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# Methyl 2-benzamido-4-(3,4-dimethoxyphenyl)-5-methylbenzoate and *N*-{5-benzoyl-2-[(*Z*)-2-methoxyethenyl]-4-methylphenyl}benzamide

# Krištof Kranjc, Marijan Kočevar and Franc Perdih\*

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, SI-1000 Ljubljana, Slovenia Correspondence e-mail: franc.perdih@fkkt.uni-lj.si

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Methyl 2-benzamido-4-(3,4-dimethoxyphenyl)-5-methylbenzoate,  $C_{24}H_{23}NO_5$ , (Ia), and N-{5-benzoyl-2-[(Z)-2-methoxyethenyl]-4-methylphenyl}benzamide, C<sub>24</sub>H<sub>21</sub>NO<sub>3</sub>, (IIa), were formed via a Diels-Alder reaction of appropriately substituted 2H-pyran-2-ones and methyl propiolate or (Z)-1-methoxybut-1-en-3-yne, respectively. Each of these cycloadditions might vield two different regioisomers, but just one was obtained in each case. In (Ia), an intramolecular  $N-H \cdots O$ hydrogen bond closes a six-membered ring. A chain is formed due to aromatic  $\pi$ - $\pi$  interactions, and a three-dimensional framework structure is formed by a combination of  $C-H \cdots O$ and C-H··· $\pi$ (arene) hydrogen bonds. Compound (IIa) was formed not only regioselectively but also chemoselectively, with just the triple bond reacting and the double bond remaining unchanged. Compound (IIa) crystallizes as N-H···O hydrogen-bonded dimers stabilized by aromatic  $\pi$ - $\pi$ interactions. Dimers of (IIa) are connected into a chain by weak C-H··· $\pi$ (arene) interactions.

#### Comment

The Diels–Alder reaction is one of the most important synthetic tools for the construction of new C–C bonds (Nicolaou *et al.*, 2002). 2*H*-Pyran-2-ones are useful dienes for such transformations (Afarinkia *et al.*, 1992; Woodard & Posner, 1999). During our research we have already investigated a set of Diels–Alder reactions between substituted 2*H*-pyran-2-ones as dienes and various alkynes as dienophiles (Kranjc *et al.*, 2004). As an intermediate, an oxabicyclo[2.2.2]octadiene system is formed in this reaction, but it has not been isolated so far. This intermediate must therefore be spontaneously transformed into the final benzamide product *via* elimination of CO<sub>2</sub> with a retro-Diels–Alder reaction. In the two cases presented here, we have been studying the regioselectivity of these reactions, whereby there are two possible ways that the dienophile can attack the diene.

In the case of (I), the dienophile was methyl propiolate and its cvcloaddition could vield either (Ia) or (Ib) (see reaction scheme; Kranjc & Kočevar, 2005). On the basis of <sup>1</sup>H NMR spectroscopy it was determined that just one product was obtained. In order to determine the regioselectivity of the Diels-Alder reaction, the single-crystal X-ray diffraction analysis of (I) was performed and showed that the correct structure was (Ia). In the second case, we used (Z)-1-methoxybut-1-en-3-vne as the dienophile (Kranjc & Kočevar, 2008). Here, besides the regioselectivity as in the case of (I), the chemoselectivity was also important, *i.e.* whether the triple bond of the dienophile would react preferentially over the double bond. As in the previous case, the Diels-Alder reaction gave just one type of product, (IIa). Single-crystal X-ray diffraction analysis showed that the triple bond has reacted exclusively and the double bond in (IIa) retains the Z orientation.



In the crystal structure of (I*a*), there is an intramolecular hydrogen bond between the amide N1–H2 group and the carbonyl O1 atom from the neighbouring acetyl group, with graph-set motif S(6) (Bernstein *et al.*, 1995) (Fig. 1 and Table 1). The acetyl and amide units deviate slightly from coplanarity with the C1–C6 benzene ring, with torsion angles C3–C2–C7–O1 =  $3.5(3)^{\circ}$  and C9–N1–C3–C4 =  $-11.2(3)^{\circ}$ . Such coplanarity is common when the amide unit is involved in intramolecular hydrogen bonding and is also observed in, for example, methyl 2-[(methoxyacetyl)amino]-benzoate (Alam *et al.*, 2010) and diethyl 2-amino-5-[(2-



## Figure 1

The molecular structure of (Ia), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is indicated by a dashed line.





A packing diagram for (Ia). Dashed lines indicate  $\pi$ - $\pi$  interactions and hydrogen bonds. Chains running parallel above and below are indicated by arbitrary colours (blue and red in the electronic version of the journal) for clarity. Also for the sake of clarity, H atoms not involved in the motif shown have been omitted.

methoxybenzoyl)amino]terephthalate (Wu *et al.*, 2004). It might thus be expected that larger deviations from planarity might disable the intramolecular hydrogen bonding. However, there are interesting examples in the literature, such as methyl 2-{[2-( $\{2-[(tert-butoxycarbonyl)amino]benzoyl\}amino)-2-methyl$  $propanoyl]amino}benzoate (Prabhakaran$ *et al.*, 2008), whereintramolecular hydrogen bonding is present, even though theaminocarbonyl and*tert-butoxycarbonylamino*groups aretwisted out of the plane by 28.5 and 17.9°, respectively. An $even larger twist of 59.4° is found in ethyl 2-({[3-bromo-1-(3$ chloropyridin-2-yl)-1*H*-pyrazol-5-yl]carbonyl<math>amino)-5-chloro-3-methylbenzoate (Dong *et al.*, 2009) due to steric interference





caused by the methyl substituent at the *ortho* position to the amide group, but intramolecular hydrogen bonding is, surprisingly, still preserved. These examples show that one cannot predict solely from the twist angle whether intra- or intermolecular hydrogen bonding will occur.

The orientations of all three aromatic rings in (Ia) are influenced by their ability to form  $\pi - \pi$  interactions. Benzene rings C1-C6 (centroid Cg1) and C10-C15 (centroid Cg2) are involved in  $\pi$ - $\pi$  interactions, with a  $Cg1 \cdots Cg2(1-x, -y, -z)$ centroid-centroid distance of 3.9171 (10) Å, a dihedral angle between the rings of 8.68  $(8)^{\circ}$ , a perpendicular distance from centroid Cg1 to the plane of the C10-C15 ring of 3.507 Å, and an angle between the intercentroid vector and the normal to the second ring of 26.45° (see Fig. 2). The planes of benzene rings C1-C6 and C16-C21 (centroid Cg3) are twisted by 49.43 (7)° and therefore enable a  $\pi$ - $\pi$  interaction between two parallel C16–C21 rings, with a  $Cg3\cdots Cg3(2-x, 1-y, -z)$ centroid-centroid distance of 3.9646 (9) Å, a perpendicular distance from the centroid Cg3 to the plane of the other ring of 3.6313 (6) Å and a slippage between the centroids of 1.591 Å. These interactions are consistent with well defined  $\pi$ - $\pi$ stacking interactions (Hunter & Sanders, 1990; Choudhury & Chitra, 2010), although the interplanar separations are somewhat greater than the graphite spacing of 3.35 Å (Bacon, 1951). According to Janiak (2000), these interactions can be regarded as medium strong, since strong interactions exhibit rather short centroid–centroid contacts ( $Cg \cdots Cg < 3.8 \text{ Å}$ ), small slip angles ( $<25^{\circ}$ ) and vertical displacements (<1.5 Å), which translate into a sizeable overlap of the aromatic planes. In comparison, medium-to-weak interactions exhibit rather long centroid–centroid distances (>4.0 Å) together with large slip angles (> $30^{\circ}$ ) and vertical displacements (>2.0 Å) (Janiak,

2000; Yang *et al.*, 2005; Dorn *et al.*, 2005). A chain is formed due to these  $\pi$ - $\pi$  interactions and the supramolecular aggregation is controlled by a combination of C13-H13···O3(1-x,  $-\frac{1}{2} + y, \frac{1}{2} - z$ ) hydrogen bonding between the phenyl ring of the benzoylamine group and the carbonyl atom of the amide group, and C24-H24B···O5(-x, 2 - y, 1 - z) hydrogen bonds between the methyl and one of the methoxy groups (Fig. 2 and Table 1).

In contrast with (Ia), where the amide group has a suitable hydrogen-bond acceptor in the ortho position, compound (IIa) has the closest suitable hydrogen-bond acceptor at the meta position and hence, due to this large separation, an intramolecular interaction is not possible (Fig. 3). Indeed, the crystal structure of (IIa) contains centrosymmetric hydrogenbonded dimers facilitated by N1-H2···O2(-x, 1-y, 1-z) interactions involving the amide and benzoyl groups of adjacent molecules. The dimers can be described by the graph-set motif  $R_2^2(14)$  (Table 2). This dimeric structure is further stabilized by a medium-strong  $\pi$ - $\pi$  interaction between two parallel C1-C6 rings (centroid Cg1) of two adjacent molecules, with a  $Cg1\cdots Cg1(-x, 1 - y, 1 - z)$  centroid-to-centroid distance of 3.8081 (13) Å, a perpendicular distance from the centroid of one ring to the plane of the other of 3.4212 (8) Å and a slippage between the centroids of 1.672 Å (Fig. 4). Intermolecular hydrogen bonding is associated with a large twist of the benzamide and benzoyl groups out of the C1-C6 plane, with torsion angles  $C10-N1-C3-C4 = 70.6 (3)^{\circ}$  and  $C6-C5-C17-O2 = -37.5 (3)^{\circ}$ . We found no similar sandwich-like dimers with a benzamide group. Dimers with nearly coplanar molecules are present in 3-(acetylamino)benzoic acid (Hansen et al., 2007) and are further hydrogen bonded via the carboxyl group. The vast majority of compounds containing a benzamide group form infinite hydrogen-bonded chains or layers. There is great variability in the observed twist angles between the planes of the benzene ring and the benzamide group in the known examples, with values up to  $60^{\circ}$  (see, for example, Adams et al., 2001; Nimmanpipug et al., 2002; Saeed et al., 2009).

Compound (IIa) has an additional ethenyl group with preserved Z geometry around the double bond. This ethenyl group is conjugated with the C1–C6 benzene ring but deviates from coplanarity by  $16.19 (15)^{\circ}$ . In the related compounds (Z)-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenoic acid (Langer et al., 2004) and trichloro(pentamethylcyclopentadienyl)(tetrahydrofuran)(p-tolylethenoxy)tantalum (Meyer et al., 1990), somewhat smaller deviations of 0.15 and 6.7°, respectively, were observed. Larger deviations in the range 20–25.9° can be found in, for example, (Z)-1-chloro-2-(p-tolyl)ethenyl benzoate (Bejot et al., 2005) and 2-phenyl-1-(1-acetoxy-2-phenylethenyl)cyclopropane (Miki et al., 2003). Even larger deviations from planarity would disable the conjugation of the ethenyl group with the benzene ring, as observed in methyl (2E)-(4-methoxyphenyl)(1,3-oxazolidin-2ylidene)ethanoate (Beccalli et al., 1997) and (E)-methyl 2-[2-(6-chloropyrimidin-4-yloxy)phenyl]-3-methoxyacrylate (Ma et al., 2007), with torsion angles of 48.7 and 71.6°, respectively. In both cases, the large torsion angles are caused by the presence



#### Figure 4

A packing diagram for (II*a*). Dashed lines indicate  $\pi$ - $\pi$  interactions and hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

of sterically demanding groups, either on the ethenyl group, as in the former compound, or on the benzene ring in the *ortho* position to the ethenyl group, as in the latter case.

Dimers of (II*a*) are connected into a chain by weak C14– H14...Cg3(-x, 1 – y, -z) interactions (Cg3 is the centroid of the C18–C23 ring) (Fig. 4 and Table 2). These interactions have an influence on the O2–C17–C18–C23 torsion angle, which is -28.3 (3)°, leading to a twist of 61.22 (12)° between the planes of benzene rings C1–C6 and C18–C23. No additional  $\pi$ - $\pi$  interactions were found in the crystal structure of (II*a*).

## **Experimental**

For the preparation of (Ia) (Kranjc & Kočevar, 2005), a mixture of N-[5-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-2H-pyran-3-yl]benzamide (365 mg, 1 mmol) and methyl propiolate (168 mg, 2 mmol) in xylene (3 ml) was heated under reflux for 16.5 h. The volatile components were removed under reduced pressure and the residue was treated with cold methanol (2–3 ml). The precipitated material was filtered off, washed with cold methanol (1–2 ml) and recrystallized from methanol (m.p. 458.5–461 K).

For the preparation of (II*a*) (Kranjc & Kočevar, 2008), a mixture of N-(5-benzoyl-6-methyl-2-oxo-2*H*-pyran-3-yl)benzamide (667 mg, 2 mmol) and (*Z*)-1-methoxybut-1-en-3-yne (50% solution in MeOH) (656 mg, 8 mmol) in toluene (3 ml) was irradiated in a closed vial in a focused microwave apparatus (Discover by CEM, Matthews, North Carolina, USA) for 45 min. The final temperature was set at 423 K, the power at 120 W and the ramp time at 5 min. The volatile components were removed under reduced pressure, and the remaining solid was treated with methanol (1.5 ml) and cooled. The precipitated material was filtered off, washed with cold methanol (1 ml) and recrystallized from methanol (m.p. 447–449 K).

#### Compound (Ia)

Crystal data

C<sub>24</sub>H<sub>23</sub>NO<sub>5</sub>  $M_r = 405.43$ Monoclinic,  $P2_1/c$  a = 7.6516 (1) Å b = 14.7810 (3) Å c = 17.8063 (4) Å  $\beta = 95.8175$  (8)°

#### Data collection

Nonius KappaCCD area-detector diffractometer Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)  $T_{\rm min} = 0.981, T_{\rm max} = 0.981$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$  $wR(F^2) = 0.126$ S = 1.024566 reflections

#### Compound (IIa)

#### Crystal data

 $\begin{array}{l} {\rm C}_{24}{\rm H}_{21}{\rm NO}_{3} \\ M_{r} = 371.42 \\ {\rm Triclinic}, \ P\overline{1} \\ a = 9.6722 \ (2) \ {\rm \AA} \\ b = 10.0140 \ (2) \ {\rm \AA} \\ c = 11.5677 \ (3) \ {\rm \AA} \\ \alpha = 71.422 \ (1)^{\circ} \\ \beta = 84.479 \ (1)^{\circ} \end{array}$ 

#### Data collection

Nonius KappaCCD area-detector diffractometer Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)  $T_{\rm min} = 0.984, T_{\rm max} = 0.993$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.062$  $wR(F^2) = 0.155$ S = 1.034442 reflections  $V = 2003.49 (7) Å^{3}$ Z = 4 Mo K\alpha radiation \mu = 0.09 mm^{-1} T = 293 K 0.2 \times 0.2 \times 0.2 mm

8696 measured reflections 4566 independent reflections 3167 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.033$ 

275 parameters H-atom parameters constrained 
$$\begin{split} &\Delta\rho_{max}=0.18~\text{e}~\text{\AA}^{-3}\\ &\Delta\rho_{min}=-0.17~\text{e}~\text{\AA}^{-3} \end{split}$$

 $\gamma = 67.753 (1)^{\circ}$   $V = 982.60 (4) \text{ Å}^{3}$  Z = 2Mo K\alpha radiation  $\mu = 0.08 \text{ mm}^{-1}$  T = 293 K $0.2 \times 0.2 \times 0.08 \text{ mm}$ 

6912 measured reflections 4442 independent reflections 2768 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.030$ 

 $\begin{array}{l} 255 \text{ parameters} \\ \text{H-atom parameters constrained} \\ \Delta \rho_{\text{max}} = 0.21 \text{ e } \text{ Å}^{-3} \\ \Delta \rho_{\text{min}} = -0.20 \text{ e } \text{ Å}^{-3} \end{array}$ 

## Table 1

Hydrogen-bond geometry (Å, °) for (Ia).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$	
N1-H2···O1	0.95	1.83	2.6741 (17)	146	
C13-H13···O3 <sup>i</sup>	0.93	2.53	3.450 (2)	172	
$C24 - H24B \cdots O5^{ii}$	0.96	2.57	3.420 (2)	148	

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

#### Table 2

Hydrogen-bond geometry (Å,  $^{\circ}$ ) for (IIa).

Cg3	is	the	centroid	of	the	C18-	C23	ring
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$D - H \cdots A$	$D-{\rm H}$	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$N1 - H2 \cdots O2^{i}$	0.82	2.27	3.021 (2)	153
C14 - H14 \cdots Cg3^{ii}	0.93	2.99	3.820 (4)	150

Symmetry codes: (i) -x, -y + 1, -z + 1; (ii) -x, -y + 1, -z.

All H atoms were initially located in difference Fourier maps. H atoms bonded to C atoms were subsequently treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic and alkenyl) or 0.98 Å (CH<sub>3</sub>), and with  $U_{iso}(H) = kU_{eq}(C)$ , where k = 1.5 for methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms. H atoms bonded to N atoms were treated as riding, with  $U_{iso}(H) = 1.5U_{eq}(N)$ .

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3044). Services for accessing these data are described at the back of the journal.

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