

## The Crystal Structure of Butane-1,2,3,4-tetracarboxylic Dianhydride

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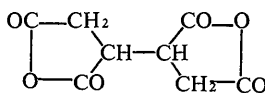
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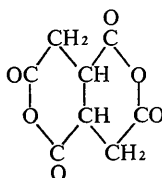
The crystal and molecular structure of butane-1,2,3,4-tetracarboxylic dianhydride,  $C_8H_6O_6$ , has been determined by a three-dimensional X-ray analysis using visually estimated  $Cu K\alpha$  data. The crystals are orthorhombic, space group  $Pcab$  with cell dimensions:  $a=9.01$ ,  $b=13.89$ ,  $c=6.59$  Å and  $Z=4$ . Phases for 183 reflexions were found by symbolic addition procedures and the subsequent refinements were carried out by the block-diagonal least-squares method with anisotropic temperature factors to an  $R$  value of 0.094, using the 801 observed reflexions. The molecule has a centre of symmetry and consists of two five-membered rings bridged by a carbon-carbon single bond. An intermolecular carbon-oxygen approach as short as 2.89 Å was observed, which is shorter than the sum of the van der Waals radii.

### Introduction

Butane-1,2,3,4-tetracarboxylic dianhydride,  $C_8H_6O_6$ , was synthesized by oxidation and dehydration of the Diels-Alder adduct formed by butadiene and maleic anhydride (Asahara & Fukui, 1967; *Methoden der Organischen Chemie*, 1952). Two possible structures have been proposed for the compound:



(I)



(II)

In order to establish the molecular structure the compound has been subjected to X-ray analysis.

### Experimental

The crystals are colourless and tabular. Specimens for X-ray work were selected from the original samples without further treatment. The cell dimensions were obtained from zero-level Weissenberg photographs ( $Cu K\alpha$ ,  $\lambda=1.5418$  Å) about the  $a$  and  $c$  axes. Powder diffraction lines of copper were superposed on the films for calibration purposes.

#### Crystal data

$C_8H_6O_6$ , m.p. ca. 260°C  
M.W. 198.1

#### Orthorhombic

$a = 9.009 \pm 0.005$  Å  
 $b = 13.893 \pm 0.006$   
 $c = 6.590 \pm 0.005$

$$U = 824.9 \text{ \AA}^3$$

$$D_m = 1.59 \text{ g.cm}^{-3}$$

$$Z = 4$$

$$D_x = 1.59 \text{ g.cm}^{-3}$$

Systematic absences:  $hk0$ , when  $k = 2n + 1$ ;

$h0l$ , when  $h = 2n + 1$ ;

$0kl$ , when  $l = 2n + 1$ .

Space group  $Pcab$  (No. 61)

$$F(000) = 408$$

$$\mu(Cu K\alpha) = 12.43 \text{ cm}^{-1}$$

The multiple-film Weissenberg photographs were taken with  $Cu K\alpha$  radiation. Intensity data were collected for eight layers  $0kl-7kl$  about the  $a$  axis and four layers  $hk0-hk3$  about the  $c$  axis. The intensities were estimated visually by comparison with a standard scale. In all, 801 non-zero reflexions were observed. The usual Lorentz, polarization and spot shape corrections were applied, but no absorption correction was made. At a later stage of the refinement extinction corrections were found necessary for strong reflexions. They were corrected according to:  $I_o = I_{corr} \exp(-g \cdot I_{corr})$ .

### Determination of the structure

The general position of the space group  $Pcab$  is eight-fold. Since there are only four molecules in the unit cell, the centre of gravity of each molecule must lie on a centre of symmetry.

The structure was solved by obtaining the values of the phases directly by means of the symbolic addition procedure (Karle & Karle, 1963). The program *SIGMA* written by Ashida was utilized to list the relationships for each reflexion and to calculate the associated probabilities. The reflexions 3,11,1, 5,11,2 and 3,4,7 were chosen to define the origin. Symbols were assigned to the phases of three additional reflexions. These six assignments, which form the basic set

for applying the  $\Sigma_2$  formula, are shown in Table 1. Through the application of the  $\Sigma_2$  formula it was found from the relationships among the symbols that  $a$  is positive and  $b$  and  $c$  are negative. 183 phases for 252 reflexions with  $E \geq 1.00$  were determined. After the refinement only one of these was found to be incorrect. The molecule was clearly resolved on the  $E$  map computed from these phases. It was found that the structure corresponds to (I). Calculation of all the observed structure factors gave an  $R$  value of 0.35. The full set of data and individual isotropic temperature factors were then used in five cycles of the block-diagonal least-squares refinement. The  $R$  value dropped to 0.197.

Table 1. Initial phase assignment

$h$	$k$	$l$	$E_h$	Sign	Number of $\Sigma_2$ relations for the reflexion
3	11	1	3.05	+	40
5	11	2	2.89	+	24
3	4	7	2.48	+	14
8	2	0	2.21	$a$	17
2	12	2	2.98	$b$	27
1	11	4	2.68	$c$	20

Anisotropic thermal parameters were introduced and the  $R$  value came down to 0.129. Hydrogen atoms were located by calculation and were included in the least-squares refinement with isotropic temperature factors. After correction for extinction of sixteen reflexions, six more cycles of the least-squares refinement were carried out. The  $R$  value dropped to 0.094 for all the 801 observed reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). At the final stage of the refinement the following weighting scheme was employed:  $1/w = c - b|F_o| + a|F_o|^2$  for  $5 < |F_o| \leq 88.1 (=|F_{\max}|)$  and  $1/w = d$  for  $|F_o| \leq 5$ , where  $a = 8.95 \times 10^{-4}$ ,  $b = 4.92 \times 10^{-2}$ ,  $c = 1.57$  and  $d = 5.00$ .

The final positional and thermal parameters are listed in Table 2, together with their estimated standard deviations. The observed and calculated structure factors are compared in Table 3. The thermal parameters are illustrated by an *ORTEP* plot in Fig. 1, together with the numbering scheme (Johnson, 1965). The motion appears to consist chiefly of a rigid-body libration about the centre of gravity, largely perpendicular to the molecular planes.

Table 2. Final positional and thermal parameters with their standard deviations ( $\times 10^4$ )

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Estimated standard deviations are given in parentheses for the least significant figures.									
C(1)	4966 (4)	5517 (2)	4601 (5)	94 (5)	22 (2)	128 (8)	3 (5)	8 (11)	-7 (7)
C(2)	5472 (4)	6306 (2)	6083 (6)	108 (5)	24 (2)	194 (10)	4 (5)	-55 (14)	-20 (7)
C(3)	4361 (5)	7091 (3)	5752 (6)	114 (6)	25 (2)	185 (10)	5 (6)	16 (14)	-14 (7)
C(4)	3438 (5)	5820 (3)	4028 (6)	109 (6)	28 (2)	170 (9)	14 (5)	-40 (13)	-2 (7)
O(1)	4350 (4)	7904 (2)	6333 (5)	200 (6)	26 (1)	318 (10)	19 (5)	-68 (13)	-62 (6)
O(2)	3173 (3)	6763 (2)	4595 (4)	110 (4)	26 (1)	200 (7)	24 (4)	-41 (9)	-24 (5)
O(3)	2506 (4)	5381 (2)	3122 (5)	158 (5)	40 (1)	333 (11)	10 (6)	-248 (13)	-35 (7)
$B^*$									
H(C11)	575 (6)	547 (4)	350 (8)	4.7 Å <sup>2</sup>					
H(C21)	544 (5)	612 (3)	754 (8)	2.9					
H(C22)	665 (5)	651 (3)	586 (7)	2.3					

\* Isotropic thermal parameters. The anisotropic thermal parameters were introduced in the form:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

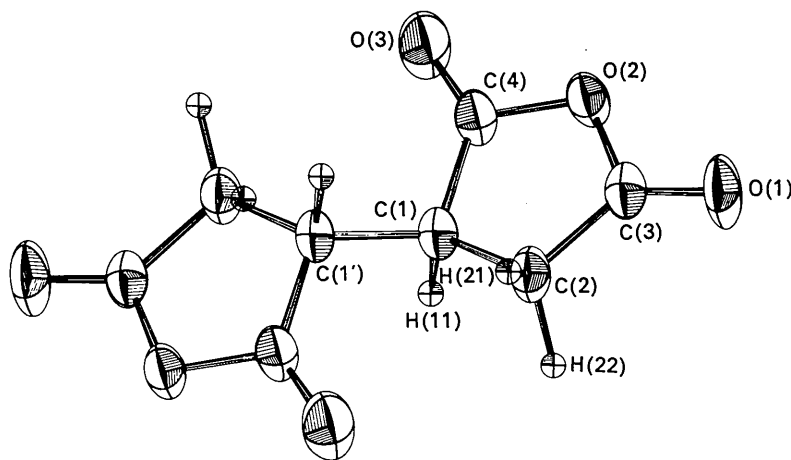


Fig. 1. Molecular conformation observed in the crystal structure of butane-1,2,3,4-tetracarboxylic dianhydride, showing atomic numbering used and the anisotropic thermal ellipsoids.



Table 5. Deviations of atoms from the best plane

The best plane through a half molecule has the equation

$$-0.4301X - 0.3456Y + 0.8339Z = -1.9301,$$

where  $X$ ,  $Y$  and  $Z$  are the coordinates in Å referred to the  $a$ ,  $b$  and  $c$  axes respectively.

	Deviation
C(1)	-0.116 Å
C(2)	0.124
C(3)	-0.004
C(4)	0.017
O(1)	-0.071
O(2)	-0.022
O(3)	0.091

Table 6. Intermolecular atomic distances less than 3.5 Å

Estimated standard deviations are given in parentheses for the least significant figures.

Atom in half molecule (1)*	To atom	In half molecule*	Distance
C(1)	O(1)	(3)	3.134 (5) Å
C(2)	O(1)	(3)	3.320 (6)
C(3)	O(1)	(3)	3.135 (6)
	H(C21)	(3)	3.27 (5)
	H(C22)	(5)	3.12 (4)
C(4)	O(1)	(3)	3.203 (5)
	H(C11)	(4)	3.44 (5)
O(1)	H(C21)	(3)	2.85 (5)
	H(C22)	(5)	2.58 (4)
O(2)	C(3)	(2)	3.440 (5)
	O(1)	(3)	3.132 (5)
	H(C21)	(3)	3.47 (5)
	H(C22)	(3)	3.44 (4)
	H(C22)	(5)	2.88 (4)
O(3)	C(1)	(2)	3.222 (5)
	C(2)	(2)	3.264 (5)
	C(3)	(2)	3.303 (5)
	C(4)	(2)	2.894 (6)
	O(2)	(2)	3.076 (4)
	O(3)	(2)	3.295 (7)
	H(C21)	(2)	2.87 (5)
	C(1)	(4)	3.165 (5)
	H(C11)	(4)	2.25 (5)
H(C11)	O(1)	(3)	2.68 (5)
	H(C22)	(6)	3.26 (7)
H(C22)	O(1)	(3)	3.22 (5)
	H(C21)	(6)	3.46 (7)

\* As illustrated in Fig. 2.

(1)	(	$x$	$y$	$z$ )
(2)	(	$\frac{1}{2}-x$	$y$	$-\frac{1}{2}+z$ )
(3)	(	$1-x$	$1\frac{1}{2}-y$	$-\frac{1}{2}+z$ )

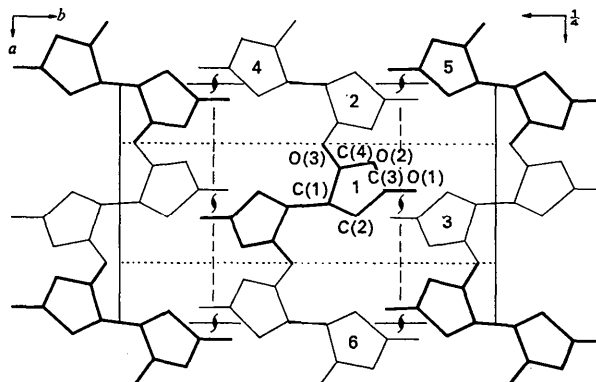
Fig. 2. A projection of the structure along the  $c$  axis.

Table 6 (cont.)

(4)	(	$-\frac{1}{2}+x$	$1-y$	$\frac{1}{2}-z$ )
(5)	(	$-\frac{1}{2}+x$	$1\frac{1}{2}-y$	$z$ )
(6)	(	$1\frac{1}{2}-x$	$y$	$-\frac{1}{2}+z$ )

Calculations were performed on the HITAC 5020E at the Computer Centre of the University and on the FACOM 270-30 computer of this Institute.

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