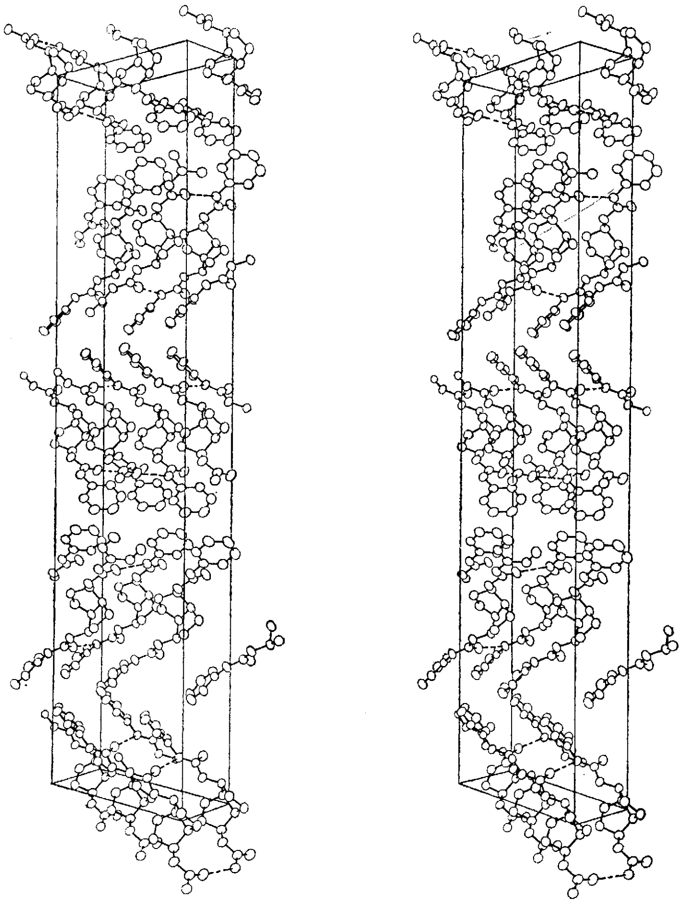

FIGURE 2 Stereodiagram of the contents of a unit cell of (II). Intermolecular N–H · · · O hydrogen bonds are shown by broken lines

There are no simple bicyclo[3.3.0]octane derivatives reported in the literature [8] with which to compare this molecule. The closest analogue to it appears to be β-D-glucurono-γ-lactone [9] which contains two fused five-membered rings (lactone and furanose) making a dihedral angle of 111·3°. The dihedral angle between

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[8] 'Molecular Structures and Dimensions,' ed. O. Kennard, D. G. Watson, and W. G. Town, vol. 5, Oosthock, Utrecht, 1974.

[9] S. H. Kim, G. A. Jeffrey, R. D. Rosenstein, and P. W. R. Corfield, *Acta Cryst.*, 1967, **22**, 733.

the best least-squares planes of the five-membered rings in (II) is 101·3°.

Mathieson [10] has made a survey of several structures containing ester groups in the equatorial position of six-membered rings in the chair conformation; in all these structures, the ester group was oriented so that it was coplanar with the axial hydrogen atom of the ring carbon atom. This preference was ascribed to an interaction between the hydrogen and the double-bonded oxygen in the ester group. This situation does not prevail here. Ring carbon atom C(2) is 0·16 Å, and the *exo*-hydrogen H(21) is 0·96 Å, from the plane of the ester group NCO_2 (Table 4); as a consequence the O(2) · · · H(21) separation is 2·51 Å. The phenyl ring is planar (Table 4) but its plane makes an angle of 32·1° with that of the ester group in order to reduce the interaction between the hydrogen H(111) on C(11) and ester oxygen O(2). The H(111) · · · O(2) distance 2·42 Å is the shortest H · · · O contact in the structure.

The bond lengths (Figure 1) are all close to the commonly accepted values for these bonds. The bond angles show some effect of steric strain; thus angle O(1)–C(2)–C(1) [114·7(2)°] is considerably greater than O(1)–C(2)–C(3) [107·4(2)°] which would increase the O(1) · · · C(4′)H separation. Similarly, in the phenylurethane group, angle N–C(6)–C(11) [123·4(2)°] is larger than angle N–C(6)–C(7) [117·4(2)°] to increase the O(2) · · · H(111) separation.

A stereodiagram of the crystal structure is shown in Figure 2. The molecules are linked in infinite chains along the *a* direction by N–H · · · O hydrogen bonds [3·084(7) Å]. All other intermolecular contacts correspond to or, are greater than, van der Waals distances.

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[4/1605 *Received*, 31*st July*, 1974]

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[10] A. McL. Mathieson, *Tetrahedron Letters*, 1965, 4137.