

THE BAYER-VILLIGER OXIDATION OF DIAMANTANONE AND THE STRUCTURE OF 11-OXO-10-OXAPENTACYCLO[7,4,1,1^{4,13},0^{2,7},0^{6,12}]-PENTADECANE

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The studied substance was prepared by the Bayer-Villiger oxidation of diamantanone and identified by ¹H and ¹³C NMR spectroscopy. The structure of the compound was solved by direct methods and refined to the value $R = 0.052$ for 845 observed reflections ($I > 1.96\sigma(I)$). The substance crystallizes in the orthorhombic space group $Pnmm$; $a = 23.595(4)$, $b = 10.284(2)$, $c = 6.676(1)$ Å. The unit cell of the crystal structure of 11-oxo-10-oxapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane contains four ordered and two disordered molecules. The disordered molecule is described by averaging the image of the ordered molecule and its inverse image. Thus, the unit cell contains 6 formula units (part of the atoms have fractional occupation factors) even though the multiplicity of the general position in the $Pnmm$ group is 8.

The increasing interest in the study of the reactions of an ideal model system – adamantane – has recently spread to the second member of this homologous series of diamantoid hydrocarbons, diamantane. A total of 152 original scientific papers¹ have been published on this substance since 1965, when the synthesis of this interesting compound was first described². A description of the crystal structure of this substance was published³ in parallel with the description of the synthesis of diamantane. The symmetry of diamantane is disturbed when its six-membered ring is expanded to a seven-membered ring. An example is the preparation of 2(3)-azahomodiamantanones (lactams) by Beckmann rearrangement of diamantanone oximes⁴.

The oxidation of diamantanone by peroxyacetic acid yields a mixture of two isomeric 2(3)-oxahomodiamantanones, 10-oxo-11-oxapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane (lactone I) and 11-oxo-10-oxapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane (lactone II).

In the structure of the products, the Bayer–Villiger reaction is the oxygen analogue of the Beckmann rearrangement of oximes. The first phase of the reaction involves the protonation of the carbonyl oxygen with subsequent addition of the peroxyacid. The peroxide formed is split through nucleophilic attack of one of the two “substituents” of the carbonyl carbon on the oxygen atom to form the protonated form of the cyclic ester. In unsymmetrically branched cyclic ketones in the α position, the oxygen atom moves in between the carbonyl carbon and the carbon at which the branching occurs. Diamantanones are branched at the C2 and C4 carbons and a mixture of lactones is formed, with a ratio in the reaction mixture that is affected by the branching at the C1 and C7 carbons. The ratio of *I* and *II* in the reaction mixture is independent of the reaction temperature and has a value of 4 : 1. These results are in agreement with the results obtained for the Beckmann rearrangement of diamantanone oximes^{4,5}, where a mixture of 10-oxo-11-aza-2(3)-homodiamantane and 11-oxo-10-aza-2(3)-homodiamantane is formed in roughly a ratio of 7 : 3.

Lactone *I* has not yet been prepared, while lactone *II* was first described by the authors^{6,7}, who prepared this substance by cyclization of tetracyclo[7,3,1,0^{2,7},0^{6,11}]-tridec-3-en-12-carboxylic acid in conc. sulphuric acid medium with a yield of 90%. The ¹H NMR and IR spectra published by these authors agree with our results.

EXPERIMENTAL

Preparation of Vicinal Oxo-2(3)-oxahomodiamantanes

Diamantanone (40.4 g; 0.2 mol) was dissolved in 500 ml of glacial acetic acid. Sodium acetate (40 g) was added to the solution and dissolved; then 200 ml of 40% peroxyacetic acid were added dropwise with stirring. Addition was regulated so that the temperature of the reaction mixture did not exceed 40°C. After addition of all the peroxyacid, the reaction mixture was left to stand overnight at room temperature. The reaction products were poured onto ice and the excess peroxyacid was removed by addition of solid sodium sulphite; the acetic acid was neutralized by addition of solid potassium hydrogen carbonate. The lactones were extracted with chloroform, washed with water and dried with sodium sulphate. The chloroform was distilled off to yield 42.4 g of a raw mixture of the two isomeric oxo-2(3)-oxahomodiamantanes. The raw product was recrystallized twice from methanol to yield 27 g of pure product lactone *I*. Melting point 188–189°C (benzene). Elemental analysis for C₁₄H₁₈O₂ (218.3) calculated: 77.03% C, 8.31% H; found 76.80% C, 8.17% H. The mass spectrum was measured on a JEOL 303 instrument with ionization by an electron impact of 75 eV. The mass spectrum contains the following ions *m/z* (%): 218 (2, M⁺), 202 (4), 175 (14), 174 (100), 159 (4), 145 (10), 131 (17), 117 (30), 105 (13), 96 (47), 91 (51), 80 (51), 79 (61). The NMR spectrum was measured on a BRUKER AM-400 instrument by the FT technique in C²HCl₃ with tetramethylsilane as an internal standard at a temperature of 35°C and frequency of 100.62 MHz. ¹H NMR (δ , ppm): 4.26 (1 H, C9), 2.97 (1 H, C12), 1.7–2.15 (16 H). ¹³C NMR (δ , ppm): 35.98 (C1), 35.17 (C2), 38.14 (C3), 25.70 (C4), 38.01 (C5), 37.68 (C6), 35.98 (C7), 31.72 (C8), 39.99 (C9), 178.34 (C10), 82.21 (C12), 37.68 (C13), 31.72 (C14), 38.01 (C15).

After crystallization of lactone *I*, lactone *II* was concentrated to about 55% in the mother liquor. It was obtained from the mixture as the salt of the hydroxyacid by alkaline hydrolysis

in methanol. Repeated alkaline hydrolysis yielded 5 g of pure lactone *II*. Melting point, ^1H NMR and IR agree with the results of authors^{6,7}. Elemental analysis: found 76.90% C, 8.42% H. The mass spectrum contains the following ions m/z (%): 218 (6, M^+), 202 (1), 175 (16), 174 (100), 159 (4), 145 (8), 131 (16), 117 (25), 105 (14), 96 (42), 91 (48), 81 (34), 80 (54), 79 (60). ^{13}C NMR (δ , ppm): 35.90 (C1), 34.80 (C2), 37.98 (C3), 26.00 (C4), 38.44 (C5), 33.13 (C6), 35.90 (C7), 36.94 (C8), 71.66 (C9), 177.4 (C11), 53.69 (C12), 33.13 (C13), 36.94 (C14), 38.44 (C15). The density was measured by the flotation method in a calcium nitrate solution.

Crystal Structure Determination

Preliminary values of the lattice parameters and space group were found by the analysis of the Weissenberg patterns. X-ray measurement were carried out on an Enraf-Nonius CAD4 four-circle diffractometer using a single crystal with dimensions of $0.50 \times 0.35 \times 0.30$ mm. The MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation employed was monochromatized using a graphite monochromator. The lattice parameters were refined from the positions of 25 centred reflections ($38^\circ < 2\theta < 40^\circ$). The reflection intensity was measured in the interval $2\theta < 60^\circ$ by the $\omega/2\theta$ scan technique with a scan rate of $2.06 - 16.48^\circ/\text{min}$. A total of 11 638 reflections were measured in the range $-8 \leq h \leq 8$, $-14 \leq k \leq 14$, $0 \leq l \leq 30$, with systematic extinction $0kl: k + l = 2n + 1$ and $h0l: h + l = 2n + 1$, corresponding to centrosymmetric space group $Pnmm$ and noncentrosymmetric $Pnn2$. Elimination of reflections with negative intensities and averaging of equivalent reflections yielded 1 723 independent reflections, of which 845 were considered as observed ($I > 1.96\sigma(I)$). The intensity of two standard reflections (0-1-7 and 020) were monitored periodically after each 200 measured reflections. Fluctuations in their intensities were less than 1%. Correction for absorption and extinction was negligible. The basic crystallographic data are given in Table I.

Because of the difference between the orthorhombic unit cell found and the number of formula units ($Z = 6$), the phase problem was solved using all 11 638 reflections by direct methods in the $P1$ space group. After determination of the positions of most of the nonhydrogen atoms, the structure was solved in the $Pnmm$ space group; the remaining nonhydrogen atoms were found from the difference Fourier maps. The positions of the hydrogen atoms were generated from the assumed geometry. The structural parameters were refined by the full-matrix least squares method by minimization of the function $\sum w(|F_o| - |F_c|)^2$ using the weighting scheme $1/(\sigma^2 \cdot (F_o) + 0.0009F_o^2)$. A total of 172 parameters were refined: the scale factor and the positional and anisotropic temperature parameters of the nonhydrogen atoms with the exception of the temperature parameters of atoms C3^n and C11^n , which were isotropically refined. For the ordered molecules, the positions and isotropic temperature parameters of the hydrogen atoms were refined; for the disordered molecules, the positions of the hydrogen atoms were fixed and

TABLE I
Basic crystallographic data

$a = 23.595(4) \text{ \AA}$	$\rho_o = 1.30 \text{ Mg m}^{-3}$
$b = 10.284(2) \text{ \AA}$	$\rho_c = 1.343 \text{ Mg m}^{-3}$
$c = 6.676(1) \text{ \AA}$	space group $Pnmm$
$V = 1 619.9(5) \text{ \AA}^3$	$\mu(\text{MoK}_\alpha) = 0.08 \text{ mm}^{-1}$
$Z = 6$	$F(000) = 708$

the isotropic temperature parameters had the values of their bonding partners. In the last refinement cycle, the value was $(\Delta/\sigma)_{\max} = 0.03$. The final values of the reliability factors were $R = 0.052$ and $wR = 0.070$. The highest maximum on the final difference Fourier map was $0.24 \text{ e}/\text{\AA}^3$. The following programs were employed: SHELXS 86 (ref.⁸), SDP system (ref.⁹), PARST (ref.¹⁰). The atomic scattering factors were those incorporated in the SDP system. Calculations were carried out on PDP 11/73 and EC 1033 computers.

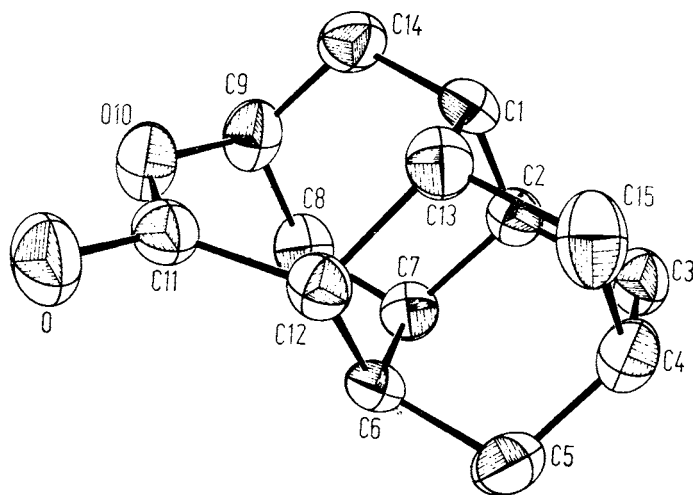


FIG. 1

The molecule of 11-oxo-10-oxapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane. 45% ellipsoids

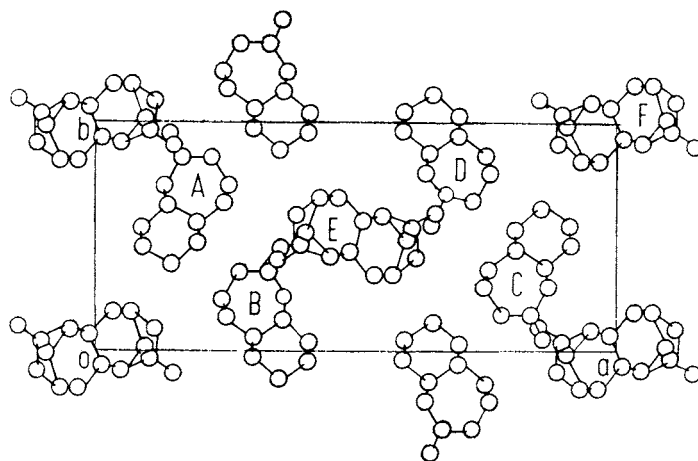


FIG. 2

Projection of the structure into the xy plane

RESULTS AND DISCUSSION

The crystal structure of 11-oxo-10-oxapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane contains ordered and disordered molecules. The ordered molecule (Fig. 1) occupies four positions in the unit cell (designated A, B, C, D) (Fig. 1), while the disordered molecule occupies two positions (E, F). The disordered molecule is the average image of the ordered molecule and its inverse image. The inversion centre lies at the middle of the C1ⁿ–C6ⁿ connecting line and is identical with the crystallographic centre of symmetry. The ordered molecule has part of its atoms in the plane of symmetry, which thus have occupation factor 0.5 (Table II). The disordered molecule has both a plane and centre of symmetry, which decreases the occupation factors for

TABLE II

The fractional coordinates of the nonhydrogen atoms ($\cdot 10^4$), their occupation factors and equivalent temperature parameters ($\cdot 10^3$). $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. The atoms of the ordered molecules are without indices, atoms of disordered molecules are denoted by index n

Atom ^a	Multiplicity	x	y	z	$U_{eq}, \text{Å}^2$
O	0.50	3 568(1)	4 504(2)	0	68(2)
O10	0.50	2 772(1)	3 439(3)	0	62(2)
C1	1.00	3 049(1)	595(3)	–1 843(4)	49(2)
C2	0.50	3 035(2)	–289(4)	0	46(2)
C3	0.50	3 534(2)	–1 228(4)	0	57(3)
C4	0.50	4 081(2)	–469(4)	0	56(2)
C5	1.00	4 108(1)	384(3)	1 870(5)	65(2)
C6	1.00	3 607(1)	1 350(3)	1 866(4)	48(1)
C8	1.00	2 527(1)	1 464(3)	1 892(5)	62(2)
C9	0.50	2 440(2)	2 234(4)	0	60(3)
C11	0.50	3 335(2)	3 444(4)	0	49(2)
C12	0.50	3 674(2)	2 213(4)	0	45(2)
O ⁿ	0.25	1 503(2)	–1 014(6)	0	72(4)
O10 ⁿ	0.25	1 140(3)	940(4)	0	73(4)
C1 ⁿ	1.00	124(1)	–676(3)	–1 829(5)	75(2)
C2 ⁿ	0.50	494(2)	–888(4)	0	57(3)
C3 ⁿ	0.25	967(4)	153(9)	0	62(2)
C4 ⁿ	0.50	698(2)	1 684(5)	0	112(4)
C5 ⁿ	1.00	343(2)	1 688(4)	1 886(7)	136(3)
C11 ⁿ	0.25	1 060(3)	–361(7)	0	41(2)

^a The atomic numbering is in agreement with the convention used in a previous work⁴. Designation of equivalent atoms: C7 \equiv C1ⁱ, C13 \equiv C6ⁱ, C14 \equiv C8ⁱ, C15 \equiv C5ⁱ, C6ⁿ \equiv C1ⁿⁱⁱ, C7ⁿ \equiv C7ⁿⁱ, C8ⁿ \equiv C5ⁿⁱⁱⁱ, C9ⁿ \equiv C4ⁿⁱ, C12ⁿ \equiv C2ⁿⁱⁱ, C13ⁿ \equiv C1ⁿⁱⁱⁱ, C14ⁿ \equiv C5ⁿⁱⁱ, C15ⁿ \equiv C5ⁿⁱ. Symmetry code: i) x, y, –z; ii) –x, –y, –z; iii) –x, –y, z.

some atoms to 0.25 (Table II). This plane of symmetry is based on either $z = 0$ or $z = 0.5$ and is perpendicular to the c axis. Thus, the unit cell contains six formula units even though the multiplicity of the general position in the $Pn\bar{m}$ group is 8. The mutual orientation of the ordered and disordered molecules (A, B, C, D, E, F) in the unit cell is given in Fig. 2.

Table III lists the interatomic distances, angles and torsion angles for the ordered and disordered molecules and deviations of the atoms from the planes fitted through the disordered and ordered molecules. The differences in these values for the two molecules are apparently a result of the inevitable imprecision in the model of the

TABLE III
Interatomic distances (Å) angles (in °), torsion angles (in °) and deviations of the atoms (Å) from the $Z = 0$ plane

Bonds	Ordered molecules	Disordered molecules	Angles	Ordered molecules	Disordered molecules
O—C11	1.221(5)	1.242(9)	O—C11—O10	117.0(3)	114.7(5)
O10—C9	1.466(5)	1.294(8)	O—C11—C12	121.0(3)	125.2(5)
O10—C11	1.328(5)	1.351(8)	O10—C9—C8	111.8(1)	116.6(2)
C1—C2	1.530(4)	1.517(4)	C9—O10—C11	122.5(3)	118.2(5)
C1—C13	1.529(4)	1.509(4)	O10—C11—C12	122.1(3)	120.1(5)
C1—C14	1.522(4)	1.516(2)	C2—C3—C4	109.5(3)	111.9(5)
C2—C3	1.523(6)	1.547(10)	C3—C4—C5	109.5(1)	102.1(2)
C3—C4	1.508(7)	1.698(10)	C4—C5—C6	109.7(2)	112.3(3)
C4—C5	1.527(4)	1.512(5)	C5—C6—C12	107.1(2)	109.9(3)
C5—C6	1.544(4)	1.516(2)	C2—C7—C6	109.2(2)	110.8(2)
C6—C12	1.538(4)	1.517(4)	C2—C7—C8	110.4(2)	109.9(3)
C8—C9	1.505(4)	1.512(5)	C6—C7—C8	113.5(2)	110.5(3)
C11—C12	1.498(6)	1.441(9)	C6—C12—C11	115.7(1)	118.6(1)
			C1—C13—C12	111.9(2)	110.8(2)
Torsion angles			C1—C13—C15	109.4(2)	110.5(3)
O—C11—C12—C6	116.0(4)	113.5(6)	C1—C14—C9	113.7(2)	112.3(3)
C1—O10—C9—C8	64.7(4)	68.7(6)			
	Atom	Deviation	Atom	Deviation	
	C1	1.230(3)	C1 ⁿ	1.221(3)	
	C5	1.248(3)	C5 ⁿ	1.259(5)	
	C6	1.246(3)			
	C8	1.263(3)			

disordered molecule. Consequently, only the geometric characteristics of the ordered molecule will be considered below.

Compared to the similar molecule 11-oxo-10-azapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]-pentadecane⁶, the C11—C12 bond in the studied molecule is shortened from 1.518(4) to 1.498(6) Å. In agreement with this value, the O10—C11—C12 angle is increased to 122.1(3)° compared with the N10—C11—C12 angle (120.0(2)°). In contrast to the 11-oxo-10-oxapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane molecule, the 11-oxo-10-azapentacyclo[7,4,1,1^{4,13},0^{2,7},0^{6,12}]pentadecane molecule is not symmetric about the plane fitted through the C2, C3, C4, C9, N10, C11 and C12 atoms and the deviation of the O atom from this plane equals 0.17 Å.

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