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2,6-Dibenzoyl-1,4-benzoquinone

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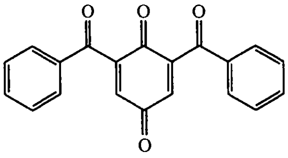
Abstract

In contrast to the stacking characteristic of quinones, the title compound, $C_{20}H_{12}O_4$, forms a two-dimensional network of C—H···O hydrogen bonds. The molecule has an unsymmetrical butterfly shape with the two benzoyl O atoms lying out of the plane of the quinonoid ring. The unusual conformation is a result of the crystal packing and the numerous weak hydrogen bonds.

Comment

C—H···O hydrogen bonds play an important role in the crystal structures of many organic compounds (Desiraju, 1996). It is well known that the strength of C—H···O hydrogen bonds depends on the acidity of the relevant C—H group. In this context, the title compound, 2,6-dibenzoyl-1,4-benzoquinone, (I), is of interest because it has a profusion of potential C—H···O hydrogen-bond donors (quinone and phenyl C—H) and acceptors (quinone and benzoyl C=O) in the molecular skeleton. The molecule can exist in three different conformations: the quinone ring and benzoyl carbonyl groups coplanar; the benzoyl carbonyl groups twisted out of the quinonoid plane and on the same face; the benzoyl carbonyl groups twisted out of the quinonoid plane but on opposite faces. The crystal structure of the title compound was undertaken to ascertain if there is any connection between the molecular conformation in the crystal and the intermolecular C—H···O hydrogen-bonding pattern.



(I)

In the crystal structure of the title quinone, both the benzoyl O atoms are out of the plane of the quinonoid ring; O7 is twisted out of the plane by 112.2 (4)° and O14 by −77.0 (4)°. The quinonoid H11 atom forms a C—H···O hydrogen bond with the benzoyl O14 atom of the [100]-translated molecule [C···O 3.154 (4) Å]. These molecules form another C—H···O bond between the quinonoid H9 and the benzoyl O7 atom [C···O 3.406 (4) Å]. The phenyl H18 and H19 atoms form C—H···O hydrogen bonds with quinonoid O10 atoms of distinct *b*-glide related molecules [C···O 3.368 (5) and 3.602 (5) Å]. Additional C—H···O bonds are formed between the phenyl H atoms, H2 and H3, and the benzoyl O7 atom of the screw-axis related molecule along [100] [C···O 3.502 (5) and 3.539 (5) Å]. In effect, the structure is two-dimensionally C—H···O hydrogen bonded. Short C20···H20 contacts of 2.744 (5) Å are present between phenyl rings in *a*-glide related molecules. The unsymmetrical butterfly shape of the molecule is unexpected and may be attributed to the numerous C—H···O hydrogen bonds that determine the molecular conformation in the crystal. The characteristic stacking, typical of quinones (Bernstein, Cohen & Leiserowitz, 1974), is not found here.

Crystal structures where the two- and three-dimensional networks are supported solely by C—H···O hydrogen bonding have not been generally discussed in detail, perhaps because of the supposed weakness of this interaction; the crystal structure of trimethylisocyanurate has such a complex three-dimensional network. Its structure was originally determined without H-atom positions (Belaj & Nachbaur, 1987). We subsequently redetermined the structure with the H atoms included (Thalladi, Panneerselvam, Carrell, Carrell & Desiraju, 1995). Although the C—H···O hydrogen bond is definitely weak, the phenomenon may be significant when several such hydrogen bonds are found in a crystal and when factors such as cooperativity and polarization become important.

When crystal-packing forces and hydrogen bonding are important, changes in the molecular conformation are likely. In order to rationalize the skewed conformation of the molecule in the crystal, *AM*1 semi-empirical

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calculations were performed (*Cerius*^{2}; Molecular Simulations, 1996) on the isolated molecule. The optimized structure has a symmetrical butterfly shape with both benzoyl O atoms pointing away from the quinonoid O13 atom and both phenyl rings nearly perpendicular to the quinonoid ring (torsion angles 88 and −99°). The conformation in the crystal is stabilized by the packing energy which was calculated (*Cerius*^{2}) to be around −175 kJ mol^{-1} (per molecule). Part of this crystal packing energy (−13 kJ mol^{-1}) is accounted for by the numerous C—H···O hydrogen bonds found in the structure.

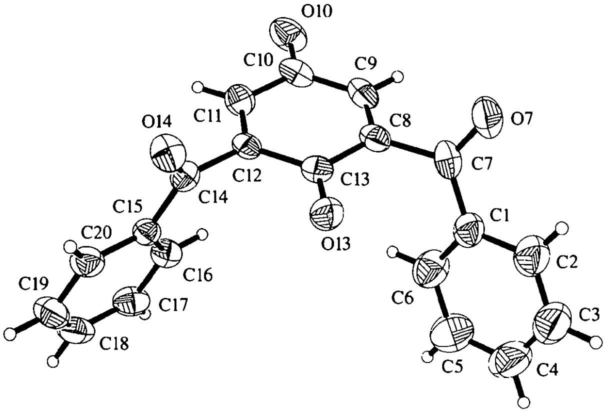

Fig. 1. The molecular structure of the title compound with the atom-labelling scheme and 50% probability displacement ellipsoids.

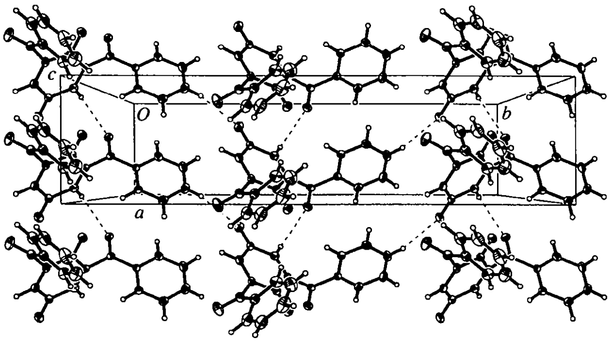

Fig. 2. The network of C—H···O hydrogen bonds in the crystal structure of the title compound.

Experimental

Crystals of 2,6-dibenzoyl-1,4-benzoquinone (Bogert & Howels, 1930) of dark yellow colour (m.p. 436 K) suitable for X-ray diffraction were obtained by recrystallization from dichloromethane.

Crystal data

$C_{20}H_{12}O_4$
M_r = 316.30

Mo $K\alpha$ radiation
λ = 0.71073 Å

Orthorhombic
Pbca
a = 5.1928 (5) Å
b = 20.405 (2) Å
c = 29.517 (3) Å
V = 3127.6 (5) Å^3
Z = 8
D_x = 1.343 Mg m^{-3}
D_m = 1.340 Mg m^{-3}
D_m measured by flotation

Cell parameters from 512 reflections
θ = 1.38–23.42°
μ = 0.094 mm^{-1}
T = 183 (2) K
Needle
0.30 × 0.25 × 0.15 mm
Yellow

Data collection

SMART diffractometer
CCD area-detector scans
Absorption correction: none
11 866 measured reflections
2263 independent reflections
1428 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.0978
$\theta_{\rm max}$ = 23.42°
$h = -5 \rightarrow 5$
$k = -22 \rightarrow 21$
$l = -25 \rightarrow 32$

Refinement

Refinement on F^2
$R(F)$ = 0.0517
$wR(F^2)$ = 0.1448
S = 1.023
2263 reflections
217 parameters
H-atom parameters constrained riding

$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.220 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.198 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O7—C7	1.216 (4)	O13—C13	1.224 (4)
O10—C10	1.222 (4)	O14—C14	1.224 (4)
O7—C7—C8—C13	112.2 (4)	C13—C12—C14—O14	−77.0 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O14$^{\rm i}$	0.93	2.524 (4)	3.154 (4)	125.3 (3)
C9—H9···O7$^{\rm i}$	0.93	2.792 (5)	3.406 (4)	124.5 (4)
C2—H2···O7$^{\rm ii}$	0.93	2.859 (5)	3.502 (5)	127.3 (4)
C3—H3···O7$^{\rm ii}$	0.93	2.935 (5)	3.539 (5)	124.0 (4)
C18—H18···O10$^{\rm iii}$	0.93	2.490 (5)	3.368 (5)	155.6 (4)
C19—H19···O10$^{\rm iv}$	0.93	2.906 (5)	3.602 (5)	132.7 (4)

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

It was obvious during the data collection that the crystal was not diffracting well (only 63% of the data could be labelled as 'observed' at the 2σ level to $\theta_{\rm max}$ = 23.42°) and we made a decision to terminate data collection at this point which is slightly below the $\theta_{\rm max}$ value of 25° recommended in *Notes for Authors*.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1318). Services for accessing these data are described at the back of the journal.

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(*E*)-2-Buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]-binaphthalen-2-yl)propanimidate and (*E*)-2-Buten-1-yl (*S*)-*N*-(2′-Methoxy-3-methyl-[1,1′]binaphthalen-2-yl)propanimidate†

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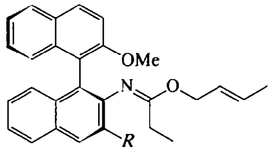
Abstract

In the structures of both of the title compounds, (*E*)-2-buten-1-yl (*S*)-*N*-(2′-methoxy-[1,1′]binaphthalen-2-yl)propanimidate, $C_{28}H_{27}NO_2$, (I), and it's methyl-substituted derivative, $C_{29}H_{29}NO_2$, (II), the C═N bond has an *E* configuration. In compound (II), the position of the additional methyl group is confirmed.

Comment

N-Arylimidates such as compound (I), derived from the axially chiral auxiliary (*S*)-2′-methoxy-[1,1′]binaphthalen-2-ylamine, are useful substrates for a highly diastereoselective and enantioselective Claisen rearrangement which produces, after hydrolysis, α,β-disubstituted γ,δ-unsaturated carboxylic acids with two new stereogenic centres (Metz & Hungerhoff, 1996). In order to optimize the inducing power of the auxiliary, we introduced a methyl group in the 3-position of the binaphthyl moiety. Details of the synthetic work have been published elsewhere (Metz & Hungerhoff, 1997).



(I) *R*=H
(II) *R*=Me

The crystals used in this work were obtained from petroleum ether/ether solutions. Structural studies of compounds (I) and (II) were undertaken in order to establish the geometry of the C═N bond. The X-ray crystal structures [compounds (I) and (II) are shown in Figs. 1 and 2, respectively] confirmed the anticipated *E* configuration. Related *N*-phenylimidates are also *E* configured, as shown by ^{1}H NMR NOE measurements (Metz & Linz, 1994). Furthermore, the structural investigation determined the correct position of the additional methyl substituent in the naphthyl moiety of (II).

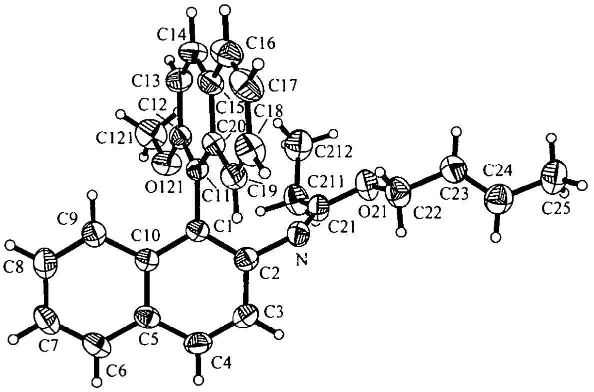


Fig. 1. *XP* (Siemens, 1990) (50% probability) plot of compound (I) with the atomic numbering scheme.

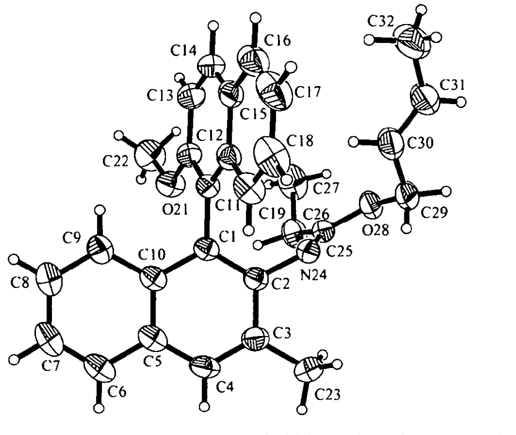


Fig. 2. *XP* (Siemens, 1990) (50% probability) plot of compound (II) with the atomic numbering scheme.

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† Dedicated to Dr Klaus Fleischmann on the occasion of his 60th birthday.