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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.110
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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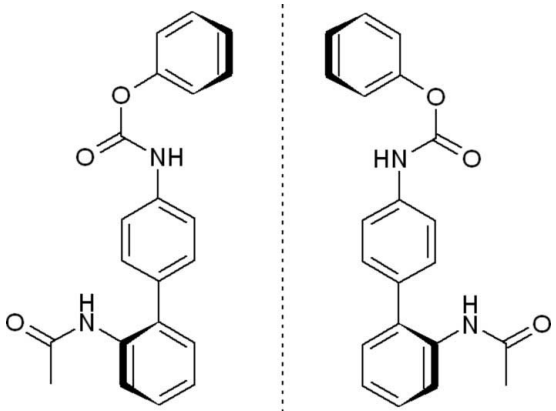
The crystal structure of the title compound, $C_{21}H_{18}N_2O_3$, reveals an interesting case of axial conformational chirality. Due to the symmetry requirements of the space group ($P2_1/n$), conformational stereoisomers of both *P* and *M* helicity are present.

Comment

The crystal structure of the title biphenyl compound, (I), is reported here. Various types of heterocyclic compounds can be prepared via the use of biphenyl precursors. In our study, compound (I) is a key intermediate for the synthesis of a novel class of phenanthridinium derivatives with potentially high biological activity (Radić Stojković *et al.*, 2006). The structure elucidation of these compounds, including that of this biphenyl intermediate, is of great importance for understanding the molecular mechanisms of their biological activities.



(I)-*M* (I)-*P*

Compound (I) is axially chiral due to hindered rotation of the biphenyl system. Rotation of the phenyl ring bound to the ester Osp^3 atom is free in solution, but hindered in the solid state, resulting in two conformational enantiomers (Dodziuk, 1992), as depicted in the scheme. Stereodescriptors *M* and *P* can be assigned to the enantiomers with respect to the rotation around the C8—C9 bond (Fig. 1). According to the CIP (Cahn–Ingold–Prelog) rules (McNaught & Wilkinson, 1997), atom C8 has a higher priority, since it is bound to atom N1. Thus, *P* helicity is defined for the molecule in Fig. 1. Torsion angles describing the *P* conformational enantiomer are listed in Table 1; the biphenyl moieties have (+)- and (−)-synclinal conformations for the *P* and *M* enantiomers, respectively.

A medium-strong N—H···O hydrogen bond (Table 2) links the molecules into infinite chains extending in the [101] direction. The chains, generated by the *n*-glide plane, consist

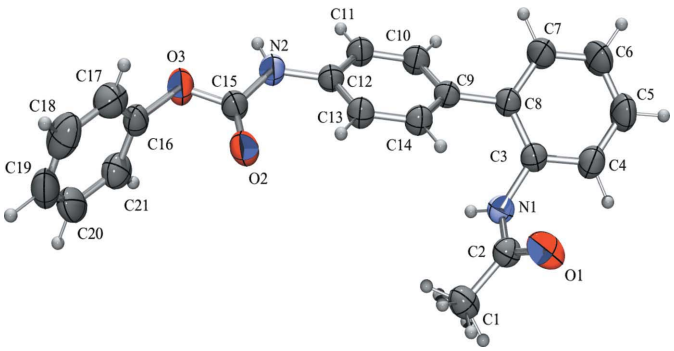


Figure 1
The molecular structure of the *P* conformational enantiomer of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii. Both disorder components of the methyl group C1 are shown.

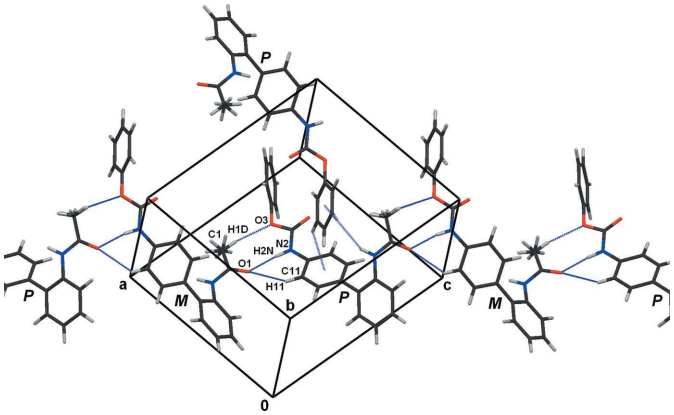


Figure 2
A hydrogen-bonded chain of (I), extending in the [101] direction. Hydrogen bonds are indicated by dashed lines. The helicity of each molecule is indicated. One C—H···π interaction is also shown.

of alternating *M* and *P* molecules (Fig. 2) related by inversion centres. However, another strong H-atom donor, N1—H1N, uses none of the potential acceptors (two carbonyl O atoms and one ester Osp^3 atom), but is involved in an unusual N—H···π interaction with the C16–C21 phenyl ring. The N1—H1N group is directed towards atom C19^{v}, the N···C distance being 3.505 (4) Å [symmetry operator: (v) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$]. There is also a C—H···π interaction between atom C18 and a symmetry-related C9–C14 benzene ring, shown in Fig. 2; the distance between C18 and the ring centroid is 3.581 (6) Å. The hydrogen-bonded chains are cross-linked into a three-dimensional network by four weak C—H···O hydrogen bonds (Table 2).

Experimental

The title compound was prepared by the modified method of Bergmann & Zervas (1932), according to the procedures of Takamiya *et al.* (1978), Berkowitz & Pedersen (1994), Salvatore *et al.* (2001), Toth *et al.* (2005) and Woll *et al.* (2002). *N*,*N*-Dimethylaniline (1.150 ml, 1.1 g, 9.07 mmol) was added to a stirred solution of 4′-aminobiphenyl-2-yl-acetamide (1.14 g, 5.04 mmol) in anhydrous ethanol (25 ml). To this, a solution of phenyl chloroformate [924.7 (1) µl, 947 mg, 6.05 mmol] in ethanol (2 ml) was added slowly and the reaction mixture was refluxed for 2 h. The solvent was then evaporated from the reaction mixture. The reaction mixture was dissolved in ethyl acetate (20 ml), washed with water (2 × 20 ml) and concentrated to a solid under reduced pressure. The product was purified by recrystallisation from dichloromethane–petroleum ether (10:1 *v*/*v*) to give 1.51 g of slightly brown crystals of (I) (yield 86%; m.p. 456 K). Crystals of (I) suitable for diffraction analysis were obtained by dissolving the compound (ca 15 mg) in a minimal volume of hot methanol. The vial was sealed with Parafilm, placed in a refrigerator (283 K) and the solvent allowed to evaporate slowly until crystals of suitable quality were observed.

Crystal data

$C_{21}H_{18}N_2O_3$
M_r = 346.37
Monoclinic, $P2_1/n$
a = 11.260 (13) Å
b = 12.74 (2) Å
c = 12.81 (2) Å
β = 100.76 (13)°
V = 1805 (5) Å^3
Z = 4
D_x = 1.275 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 0.7 mm^{-1}
T = 293 (2) K
Prism, colourless
0.32 × 0.3 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
non–profiled $\omega/2\theta$ scans
Absorption correction: none
7498 measured reflections
3756 independent reflections
2854 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 76.5°
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.110
S = 1.02
3756 reflections
296 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.2871P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0032 (4)

Table 1
Selected torsion angles (°).

C9—C8—C3—N1	6.5 (2)	C15—N2—C12—C11	159.5 (2)
C10—C9—C8—C3	−135.2 (2)	C15—O3—C16—C17	93.9 (2)
C12—N2—C15—O3	−176.1 (1)	N2—C15—O3—C16	−178.2 (1)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···O1^{i}	0.91 (2)	1.96 (2)	2.855 (5)	169 (2)
C1—H1D···O3^{ii}	0.96	2.39	3.328 (6)	166
C4—H4···O2^{iii}	0.98 (2)	2.57 (2)	3.434 (6)	147 (1)
C10—H10···O2^{iv}	0.99 (2)	2.35 (2)	3.318 (6)	164 (1)
C11—H11···O1^{i}	0.97 (2)	2.65 (2)	3.410 (6)	136 (1)

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

The H atoms bound to atom C1 were modelled as a disordered methyl group, with C—H = 0.96 Å, U_{iso}(H) = 1.5U_{eq}(C) and occupancy factors of 0.5, while all other H atoms were located in a difference electron-density map and refined freely.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *PLATON* (Spek, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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