Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1406). Services for accessing these data are described at the back of the journal.

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3,6-Dichlorophthalic Anhydride

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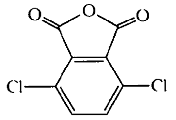
Abstract

The molecular structure of 3,6-dichlorophthalic anhydride, $C_8H_2Cl_2O_3$, is normal. The molecules pack in ribbons held together by O···Cl, O···H and Cl···H interactions. The ribbons pack in a herring-bone arrangement.

Comment

The packing motifs of 4,5-dichlorophthalic anhydride, 4,5-dibromophthalic anhydride and 4,5-benzofurazan 1-oxide are closely related and involve two-dimensional sheets of molecules held together by Cl···O or Br···O and C—H···O or C—H···N interactions (Ojala *et al.*, 1998). In 3,6-dibromobenzofurazan 1-oxide, the molecules are again arranged in two-dimensional sheets, with two different kinds of sheets occurring in the same structure (Britton, 1992). The structure of the title compound, (I), has been determined, to see whether there is a similar packing arrangement based on two-dimensional sheets.



(I)

The anisotropic displacement ellipsoids and the atom-labeling scheme are shown in Fig. 1. The bond lengths and angles are normal. The molecule deviates slightly from planarity. Each ring is close to planarity but the two rings are bent from coplanarity by 1.8 (1)°. This is similar to the situation in both phthalic anhydride (Bates & Cutler, 1977) and 3-methylphthalic anhydride (Bocelli & Cantoni, 1995). In addition, the Cl atoms and the exocyclic-O atoms are bent out of the planes of the rings to relieve the crowding between them. This is similar to the behavior in tetrachlorophthalic anhydride (Rudman, 1971).

The packing (Fig. 2) does not include two-dimensional layers. Using the van der Waals radii suggested by Pauling (1960), there are five intermolecular distances shorter than normal. The O3 and Cl1 atoms

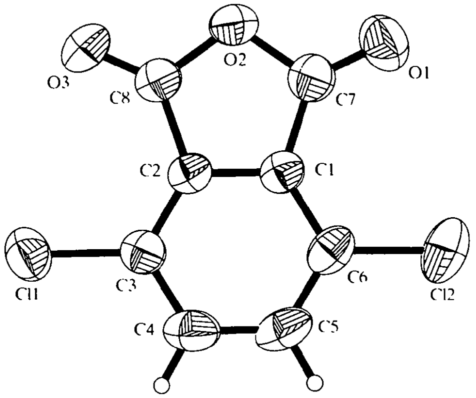


Fig. 1. The molecular structure of 3,6-dichlorophthalic anhydride, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level; H atoms are shown as spheres of arbitrary size.

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are both 3.095 (2) Å from the Cl1 and O3 atoms, respectively, in the molecule at $(-x, -y, 1-z)$, which can be compared with the suggested distance of 3.20 Å. The overall arrangement of the pair of molecules is virtually identical to that found in tetrachlorophthalic anhydride (Rudman, 1971). Looking at the overall arrangement of C8—O3···Cl1—C3, the C—O···Cl angle, the O···Cl distance and the O···Cl—C angle are, respectively, 156.9 (2)°, 3.095 (2) Å and 172.9 (3)° in the dichloro compound, compared with 156.9°, 3.101 Å and 173.4° in the tetrachloro compound. If these interactions are regarded as the Lewis base O atom (using an unshared pair in an sp^2-hybrid orbital) approaching the Lewis acid Cl atom (which is expanding its outer shell from four to five pairs of electrons), the expected angles would be C—O···Cl near 120° and O···Cl—C near 180°.

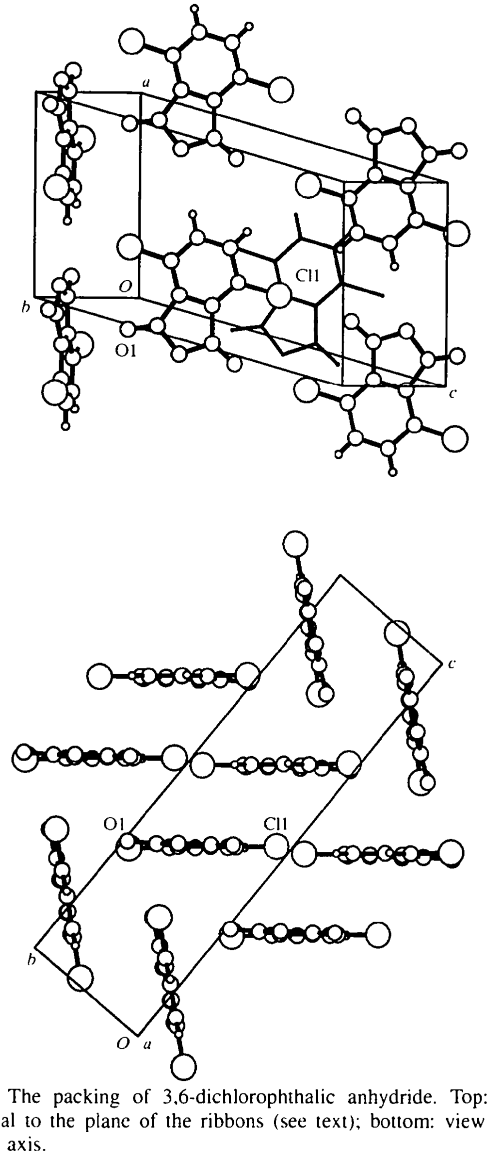

Fig. 2. The packing of 3,6-dichlorophthalic anhydride. Top: view normal to the plane of the ribbons (see text); bottom: view along the *a* axis.

If the pair of molecules described in the preceding paragraph is regarded as forming a loose dimer, the dimers are collected into nearly planar ribbons by what might be described as C—H hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Desiraju, 1991). The C4—H4···Cl1$(1-x, -y, 1-z)$ contact has a C—H···Cl angle of 172° and an H···Cl distance of 3.06 Å, based on the idealized H-atom position (C—H 0.93 Å). Similarly, the C5—H5···O2$(1+x, y, z)$ contact has a C—H···O angle of 174° and an H···O distance of 2.59 Å. The H···Cl distance is slightly longer than the suggested 3.00 Å, while the H···O distance is slightly shorter than the suggested 2.60 Å.

The ribbons are stacked into layers. The shortest distance between layers, relative to the suggested van der Waals distances, is the Cl1···Cl$(x, y-1, z)$ distance of 3.456 (3) Å (*cf.* 3.50 Å suggested). This is slightly shorter than the average distance between molecular planes of 3.472 Å.

The stacks of ribbons interact with adjacent stacks in a herring-bone fashion, as can be seen in the bottom view in Fig. 2. The closest distances between adjacent stacks are O1···C7 2.980 (3) and O1···C1 3.063 Å, with both C1 and C7 in the same molecule at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$; these distances should be compared with the suggested distance of 3.10 Å.

Experimental

A crystal suitable for the diffraction study was found in the original sample (Aldrich Chemical Co.).

Crystal data

$C_8H_2Cl_2O_3$
$M_r = 217.00$
Monoclinic
$P2_1/c$
$a = 7.998\ (5)$ Å
$b = 5.413\ (2)$ Å
$c = 19.435\ (5)$ Å
$\beta = 100.06\ (4)°$
$V = 828.5\ (6)$ Å^3
$Z = 4$
$D_x = 1.740$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 10$–$23°$
$\mu = 0.75$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.50 × 0.30 × 0.25 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.77$, $T_{max} = 0.83$
3972 measured reflections
1988 independent reflections

1434 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.96°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 7$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 70 min
intensity decay: < 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.04$
$wR(F^2) = 0.11$
$S = 1.03$
1987 reflections
118 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.245P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cl1—C3	1.723 (2)	Cl2—C6	1.713 (3)
O1—C7	1.185 (3)	O3—C8	1.186 (3)
O2—C8	1.389 (3)	O2—C7	1.393 (3)
C1—C7	1.478 (3)	C2—C8	1.477 (3)
C1—C6	1.380 (3)	C2—C3	1.376 (3)
C5—C6	1.384 (4)	C3—C4	1.389 (3)
C1—C2	1.380 (3)	C4—C5	1.376 (4)
C2—C1—C6	121.1 (2)	C3—C2—C1	121.3 (2)
C1—C6—C5	117.6 (2)	C2—C3—C4	117.9 (2)
C4—C5—C6	121.5 (2)	C5—C4—C3	120.6 (2)
C2—C1—C7	107.9 (2)	C1—C2—C8	107.8 (2)
O2—C7—C1	106.8 (2)	O2—C8—C2	107.0 (2)
O1—C7—O2	120.9 (2)	O3—C8—O2	121.0 (2)
C8—O2—C7	110.5 (2)		

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1995). Molecular graphics: *SHELXTL* and *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1409). Services for accessing these data are described at the back of the journal.

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17,17-Ethylenedioxyandrost-4-ene-3,6-dione and 17,17-Ethylenedioxyandrosta-1,4-diene-3,6-dione

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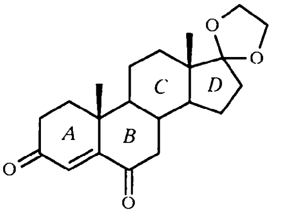
Abstract

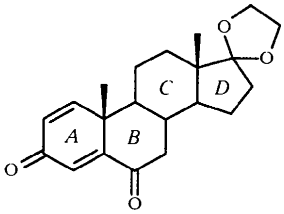
The crystal structures of 17,17-ethylenedioxyandrost-4-ene-3,6-dione, $C_{21}H_{28}O_4$, and 17,17-ethylenedioxyandrosta-1,4-diene-3,6-dione, $C_{21}H_{26}O_4$, intermediates in the synthesis of heteroandrogenic aromatase inhibitors, have been determined. Both structures are stabilized by C—H···O hydrogen bonds, highlighting the importance of weak interactions in influencing packing motifs in general and the conformation of the flexible dioxolane ring in particular.

Comment

The presence of a 4-ene-3,6-dione moiety in the *A*/*B* rings of a steroid skeleton is known to enhance the biological activity of such steroids, notably as aromatase inhibitors for the treatment of estrogen-dependent breast cancer (Numazawa *et al.*, 1993). The title compounds, 17,17-ethylenedioxyandrost-4-ene-3,6-dione, (I), and 17,17-ethylenedioxyandrosta-1,4-diene-3,6-dione, (II), were synthesised for elaboration to more complex *A*/*B*/*D* ring androgens and *A*-ring heteroandrogens (Nangia & Anthony, 1996, 1997). The conjugation in the enone (or enedione) portion of the molecule plays an important role in determining the stability of various *A*-ring conformations and in turn is able to influence the steroid–receptor interactions that control hormonal responses (Duax *et al.*, 1994).



(I)



(II)

In compound (I) (Fig. 1), ring *A* adopts the 1-α sofa conformation, ring *B* adopts a half-chair conformation,

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