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The Crystal Structure of (1*Z*,2*E*)-1,2-Naphthoquinone Dioxime

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The crystal structure of the title compound has been determined and refined using three-dimensional X-ray diffraction data. The unit cell is monoclinic, $P2_1/c$ (No. 14), with $Z=4$ and cell parameters $a=7.082(12)$, $b=9.046(11)$, $c=13.845(11)$ Å, $\beta=100.2(1)°$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to a final R value of 0.049 for 924 observed reflections. The estimated standard deviations in the bond lengths were in the range 0.004 – 0.006 Å. The two oxime groups are intramolecularly hydrogen bonded, with the O···N distance of 2.490(5) Å, and the separate molecules are joined together by an intermolecular hydrogen bond of 2.729(4) Å between oxygen atoms of neighbouring oxime groups.

Our studies on 1,2-naphthoquinone monoximes [1] and the metal chelates formed by them,[2] have led us to investigate the *vicinal* dioxime compounds derived from aromatic nuclei. It is well known that the complex formation ability of the $-C(=NOH)-C(=NOH)-$ group is greatly influenced by the spatial arrangement of the two oxime groups. For instance, the specific action of the grouping towards nickel ions has been attributed to the *anti* isomers of the compounds.[3] On the other hand, it has been stated that aromatic rings destroy such action, and no scarlet nickel chelates are formed by the dioximes of 1,2-benzoquinone or 1,2-naphthoquinone,[3] for which stable *amphi* configurations could be expected. The relationship between the stability of the isomeric form of the ligand and its capability for complex formation is not, however, very clear-cut.

This paper is a part of our study on the structures of analytically interesting organic ligands and their metal chelates. The present type of compounds has been submitted to investigation since the numerous reports on *vic*-dioximes and *vic*-dioximates in the literature have mainly been directed to the aliphatic compounds, and information about the chemistry of their aromatic counterparts is very limited; *e.g.* no results from crystal structure studies of such ligands are available.

EXPERIMENTAL

Crystal preparation and analysis. 1,2-Naphthoquinone dioxime was prepared from 1-nitroso-2-naphthol (E. Merck AG) and hydroxylamine hydrochloride. Methanolic solution containing equimolar quantities of 1-nitroso-2-naphthol and hydroxylamine hydrochloride together with a few drops of 2 M HCl was boiled under reflux for 8 h. When the hot solution was poured into excess of water, 1,2-naphthoquinone dioxime and small amounts of the corresponding anhydride compound were precipitated as a light yellow compact mass. The product was purified by dissolving into cold diluted sodium hydroxide solution, filtering off the insoluble anhydride, and reprecipitating the dioxime by adding diluted HCl. 1,2-Naphthoquinone dioxime was recrystallized from warm 1:1 aqueous ethanol from which it separated on gradual cooling as yellow needles; m.p. 163 °C. Anal. $C_{10}H_8O_2N_2$: C, H, N.

Crystal and intensity data. Weissenberg photographs showed that crystals are monoclinic and that the space group, from systematic absences, is $P2_1/c$. The unit cell dimensions were refined using data obtained from powder photographs taken with a Hägg-Guinier camera using Cu$K\alpha$ radiation and calcium fluoride as internal standard. The density was determined by the flotation method. Crystal data for $C_{10}H_8O_2N_2$ are:

Space group $P2_1/c$ (No. 14)
$a=7.082(12)$ Å, $b=9.046(11)$ Å, $c=13.845(11)$ Å
$\beta=100.2(1)°$, $Z=4$, $D_m=1.44$ g cm^{-3}, $D_x=1.432$ g cm^{-3}
μ(Cu$K\alpha$) = 8.6 cm^{-1}

Table 1. Fractional atomic coordinates (× 10^4) and anisotropic thermal parameters (× 10^3) for non-hydrogen atoms. Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$.

Atom	*X/a*	*Y/b*	*Z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	1031(5)	4227(4)	2529(2)	84(2)	58(2)	37(2)	9(2)	7(1)	5(1)
O2	1113(4)	694(3)	4008(2)	75(2)	42(1)	56(2)	0(1)	−1(1)	2(1)
N1	1657(4)	5177(3)	3314(2)	60(2)	52(2)	36(2)	10(2)	10(1)	5(1)
N2	1246(4)	2143(3)	3718(2)	45(2)	41(2)	44(2)	4(1)	4(1)	1(1)
C1	2000(4)	4605(4)	4192(2)	26(2)	46(2)	38(2)	8(1)	9(1)	4(1)
C2	1786(5)	3034(4)	4458(2)	31(2)	44(2)	39(2)	7(1)	9(1)	1(1)
C3	2128(5)	2618(4)	5485(2)	39(2)	49(2)	43(2)	5(2)	5(2)	10(2)
C4	2643(5)	3620(4)	6188(2)	39(2)	61(2)	36(2)	10(2)	5(1)	5(2)
C5	3436(5)	6177(5)	6756(3)	37(2)	68(3)	50(2)	5(2)	2(2)	−12(2)
C6	3661(6)	7639(5)	6562(3)	41(2)	69(3)	71(3)	6(2)	3(2)	−23(2)
C7	3402(6)	8127(5)	5589(3)	41(2)	49(2)	84(3)	2(2)	11(2)	−9(2)
C8	2893(5)	7149(4)	4822(3)	44(2)	49(2)	60(2)	2(2)	11(2)	2(2)
C9	2615(5)	5661(4)	5003(2)	24(2)	49(2)	43(2)	7(1)	8(1)	2(1)
C10	2912(5)	5157(4)	5986(2)	31(2)	55(2)	42(2)	7(2)	6(1)	−2(2)

A crystal with approximate dimensions 0.6 × 0.4 × 0.3 mm was chosen for the data collection. Ni-filtered Cu radiation (Cu$K\alpha$, λ = 1.5418 Å) and a Stoe-Güttinger diffractometer were used to measure the intensities from the levels $0kl-6kl$. The total number of reflections was 1349, of which 924 were considered observed, being stronger than $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity based on counting statistics. The data set was corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement. The structure was determined by direct methods, using the X-RAY system (1972).[4] Scattering factors for the non-hydrogen atoms were taken from Ref. 5 and those for the hydrogen atom from Ref. 6.

The full-matrix least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$ was performed with weights $w=1/(10.0+|F_o|+0.0025|F_o|^2)$. The atomic coordinates and temperature factors for the non-hydrogen atoms were refined first isotropically and then anisotropically. The resulting R value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was 0.080. A difference Fourier map calculated at this stage showed clearly the positions of all hydrogen atoms. The hydrogen atoms were then included in the subsequent refinement cycles with isotropic thermal parameters. After the last cycle the R value for 924 reflections was 0.049.

The atomic coordinates and thermal parameters together with their standard deviations are given for the non-hydrogen atoms in Table 1 and for the hydrogen atoms in Table 2. A list of the observed and calculated structure factors is available on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The molecular structure of the compound is shown in Fig. 1, where the bond lengths and angles are also given. It can be seen that in the *amphi* configuration of the oxime groups the N1 – O1 bond is turned away from the C8 carbon atom. Such orientation is not self-evident since the turning of the 1-oxime group towards the C8 carbon atom has been observed at least in potassium 1,2-naphthoquinone-1-oxime-7-sulfonate monohydrate.[1] The present two oxime C=N [1.304(4) and 1.306(4) Å] and N – O [1.394(4) and 1.379(4) Å] distances are

Table 2. Fractional atomic coordinates (× 10^3) and isotropic thermal parameters (× 10^2) for hydrogen atoms. Estimated standard deviations are given in parentheses.

Atom	*X/a*	*Y/b*	*Z/c*	*U*
H(O1)	79(7)	325(6)	278(3)	7.4(15)
H(O2)	45(9)	18(7)	346(4)	15.8(23)
H(C3)	192(6)	163(5)	563(3)	7.2(14)
H(C4)	291(6)	329(4)	686(3)	6.0(12)
H(C5)	357(6)	574(4)	745(3)	6.6(12)
H(C6)	396(6)	840(5)	716(3)	8.4(14)
H(C7)	345(7)	924(5)	545(3)	8.5(14)
H(C8)	272(6)	754(4)	414(3)	5.8(11)

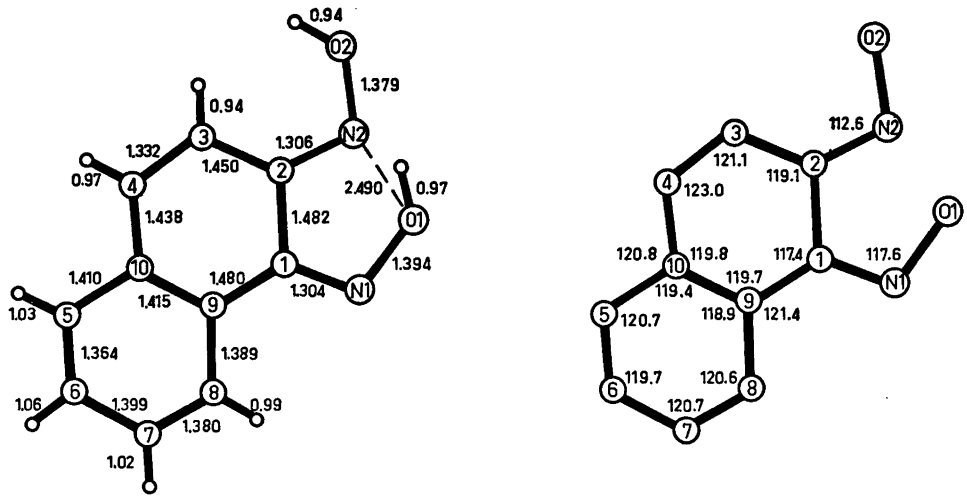

Fig. 1. Schematic representation of the molecule showing bond lengths (Å) and angles (°). The e.s.d.'s for bond lengths are in the range 0.004 – 0.006 Å, and for angles, 0.3 – 0.4°.

closely equal. Their values compare well with the corresponding bond lengths found in several other oximes: 1.30 ± 0.02 and 1.38 ± 0.02 Å.[1,7]

The naphthalene C – C bond lengths are also as expected; the quinonoid nature of the compound is discovered in the short C3 – C4 bond [1.332(5) Å], whereas the hexagonal C5 – C10 carbon ring has maintained its aromatic character. A similar distribution of the C – C bond lengths has been observed in several 1,2-naphthoquinone monoxime compounds.

A part of the molecular packing is shown in Fig. 2. The structure may be described as built up of infinite serpentine chains of the molecules, running nearly along the *b* axis. The O2 – H(O2) and H(O2)···O1($x, y-\frac{1}{2}, -z+\frac{1}{2}$) distances of 0.94(6) and 1.79(6) Å, together with the value of the O2 – H(O2)···O1 angle [174(6)°], indicate that the adjacent molecules are joined together by means of the hydrogen bond from the O2 oxime oxygen to the neighbouring O1 oxime oxygen. The intermolecular O1···O2 distance is 2.729(4) Å. This type of hydrogen bonding is somewhat uncommon, since most of the oximes whose structures are accurately known associate in the solid state *via* O – H···N hydrogen bond of length about 2.8 Å.[7]

The intramolecular hydrogen-bridged O1··· N2 distance in the molecule is 2.490(5) Å. The position of the H(O1) hydrogen atom can be located at a distance of 0.97(5) Å from the oxygen and 1.63(5) Å from the nitrogen atom, so that the O – H···N angle is 145(4)°. It was unexpected to find out that comparable intra-

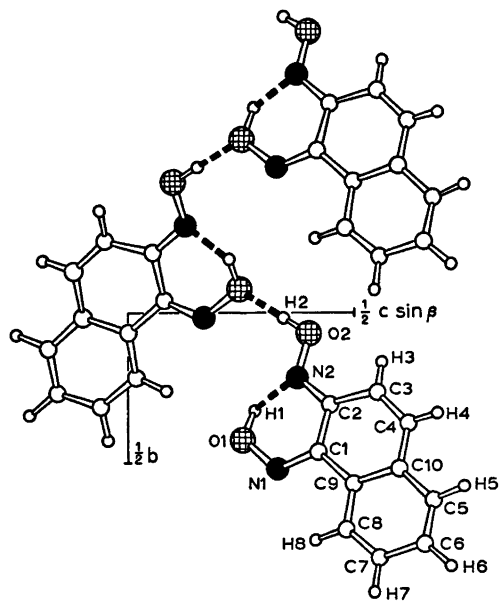

Fig. 2. Partial packing diagram of the compound as viewed down the *a*-axis. The broken lines represent hydrogen bonds.

Table 3. The least-squares plane defined by the naphthalene carbon ring C1 – C10. Deviations (Å) of different atoms from the plane are given.

Atom	Distance	Atom	Distance	Atom	Distance
C1	−0.023	C6	−0.020	N1	−0.100
C2	−0.004	C7	0.003	N2	−0.029
C3	0.005	C8	−0.020	O1	−0.163
C4	0.005	C9	0.007	O2	0.022
C5	−0.004	C10	0.011		

molecular hydrogen bonds which involve N and O atoms are hardly available. The present N···O separation is nevertheless quite similar to the comparable O···O bond lengths frequently reported in the literature, *e.g.* 2.473 Å in β-5-propoxy-*o*-quinone-2-oxime.[8] In such cases symmetrical hydrogen bridges are usually proposed.

The CNO angle in typical oximes is relatively constant around 112 – 113°.[1,7] In the present compound the C1 – N1 – O1 angle is opened up by about 5° from the expected value, while the C2 – N2 – O2 angle is unaffected. The effect of the intramolecular hydrogen bonding on the planarity of the molecule is also worth noting. The naphthalene carbon ring is relatively planar, the largest deviation from the mean plane being 0.023 Å for the C1 carbon atom. The N2 and O2 atoms lie approximately in the naphthalene mean plane, but the N1 and O1 atoms are markedly displaced from it (Table 3). A further interesting finding is that the outside angle C3 – C2 – N2 [125.7(3)°] is significantly larger than the inside angle C1 – C2 – N2 [115.2(3)°], a phenomenon that has been found in several related structures, *e.g.* 1,2-naphthoquinone-2-oxime compounds. It may be noted that almost the same difference is observed between the values of the inside angle C2 – C1 – N1 [127.0(3)°] and the outside angle C9 – C1 – N1 [115.6(3)°]. As a whole, it is obvious that the only marked distortions of the geometry and orientation of the present 1,2-oxime groups are associated with the oxime group on the C1 carbon atom.

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