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Two polymorphs of 4-propyl-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-5,6-dione

Erli Sugiono[a] and Michael Bolte[b]*

[a]Institut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany, and [b]Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany
Correspondence e-mail: bolte@chemie.uni-frankfurt.de

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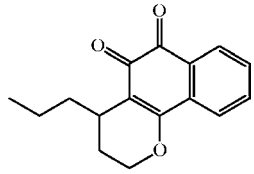
Two polymorphs of the title compound, $C_{16}H_{16}O_3$, have been obtained from the same solution. One polymorph, (I_m), crystallizes in the monoclinic space group $P2_1$, while the other, (I_o), crystallizes in the orthorhombic space group $P2_12_12_1$. The cell constants of the two polymorphs are surprisingly similar. Whereas the *a* and *b* axes are equal in the two structures, the *c* axis in (I_o) is twice as long as that in (I_m). The monoclinic angle β is 95.084 (9)° compared with 90° in the orthorhombic crystal system. The cell volume of (I_m) is almost exactly half of the cell volume of (I_o). The packing motifs are also very similar in the two structures. However, whereas the molecules in (I_m) are related by a twofold screw axis just in the direction of the *b* axis, in (I_o) there are twofold screw axes along all three directions of the unit cell.

Comment

β-Lapachone is a naturally occurring plant quinone primarily isolated from the Central and South American lapacho tree (*Tabebuia avellanedae*). β-Lapachone (2,2-dimethyl-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-5,6-dione) and its derivatives exhibit a number of important pharmacological properties, such as antibacterial, antifungal, antitrypanosomal, antimalarial and antitumor activities (Guiraud *et al.*, 1994; de Andrade-Neto *et al.*, 2004; Ferreira *et al.*, 2006). The title compound, (I), was synthesized from 2-hydroxy-1,4-naphthoquinone, α,β-unsaturated aldehyde and diarylprolinol catalyst, and recrystallized from CH_3OH/hexane/CH_2Cl_2 (Rueping *et al.*, 2008). In the same reaction vessel, two different kinds of crystals were found, *viz.* orange plates and orange needles. Since the cell parameters of the two crystal types were different, for both types a full crystal structure determination was carried out. As a result, two polymorphs were encountered. The plates were an orthorhombic form, (I_o), whereas the needles were a monoclinic form, (I_m).

Perspective views of the two polymorphs of the title compound are shown in Figs. 1 and 2. Bond lengths and angles can be regarded as normal (Cambridge Structural Database,



(I)

Version 5.28 of November 2006 plus two updates; *Mogul*, Version 1.1; Allen, 2002; Bruno *et al.*, 2004). The 1,2-naphthoquinone units are planar [the r.m.s. deviations for the ten C atoms are 0.014 and 0.016 Å for (I_m) and (I_o), respectively]. The 3,4-dihydro-2*H*-pyran rings adopts a half-chair conformation and exhibits local twofold rotational symmetry (Tables 1 and 2). The propyl chains adopt a *trans* conformation (Tables 1 and 2). The molecular conformations of the two polymorphs are almost identical. A least-squares fit of all non-H atoms gives an r.m.s. deviation of 0.013 Å.

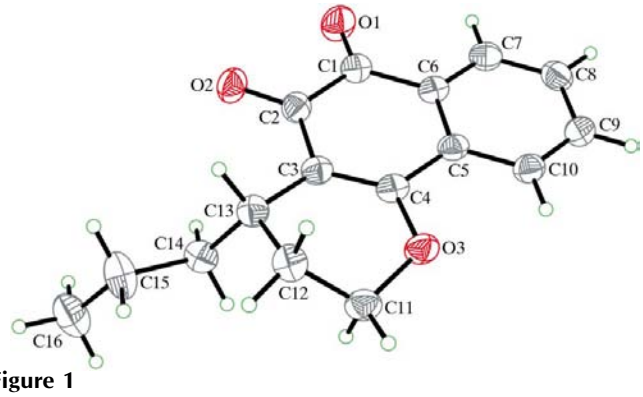


Figure 1
A perspective view of (I_m), showing the atom numbering. Displacement ellipsoids are shown at the 50% probability level.

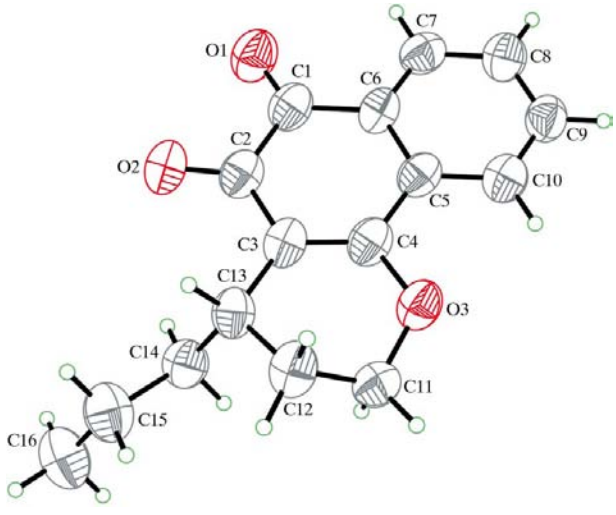


Figure 2
A perspective view of (I_o), showing the atom numbering. Displacement ellipsoids are shown at the 50% probability level.

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The packing patterns on the other hand show some interesting similarities and differences. Whereas the *a* and *b* axes are equal in the two structures, the *c* axis in (I_o) is twice as long as that in (I_m), and the monoclinic angle β of 95.084 (9)° differs significantly from that of 90° in the orthorhombic crystal system. The cell volume of (I_m) is almost exactly half of the cell volume of (I_o). The packing motifs are also very similar in the two structures (Figs. 3 and 4). If only the central two columns of molecules in the packing of (I_o) are compared with only the right or left two columns in the packing of (I_m), the patterns seem to be the same, because the aromatic rings in two neighbouring molecules approach one another in the same manner. The reason for this similarity is that these molecules are related by a twofold screw axis running in the same direction in both structures, *i.e.* along *b* in (I_m) and along *a* in (I_o). However, the propyl chains of two neighbouring molecules approach each other in a completely different way.

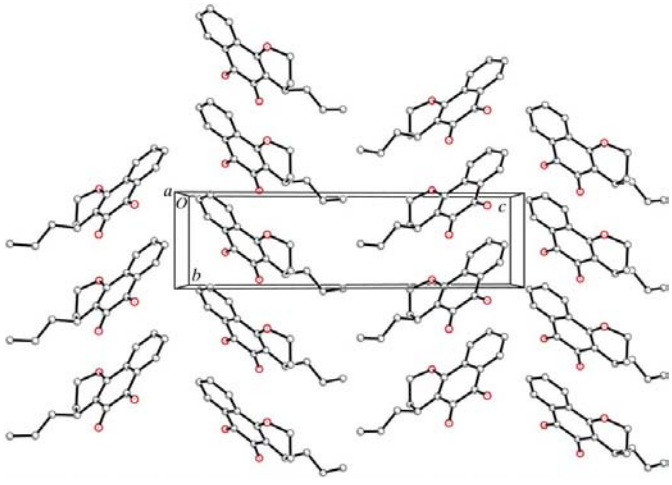

Figure 3
The packing of (I_m) viewed along the *a* axis. H atoms have been omitted for clarity.

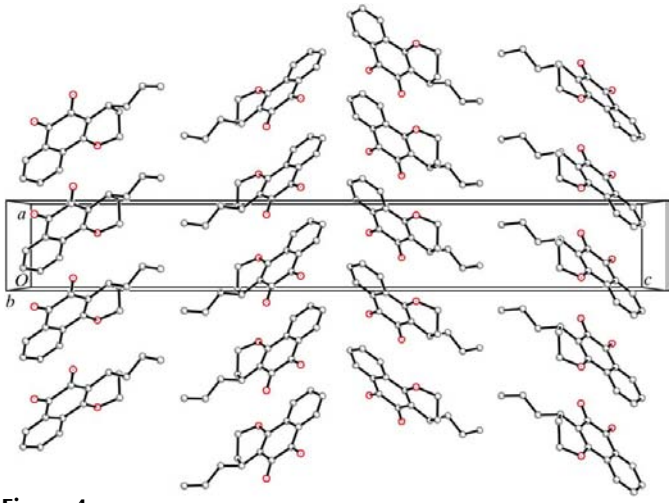

Figure 4
The packing of (I_o) viewed along the *b* axis. H atoms have been omitted for clarity.

Whereas in (I_m) two molecules are again related by a twofold screw axis along *b* (in the plane of the paper), in (I_o) two molecules are related by a twofold screw axis along *b* (perpendicular to the plane of the paper). In other words, the propyl chains in (I_m) all point in the same direction (downwards in Fig. 3), whereas the propyl chains in (I_o) point upwards and downwards (Fig. 4). This difference is the reason for the appearance of two polymorphic forms of the title compound.

Experimental

Full experimental details will be published elsewhere (Rueping *et al.*, 2008).

Polymorph (I_m)

Crystal data

$C_{16}H_{16}O_3$
M_r = 256.29
Monoclinic, $P2_1$
a = 6.3201 (7) Å
b = 5.2972 (8) Å
c = 19.429 (2) Å
β = 95.084 (9)°
V = 647.90 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 173 (2) K
0.22 × 0.04 × 0.04 mm

Data collection

Stoe IPDSII two-circle diffractometer
6418 measured reflections
1331 independent reflections
1021 reflections with $I > 2\sigma(I)$
R_{int} = 0.099

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.087
S = 0.97
1331 reflections
173 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

C11—O3—C4—C3	10.8 (4)	C4—C3—C13—C12	12.2 (4)
C13—C3—C4—O3	5.5 (5)	C11—C12—C13—C3	−43.4 (3)
C4—O3—C11—C12	−44.0 (4)	C13—C14—C15—C16	177.3 (3)
O3—C11—C12—C13	61.5 (3)		

Polymorph (I_o)

Crystal data

$C_{16}H_{16}O_3$
M_r = 256.29
Orthorhombic, $P2_12_12_1$
a = 5.2833 (7) Å
b = 6.3043 (8) Å
c = 38.753 (6) Å
V = 1290.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 173 (2) K
0.19 × 0.18 × 0.03 mm

Data collection

Stoe IPDSII two-circle diffractometer
8057 measured reflections
1399 independent reflections
738 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.108
S = 0.83
1399 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 2
Selected torsion angles (°) for (I_o).

C11—O3—C4—C3	13.8 (5)	C4—C3—C13—C12	13.6 (5)
C13—C3—C4—O3	3.2 (6)	C11—C12—C13—C3	−44.3 (5)
C4—O3—C11—C12	−46.4 (5)	C13—C14—C15—C16	179.2 (4)
O3—C11—C12—C13	62.4 (5)		

Because of the absence of anomalous scatterers, Friedel pairs were merged prior to refinement. All H atoms could be located by difference Fourier synthesis. They were refined with fixed individual displacement parameters [U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl})] using a riding model, with C—H distances ranging from 0.95 to 1.00 Å.

For both polymorphs, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3197). Services for accessing these data are described at the back of the journal.

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