

(E)-3,6-Dihydroxy-2-methyl-1,4-benzoquinone 4-Methoxyimine N-Oxide

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Abstract. $C_8H_9NO_5$, $M_r = 199.17$, triclinic, $P\bar{1}$, $a = 4.470$ (4), $b = 9.733$ (6), $c = 10.526$ (6) Å, $\alpha = 103.88$ (5), $\beta = 100.20$ (5), $\gamma = 95.84$ (5)°, $U = 432.5$ (5) Å³, $D_x = 1.529$ g cm⁻³, $Z = 2$, $\mu = 0.7$ cm⁻¹ (Mo $K\alpha$). The structure contains bifurcated hydrogen bonds. Refinement proceeded to $R = 0.049$ for 1333 unique reflexions.

Introduction. The structure determination was undertaken to identify the product of the reaction between diazomethane and 1,3,6-trihydroxy-2-methyl-4-nitrobenzene. A preliminary communication has been published (Jones, Kennard, Sheldrick, Raphael & Ravenscroft, 1977).

Red crystals were obtained from acetonitrile as elongated irregular prisms. Intensities were measured on an automated Syntex $P2_1$ four-circle diffractometer with Mo $K\alpha$ radiation, graphite monochromator, and a crystal $0.55 \times 0.25 \times 0.1$ mm. 3209 reflexions were measured in the range $0 < 2\theta < 65^\circ$. Lp corrections were applied; averaging equivalent reflexions gave 1333 unique reflexions with $F > 4\sigma(F)$. Cell dimensions were obtained by least squares from 15 strong reflexions.

Attempts to solve the structure by multisolution Σ_2 sign expansion with the program *SHELX* gave no sensible E maps. The program *XCSD* was then used; this incorporates a pseudotangent refinement to select the starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) and the negative quartet test *NQEST* (De Titta, Edmonds, Langs & Hauptman, 1975). The resulting E map had merit figures *NQEST* -0.912 , $R\alpha$ (Roberts *et al.*, 1973) 0.068 , RA (a point-atom R based on observed peaks) 0.331 ; however, the map showed only a planar network of six-membered rings. 13 of the highest peaks were chosen as a starting point for an iterative procedure, involving refinement of site occupation factors followed by difference syntheses to locate a new set of atoms. No progress, however, could be made in $P\bar{1}$. When the space group was changed to $P1$ and the procedure repeated, all but three atoms of two molecules related by a centre of symmetry were located. Isotropic refinement (to $R = 0.23$), followed by a difference synthesis, revealed the missing atoms. The space group was changed back to $P\bar{1}$; anisotropic

refinement (to $R = 0.08$) and a difference synthesis showed the three non-methyl H atoms, but the methyl H atoms appeared to be disordered. In the final stages of refinement both methyl groups were successfully refined to a model of twofold disorder (Jones &

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	4685 (4)	1628 (2)	1196 (2)	
C(2)	7170 (5)	2788 (2)	1451 (2)	
C(3)	9148 (5)	3220 (2)	2657 (2)	
C(4)	8796 (5)	2489 (2)	3698 (2)	
C(5)	6361 (5)	1325 (2)	3454 (2)	
C(6)	4394 (5)	916 (2)	2270 (2)	
C(7)	7504 (6)	3503 (3)	355 (2)	
C(8)	12538 (7)	2598 (3)	7003 (2)	
N(1)	10806 (4)	2910 (2)	4851 (2)	
O(1)	13016 (4)	3921 (2)	5202 (2)	
O(2)	10395 (4)	2106 (2)	5761 (2)	
O(3)	11422 (4)	4312 (2)	2868 (2)	
O(4)	2779 (4)	1214 (2)	125 (2)	
O(5)	2073 (4)	-170 (2)	2002 (2)	
H(1)	12556 (52)	4430 (25)	3666 (24)	55 (4)
H(2)	954 (52)	-267 (25)	1174 (24)	55 (4)
H(3)	6090 (49)	898 (24)	4104 (22)	55 (4)
H(4)	11908	1925	7622	81 (6)
H(5)	12401	3698	7477	81 (6)
H(6)	14858	2506	6874	81 (6)
H(7)	5745	3053	-539	59 (5)
H(8)	9738	3390	122	59 (5)
H(9)	7369	4624	736	59 (5)
H(4')	11253	2914	7775	81 (6)
H(5')	14203	3494	7027	81 (6)
H(6')	13711	1722	7172	81 (6)
H(7')	7866	2754	-523	59 (5)
H(8')	9490	4325	752	59 (5)
H(9')	5497	3988	90	59 (5)

Table 2. Bond lengths (Å)

C(1)–C(2)	1.440 (4)	C(1)–C(6)	1.479 (4)
C(2)–C(3)	1.358 (4)	C(2)–C(7)	1.504 (5)
C(3)–C(4)	1.464 (4)	C(4)–C(5)	1.430 (4)
C(5)–C(6)	1.337 (4)	C(4)–N(1)	1.322 (3)
C(1)–O(4)	1.237 (3)	C(3)–O(3)	1.341 (3)
C(6)–O(5)	1.343 (3)	C(8)–O(2)	1.420 (4)
N(1)–O(1)	1.257 (3)	N(1)–O(2)	1.399 (4)
O(3)–H(1)	0.875 (24)	O(5)–H(2)	0.902 (24)
C(5)–H(3)	0.900 (27)		

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Kennard, 1977); site occupation factors refined to 0.20 [H(4'),H(5'),H(6')]; 0.80 [H(4),H(5),H(6)]; 0.58 [H(7'),H(8'),H(9')]; and 0.42 [H(7),H(8),H(9)] (all e.s.d.'s 0.01). H(1), H(2) and H(3) refined freely. Chemically similar H atoms were allotted equal isotropic temperature factors. Convergence was reached at $R = 0.0492$, with a corresponding $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$ of 0.0534; the weighting scheme was $w = 1/[\sigma^2(F) + 0.001 F^2]$, which gave mean values of $w\Delta^2$ independent of $\sin \theta$ or $|F_o|$. A final difference map showed no peaks $> 0.33 \text{ e } \text{Å}^{-3}$. Final atomic parameters are given in Table 1,* bond lengths and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33172 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

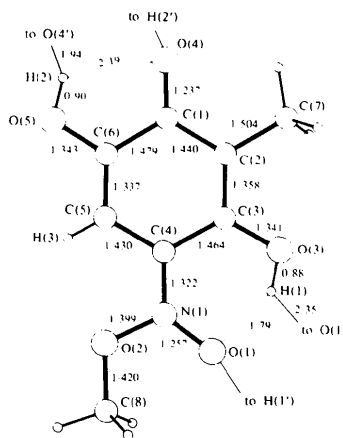


Fig. 1. Single molecule showing the atomic numbering, bond lengths and hydrogen-bonding contacts (Å) (narrow lines). Only one position of the disordered methyl groups is shown.

Table 3. Bond angles (°)

C(1)–C(2)–C(7)	118.5 (3)	C(1)–C(6)–C(5)	121.7 (3)
C(2)–C(1)–C(6)	118.3 (3)	C(3)–C(2)–C(1)	120.3 (3)
C(3)–C(2)–C(7)	121.2 (3)	C(3)–C(4)–C(5)	120.3 (3)
C(4)–C(3)–C(2)	120.0 (3)	C(4)–C(5)–C(6)	119.4 (3)
C(3)–C(4)–N(1)	118.6 (3)	C(5)–C(4)–N(1)	121.0 (3)
C(1)–C(6)–O(5)	117.0 (3)	C(2)–C(1)–O(4)	122.9 (3)
C(2)–C(3)–O(3)	118.9 (3)	C(4)–C(3)–O(3)	121.1 (3)
C(5)–C(6)–O(5)	121.3 (3)	C(6)–C(1)–O(4)	118.9 (3)
C(4)–N(1)–O(1)	127.6 (3)	C(4)–N(1)–O(2)	114.8 (3)
N(1)–O(2)–C(8)	113.8 (3)	O(1)–N(1)–O(2)	117.6 (3)
C(3)–O(3)–H(1)	108.2 (18)	C(6)–O(5)–H(2)	108.7 (17)
C(4)–C(5)–H(3)	120.5 (13)	C(6)–C(5)–H(3)	120.0 (13)

Table 4. Torsion angles (°) involving non-hydrogen atoms

Sign convention as defined by Klyne & Prelog (1960).

C(1)–C(6)–C(5)–C(4)	0.6 (3)
C(2)–C(1)–C(6)–C(5)	0.2 (3)
C(2)–C(1)–C(6)–O(5)	–179.4 (2)
C(3)–C(2)–C(1)–C(6)	–1.0 (3)
C(3)–C(2)–C(1)–O(4)	178.4 (2)
C(3)–C(4)–N(1)–O(2)	–176.8 (2)
C(3)–C(4)–N(1)–O(1)	2.3 (3)
C(3)–C(4)–C(5)–C(6)	–0.5 (3)
C(4)–C(3)–C(2)–C(1)	1.1 (3)
C(4)–N(1)–O(2)–C(8)	–178.6 (2)
C(4)–C(3)–C(2)–C(7)	–179.1 (2)
C(5)–C(4)–C(3)–C(2)	–0.4 (3)
C(5)–C(4)–C(3)–O(3)	–179.9 (2)
C(5)–C(4)–N(1)–O(1)	–179.0 (2)
C(5)–C(4)–N(1)–O(2)	1.9 (3)
C(7)–C(2)–C(1)–C(6)	179.2 (2)
C(7)–C(2)–C(1)–O(4)	–1.5 (3)
N(1)–C(4)–C(3)–C(2)	178.3 (2)
N(1)–C(4)–C(3)–O(3)	–1.2 (3)
N(1)–C(4)–C(5)–C(6)	–179.1 (2)
O(1)–N(1)–O(2)–C(8)	2.2 (3)
O(3)–C(3)–C(2)–C(1)	–179.4 (2)
O(3)–C(3)–C(2)–C(7)	0.5 (3)
O(4)–C(1)–C(6)–C(5)	–179.3 (2)
O(4)–C(1)–C(6)–O(5)	1.2 (3)
O(5)–C(6)–C(5)–C(4)	–179.9 (2)

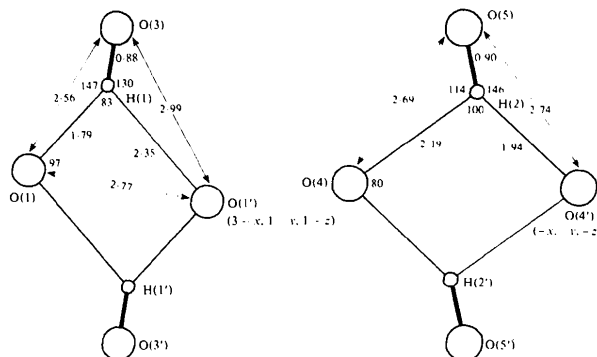


Fig. 2. Geometry of the bifurcated hydrogen bonding. Primes indicate symmetry-related atoms. Lengths are in Å, angles in degrees.

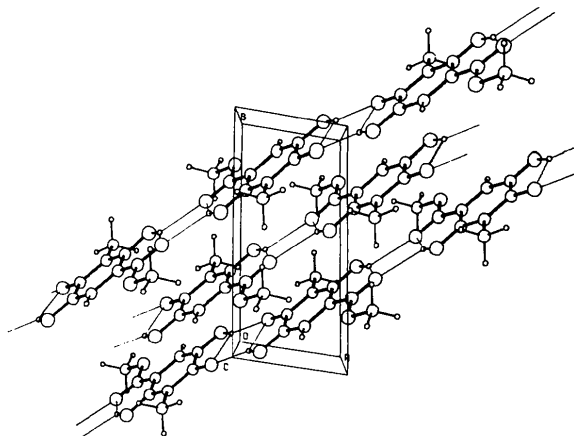
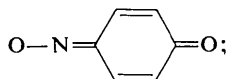


Fig. 3. Packing diagram showing the chains of molecules.

angles and torsion angles in Tables 2, 3 and 4. Diagrams of the structure are given in Figs. 1, 2 and 3.

At the end of the refinement, an *E* map calculated from correctly phased *E*'s > 1.5 contained, in addition to the correct atomic sites, a number of spurious peaks completing a planar hexagonal network similar to those initially obtained by direct methods. The difficulties encountered in direct methods can therefore be attributed to an amplitude termination effect (Bürgi & Dunitz, 1971).

Discussion. The bond lengths establish the quinonoid nature of the compound, as they are similar to those of the related molecules *p*-methoxyindophenol *N*-oxide (Romers & Hesper, 1966); α - and β -2-chloro-*p*-benzoquinone 4-oxime acetate (Fischmann, MacGillavry & Romers, 1961*a,b*); and α -2-chloro-5-methyl-*p*-benzoquinone 4-oxime (Romers & Fischmann, 1960). These were the only structures found in a connectivity search of the Cambridge Crystallographic Data Centre files for the fragment



no *p*-benzoquinone oxime *N*-oxide has been crystallographically investigated prior to this work.

The current structure shows highly significant differences in lengths of ring bonds of the same formal

Table 5. Bond lengths (Å) for structures cited in the Discussion

Bond type	Range	Mean	Current structure
C—C*	1.437–1.54	1.482	1.453 (mean)
C=C*	1.29–1.38	1.339	1.348 (mean)
C=O	1.20–1.248	1.217	1.237
C=N	1.28–1.37	1.324	1.322
N—O	1.32–1.40	1.373	1.399 [N(1)—O(2)]
N→O	1.266 (one value only)		1.257 [N(1)—O(1)]

* In quinonoid rings only.

Table 6. Deviations from mean ring plane (Å)

Equation of plane: $-3.3151x + 6.2991y + 3.2717z = -0.1394$

C(1)*	0.003	C(6)*	0.003	O(2)	-0.095
C(2)*	-0.007	C(7)	-0.026	O(3)	0.008
C(3)*	0.004	C(8)	-0.089	O(4)	0.024
C(4)*	0.001	N(1)	-0.023	O(5)	0.000
C(5)*	-0.005	O(1)	-0.004		

* Atoms used to calculate mean plane.

order (Fig. 1). The structures cited above also show a considerable range of values for lengths of such bonds (Table 5). The accuracy of the earlier structures was, however, low (e.s.d.'s for C—C of order 0.04 Å).

The molecule shows some deviations from planarity (Tables 4, 6). The major deviations are for the oxime group, in particular O(2) and C(8). This may be because of repulsive interaction between O(2) and H(3) [$O(2) \cdots H(3) = 2.35 \text{ \AA}$].

Each hydroxyl group participates in one intramolecular and one intermolecular hydrogen bond (Fig. 2), acting as donor for both. Such bifurcated hydrogen bonding was discussed by Donohue (1968). O(5) is involved in a bifurcated hydrogen bond, with the donor H(2) at similar distances from the two acceptor atoms O(4) and O(4'). The hydrogen bonds involving O(3) are asymmetric with the donor H(1) markedly closer to O(1) than to O(1'). Fig. 3 shows that the effect of the hydrogen bonding is to link the molecules into infinite flat parallel chains.

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