

Tableau 4. Angles valentiels (°)

C(2)—C(1)—C(8)	87,7 (3)	C(10)—C(11)—C(12)	115,4 (3)
C(2)—C(1)—C(12)	121,7 (3)	C(11)—C(12)—C(1)	111,1 (3)
C(2)—C(1)—O(1)	115,7 (3)	C(10)—C(13)—C(14)	108,2 (4)
C(8)—C(1)—C(12)	112,5 (3)	C(10)—C(13)—C(15)	109,6 (4)
C(8)—C(1)—O(1)	106,4 (3)	C(10)—C(13)—C(16)	113,2 (3)
C(12)—C(1)—O(1)	109,9 (3)	C(14)—C(13)—C(15)	108,7 (4)
C(1)—C(2)—C(3)	142,8 (4)	C(14)—C(13)—C(16)	108,4 (4)
C(1)—C(2)—C(7)	92,5 (3)	C(15)—C(13)—C(16)	108,6 (4)
C(3)—C(2)—C(7)	124,6 (4)	C(1)—O(1)—C(17)	116,4 (3)
C(2)—C(3)—C(4)	115,3 (5)	O(1)—C(17)—O(2)	124,8 (4)
C(3)—C(4)—C(5)	121,7 (6)	O(1)—C(17)—C(18)	110,0 (3)
C(4)—C(5)—C(6)	123,7 (6)	O(2)—C(17)—C(18)	125,2 (4)
C(5)—C(6)—C(7)	112,8 (5)	C(17)—C(18)—C(19)	114,4 (3)
C(6)—C(7)—C(8)	142,1 (4)	C(17)—C(18)—C(23)	123,0 (4)
C(6)—C(7)—C(2)	121,9 (4)	C(19)—C(18)—C(23)	122,6 (4)
C(2)—C(7)—C(8)	95,8 (4)	C(18)—C(19)—C(20)	117,4 (4)
C(7)—C(8)—C(9)	117,8 (4)	C(19)—C(20)—C(21)	119,6 (4)
C(7)—C(8)—C(1)	83,9 (3)	C(20)—C(21)—C(22)	121,9 (4)
C(1)—C(8)—C(9)	111,0 (3)	C(20)—C(21)—Br	118,8 (3)
C(8)—C(9)—C(10)	107,2 (3)	C(22)—C(21)—Br	119,2 (3)
C(9)—C(10)—C(11)	110,1 (3)	C(21)—C(22)—C(23)	120,3 (4)
C(9)—C(10)—C(13)	112,5 (3)	C(22)—C(23)—C(18)	118,1 (6)
C(11)—C(10)—C(13)	112,5 (3)		

tion cycle butanique—cycle saturé sont en position *cis*, en accord avec les résultats antérieurs concernant les benzocyclobuténols. Les hypothèses conformationnelles sur les deux isomères envisagés sont exactes: ces conformations sont imposées par le groupement *tert*-butyle. Cette étude a permis d'étudier un benzo-

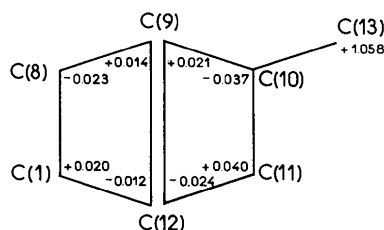


Fig. 3. Déformations du cycle saturé à six chaînons (écarts aux plans moyens en Å).

cyclobuténol présentant une nouvelle géométrie moléculaire à l'état cristallin. Toutefois, les caractéristiques du motif benzocyclobuténique ne sont pas modifiées.

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## Pyruvic Acid

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**Abstract.** C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>, *M<sub>r</sub>* = 88.07, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.867 (2), *b* = 5.247 (1), *c* = 6.993 (1) Å, β = 115.39 (1)° at -7°C, *Z* = 4, *D<sub>m</sub>* = 1.47 (floatation), *D<sub>x</sub>* = 1.49 g cm<sup>-3</sup>. *R* = 0.080 for 593 reflexions. The molecules related by a centre of symmetry are hydrogen-bonded to each other through their carboxyl groups to form a dimer.

**Introduction.** Crystals were obtained by cooling liquid pyruvic acid in a refrigerator. Although the melting

point of the material is 13.6°C, the crystal deliquesces in air at -10°C. Therefore, the diffraction experiments were carried out at -7 ± 1°C in the cold room with the crystal enclosed in a glass capillary. The space group *P*2<sub>1</sub>/*c* was deduced from the systematic absences *l* = 2*n* + 1 for *h*0*l* and *k* = 2*n* + 1 for 0*k*0 reflexions. Intensity data were collected on a Hilger & Watts four-circle diffractometer with a 0.6 × 0.5 × 0.5 mm specimen, nickel-filtered Cu *K*α radiation and the θ-2θ scanning mode. 593 non-zero intensity data were obtained up to 150° in 2θ. No correction was made for absorption or extinction.

The structure was solved from a Patterson map, and

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Table 1. *Final atomic parameters* ( $\times 10^4$ ) *for the non-hydrogen atoms*

The anisotropic thermal factors are of the form:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ . Values in the parentheses are estimated standard deviations.

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	1163 (5)	-1559 (11)	-1387 (8)	51 (5)	282 (21)	169 (13)	-54 (17)	73 (13)	-93 (26)
C(2)	2095 (4)	344 (9)	-46 (7)	49 (5)	197 (16)	130 (10)	12 (14)	86 (12)	-1 (22)
C(3)	3387 (4)	170 (9)	-21 (7)	41 (4)	196 (16)	140 (11)	-13 (14)	57 (12)	-37 (23)
O(1)	1879 (3)	1955 (7)	981 (6)	69 (4)	291 (15)	247 (11)	-16 (12)	157 (11)	-190 (20)
O(2)	4168 (3)	1953 (7)	1087 (6)	56 (4)	338 (17)	288 (11)	-85 (13)	120 (11)	-327 (23)
O(3)	3642 (3)	-1523 (6)	-961 (5)	51 (3)	233 (13)	226 (10)	-9 (11)	113 (10)	-135 (19)

Table 2. *Fractional coordinates* ( $\times 10^3$ ) *and isotropic thermal factors* ( $\text{\AA}^2$ ) *for the hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(C1)	129 (6)	-331 (14)	-133 (11)	2.9 (1.5)
H'(C1)	90 (6)	-143 (13)	-313 (10)	3.3 (1.5)
H''(C1)	27 (8)	-82 (16)	-113 (12)	5.3 (2.0)
H(O2)	509 (5)	174 (11)	82 (8)	1.5 (1.2)

Table 3. *Bond distances* ( $\text{\AA}$ ) *and angles* ( $^\circ$ )

## Bond distances

C(1)—C(2)	1.487 (7)	C(2)—C(3)	1.529 (7)
C(2)—O(1)	1.206 (6)	C(3)—O(2)	1.311 (6)
C(3)—O(3)	1.218 (6)		
C(1)—H(C1)	0.93 (7)	C(1)—H'(C1)	1.12 (7)
C(1)—H''(C1)	1.20 (9)	O(2)—H(O2)	1.19 (6)

## Bond angles

C(1)—C(2)—C(3)	116.0 (4)	C(1)—C(2)—O(1)	123.8 (5)
C(3)—C(2)—O(1)	120.2 (4)	C(2)—C(3)—O(2)	114.5 (4)
C(2)—C(3)—O(3)	121.2 (4)	O(2)—C(3)—O(3)	124.3 (5)

Table 4. *Least-squares planes and deviations of atoms* ( $\text{\AA}$ )

An asterisk indicates on atom not included in the plane. *X*, *Y*, *Z* are the coordinates in  $\text{\AA}$  along *a*, *b* and *c*\*.

## The molecular plane

$$0.0468X + 0.6043Y - 0.7953Z = 0.2514$$

C(1)	-0.035	C(2)	0.003
C(3)	-0.001	O(1)	0.034
O(2)	-0.037	O(3)	0.036

## The plane through C(1), C(2), C(3) and O(1)

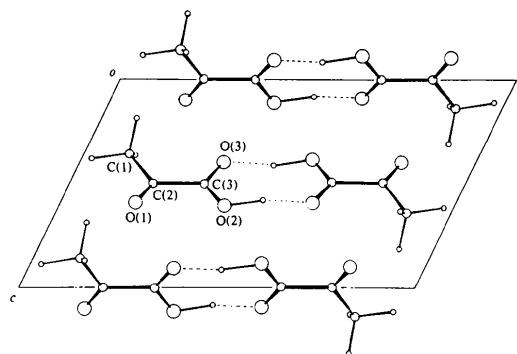
$$0.0456X + 0.6274Y - 0.7774Z = 0.2495$$

C(1)	-0.000	C(2)	0.001
C(3)	-0.000	O(1)	-0.000
O(2)*	-0.070	O(3)*	0.069

## The plane through C(2), C(3), O(2) and O(3)

$$0.0444X + 0.5779Y - 0.8149Z = 0.2385$$

C(2)	0.001	C(3)	-0.002
O(2)	0.001	O(3)	0.001
C(1)*	-0.082	O(1)*	0.065

Fig. 1. The crystal structure viewed down along the *b* axis. Dashed lines indicate hydrogen bonds.

refined by the full-matrix least-squares method. The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = (20.0/|F_o|)^2$  for  $|F_o| > 20.0$ ,  $w = 1.0$  for  $2.0 \leq |F_o| \leq 20.0$ , and  $w = 0.5$  for  $|F_o| < 2.0$ . The final *R* value ( $\sum ||F_o| - |F_c|| / \sum |F_o|$ ) was 0.080.\* The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Tables 1 and 2.

**Discussion.** Bond distances and angles are given in Table 3. No unusual value was found. The molecule is nearly planar (Table 4). The plane through C(1), C(2), C(3) and O(1) makes an angle of  $3.5^\circ$  with that through C(2), C(3), O(2) and O(3). In sodium pyruvate the corresponding angle is  $18.1^\circ$  (Tavale, Pant & Biswas, 1961), showing that the molecule is twisted in the ionized state.

The crystal is composed of hydrogen-bonded dimers arranged along the *a* axis as shown in Fig. 1. The two molecules in the dimer are related to each other by a centre of symmetry. The O...O distance of the hydro-

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31999 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

gen bond is 2.647 Å, which is in good agreement with the values observed in other carboxyl groups: 2.676 and 2.669 Å in 5-hydroxy-2,3-norbornanedicarboxylic  $\gamma$ -lactone (Chapuis, Zalkin & Templeton, 1973), 2.699 and 2.656 Å in itaconic acid (Harlow & Pfluger, 1973).

The program *FMLS* (Ashida, 1973) was used with some modifications for the full-matrix least-squares calculations. The computations were made on a FACOM 230-60 computer at Nagoya University and a HITAC 8450 computer at the Research Institute for Polymers and Textiles.

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## 2,2'-Bis(dimethylarsino)octafluorobi-1-cyclobuten-1-ylmolybdenum Tetracarbonyl

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**Abstract.**  $C_{16}H_{12}As_2F_8O_4Mo$ ,  $M_r = 666.1$ ,  $P\bar{1}$ ,  $a = 9.174$  (2),  $b = 15.692$  (4),  $c = 9.681$  (3) Å,  $\alpha = 115.93$  (1),  $\beta = 68.98$  (1),  $\gamma = 114.48$  (1)°,  $V = 1114$  Å<sup>3</sup>,  $d_o = 1.93$  (4) (by flotation),  $Z = 2$ ,  $d_c = 1.99$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation ( $\lambda = 0.70926$  Å),  $\mu(\text{Mo } K\alpha) = 36.8$  cm<sup>-1</sup>,  $F(000) = 640$ ,  $T = 20 \pm 1$ °C; final  $R$  for 2764 observed reflexions 0.069. Approximate octahedral coordination is found about Mo which is bonded to four carbonyl groups and the two As atoms of a puckered, seven-membered chelate.

**Introduction.** Crystals of the title compound were deep red. Weissenberg photographs of the layers  $hk0$  and  $hkl$ , and precession photographs of the  $h0k$  and  $0kl$  zones were taken with Cu radiation ( $\lambda = 1.5418$  Å), from which triclinic Laue symmetry was established. A cleaved fragment  $0.18 \times 0.23 \times 0.15$  mm was mounted for data collection. Accurate cell dimensions were determined from counter measurements and least-squares refinement of 12 of the strongest reflexions having  $2\theta > 25^\circ$ , on a Picker FACS-1 computer-controlled four-circle diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.70926$  Å). The take-off angle was  $1.0^\circ$ , and the crystal was mounted with  $b$  approximately parallel to the  $\varphi$  axis of the diffractometer. Intensities were collected with a symmetrical  $\theta$ - $2\theta$  scan, a base width

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of  $1.4^\circ$ , Nb-filtered Mo  $K\alpha$  radiation and a take-off angle of  $1.3^\circ$ . Background counts of 10 s were measured at each of the scan limits, and after each 70 reflexions, two standard reflexions were measured; their variation was  $\pm 5\%$ . The intensities of 3949 unique reflexions were measured and corrected for Lorentz and polarization effects but not for absorption. 2764 were classed as observed  $\{I > 2.3\sigma(I)\}$ , where  $\sigma(I) = [(T) + (t_b/t_s)^2(B_1 + B_2) + (kI)^2]^{1/2}$  where  $T$  = total count,  $B_1$  and  $B_2$  are background counts,  $t_s$  = scan time,  $t_b$  = total background time,  $k$  is a constant set to 0.03, and  $I$  is the net count}.

Solution of the Patterson function yielded positions of the Mo and two As atoms. Full-matrix least-squares refinement of scale factor and positional and isotropic thermal parameters for these three atoms gave  $R = 0.256$ . A subsequent difference map served to locate all remaining non-hydrogen atoms. Refinement of all positional and isotropic thermal parameters reduced  $R$  to 0.096. Introduction of anisotropic temperature factors for all atoms and further refinement lowered  $R$  to 0.081.\* The eight C atoms of the two cyclobutene rings showed little indication of anisotropy and were treated isotropically in further refinement. With a reduced sphere of data ( $\sin \theta/\lambda_{\max}$  cut off at  $0.4$  Å<sup>-1</sup>) a difference map located several H atoms; all other H atom positions were calculated. Final refinement of all non-hydrogen atom positional and thermal motion parameters gave a final  $R$  of 0.069 for the observed data. In the early stages of refinement, unit weights were used; in the final stages weights =  $1/\sigma_F$  were used, where  $\sigma_F = \sigma_I/L_p(2F_o)$ .

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