

Short Communications

The Crystal Structure of (1*Z*,2*E*)-1,2-Naphthoquinone Dioxime. A New Modification

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In a recent report we described the crystal and molecular structure of (1*Z*,2*E*)-1,2-naphthoquinone dioxime.¹ We have since noticed that minor changes in the recrystallization procedure yield a crystallographically different form of the compound. Because it seemed possible that a new configuration of the oxime groups had been established, an X-ray structure analysis of the new crystals was undertaken.

The new modification (=B) was obtained from the raw product of 1,2-naphthoquinone dioxime¹ on recrystallization from 75% aqueous ethanol; m.p. 165 °C. Anal. C₁₀H₈O₂N₂: C, H, N. The yellow-brown tabular crystals are monoclinic with the following crystal data: $a =$

11.993(10), $b = 11.078(10)$, $c = 13.632(12)$ Å, $\beta = 98.60(7)^\circ$, $Z = 8$, $D_m = 1.42$ g cm⁻³, $D_x = 1.396$ g cm⁻³ and $\mu(\text{MoK}\alpha) = 2.4$ cm⁻¹. The space group, from systematic absences and statistical tests, is $C2/c$ (No. 15).

The intensity data were collected with a Syntex P2₁ diffractometer using graphite monochromated Mo radiation (MoK α , $\lambda = 0.7107$ Å) and the $\theta - 2\theta$ scan technique. Out of a total of 2054 reflections having 2θ less than 60°, 960 with $I > 2\sigma(I)$ were regarded as observed. No

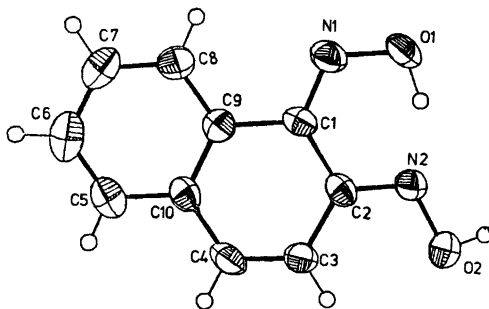


Fig. 1. Numbering and 50% probability ellipsoids of the atoms.

Table 1. Fractional coordinates ($\times 10^4$) and anisotropic thermal parameters^a ($\times 10^3$) for non-hydrogen atoms.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	2041(4)	2907(4)	6333(3)	32(2)	37(2)	37(2)	5(2)	-2(2)	-8(2)
C2	1346(4)	1795(4)	6242(3)	37(2)	38(2)	33(2)	9(2)	0(2)	-1(2)
C3	434(4)	1682(4)	5408(4)	38(3)	35(2)	52(3)	-1(2)	-7(2)	-1(2)
C4	256(4)	2540(5)	4715(4)	42(3)	52(3)	44(3)	6(2)	-14(2)	-4(2)
C5	712(5)	4498(5)	3987(4)	51(3)	63(4)	41(3)	11(3)	4(2)	7(3)
C6	1345(5)	5524(5)	4004(5)	71(4)	52(3)	64(4)	16(3)	28(3)	17(3)
C7	2233(5)	5715(5)	4786(4)	63(4)	37(3)	72(4)	-3(3)	22(3)	2(3)
C8	2459(4)	4876(4)	5529(4)	53(3)	41(3)	47(3)	-4(2)	2(2)	-7(2)
C9	1811(4)	3828(4)	5528(3)	40(2)	31(2)	39(2)	6(2)	6(2)	-6(2)
C10	923(4)	3626(4)	4742(3)	39(2)	40(2)	36(2)	9(2)	2(2)	0(2)
N1	2837(4)	3171(4)	7070(3)	53(2)	42(2)	45(2)	1(2)	-10(2)	-8(2)
N2	1603(3)	971(3)	6919(3)	43(2)	36(2)	43(2)	-2(2)	-3(2)	0(2)
O1	3088(4)	2326(4)	7826(3)	78(3)	54(2)	48(2)	-7(2)	-30(2)	3(2)
O2	928(3)	-45(3)	6780(3)	59(2)	43(2)	61(2)	-6(2)	-4(2)	14(2)

^a The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$.

Table 2. Fractional coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^3$) for the hydrogen atoms.

Atom	X/a	Y/b	Z/c	U
H(O1)	255(6)	168(6)	764(5)	9.8(22)
H(O2)	127(5)	-47(6)	722(5)	9.1(22)
H(C3)	30(4)	97(4)	535(3)	3.4(12)
H(C4)	-29(4)	244(4)	419(3)	3.8(12)
H(C5)	13(4)	435(4)	351(3)	4.2(13)
H(C6)	129(6)	613(6)	349(5)	9.9(23)
H(C7)	268(5)	642(5)	481(4)	6.9(17)
H(C8)	305(4)	503(4)	603(3)	4.1(12)

correction for absorption was carried out (crystal size $0.3 \times 0.3 \times 0.15$ mm). The methods of solving and refining the structure were the same as in Ref. 1. The weighting parameters used in the calculations were: $a=40.0$ and $b=0.04$. An R value of 8.5% was achieved by refining the non-hydrogen atoms anisotropically. All hydrogen atoms were then located from a difference Fourier map and included in the subsequent least-squares cycles with isotropic temperature factors. The final R value for 960 reflections was 5.3%. Atomic coordinates and thermal parameters are listed in Tables 1 and 2.

The structure of the molecule is visualized in Fig. 1. The interatomic distances and angles

together with the respective values of the former modification ($=A$) are listed in Table 3. The observed C-H and O-H bond lengths not seen in Table 3 vary from 0.82 to 0.97 Å, the respective standard deviations falling between 0.04 and 0.07 Å.

The two modifications have the same (1*Z*,2*E*)-configuration of the oxime groups and the differences between the corresponding bond lengths and angles are not significant. The similarity between the intramolecular hydrogen bonds in A and B is also obvious: the observed O1...N2 distances are 2.490(5) and 2.508(5) Å, respectively. The differences between the crystal forms of the two modifications arise rather from a different packing of the molecules in the structure. In B the molecules are linked together by a hydrogen bond [2.804(5) Å] from the O2 oxime oxygen to the N1 ($-x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$) nitrogen atom, whereas in A the same H(O2) was accepted by a neighbouring oxime oxygen.

A list of the observed and calculated structure factors is available on request.

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1. Näsäkkälä, M., Saarinen, H., Korvenranta, J. and Näsäkkälä, E. *Acta Chem. Scand. A* 31 (1977) 469.

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Table 3. Intramolecular distances (Å) and angles ($^\circ$) of the different modifications of (1*Z*,2*E*)-1,2-naphthoquinone dioxime. Standard deviations in bond lengths and angles are in the range 0.004–0.006 Å and 0.3–0.4 $^\circ$ for modification A, and 0.005–0.008 Å and 0.3–0.5 $^\circ$ for B.

Distance	Modification		Angle	Modification	
	A	B		A	B
C1–C2	1.482	1.482	C1–C2–C3	119.1	118.9
C1–C9	1.480	1.494	C2–C3–C4	121.3	120.8
C2–C3	1.450	1.460	C3–C4–C10	123.0	123.1
C3–C4	1.332	1.334	C4–C10–C9	119.8	120.3
C4–C10	1.438	1.443	C5–C10–C9	119.4	118.7
C5–C6	1.364	1.365	C5–C6–C7	119.7	119.6
C5–C10	1.410	1.407	C6–C5–C10	120.7	121.4
C6–C7	1.399	1.405	C6–C7–C8	120.7	120.2
C7–C8	1.380	1.372	C7–C8–C9	120.6	120.9
C8–C9	1.389	1.397	C8–C9–C10	118.9	119.3
C9–C10	1.415	1.411	C9–C1–C2	117.4	117.8
C1–N1	1.304	1.311	C10–C9–C1	119.7	119.1
C2–N2	1.306	1.302	C9–C1–N1	115.6	116.4
N1–O1	1.394	1.391	C2–C1–N1	127.0	125.8
N2–O2	1.379	1.382	C1–N1–O1	117.6	118.0
O1–N2	2.490	2.508	C1–C2–N2	115.2	116.9
			C3–C2–N2	125.7	124.3
			C2–N2–O2	112.6	113.6