Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.3186 (1)	−0.17922 (3)	0.91892 (4)	0.03759 (8)
S2	0.2064 (1)	0.07052 (3)	0.76954 (4)	0.03828 (8)
O1	−0.1105 (4)	−0.1297 (1)	0.6310 (2)	0.0563 (3)
C1	0.5273 (3)	−0.0564 (1)	1.0334 (2)	0.0304 (3)
C2	0.0954 (4)	−0.0878 (1)	0.7492 (2)	0.0368 (3)

Table 2. *Selected geometric parameters (Å, °)*

S1—C1	1.731 (1)	S2—C2	1.776 (2)
S1—C2	1.779 (2)	O1—C2	1.205 (2)
S2—C1^{i}	1.730 (1)	C1—C1^{i}	1.343 (2)
C1—S1—C2	94.82 (6)	S2^{i}—C1—C1^{i}	118.3 (1)
C1^{i}—S2—C2	94.83 (6)	S1—C2—S2	113.78 (7)
S1—C1—S2^{i}	123.61 (7)	S1—C2—O1	123.0 (1)
S1—C1—C1^{i}	118.1 (1)	S2—C2—O1	123.2 (1)
S1···S2^{ii}	3.5513 (5)	S1···S2^{iii}	3.8381 (6)

Symmetry code: (i) $1 - x, -y, 2 - z$; (ii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1320). Services for accessing these data are described at the back of the journal.

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Redetermination of 2,3-dichloro-5,6-dicyano-1,4-dihydroxybenzene†

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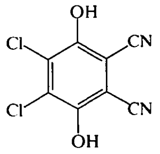
(*Received 16 November 1998; accepted 14 December 1998*)

Abstract

The crystal structure of the title compound, $C_8H_2Cl_2N_2O_2$, was reported recently [Reddy, Ovchinnikov, Shishkin, Struchkov & Desiraju (1996). *J. Am. Chem. Soc.* **118**, 4085–4089]. However, the space group has been corrected from $Pna2_1$ to $Pnma$ in the present study. The molecule lies on a mirror plane perpendicular to b.

Comment

Crystals of the title compound, 2,3-dichloro-5,6-dicyano-1,4-dihydroxybenzene (DDH), are orthorhombic and the systematic absences ($0kl$, $k+l$ odd, and $hk0$, h odd) indicate that the space group is $Pnma$ (No. 62) or $Pn2_1a$, the $a\bar{c}b$ setting of $Pna2_1$ (No. 33). Assuming the centrosymmetric space group $Pnma$, the structure solution was straightforward.



DDH

Reddy *et al.* (1996) reported the crystal structure of DDH in space group $Pna2_1$, with lattice constants a = 16.503 (2), b = 8.542 (1) and c = 6.421 (2) Å at 140 K. Their fractional coordinates of non-H atoms (x', y', z') are related to those obtained in the present paper (x, y, z) as $x' = 1 - x$, $y' = z + \frac{1}{2}$ and $z' = 0.365 = y + 0.115$. The crystal structure is essentially the same as that reported by Reddy *et al.* (1996). There are intramolecular O—H···Cl hydrogen bonds, which cause expansion of the O1—C3—C2 and O2—C6—C1 bond angles. Fig. 2 shows the intermolecular O—H···N≡C hydrogen-bond network in the $y = \frac{1}{4}$ plane, which is a crystallographic mirror plane.

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† Alternative name: 4,5-dichloro-3,6-dihydroxyphthalonitrile.

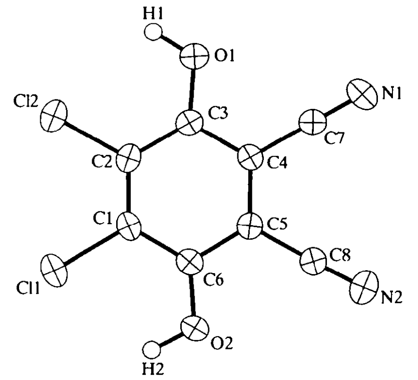

Fig. 1. The molecular structure of DDH. Displacement ellipsoids are plotted at the 50% probability level. H atoms are shown as spheres of arbitrary size.

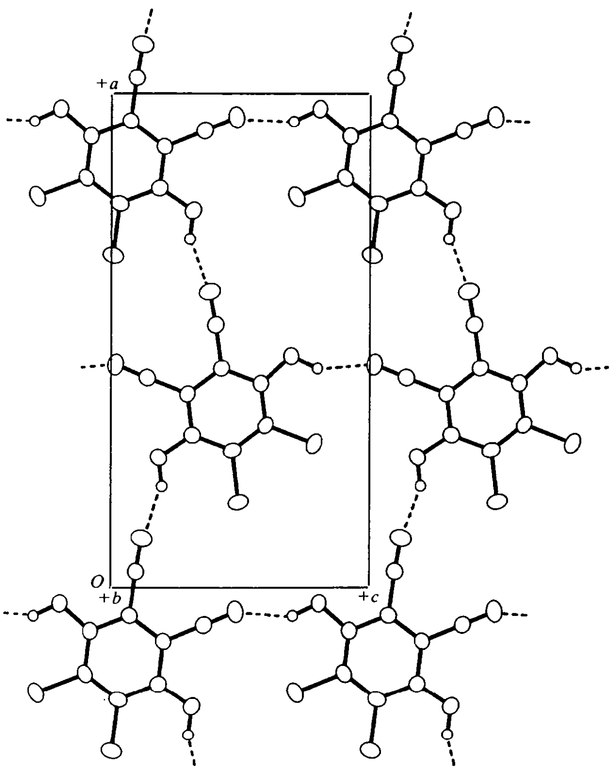

Fig. 2. Part of the crystal structure ($y = \frac{1}{4}$) projected along **b**.

Experimental

In the course of the oxidation reaction of some metal complexes by DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), a yellow compound (DDH) was obtained. Crystals were grown from an acetonitrile solution.

Crystal data

$C_8H_2Cl_2N_2O_2$
$M_r = 229.02$
Orthorhombic
Pnma
$a = 16.380\,(3)$ Å
$b = 6.536\,(2)$ Å
$c = 8.514\,(2)$ Å
$V = 911.5\,(7)$ Å^3
$Z = 4$
$D_x = 1.669$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 22 reflections
$\theta = 14.5\text{–}15.0°$
$\mu = 0.681$ mm^{-1}
$T = 296.2$ K
Prism
0.5 × 0.4 × 0.3 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.774$, $T_{\max} = 0.815$
1132 measured reflections
1132 independent reflections

974 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 8$
$l = -11 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: 1%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.058$
$S = 0.991$
1132 reflections
87 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o) + 0.00250|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.0005$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl1	0.79129 (4)	1/4	−0.28490 (6)	0.0487 (2)
Cl2	0.67384 (3)	1/4	0.00695 (7)	0.0507 (2)
O1	0.76362 (9)	1/4	0.3162 (2)	0.0489 (4)
O2	0.96916 (10)	1/4	−0.1952 (2)	0.0520 (5)
N1	0.9522 (1)	1/4	0.4823 (2)	0.0643 (7)
N2	1.0999 (1)	1/4	0.1207 (2)	0.0538 (6)
C1	0.8295 (1)	1/4	−0.0972 (2)	0.0359 (5)
C2	0.7772 (1)	1/4	0.0312 (3)	0.0368 (5)
C3	0.8088 (1)	1/4	0.1856 (2)	0.0373 (5)
C4	0.8935 (1)	1/4	0.2043 (2)	0.0357 (5)
C5	0.9454 (1)	1/4	0.0736 (2)	0.0346 (5)
C6	0.9146 (1)	1/4	−0.0780 (2)	0.0362 (5)
C7	0.9262 (1)	1/4	0.3605 (2)	0.0437 (6)
C8	1.0321 (1)	1/4	0.0973 (2)	0.0384 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cl1—C1	1.716 (2)	O2—C6	1.339 (3)
Cl2—C2	1.706 (2)	N1—C7	1.121 (3)
O1—C3	1.335 (3)	N2—C8	1.128 (3)
O1—C3—C2	124.9 (2)	O2—C6—C1	125.2 (2)
O1—C3—C4	117.1 (2)	O2—C6—C5	116.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl2	0.96	2.58	3.016 (2)	108
O2—H2···Cl1	0.96	2.52	3.012 (2)	112
O1—H1···N2$^{\rm i}$	0.96	1.84	2.735 (3)	153
O2—H2···N1$^{\rm ii}$	0.96	1.87	2.760 (3)	152

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $x, y, z - 1$.

Refinement was carried out based on all independent reflections. The threshold $I > 2\sigma(I)$ was used only for calculation of the R factor. The hydroxyl H atoms were located from difference syntheses and only displacement parameters were refined, assuming ideal bond lengths (O—H 0.96 Å).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1998). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1531). Services for accessing these data are described at the back of the journal.

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N-Propylimidazolidinetrione and *N*-methyl-*N*′-phenylethylimidazolidinetrione

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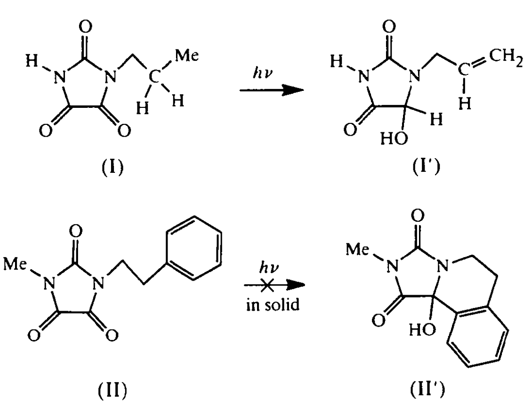
Abstract

In crystals of *N*-propylimidazolidinetrione, $C_6H_8N_2O_3$, (I), and *N*-methyl-*N*′-phenylethylimidazolidinetrione, $C_{12}H_{12}N_2O_3$, (II), the *N*-alkyl side chains have *trans* conformations. Photoirradiation of (I) gives the *N*-allyl derivative both in solution and in the solid state. (II) is photoreactive, yielding a tricyclic compound in solution, but not in the solid state. The photostability of (II) in the crystalline state may be due to the reaction cavity which does not allow the *N*′-phenylethyl moiety to make a large conformational change for cyclization.

Comment

The photoreactivities of imidazolidinetriones in solution vary with the substituents on the N atoms (Aoyama *et al.*, 1984). An intramolecular disproportionation reaction occurs for (I) and a cyclization reactions occurs for (II). The intermediate of the reactions seems to be the 1,4-biradical formed by γ-hydrogen abstraction by the α-dicarbonyl group (Aoyama *et al.*, 1984). Recently, the photoreactivities in the solid state have also been investigated for these compounds by one of the authors (HA). The yield of (I′) was *ca* 30% after irradiation for 12 h with a 1000 W high-pressure Hg lamp, but there was no yield of (II′). The yields of the photoproducts were estimated *via* their ^{1}H NMR spectra. The crystal structure analyses have been carried out to investigate the geometrical factors which might determine the reactivity in the solid state. The distances between the carbonyl oxygen, O3, and one of the γ-H atoms bonded to C10 are 3.42 (4) Å in (I), and 3.17 Å (no standard uncertainty due to a riding model) in (II). The $C8{=}O3\cdots H$ angles are 74.6 (7) and 76.4°, respectively. Therefore, the conformations in (I) and (II) are both suitable for intramolecular hydrogen abstraction. It is supposed that the reaction of (I) takes place with little structural change, but that of (II) does not because a large conformational change of the ethylphenyl group is not allowed in the crystal. The C6=O1 bond length in (I) is 0.022 (4) Å longer than that in (II). This elongation of the carbonyl bond is attributed to the hydrogen bonding of O1 in (I), which does not occur in (II). Similar effects were reported for imidazolidinetrione (Weber & Craven, 1987).



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