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2-Amino-7-methoxy-3H-phenoxazin-3-one

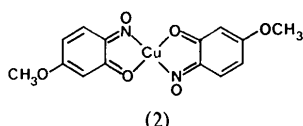
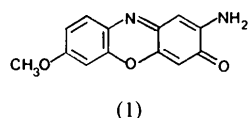
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Abstract. $C_{13}H_{10}N_2O_3$, $M_r = 242.23$, monoclinic, $P2_1/n$ [equivalent positions $\pm (x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$], $a = 21.976$ (3), $b = 3.901$ (4), $c = 12.523$ (3) Å, $\beta = 95.68$ (2)°, $U = 1068.3$ (1.4) Å³, $Z = 4$, $D_c = 1.506$ Mg m⁻³, μ (Mo $K\alpha$) = 0.067 mm⁻¹, $F(000) = 504$. The structure was solved from diffractometer data by direct methods and refined to $R = 0.052$ for 598 observed reflections. The phenoxazinone ring is almost planar and its geometry closely resembles that of the same heterocyclic fragment in the structure of the antibiotic actinomycin.

Introduction. In parallel with our chemical studies on the synthetic potential of the reactions of metal complexes of 2-nitrosophenols (monoximes of 1,2-quinones) with phosphines, amines and phenols (Charalambous, Kensett & Jenkins, 1977), we are investigating the X-ray structures of the heterocyclic products of these reactions. The phenoxazinone (1) reported here was obtained from the reaction of bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) (2) with 1,2-diaminoethane. Phenoxazines are of interest both as dyestuffs (Ionescu & Mantsch, 1967) and as natural products which show biological activity such as the antibiotics of the actinomycin group (Brockmann & Muxfeldt, 1958).



Data were collected from a crystal $0.38 \times 0.10 \times 0.02$ mm. 1918 intensities were recorded ($3.0 \leq \theta \leq 30.0^\circ$) on a Philips PW1100 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, a θ - 2θ scan mode, and a constant scan width of 0.80° . Lp corrections were applied. No absorption correction was made. Equivalent reflections were averaged to give 598 unique observed intensities [$F > 6\sigma(F)$]. Cell dimensions were derived from the angular measurements of 25 strong reflections ($10.0 < \theta < 15.0^\circ$). The structure was solved by multiresolution Σ_2 sign expansion for terms with $E > 1.2$. All the non-hydrogen atoms were located from the E map with the second-highest combined figure of merit (2.766). The structure was refined by full-matrix least-squares calculations using isotropic thermal parameters. All the H atoms were located from a difference map and were included in the refinement without constraints. Neutral-atom scattering factors were used (Cromer & Mann, 1968). The refinement converged to $R = 0.052$ and $R_w = \sum w^{1/2} |F_o| - |F_c| / \sum w^{1/2} |F_o| = 0.045$ with $w = 1/(\sigma^2 F_o)$. The final coordinates are listed in Table 1, bond lengths and angles in Table 2.* Computations were performed with *SHELX 76* (Sheldrick, 1976).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36204 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$; for H $\times 10^2$)

	x	y	z	U
C(1)	0.3219 (3)	0.343 (2)	0.7737 (6)	32 (2)
C(2)	0.3557 (3)	0.163 (2)	0.7093 (6)	36 (2)
N(2)	0.3373 (4)	0.086 (2)	0.6054 (5)	34 (2)
C(3)	0.4177 (3)	0.038 (2)	0.7496 (6)	38 (2)
O(3)	0.4485 (2)	-0.1266 (14)	0.6898 (3)	35 (2)
C(4)	0.4391 (3)	0.114 (2)	0.8603 (5)	34 (2)
C(4a)	0.4035 (3)	0.2890 (19)	0.9214 (5)	32 (2)
O(5)	0.4252 (2)	0.3513 (13)	1.0265 (3)	24 (2)
C(5a)	0.3881 (3)	0.5180 (13)	1.0916 (5)	29 (2)
C(6)	0.4102 (3)	0.555 (2)	1.1988 (6)	34 (2)
C(7)	0.3727 (3)	0.713 (2)	1.2667 (6)	37 (2)
O(7)	0.3869 (2)	0.7579 (14)	1.3747 (4)	33 (2)
C(71)	0.4424 (4)	0.602 (3)	1.4219 (8)	54 (3)
C(8)	0.3162 (3)	0.850 (2)	1.2270 (6)	39 (2)
C(9)	0.2958 (3)	0.812 (2)	1.1212 (6)	37 (2)
C(9a)	0.3314 (3)	0.6404 (19)	1.0491 (5)	32 (2)
N(10)	0.3079 (2)	0.5856 (15)	0.9448 (4)	25 (3)
C(10a)	0.3424 (3)	0.4140 (19)	0.8835 (5)	31 (2)
H(1)	0.281 (2)	0.457 (14)	0.751 (4)	4 (2)
H(N2a)	0.363 (4)	-0.05 (2)	0.570 (7)	5 (3)
H(N2b)	0.302 (2)	0.113 (17)	0.584 (4)	3 (2)
H(4)	0.481 (2)	-0.002 (14)	0.888 (4)	4 (2)
H(6)	0.448 (2)	0.448 (14)	1.227 (4)	3 (2)
H(71a)	0.442 (4)	0.68 (2)	1.504 (7)	6 (2)
H(71b)	0.474 (2)	0.715 (15)	1.399 (4)	4 (2)
H(71c)	0.438 (3)	0.324 (17)	1.411 (4)	6 (2)
H(8)	0.296 (2)	0.968 (17)	1.279 (5)	6 (2)
H(9)	0.259 (2)	0.900 (15)	1.088 (4)	5 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)—C(2)	1.347 (9)	C(1)—C(10a)	1.430 (9)
C(2)—C(3)	1.487 (8)	C(2)—N(2)	1.358 (9)
N(2)—H(N2a)	0.91 (9)	N(2)—H(N2b)	0.81 (5)
C(3)—C(4)	1.450 (9)	C(3)—O(3)	1.238 (8)
C(4a)—O(5)	1.376 (7)	C(4)—C(4a)	1.334 (8)
O(5)—C(5a)	1.373 (7)	C(4a)—C(10a)	1.464 (8)
C(5a)—C(9a)	1.390 (8)	C(5a)—C(6)	1.389 (8)
C(7)—O(7)	1.369 (7)	C(6)—C(7)	1.384 (9)
C(7)—C(8)	1.397 (9)	O(7)—C(71)	1.437 (9)
C(9)—C(9a)	1.420 (8)	C(8)—C(9)	1.364 (9)
N(10)—C(10a)	1.315 (7)	C(9a)—N(10)	1.373 (7)

C—H 0.89 (6) to 1.09 (6), mean = 0.99 (4)

C(2)—C(1)—C(10a)	122.5 (8)	C(1)—C(2)—C(3)	120.6 (8)
C(1)—C(2)—N(2)	124.1 (8)	C(3)—C(2)—N(2)	115.4 (7)
C(2)—C(3)—C(4)	117.2 (8)	O(3)—C(3)—C(2)	120.2 (7)
O(3)—C(3)—C(4)	122.6 (7)	C(3)—C(4)—C(4a)	120.0 (7)
C(4)—C(4a)—O(5)	118.2 (6)	C(4)—C(4a)—C(10a)	123.8 (7)
O(5)—C(4a)—C(10a)	118.1 (6)	C(4a)—O(5)—C(5a)	118.9 (5)
O(5)—C(5a)—C(6)	116.9 (7)	O(5)—C(5a)—C(9a)	119.9 (6)
C(6)—C(5a)—C(9a)	123.2 (7)	C(5a)—C(6)—C(7)	117.9 (8)
C(6)—C(7)—C(8)	120.9 (7)	C(6)—C(7)—O(7)	124.9 (7)
O(7)—C(7)—C(8)	114.2 (7)	C(7)—O(7)—C(71)	117.0 (7)
C(7)—C(8)—C(9)	120.0 (8)	C(8)—C(9)—C(9a)	121.3 (8)
C(9)—C(9a)—N(10)	120.0 (6)	C(5a)—C(9a)—N(10)	123.3 (7)
C(5a)—C(9a)—C(9)	116.6 (7)	C(9a)—N(10)—C(10a)	116.8 (6)
N(10)—C(10a)—C(1)	121.0 (7)	C(4a)—C(10a)—C(1)	116.0 (7)
C(4a)—C(10a)—N(10)	123.0 (6)		

Important intermolecular distances

N(10)···H(N2b)	2.40 (5)	O(5)···H(4 ⁱⁱ)	2.62 (5)
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Symmetry transformations: (i) $\frac{1}{2} - x, \frac{1}{2} + y, 1\frac{1}{2} - z$; (ii) $1 - x, -y, 2 - z$.

Discussion. A perspective view of the molecule is shown in Fig. 1 with the numbering scheme. The analysis established the configuration (1) for the prod-

uct of the reaction of 1,2-diaminoethane with bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II), (2).

The bond lengths within the quinoidal portion of the phenoxazinone nucleus show the pattern of bond fixation expected for the Kekulé formula shown, with the double-bond pattern of: C(3)—O(3) 1.238 (8), C(4)—C(4a) 1.334 (8), C(1)—C(2) 1.347 (9) and C(10a)—N(10) 1.315 (7) \AA . Bond lengths within the phenyl ring are normal with C—C distances of 1.364 (9) to 1.420 (8) \AA , mean 1.391 (6) \AA . The corresponding C—C single-bond distances in the quinoidal ring range from 1.430 (9) to 1.487 (8) \AA , mean 1.458 (7) \AA . The C—O distances at O(5) of 1.376 (7) and 1.373 (7) \AA agree with the mean value found for dioxin C—O distances of 1.383 (7) \AA (Singh & McKinney, 1978; Schwetz, Norris, Sparchu, Rowe, Gehring, Emerson & Gerbig, 1973).

The ring geometry is similar to that reported for the chromophore in the structure of the actinomycin D—deoxyguanosine complex (Jain & Sobell, 1972). The major difference between this structure and the phenoxazinone ring in the complex is in the C—NH₂ distance. However, in the latter structure there was a problem of disorder due to a non-crystallographic two-fold symmetry element about the N(10)···O(5) line, resulting in less accurate parameters for this part of the molecule.

The phenoxazinone ring system in (1) and in the actinomycin complex are almost planar with maximum deviations from the [C₁₂NO] plane of 0.10 (1) \AA and 0.15 \AA respectively.

The molecule (1) is only slightly folded about the O(5)···N(10) line, angle of fold 5.0 (6)°. Similar small angles of fold have been found for dioxin molecules (Cantrell, Webb & Mabis, 1969; Singh & McKinney, 1978; Schwetz *et al.*, 1973). In the crystal structure of the reduced heterocycle, phenoxazine, the angle of fold is 171 (1)° (Singhabhandhu, Robinson, Fany & Geiger, 1975). In the related phenothiazines and phenoxthionines, angles of fold range from 126 to 158° (Hosoya, 1966; Gillean, Phelps & Cordes, 1973; McDowell, 1976), whereas the phenazines are relatively planar (Riganti, Locchi, Curti & Bovio, 1965).

In the actinomycin complex the exocyclic angles for the substituent atoms at C(1), C(9), C(4) and C(6) are

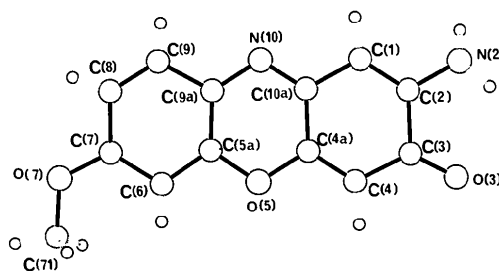


Fig. 1. ORTEP (Johnson, 1965) perspective view of 2-amino-7-methoxy-3H-phenoxazin-3-one (1).

all about 120° [$118.2(1.2)$ – $122.8(1.2)^\circ$]. For (1) all the H atoms were successfully refined and a small degree of strain was found to result from the short N(10)–C(10a) bond. The bond angles H(1)–C(1)–C(10a) and H(9)–C(9)–C(9a) are less than 120° [$113(2)$ and $111(2)^\circ$ respectively]; the atoms H(1) and H(9) are forced inwards as the longer C–O(5) bond lengths cause the atoms H(4) and H(6) to be splayed outwards with H(4)–C(4)–C(4a) and H(6)–C(6)–C(5a) angles of $125(2)$ and $122(2)^\circ$. This is also reflected in the differences between the angles of $118.9(6)$ and $116.8(6)^\circ$ at O(5) and N(10).

The 7-methoxy substituent is twisted only slightly out of the [C₁₂NO] least-squares plane with deviations of O(7) and C(71) of $0.37(1)$ and $0.21(1)$ Å, respectively.

The only intramolecular contact of significance is between O(3) and H(N2a) of $2.33(6)$ Å. Only weak intermolecular interactions occur (Table 2).

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A Neutron Diffraction Study of 1,1'-Ethylenebis(piperidine 1-oxide) Monoperchlorate*

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Abstract. C₁₂H₂₅N₂O₂⁺.ClO₄⁻ [PEtP(NO)₂.HClO₄], triclinic, *P*1̄, *a* = 6.281(1), *b* = 12.443(1), *c* = 10.490(1) Å, α = 102.48(1), β = 99.18(1), γ = 85.84(1)°, *Z* = 2, μ(measured) = 0.285 mm⁻¹ for λ =

1.210 Å. Final *R* = 0.060 for 2037 reflexions and 416 parameters. The intramolecular O···H···O bridge is 2.429(5) Å with an O···H···O angle of 175.1(6)°. The proton is, within experimental error, centrally located in the bridge, the two O···H distances being 1.225(7) and 1.206(7) Å. Thermal motion within the hydrogen-bond bridge indicates a single-minimum potential well. The geometry of the PEtP(NO)₂ skeleton is practically identical with that deduced from X-ray data.

* Hydrogen Bond Studies. CXLIII. Part CXLII: Küppers, Kvik & Olovsson (1981).

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