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2-(Pyrrolidin-1-yl)-1,4-naphthoquinone and 2-phenylsulfanyl-3-(pyrrolidin-1-yl)-1,4-naphthoquinone

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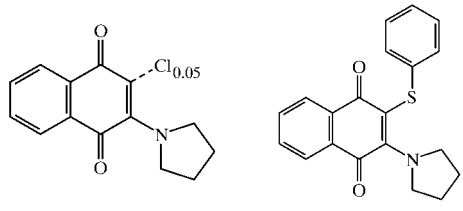
The structure of 2-(pyrrolidin-1-yl)-1,4-naphthoquinone, $C_{14}H_{12.95}Cl_{0.05}NO_2$, (I), is actually a 0.95:0.05 mixture including 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone as a minor impurity, but (I) was resolved as a single molecule containing a Cl atom with 5% occupancy at the 3-position. Compound (I) was prepared from the fully chloro-substituted analogue in an attempt to produce the disubstituted pyrrolidinyl derivative. 2-Phenylsulfanyl-3-(pyrrolidin-1-yl)-1,4-naphthoquinone, $C_{20}H_{17}NO_2S$, (II), was also prepared from 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone, using a strong exocyclic nucleophile. The structure of (II) differs from previous structures of 2,3-dichloro-1,4-naphthoquinone and its derivatives in that the naphthoquinone ring is non-planar.

Comment

In 2,3-dichloro-1,4-naphthoquinone, also known as dichlone (Métras, 1961; Ikemoto *et al.*, 1977), the two C═O groups activate the 2- and 3-position Cl atoms, rendering both equally reactive towards nucleophiles. In such a reaction, Michael addition followed by the elimination of HCl leaves a donating atom attached directly to the quinone. This attachment immediately deactivates the neighbouring Cl atom, making any additional displacement of that atom very difficult. Dichlone and its derivatives display both herbicidal and pesticidal activity (Merck Index, 1996), and for this reason we have recently initiated a study of the syntheses and structures of 2-substituted dichlone derivatives prepared by nucleophilic attack on dichlone itself. There are currently 11 known structures of this type and one common feature is that all contain an essentially planar naphthoquinone moiety. As an extension to our synthetic work on dichlone, we have been attempting to prepare analogues substituted in both Cl positions with the same type of nucleophile. This was initially undertaken by prolonging the reaction time in a 2 molar excess of nucleophile, but without success. However, one reaction that did produce an unexpected result is that of dichlone with pyrrolidine. The structure of 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone has been reported previously (Lynch & McClenaghan, 2000) and we report here the structure of the non-chlorinated derivative, (I), the molecule having lost the Cl atom by prolonged reflux in the presence of a second mole of nucleophile. Furthermore, we were successful in reacting a very strong nucleophile, but not pyrrolidine, with 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone, and the structure of that material is also reported here, namely 2-phenylsulfanyl-3-(pyrrolidin-1-yl)-1,4-naphthoquinone, (II). These two structures are significant and give important information with respect to the way forward in our study of dichlone and its derivatives.



(I) (II)

The structure of 2-(pyrrolidin-1-yl)-1,4-naphthoquinone, (I), is actually a 0.95:0.05 mixture of 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone and the reported molecule, containing a Cl atom with 5% occupancy at the 3-position (Fig. 1). This indicates that the process of removal of the second Cl atom was almost but not fully complete when the reaction was stopped. The chemistry underpinning this process requires further detailed study to determine why the removal of the second Cl atom occurred under the reaction conditions and what the other products may be. Another important question is why the two analogues cocrystallized instead of the major product crystallizing on its own. A comparison of the fully chloro-substituted structure with that of (I) reveals similarities between the planar naphthoquinone rings but significant differences between the twists of the pyrrolidinyl rings. Table 1 lists the torsion angles associated with the pyrrolidinyl ring in

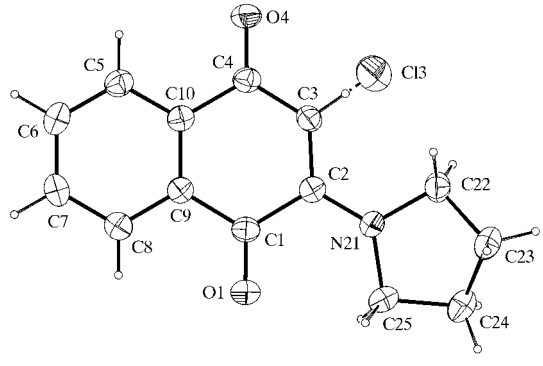


Figure 1
The molecular configuration and atom-numbering scheme for (I), shown with 50% probability ellipsoids.

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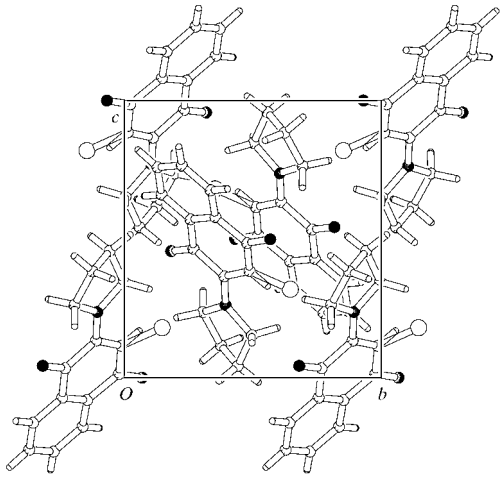

Figure 2
Packing diagram for (I), viewed down the *a* axis.

(I); the corresponding angles in the structure of the fully chloro-substituted analogue are −156.5 (2), 160.5 (2), 35.9 (2), −44.7 (2), 35.8 (2), 172.2 (2) and 16.7 (2)°, respectively. The full Cl atom deviates by *ca* 6° from the naphthoquinone plane, whereas the 5%-occupancy Cl atom in (I) deviates by *ca* 17°, although this may be accentuated by the small partial occupancy and related thermal motion. The differences in the conformation of the two pyrrolidinyl groups may also be insignificant considering that this group has a range of motion within the four CH_2 groups. Therefore, in (I), the few molecules of the fully chloro-substituted analogue align their pyrrolidinyl conformation to that of the dominant non-chloro-substituted molecules, while the Cl atoms had no effect on either the neighbouring pyrrolidinyl ring or the packing of the surrounding molecules. In neither molecule are there strong hydrogen-bonding elements to instigate any particular self-assembly pattern and although both the fully chloro-substituted structure and (I) pack in $P2_1/c$, the networks of C—H···O close contacts [see Table 2 for details of these contacts in (I)] are totally different (Figs. 2 and 3).

The structure of 2-phenylsulfanyl-3-(pyrrolidin-1-yl)-1,4-naphthoquinone, (II) (Fig. 4), has chemical significance in that it gives some indication of the types of nucleophilic groups needed to react with the second deactivated Cl atom of a dichlone derivative. The only other similar structure is *N*-(3-piperidino-1,4-dihydro-1,4-dioxo-2-naphthyl)-4-aminoacetophenone oxime (Rubashko *et al.*, 1994), in which the substituent that replaced the second Cl atom is connected *via* an exocyclic nucleophile. In both structures, steric hindrance is not a contributing factor to the impedance of the reaction at the second Cl atom, whereas it would be important for any second attacking endocyclic nucleophile. Thus, disubstituted dichlone derivatives similar to (II) are possible, but at least one nucleophile needs to be both strong and non-hindering, although we have yet to study whether or not the order in which nucleophiles are attached is significant. Structurally, compound (II) differs from all other dichlone derivatives in that the naphthoquinone moiety does not approximate planarity (Fig. 5). The non-planar conformation of (II) is best indicated by the C3—C2—C1—C9 torsion angle, which has a value of 34.5 (2)°, whereas the equivalent angles in both the fully chloro-substituted structure and (I) are −5.3 (2) and

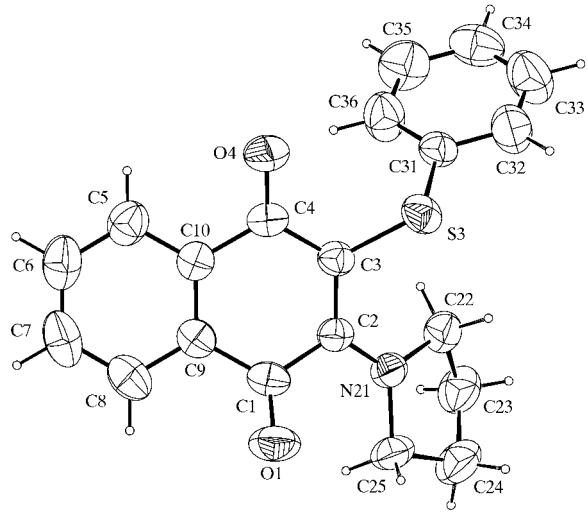

Figure 4
The molecular configuration and atom-numbering scheme for (II), shown with 50% probability ellipsoids.

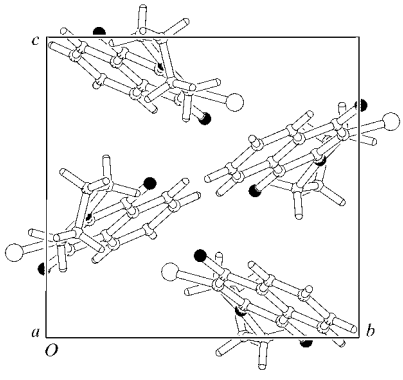

Figure 3
Packing diagram for 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone (Lynch & McClenaghan, 2000), viewed down the *a* axis.

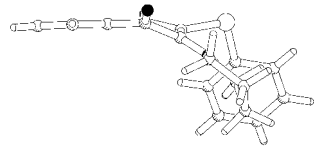

Figure 5
Side-on view of (II), showing the non-planarity of the naphthoquinone moiety.

4.7 (2)°, respectively. The dihedral angle between the phenyl and aromatic rings of the naphthoquinone moiety is 52.4 (2)°. The torsion angles of the pyrrolidinyl ring in (II) (Table 3) are

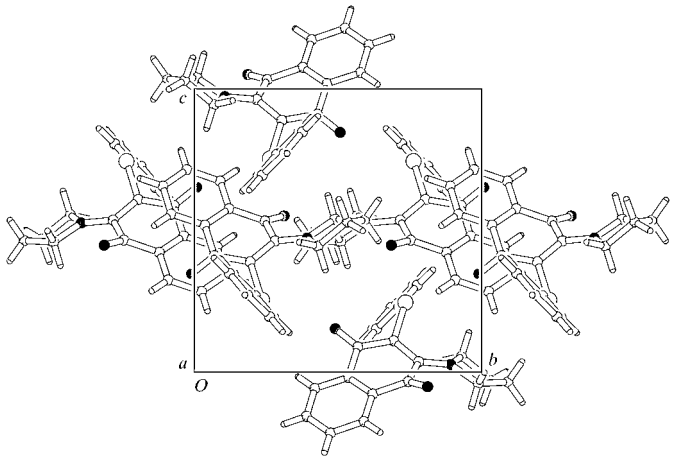

Figure 6
Packing diagram for (II), viewed down the *a* axis.

different to the equivalent angles in both the fully chloro-substituted structure (listed above) and (I) (Table 1), while only one C—H···O close contact is noted in Table 4. A packing diagram of (II) is shown in Fig. 6.

Experimental

Compounds (I) and (II) were obtained from Key Organics Ltd and crystals were grown from ethanol solutions. Compound (I) was prepared by refluxing a 1:2 molar equivalence of 2,3-dichloro-1,4-naphthoquinone and pyrrolidine in dimethylformamide for 8 h. Compound (II) was prepared by refluxing a 1:1:1 molar equivalence of 2-chloro-3-(pyrrolidin-1-yl)-1,4-naphthoquinone, thiophenol and triethylamine in dimethylformamide for 20 min.

Compound (I)

Crystal data

$C_{14}H_{12.95}Cl_{0.05}NO_2$
M_r = 228.98
Monoclinic, $P2_1/c$
a = 11.5759 (5) Å
b = 9.3063 (4) Å
c = 11.5275 (4) Å
β = 118.896 (2)°
V = 1087.24 (8) Å^3
Z = 4
D_x = 1.399 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4944 reflections
θ = 2.9–27.5°
μ = 0.11 mm^{-1}
T = 150 (2) K
Block, red
0.25 × 0.20 × 0.15 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.974, T_{max} = 0.984
8163 measured reflections
2470 independent reflections
1680 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°
$h = -14 \rightarrow 15$
$k = -12 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.123
S = 1.01
2470 reflections
168 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C1—C2—N21—C22	−171.2 (1)	C23—C24—C25—N21	29.3 (2)
C2—N21—C22—C23	164.8 (1)	C24—C25—N21—C2	171.6 (1)
N21—C22—C23—C24	32.1 (2)	C25—N21—C2—C1	7.6 (2)
C22—C23—C24—C25	−38.3 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O4^{i}	0.95	2.49	3.366 (2)	153
C25—H252···O4^{ii}	0.99	2.57	3.328 (2)	133

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

Compound (II)

Crystal data

$C_{20}H_{17}NO_2S$
M_r = 335.42
Monoclinic, $P2_1/c$
a = 13.205 (3) Å
b = 11.387 (2) Å
c = 11.220 (2) Å
β = 93.12 (3)°
V = 1684.6 (6) Å^3
Z = 4
D_x = 1.322 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8654 reflections
θ = 2.9–27.5°
μ = 0.20 mm^{-1}
T = 150 (2) K
Needle, red
0.46 × 0.04 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.912, T_{max} = 0.994
11 174 measured reflections
3716 independent reflections
2088 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 27.5°
$h = -17 \rightarrow 17$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.126
S = 0.95
3716 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 3
Selected torsion angles (°) for (II).

C1—C2—N21—C22	158.33 (18)	C23—C24—C25—N21	−29.9 (2)
C2—N21—C22—C23	−148.64 (18)	C24—C25—N21—C2	173.47 (18)
N21—C22—C23—C24	−36.2 (2)	C25—N21—C2—C1	−5.9 (3)
C22—C23—C24—C25	41.0 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O1^{i}	0.95	2.52	3.395 (3)	152

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

The H atoms of both title compounds were included in the refinement at calculated positions as riding models, with C—H distances set at 0.95 (aryl H) and 0.99 Å (CH_2), except for atom H3 [attached to C3 in compound (I)], which was located in a difference synthesis and for which both positional and displacement parameters were refined.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*94 (Spek, 1994) and *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1143). Services for accessing these data are described at the back of the journal.

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