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N-(1-Naphthylacetyl)glycine phenacyl ester and phenacyl (1-naphthylacetoxy)acetate

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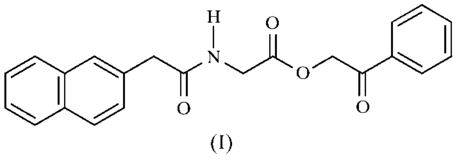
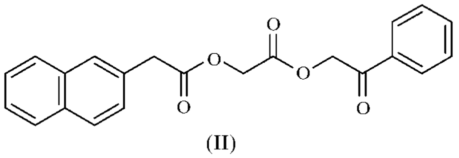
The structures of the bichromophoric compounds *N*-(1-naphthylacetyl)glycine phenacyl ester, $C_{22}H_{19}NO_4$, (I), and its oxygen analogue, phenacyl (1-naphthylacetoxy)acetate, $C_{22}H_{18}O_5$, (II), have been determined. The molecules of (I) are held together by intermolecular N—H···O hydrogen bonds between the carbonyl and N—H groups, while compound (II) does not show any hydrogen bonding in the crystal.

Comment

In recent years, research in the area of intramolecular charge and energy transfer (ET) in polychromophoric molecules has become increasingly important in connection with understanding the effects of molecular conformation, interchromophore distance and the bridging architecture on the mechanisms of the transfer process (Chattoraj *et al.*, 1991; Morrison *et al.*, 1986; Borkent *et al.*, 1978; Wagner & Klán, 1999; Klán & Wagner, 1998).



(I)



(II)

In the case of the title compounds, (I) and (II) (Figs. 1 and 2), in solution, ET between an electronically excited triplet donor (phenacyl) and an acceptor (naphthyl) moiety proceeds by an electron-exchange mechanism, which requires a close contact between the chromophores (Zabadal *et al.*, 2002). ET in (II) was found to be faster than in (I), which should be closely related to the greater flexibility of (II), *i.e.* as a result of conformations with easier contacts of the terminal chromophores.

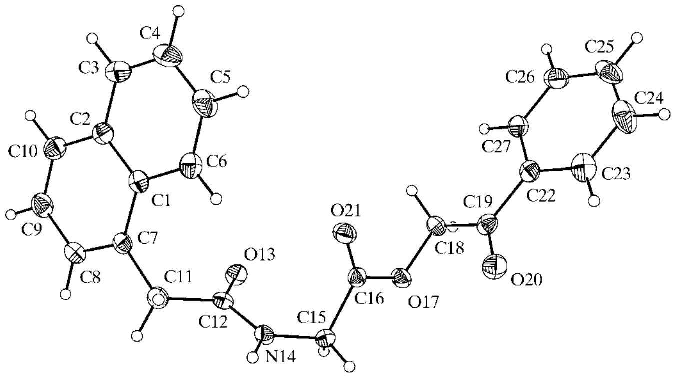


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Contrary to the remarkable difference in the molecular conformations (and corresponding ET rates) in solution, the molecular structures of (I) and (II) in the solid phase are very similar. In the crystal structure of (I), the C7···C22 distance is 9.009 (3) Å, while the same distance in (II) is 8.818 (2) Å. The mutual distance between chromophores is controlled mainly by the length and shape of the central chain. Replacing the –NH– group in (I) by –O– in (II) does not significantly affect the spatial arrangement of the bridging atoms; the r.m.s. deviations of the superimposed atomic chains (based on atoms C12, N14/O14, C15, C16, O17 and C18) is 0.1425 Å (Fig. 5). This is also reflected in the dihedral angles along the chain, where the pairs showing the greatest differences are C15—O14—C12—C11/C15—N14—C12—C11 of −166.28 (10)/−179.18 (12)° and O17—C16—C15—N14/O17—C16—C15—O14 of −161.14 (11)/172.92 (10)°.

Compound (I) forms a hydrogen-bonded polymer (see Fig. 3 and Table 1). Compared to (II), the C12═O13 double bond in (I) is elongated due to the hydrogen bonding, *viz.* 1.230 (2) *versus* 1.192 (2) Å. This is similar to what was found for the

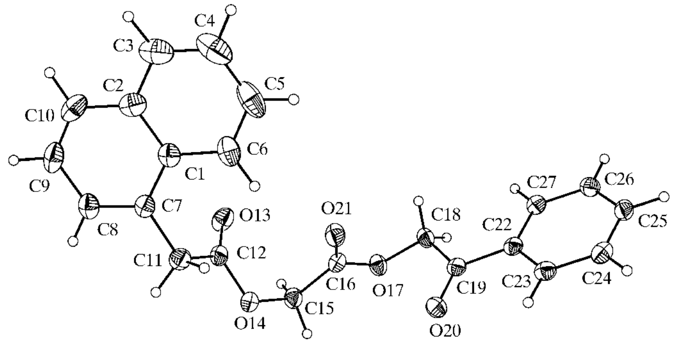


Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

analogous bond in 1-naphthaleneacetic acid [1.211 (10) Å; Rajan, 1984], which forms hydrogen-bonded dimers. The shortest contact in (II) is between atom O14 and one of the C11 H atoms of neighbouring molecules [2.551 (16) Å]; the molecules thus form a dimer, with atoms O14, C12, C11, and H11*A* and their symmetry equivalents in the other molecule forming an eight-membered ring (Fig. 4).

In spite of an exact crystallographic description of their conformations in the solid phase, the study of polychromophores in solution is of great importance, especially in flexible systems where two chromophores are connected by long bridges. The conformations, due to different driving forces in both the solid and liquid phases, differ significantly, and so the relationship of the crystal structure/ET properties is not directly obvious.

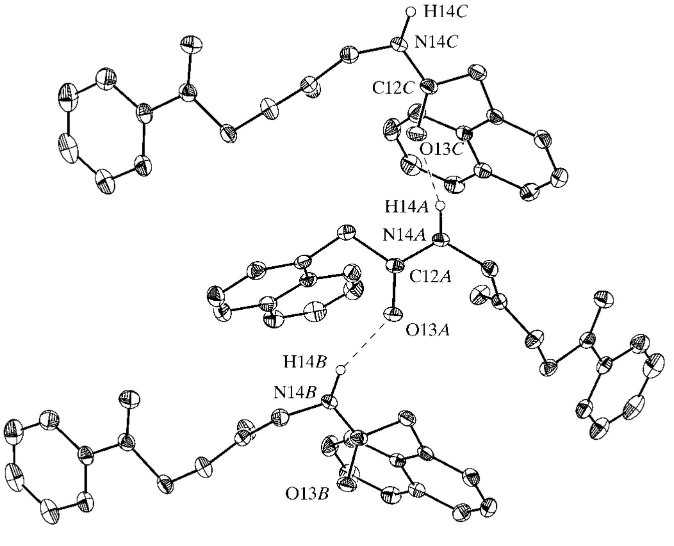


Figure 3
A packing diagram of compound (I), showing the hydrogen-bonding scheme.

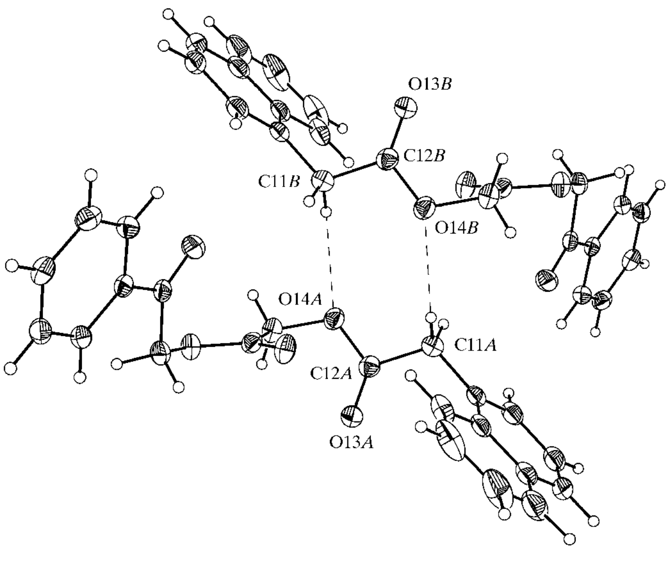


Figure 4
The van der Waals interactions in the crystal structure of (II).

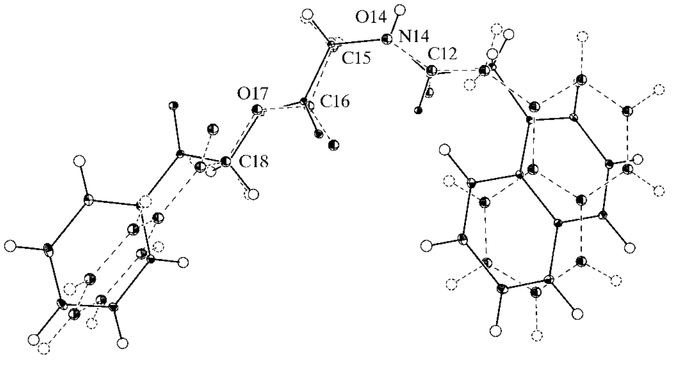


Figure 5
Superimposition of the structures of (I) and (II), based on the atoms bridging the chromophores.

Experimental

Compound (I) was synthesized by the coupling of commercially available *N*-*t*-Boc–L-Gly–OH (Fluka, Buchs, Switzerland) and phenacyl bromide (Banerjee & Falvey, 1997), brought about by stirring the mixture for 3 h under argon. The bichromophoric compound (I) was formed using DCC (*N,N*′-dicyclohexylcarbodiimide) and HOBt (1-hydroxybenzotriazole) as coupling reagents after cleavage of the *N*-*tert*-butyloxycarbonyl protecting group using 3 *M* HCl in ethyl acetate (Narita *et al.*, 1986). Single crystals of (I) were obtained by recrystallization from ethanol.

Compound (II) was prepared by the coupling of an appropriate carboxylic acid and phenacyl bromide. The acid was obtained by extending the 1-naphthaleneacetic acid with an acetyl fragment. In this procedure, the *tert*-butyl ester of bromoacetic acid was employed in addition to naphthylacetic acid (Ringshaw & Smith, 1964). The intermediate *tert*-butyl ester was then cleaved to the carboxylic acid using concentrated formic acid (Harada *et al.*, 1997). The crude product was recrystallized from a mixture of methanol and water (8:2) to give (II).

Compound (I)

Crystal data

$C_{22}H_{19}NO_4$
$M_r = 361.38$
Orthorhombic, *Pbca*
$a = 9.1467\ (18)$ Å
$b = 16.102\ (3)$ Å
$c = 24.318\ (5)$ Å
$V = 3581.5\ (12)$ Å^3
$Z = 8$
$D_x = 1.340$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 500 reflections
$\theta = 4.8$–$25.5°$
$\mu = 0.09$ mm^{-1}
$T = 120\ (2)$ K
Prism, colourless
0.50 × 0.30 × 0.20 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
19 123 measured reflections
3141 independent reflections
3034 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.024$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -19 \rightarrow 17$
$l = -28 \rightarrow 26$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.085$
$S = 1.17$
3141 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2$
$+ 1.2751P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1

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

D—H···A	D—H	H···A	D···A	D—H···A
N14—H14A···O13$^{\text{i}}$	0.88	1.98	2.7686 (15)	149

Symmetry code: (i) $\frac{1}{2}+x, y, \frac{3}{2}-z$.

Compound (II)

Crystal data

$C_{22}H_{18}O_5$
$M_r = 362.36$
Monoclinic, $P2_1/c$
$a = 8.927$ (2) Å
$b = 11.413$ (2) Å
$c = 17.875$ (4) Å
$\beta = 102.50$ (3)°
$V = 1778.0$ (7) Å^3
$Z = 4$
$D_x = 1.354$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 500 reflections
$\theta = 4.5$–27.8°
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
0.40 × 0.40 × 0.30 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
10 881 measured reflections
3128 independent reflections
2917 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$

$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 6$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.084$
$S = 1.06$
3128 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2$
$+ 0.6568P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

For both compounds, data collection: *Xcalibur* (Oxford Diffraction, 2001); cell refinement: *Xcalibur*; data reduction: *Xcalibur*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1607). Services for accessing these data are described at the back of the journal.

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