3-Amino-4'-methyl-5-ethylbiphenyl-2,4-dicarbonitrile and 3-amino-4'-(N,N-diethylamino)-5-ethylbiphenyl-2,4-dicarbonitrile

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In the title compounds, $C_{17}H_{15}N_3$ and $C_{20}H_{22}N_4$, the methyl derivative crystallizes with two molecules in the asymmetric unit, while the N,N-diethylamino derivative crystallizes with one molecule per asymmetric unit. The biphenyl twist angle for both molecular structures is approximately 45°. The molecular packing is stabilized by N—H···N hydrogen bonds.

Comment

Biphenyl derivatives have been extensively studied in the past with respect to the difference in the torsion angle between the aromatic rings, which determines the photophysical, biological and laser activities (Shukla et al., 1985; Nieger et al., 1998). The laser activity of a biphenyl compound can be enhanced by bulkier substitutions on the phenyl rings which cause deviations from coplanarity. The π-electron delocalization along the biphenyl unit will be at a maximum in a coplanar arrangement of the biphenyls (Nieger et al., 1998). Apart from the photophysical properties, biphenyl compounds are of great importance due to the activity of these molecules with regard to the central nervous system (Reboul et al., 1993). Certain fluoro-substituted biphenyl derivatives have greater affinities to
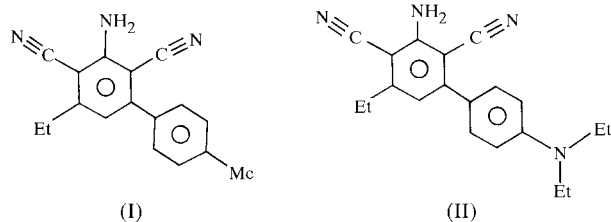
certain receptor proteins (Mckinney & Singh, 1988). The present study is part of a series of investigations on the crystal structures of biphenyl derivatives.

Compound (I) contains two molecules in the asymmetric unit, designated (IA) and (IB) (Fig. 1), and compound (II) contains one molecule per asymmetric unit (Fig. 2). The dihedral angles between the phenyl rings are 44.1 (1) and 46.7 (1)° for (IA) and (IB), respectively, and 42.1 (1)° for (II). The twisting of these rings is described by the following inter-ring torsion angles: C6A—C1A—C1A'—C6A' = −40.5 (3)° and C6B—C1B—C1B'—C6B' = −42.9 (3)° for (I); C6—C1—C1'—C6' = 43.8 (3)° for (II). The values of the torsion angles C2'—C1A'—C1A—C6A [136.7 (2)°] and C2B'—C1B'—C1B—C6B [135.0 (2)°] in (I), and C2'—C1'—C1—C6 [−131.4 (2)°] in (II) indicate that the conformation of molecules (IA) and (IB) is (+)-anticlinal and that of (II) is (−)-anticlinal. Atom C7 deviates from the mean plane of the attached phenyl ring by −0.050 (2) Å in (IA), −0.105 (3) Å in (IB) and 0.158 (2) Å in (II). The bond lengths and angles for compounds (I) and (II) are listed in Tables 1 and 3, respectively. The triple-bond distances N3—C8 and C7—N2 agree with the literature values [1.138 (7) Å; Allen et al., 1986]. The bond angles around C8 and C7 agree with the triple-bond character of C8—N3 and C7—N2 (sp hybridization). The ring–ring bond distances which connect the two phenyl rings are comparable with reported values [1.487 (7) Å; Allen et al., 1986]. The ethyl substituents in (I) and (II) are twisted out of the plane of the attached ring, as evidenced by the C6—C5—C9—C10 torsion angles. This angle has values of 33.2 (6)° and 96.6 (3)° for (IA) and (IB), respectively, and 94.5 (3)° for (II). The diethyl substituent in (II) is completely staggered. The sum of the angles around N4 in compound (II) is 360° and is indicative of the sp^2 hybridization.

The inter-ring bond distance in unsubstituted biphenyl is 1.507 Å (Trotter, 1961). The inter-ring bond distances C1A—C1A' and C1B—C1B' in (I), and C1—C1' in (II) are 1.485 (3), 1.484 (3) and 1.480 (3) Å, respectively. These values agree well with those of related structures found in polychlorinated biphenyl [1.485 (6) Å; Mckinney & Singh, 1981] and 2-fluorobiphenyl [1.483 (4) Å; Rajnikant et al., 1995], and with the theoretically calculated value of 1.488 Å between two sp^2-hybridized C atoms (Dewar & Schmeizing, 1968).

Apart from normal van der Waals interactions, the packing of the crystal is stabilized by intermolecular N—H···N hydrogen bonds. The hydrogen-bonding geometries for (I) and (II) are given in Tables 2 and 4, respectively. In both structures, the N atom of the cyano group participates in the hydrogen-bonded interaction as an acceptor atom. All N—H···N interactions have distances less than the sum of their van der Waals radii (Bondi, 1964). The molecular packing arrangement in compound (I) down the a axis is characterized by an intermolecular N—H···N hydrogen bond between (IA) and (IB), with an N1B···N3A distance of 3.166 (3) Å, and two N—H···N intermolecular interactions with the molecules related by inversion, having donor–acceptor distances of 3.228 (3) and 3.157 (3) Å. It is a layered structure, with the layers parallel to the bc plane. In compound (II), the crystal packing is stabilized by two intermolecular hydrogen bonds: N1···N2ⁱ = 3.259 (2) and N1···N3ⁱⁱ = 3.006 (2) Å [symmetry codes: (i) $2 − x, \frac{1}{2} + y, \frac{1}{2} − z$; (ii) $2 − x, −\frac{1}{2} + y, \frac{1}{2} − z$.] Each
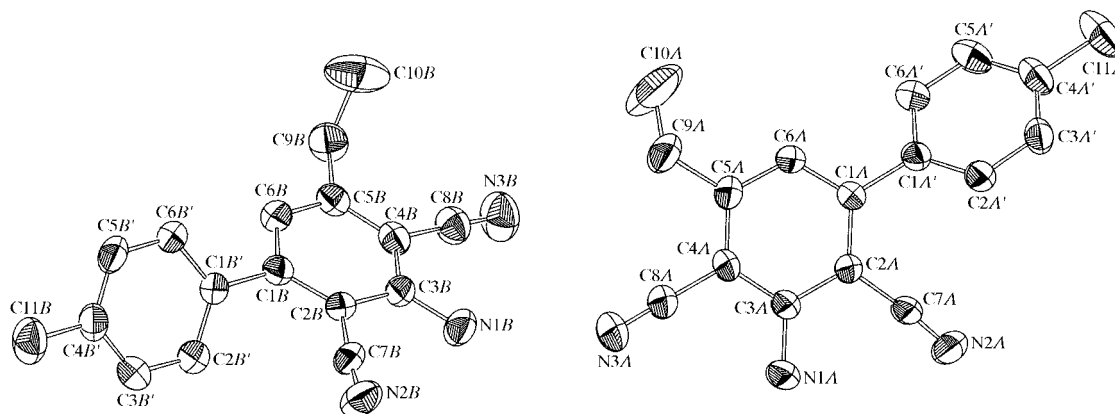
Figure 1
The molecular structure of compound (I) with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.
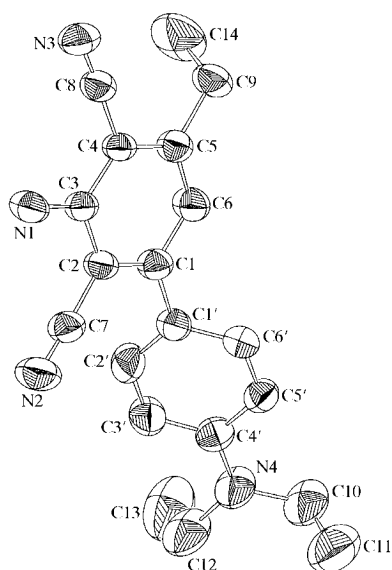

Figure 2
The molecular structure of compound (II) with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

molecule mutually donates and accepts two H atoms with symmetry-related molecules.

Experimental

The title compounds were synthesized as follows: a mixture of 5-(4-methylphenyl)pent-4-en-3-one (1.0 g, 5.74 mmol), malononitrile (0.76 g, 11.51 mmol) and a catalytic amount of pyrrolidine in ethanol (20 ml) for compound (I) and a mixture of 5-(4-diethylamino-phenyl)pent-4-en-3-one (1.0 g, 4.6 mmol), malononitrile (0.29 g, 4.39 mmol) and a catalytic amount of pyrrolidine in ethanol (20 ml) for compound (II) were used as starting materials. The mixtures were heated under reflux for 7 h, concentrated under reduced pressure and purified by column chromatography over silica gel. Elution with a petroleum ether–benzene (1:5) mixture gave the products as yellow solids. The compounds were dissolved in ethyl acetate containing a few drops of hexane. Slow evaporation of the solvent at room temperature produced crystals from which experimental samples were obtained.

Compound (I)

Crystal data

$C_{17}H_{15}N_3$
$M_r = 261.32$
Monoclinic, $P2_1/c$
$a = 7.8579 (1)$ Å
$b = 23.7627 (5)$ Å
$c = 15.3423 (2)$ Å
$\beta = 94.765 (1)°$
$V = 2854.89 (8)$ Å^3
$Z = 8$

$D_x = 1.216$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192
    reflections
$\theta = 1.45–28.33°$
$\mu = 0.074$ mm^{-1}
$T = 293 (2)$ K
Rectangular, pale yellow
$0.30 \times 0.24 \times 0.14$ mm

Data collection

Siemens SMART CCD area-
    detector diffractometer
ω scans
Absorption correction: empirical
    (*SADABS*; Sheldrick, 1996)
    $T_{min} = 0.978$, $T_{max} = 0.99$
19 861 measured reflections
6961 independent reflections

3077 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 28.31°$
$h = -10 \rightarrow 10$
$k = -31 \rightarrow 31$
$l = -10 \rightarrow 20$
Intensity decay: <2%

Table 1
Selected geometric parameters (Å, °) for (I).

N1A—C3A	1.360 (3)	N1B—C3B	1.363 (3)
N2A—C7A	1.146 (3)	N2B—C7B	1.140 (3)
N3A—C8A	1.141 (3)	N3B—C8B	1.143 (3)
C1A′—C1A	1.485 (3)	C1B′—C1B	1.484 (3)
N2A—C7A—C2A	174.7 (2)	N2B—C7B—C2B	174.8 (3)
N3A—C8A—C4A	179.0 (3)	N3B—C8B—C4B	178.6 (3)
C2A′—C1A′—C1A—C6A	136.7 (2)	C6B′—C1B′—C1B—C6B	−42.9 (3)
C6A′—C1A′—C1A—C6A	−40.5 (3)	C2B′—C1B′—C1B—C6B	135.0 (2)

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

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1B—H1B1$\cdots$N3A	0.86	2.37	3.166 (3)	154
N1A—H1A1$\cdots$N3A^i	0.86	2.52	3.228 (3)	140
N1A—H1A2$\cdots$N1B^i	0.86	2.58	3.157 (3)	126

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.067$

$wR(F^2) = 0.173$

$S = 0.970$

6961 reflections

365 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.0465P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.32$ e Å^{-3}

$\Delta\rho_{min} = -0.30$ e Å^{-3}

Extinction correction: *SHELXL*97 (Sheldrick, 1997)

Compound (II)

Crystal data

$C_{20}H_{22}N_4$

$M_r = 318.42$

Monoclinic, $P2_1/c$

$a = 10.8918 (2)$ Å

$b = 10.3458 (2)$ Å

$c = 16.5707 (2)$ Å

$\beta = 101.496 (1)°$

$V = 1829.80 (5)$ Å^3

$Z = 4$

$D_x = 1.156$ Mg m^{-3}

Mo $K\alpha$ radiation

Cell parameters from 5488 reflections

$\theta = 1.83–28.58°$

$\mu = 0.070$ mm^{-1}

$T = 293 (2)$ K

Rectangular, pale yellow

$0.40 \times 0.26 \times 0.14$ mm

Data collection

Siemens SMART CCD area-detector diffractometer

ω scans

Absorption correction: empirical (*SADABS*; Sheldrick, 1996)

$T_{min} = 0.972$, $T_{max} = 0.990$

12 556 measured reflections

4478 independent reflections

2122 reflections with $I > 2\sigma(I)$

$R_{int} = 0.079$

$\theta_{max} = 28.36°$

$h = -14 \rightarrow 12$

$k = -7 \rightarrow 13$

$l = -21 \rightarrow 22$

Intensity decay < 2%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.145$

$S = 1.000$

4478 reflections

221 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0430P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.23$ e Å^{-3}

$\Delta\rho_{min} = -0.23$ e Å^{-3}

Extinction correction: *SHELXL*97 (Sheldrick, 1997)

Extinction coefficient: 0.0115 (15)

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C3	1.349 (2)	N4—C12	1.467 (3)
N2—C7	1.141 (2)	N4—C10	1.459 (3)
N3—C8	1.140 (2)	C1'—C1	1.480 (3)
N4—C4'	1.379 (2)		
C4'—N4—C12	122.08 (18)	N2—C7—C2	175.8 (2)
C4'—N4—C10	121.39 (18)	N3—C8—C4	177.7 (2)
C12—N4—C10	116.51 (18)		
C6'—C1'—C1—C6	43.8 (3)	C2'—C1'—C1—C6	−131.4 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N2^i	0.86	2.45	3.259 (2)	158
N1—H1B···N3^{ii}	0.86	2.21	3.006 (2)	154

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

In both compounds, all H atoms were fixed geometrically and allowed to ride on the corresponding non-H atoms, with C—H = 0.96 Å and $U_{iso} = 1.5U_{eq}$ and $1.2U_{eq}$ for methyl and other H atoms, respectively.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1022). Services for accessing these data are described at the back of the journal.

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