perspective sur la Fig. 3, et les distances intermoléculaires les plus courtes sont données dans le Tableau 6. L'empilement résulte de liaisons normales de van der Waals, essentiellement par des contacts O–H et C–H. L'une de ces distances, entre O(3) et l'hydrogène H(11) du cycle d'une molécule voisine, est assez nettement inférieure à la somme des rayons de van der Waals de l'oxygène et de l'hydrogène [2,39 Å comparé à 2,60 Å]. Cette forte liaison intermoléculaire pourrait contribuer en partie à maintenir le ligand organique dans la conformation *s-cis* observée.

En conclusion, la présente détermination de la structure cristalline et moléculaire de $Mn(C_5H_5)(CO)_2(CH_2{=}CHCOCH_3)$ confirme le caractère non hétérobutadiénique du complexe, la liaison entre le ligand organique et le manganèse se faisant uniquement par la double liaison éthylénique. Le ligand organique se trouve en conformation *s-cis* (*b*). Dans la limite de précision des résultats cristallographiques, le remplacement d'un CO par le ligand $CH_2{=}CHCOCH_3$ n'affecte pas de manière significative les liaisons Mn–cycle et Mn–CO.

Références

Barbeau, C., Dichmann, K. S. & Ricard, L. (1973). *Canad. J. Chem.* **51**, 3027–3031.
Barbeau, C. & Dubey, R. J. (1973). *Canad. J. Chem.* **51**, 3684–3689.
Barbeau, C. & Dubey, R. J. (1974). *Canad. J. Chem.* **52**, 1140–1146.
Berndt, A. F. & Marsh, R. E. (1963). *Acta Cryst.* **16**, 118–123.
De Cian, A. & Weiss, R. (1972). *Acta Cryst.* B**28**, 3273–3280.
Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
Giffard, M. & Dixneuf, P. (1975). *J. Organometal. Chem.* **85**, C26–C28.
Granoff, B. & Jacobson, R. A. (1968). *Inorg. Chem.* **7**, 2328–2333.
Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
Le Borgne, G. & Grandjean, D. (1973). *Acta Cryst.* B**29**, 1040–1046.
Le Marouille, J. Y. (1972). Thèse de 3ème cycle. Rennes.
Prewitt, C. T. (1966). *Fortran* IV *Full-matrix Crystallographic Least-squares Program*, *SFLS*-5.

Acta Cryst. (1975). B**31**, 2829

The Crystal and Molecular Structure of Diglycollic Anhydride, $C_4H_4O_4$

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(*Received* 19 *February* 1975; *accepted* 7 *May* 1975)

Crystals of diglycollic anhydride are monoclinic with a = 17·080 (4), b = 5·143 (1), c = 11·716 (3) Å, β = 111·33 (2)° and space group $P2_1/c$. The structure was solved by direct methods. There are two independent molecules in the asymmetric unit. The molecules are in the boat conformation with the carbonyl groups staggered with respect to the methylene hydrogens.

Introduction

Diglycollic anhydride $C_4H_4O_4$ is the cyclized product resulting from the dehydration of diglycollic acid (Morrill, Steahly & Zienty, 1961). The crystal structure determination of diglycollic anhydride was undertaken to provide the initial atomic positions for an analysis of the charge distribution (Sygusch, Brisse & Cyr, 1975). This particular molecule was chosen because of its low molecular weight and because it is expected to be fairly rigid and free from hydrogen bonds in the solid state.

Experimental

Crystals of diglycollic anhydride were easily obtained by recrystallization from an ether solution. A crystal, 0·43 × 0·41 × 0·18 mm, was mounted on a carefully aligned Picker FACS-I diffractometer with its b axis approximately coinciding with the φ axis of the diffractometer. The unit-cell constants were obtained by a least-squares refinement of the angular measurements of 12 reflexions occurring at medium 2θ values. These dimensions and other pertinent data are presented below.

Crystal data

$C_4H_4O_4$, F.W. 116·08, $F(000)$ = 416, monoclinic, a = 17·080 (4), b = 5·143 (1), c = 11·716 (3) Å, β = 111·33 (2)°, V = 958·76 Å^3, D_x = 1·61, D_o = 1·60 g cm^{-3} (flotation), space group $P2_1/c$ ($0k0$, $k=2n$; $h0l$, $l=2n$), Z = 8, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ(Mo $K\alpha$) = 1·60 cm^{-1}, T = 20 (1)°C.

There are two independent molecules of diglycollic anhydride per asymmetric unit. To prevent sublimation, the crystal was coated with a thin film of polystyrene before data collection. Intensities for reflexions with $2\theta \leq 55°$ were collected twice with graphite-monochromatized Mo $K\alpha$ radiation and the θ–2θ scan technique with a 1° min^{-1} scan speed. A 2·2° scan range progressively increased with θ up to 2·4° for $K\alpha_1$–$K\alpha_2$ dispersion was chosen. The background was measured for 40 s on each side of the peaks. The intensities of three standard reflexions measured every 30 reflexions decreased by less than 10% over the duration of the data collection. Of the 2332 measured reflexions 412 had $I \leq 2{\cdot}0\sigma(I)$ and 239 had $I \leq 0{\cdot}5\sigma(I)$. The standard deviation $\sigma(I)$ was calculated according to $\sigma(I) = [I_T + (t/80)^2B + (0{\cdot}03I_N)^2]^{1/2}$, I_T being the total count, B the total background, I_N the net count and t the scanning time over one reflexion.

The data were placed on a common scale and corrected for Lorentz, polarization and absorption effects. The transmission factor ranged from 0·95 to 0·97. Simultaneously with the absorption correction, $\mathrm{d}A^*/\mathrm{d}\mu$ was evaluated for secondary extinction corrections (Åsbrink & Werner, 1966).

Structure determination and refinement

The structure was solved with the automatic symbolic addition program *MULTAN*. The entire structure was obtained from the first E map, revealing the two molecules in the asymmetric unit. A full-matrix least squares isotropic refinement reduced $R(|F|)$ to 0·129.

Two cycles of anisotropic refinement followed by a Fourier difference map revealed the positions of all the hydrogen atoms. From then on the refinement was continued with $|F|^2$ coefficients. The refinement included all the reflexions for which $I/\sigma(I) \geq 0{\cdot}5$. Two cycles of refinement, taking into account the newly found hydrogen atoms with isotropic temperature factors, followed by two more cycles with all atoms anisotropic yielded the final residuals $R(|F|^2) = 0{\cdot}046$ and $R_w(|F|^2) = 0{\cdot}068$.* The shift/σ ratios were all less

Table 1. *Positional and thermal parameters of the two molecules of diglycollic anhydride*, $C_4H_4O_4$

The atomic coordinates are given in fractions of unit-cell edges, $\times 10^5$ for non-hydrogen atoms, $\times 10^4$ for hydrogen atoms. The thermal parameters are given $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. The temperature factor is of the form:

$$T = \exp\,[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)].$$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1*A*)	14969 (5)	24246 (16)	27395 (7)	562 (5)	325 (4)	511 (5)	32 (2)	51 (2)	−10 (2)
O(4*A*)	6508 (5)	64801 (16)	31646 (7)	480 (5)	514 (5)	485 (5)	49 (2)	100 (2)	−9 (2)
O(21*A*)	23933 (6)	24752 (20)	46344 (9)	583 (6)	581 (6)	620 (6)	50 (3)	9 (2)	65 (2)
O(61*A*)	8791 (6)	28946 (22)	7486 (8)	793 (7)	744 (7)	489 (5)	73 (3)	78 (3)	−79 (3)
C(2*A*)	18389 (7)	35905 (22)	38719 (11)	425 (6)	377 (6)	463 (7)	−16 (3)	64 (3)	24 (3)
C(3*A*)	14771 (9)	61497 (29)	40238 (13)	569 (8)	414 (8)	392 (7)	4 (3)	71 (3)	−9 (3)
C(5*A*)	6431 (10)	63283 (28)	19601 (12)	460 (8)	424 (8)	434 (7)	42 (3)	59 (3)	9 (3)
C(6*A*)	9914 (7)	38075 (24)	17221 (11)	417 (6)	431 (7)	438 (6)	2 (3)	60 (3)	−10 (3)
H(31*A*)	1456 (8)	6216 (25)	4824 (14)	64 (9)	44 (9)	61 (9)	14 (4)	11 (4)	5 (4)
H(32*A*)	1861 (8)	7527 (28)	3936 (11)	44 (8)	39 (8)	58 (10)	−4 (4)	1 (4)	7 (4)
H(51*A*)	91 (9)	6425 (25)	1423 (12)	53 (9)	69 (11)	54 (9)	16 (4)	−3 (4)	−7 (4)
H(52*A*)	995 (9)	7694 (30)	1801 (12)	67 (11)	47 (9)	61 (10)	3 (4)	15 (4)	−3 (4)
O(1*B*)	34655 (5)	70857 (15)	11984 (7)	501 (5)	335 (5)	567 (5)	24 (2)	115 (2)	26 (2)
O(4*B*)	44048 (5)	31474 (17)	24900 (7)	492 (5)	558 (6)	425 (5)	56 (2)	55 (2)	49 (2)
O(21*B*)	25925 (6)	67687 (19)	21815 (9)	557 (5)	631 (7)	767 (7)	40 (2)	171 (3)	−4 (3)
O(61*B*)	40688 (6)	68348 (19)	−1682 (8)	719 (6)	661 (7)	560 (6)	31 (2)	155 (2)	90 (2)
C(2*B*)	31667 (7)	58113 (23)	19942 (10)	419 (6)	392 (6)	428 (6)	−22 (3)	73 (3)	−28 (3)
C(3*B*)	35950 (10)	33453 (31)	25459 (15)	589 (8)	457 (8)	462 (8)	13 (3)	117 (3)	39 (3)
C(5*B*)	43647 (10)	33384 (29)	12712 (13)	453 (8)	411 (7)	467 (7)	26 (3)	85 (3)	4 (3)
C(6*B*)	39791 (7)	58392 (23)	6888 (10)	408 (6)	404 (6)	408 (6)	−14 (2)	63 (2)	−3 (3)
H(31*B*)	3632 (9)	3319 (28)	3375 (14)	84 (11)	67 (12)	59 (11)	15 (4)	15 (5)	6 (5)
H(32*B*)	3240 (9)	1945 (29)	2094 (14)	64 (10)	38 (10)	93 (12)	−4 (4)	20 (5)	−4 (4)
H(51*B*)	4922 (9)	3282 (25)	1270 (11)	37 (8)	66 (11)	66 (10)	11 (4)	15 (4)	10 (4)
H(52*B*)	4044 (8)	1968 (26)	777 (11)	59 (10)	32 (9)	41 (9)	6 (4)	6 (4)	5 (3)

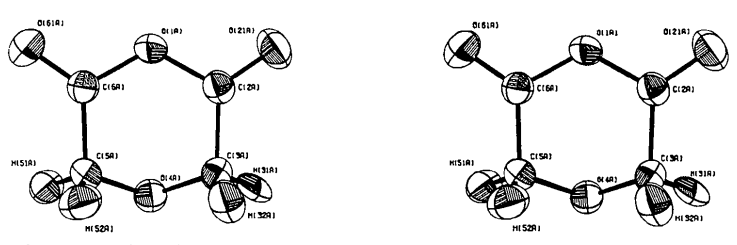

Fig. 1. Stereoscopic pair representing one molecule of diglycollic anhydride.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31119 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

than 0·1. The standard deviation of unit weight $\sigma(|F|^2)=[\sum_H w_H(|F_o|^2-|F_c|^2)^2/(m-n)]^{1/2}$, where m is the number of reflexions and n the number of parameters, was 2·17 at the end of the refinement while the secondary extinction coefficient g, was $0{\cdot}124\ (8)\times 10^5$. The scattering factors for the heavy atoms were taken from Cromer & Waber (1965) and from Stewart, Davidson & Simpson (1965) for the hydrogen atoms.

Results and discussion

The final atomic coordinates and thermal parameters are listed in Table 1. A stereoscopic view of the molecule is shown in Fig. 1. In the crystal, the diglycollic anhydride molecules exist in the boat conformation. The carbonyl groups are staggered with respect to the methylene hydrogens.

Bond distances and angles

The bond distances and angles calculated from the final coordinates and uncorrected for thermal motion have been averaged for the two molecules because respective differences amounted to less than one estimated standard deviation. The bond distances and angles are presented in Fig. 2. The estimated errors for bond distances between non-hydrogen atoms range from 0·001 to 0·002 Å and are of the order of 0·12° for bond angles. The e.s.d.'s of bond lengths involving hydrogen atoms vary from 0·012 to 0·020 Å while they are of the order of 1·2° for bond angles.

The bond distances and angles obtained here are in good agreement with the corresponding measurements in tetrachlorodibenzo-*p*-dioxin (Boer, van Remoortere, North & Neuman, 1972) and in dinitronaphthalic anhydride (Bordner & Jones, 1971). The torsional angles, presented in Table 2, have not been averaged since they do differ somewhat for the two molecules. The mean planes passing through the carbon atoms of both molecules are presented in Table 3. The deviations of the ring oxygen atoms from these planes indicate the extent of the flattening of the boat, especially at the O(21) atom. Once again the similarity of the two independent molecules is very noticeable.

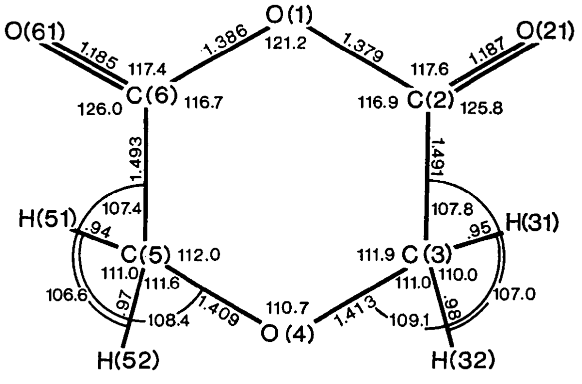

Fig. 2. Schematic diagram showing the numbering of the atoms and the bond distances and angles.

Table 2. *Torsional angles* (°)

	Molecule	
	A	*B*
O(61)–C(6)–O(1)–C(2)	163·1	164·5
C(6)—O(1)–C(2)–O(21)	−165·0	−163·7
O(61)–C(6)–C(5)–O(4)	160·5	158·0
O(4)—C(3)–C(2)–O(21)	−157·2	−160·1
O(1)—C(6)–C(5)–O(4)	−20·0	−22·5
O(1)—C(2)–C(3)–O(4)	23·0	19·8
C(2)—O(1)–C(6)–C(5)	−16·5	−15·0
C(6)—O(1)–C(2)–C(3)	14·9	16·4
C(2)—C(3)–O(4)–C(5)	−59·3	−57·3
C(6)—C(5)–O(4)–C(3)	57·3	58·7

Table 3. *Mean planes*

Equations of the least-squares planes

Plane *A*: $0{\cdot}8577X+0{\cdot}4819Y-0{\cdot}1792Z-1{\cdot}4203=0$
Plane *B*. $-0{\cdot}5092X-0{\cdot}5149Y-0{\cdot}6897Z+5{\cdot}3683=0$

Deviations from plane (Å)

	Molecule	
	A	*B*
C(2)	−0·009 (1)	0·007 (1)
C(3)	0·010 (2)	−0·008 (2)
C(5)	−0·010 (2)	0·008 (2)
C(6)	0·009 (1)	−0·007 (1)
O(1)*	−0·164 (1)	−0·164 (1)
O(4)*	−0·637 (1)	−0·630 (1)
O(21)*	0·098 (1)	0·153 (1)
O(61)*	0·165 (1)	0·110 (1)

* Atoms not included in the least-squares plane calculation.

Relation between the two molecules in the asymmetric unit

In an attempt to reduce the number of parameters the data were analysed by least-squares calculations with the constraint that the two molecules in the asymmetric unit are related by a rotation and a translation as follows: $\bar{\mathbf{X}}'=\mathbf{R}\bar{\mathbf{X}}+\bar{\mathbf{t}}$ where $\mathbf{R}$ is the rotation matrix having direction cosines l_1,l_2,l_3 defined in an orthogonal coordinate system, θ is the amount of rotation about vector $(l_1l_2l_3)$ and $\bar{\mathbf{t}}$ is the translation vector. The orthogonal reference system has X parallel to **a**, Y perpendicular to **a** and in the *ab* plane and Z perpendicular to the *ab* plane.

The translation vector has components 0·48720 (6), −0·0120 (2), −0·00294 (9) in fractions of the unit-cell edges. The direction cosines are −0·3505 (1), −0·01158 (9), 0·93648.

The axis of rotation is almost parallel to **c** and the rotation angle θ is 176·6 (1)°. This corresponds very nearly to a twofold axis of rotation. The translation is almost only along **a** and amounts very nearly to 0·5.

If a twofold axis parallel to **c** were to exist, the space group would be orthorhombic. An inspection of precession films revealed, on the *h*0*l* level, the existence of rows of intensities almost perpendicular to **c***. If we label this new direction $\mathbf{a}^{1*}$, then in the $\mathbf{a}^{1*}$–$\mathbf{c}^*$ system the reflexions will show *B* centring ($h0l$, $h+l=2n$). A

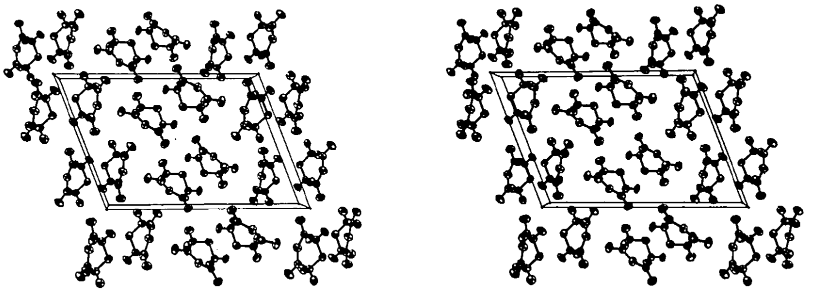

Fig. 3. Molecular packing.

new choice of axes $a_n = c_o$, $b_n = 2a_o + c_o$ and $c_n = b_o$ where n and o subscripts refer to new and old axes respectively would change the space group to *Cmma*. In such a space group having 16 equivalent positions, the molecule would be required to have an internal mirror plane. A comparison of bond distances and angles from Fig. 2 and torsional angles in Table 2 indicates that indeed the molecule very nearly has a mirror plane of symmetry.

Rigid body and charge density refinement

The intensity data were then treated by a charge density and rigid-body refinement which included librational motion as recently described by Sygusch, Brisse & Cyr (1975). The bond distances so obtained do not differ by more than one e.s.d. from the corresponding distances resulting from a conventional refinement (Fig. 2).

Packing of the molecules

The packing of the molecules is shown in Fig. 3, and the intermolecular contacts shorter than 3·2 Å are listed in Table 4. Two neighbouring molecules are packed in such a way that the O(21) atom of one of the molecules fits between the two hydrogen atoms H(32) and H(52) of the other. There is no hydrogen bonding and therefore the molecules are held together by van der Waals forces only.

The financial assistance of the National Research Council of Canada is gratefully acknowledged.

Table 4. *Intermolecular contacts*

From atom	to atom	Position*	Distance (Å)
C(2*A*)	O(21*B*)	1	3·178 (2)
C(6*A*)	O(21*B*)	1	3·003 (2)
C(6*A*)	O(4*A*)	4	3·096 (2)
O(21*A*)	C(2*B*)	2	3·097 (2)
O(21*A*)	C(6*B*)	2	3·055 (2)
C(6*B*)	O(4*B*)	4+*a*	3·049 (2)
O(1*A*)	H(32*A*)	1+*c*	2·84 (1)
O(1*A*)	H(52*A*)	1+*c*	2·68 (1)
O(21*A*)	H(32*B*)	2	2·73 (2)
O(21*A*)	H(52*B*)	2	2·66 (1)
O(1*B*)	H(32*B*)	1+*b*	2·79 (2)
O(1*B*)	H(52*B*)	1+*b*	2·81 (1)
O(21*B*)	H(32*A*)	1	2·79 (1)
O(21*B*)	H(52*A*)	1	2·64 (2)

* First symbol: Equivalent position: 1: x,y,z; 2: $x,\frac{1}{2}-y,\frac{1}{2}+z$; 3: $-x,-y,-z$; 4: $-x,\frac{1}{2}+y,\frac{1}{2}-z$. Second symbol: cell translation.

References

Boer, F. P., van Remoortere, F. P., North, P. P. & Neuman, M. A. (1972). *Acta Cryst.* **B28**, 1023–1029.

Bordner, J. & Jones, L. A. (1971). *J. Cryst. Mol. Struct.* **2**, 79–87.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Morrill, H. L., Steahly, G. W. & Zienty, F. B. (1961). *J. Org. Chem.* **26**, 4103–4104.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sygusch, J., Brisse, F. & Cyr, T. (1975). *Chem. Phys.* Submitted for publication.

Åsbrink, S. & Werner, P. E. (1966). *Acta Cryst.* **20**, 407–410.