

Octasubstituted biphenylenes: is there a favoured conformation?

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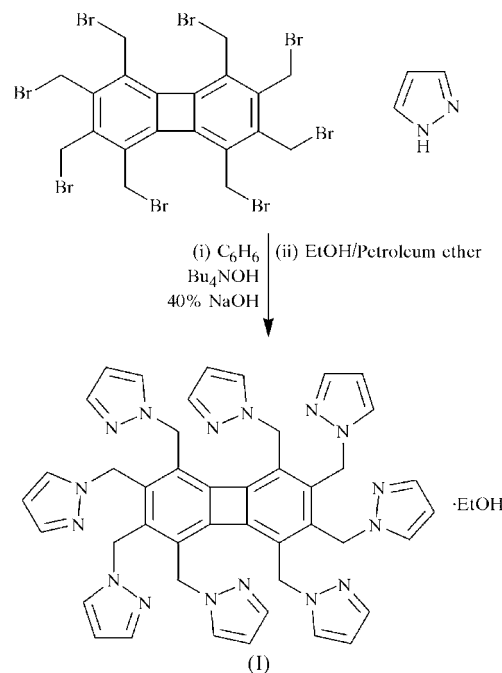
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Octakis(pyrazol-1-ylmethyl)biphenylene ethanol solvate, $C_{44}H_{40}N_{16} \cdot C_2H_6O$, has two independent centrosymmetric molecules, one of which is hydrogen bonded to the solvent molecule. One molecule adopts an arrangement with three arms up and one down in each benzene ring, whilst the other molecule has a conformation with two adjacent arms on the same side of the ring. In neither case is the expected fully alternating form observed.

Comment

We have long been involved in the synthesis and study of new N-heterocyclic ligands for use in coordination and metallo-supramolecular chemistry (Steel, 2005). In particular, we have prepared a large library of ligands that contain a central arene core to which are appended various heterocycles *via* flexible linker units (McMorran & Steel, 2002; McMorran *et al.*, 2004). In the course of designing new ligands, we have employed the concept of 'pre-organization' (Henrich & Anslyn, 2002). This relies on the principle that six bulky substituents attached to a benzene ring will tend to arrange themselves on alternating faces of the ring in an *ababab* fashion [*a* and *b* being above and below the plane of the ring, respectively, as defined by MacNicol *et al.* (1985)]. For example, hexakis(pyrazol-1-ylmethyl)benzene adopts this conformation (Hartshorn & Steel, 1995). A common extension of this approach is to differentiate the two faces of the ring with differing 1,3,5- and 2,4,6-substituents, as, for example, in 1,3,5-triethyl-2,4,6-tris-(pyrazol-1-ylmethyl)benzene (Hartshorn & Steel, 1997). We were interested to know whether this design concept could be extended to larger aromatic systems, such as biphenylenes. The X-ray crystal structure of octaethylbiphenylene revealed that this compound adopts an *ababbaba* conformation in the solid state rather than the fully alternating *abababab* conformation that was calculated to be the most stable (Taha *et al.*, 2000; Marks *et al.*, 2003). However, we previously prepared the new eight-armed ligand octakis(2-pyridylsulfanylmethyl)biphenylene and were encouraged to find that in the solid state

it was pre-organized into the fully alternating *abababab* conformation (McMorran & Steel, 2003). We now report the synthesis of octakis(pyrazol-1-ylmethyl)biphenylene and the X-ray crystal structure of its ethanol solvate, (I).



The new ligand octakis(pyrazol-1-ylmethyl)biphenylene was prepared by an eightfold phase-transfer catalyzed alkylation of octakis(bromomethyl)biphenylene with pyrazole. It was purified by chromatography followed by recrystallization and was characterized by microanalysis, 1H NMR spectroscopy and electrospray mass spectrometry. In order to ascertain the conformation of this compound, we sought to determine its X-ray structure. The analysis of (I) reveals that it crystallizes as the ethanol solvate, with two independent half molecules of the ligand in the asymmetric unit. The two independent molecules each lie on crystallographic centres of inversion. Fig. 1 shows a perspective view of the two molecules with unique and attached atoms labelled. The ethanol solvent molecule is hydrogen bonded to pyrazole atom N62 in one molecule of the ligand (Table 2). The planes of the pyrazole rings are inclined to the plane of the adjacent biphenylene unit at angles that range between $67.9(2)$ and $112.8(2)^\circ$. The duplicated pattern of bond lengths and angles within the biphenylene core (see Table 1) also parallels those observed in other structurally characterized octasubstituted biphenylenes (Hubig *et al.*, 2000; Le Magueres *et al.*, 2001*a,b*; Lu *et al.*, 2002). These suggest that there is some bond localization in such molecules.

The two independent molecules have different arrangements of the arms with respect to the biphenylene plane. In the molecule shown in Fig. 1(a), the arms have an *aababbab* arrangement (C1–C4), whereas in the molecule shown in Fig. 1(b), the arms have an *abbabaab* arrangement (C1'–C4'). Thus, in neither case do the arms adopt the fully alternating form that might be expected to be energetically most favourable. Fig. 2 shows an overlay of the two independent

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molecules and serves to show that within each benzene ring, two arms have very similar orientations, one shows a significant twisting in the orientation of the pyrazole ring and the fourth arm exists on opposite sides of the central plane.

Since all four octasubstituted biphenylenes have different relative orientations of the substituents it appears that the answer to the title question is that there is a much lower preference for the fully alternating conformation in these derivatives than in the benzene analogues. We do not believe that the conformations of the two independent molecules are strongly influenced by crystal packing. The molecule with the unusual *aababbab* arrangement (see discussion below) is not involved in the hydrogen bond mentioned above. Apart from this hydrogen bond, the shortest intermolecular contact is between atoms N82 and H74 of adjacent molecules related by a centre of inversion. This distance is 2.453 (3) Å, which is not

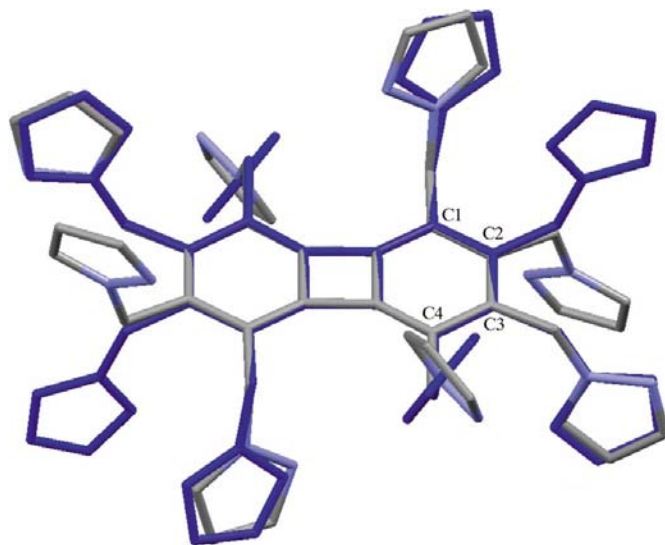


Figure 2

An overlay of the two independent molecules, with selected labels relating to Fig. 1. The darker (blue in the electronic version of the paper) single colour atoms represent the Fig. 1(a) (unprimed atoms) molecule.

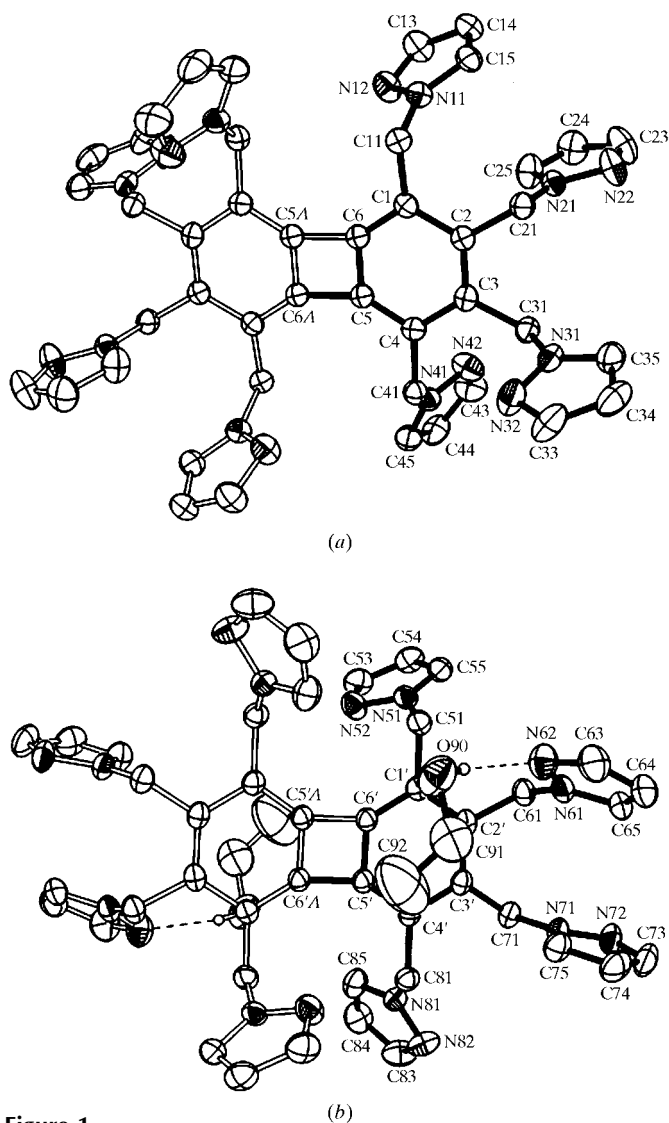


Figure 1

Perspective views of the two independent centrosymmetric molecules. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent hydrogen bonds. H atoms have been omitted, except for that of the solvent OH group.

unusually short (Mascal, 1998). In order to gain more insight into the reasons for this lack of conformational preference, we carried out a search of the Cambridge Structural Database (CSD; Version 5.28, update of January 2007; Allen, 2002) to survey the conformations of octasubstituted naphthalenes which represent a closer analogy to the biphenylenes. Table 3 lists the conformational arrangements of substituents in octasubstituted biphenylenes and naphthalenes. From this it can be seen that octakis(bromomethyl)naphthalene is the only naphthalene derivative that has the fully alternating arrangement. Table 3 also shows that in all but two examples each ring has two *a* arms and two *b* arms. Furthermore, in all cases the substituents in adjacent *peri* positions (analogous to C1 and C4 in Fig. 2, but conventionally labelled C1/C8 and C4/C5 for naphthalenes) are on opposite sides of the central plane. This is a well known effect that reduces *syn-peri* steric effects (Marks *et al.*, 2003). Such an effect is certain to be much less important in the biphenylenes than in the naphthalenes. We believe that an important reason for the scarcity of the fully alternating form in the octasubstituted biphenylenes and naphthalenes is that, unlike the hexasubstituted benzenes, this orientation is not centrosymmetric, a situation that minimizes dipole moments.

Experimental

Octakis(bromomethyl)biphenylene (120 mg, 0.134 mmol), pyrazole (83 mg, 1.22 mmol), benzene (15 ml), 40% aqueous KOH (3 ml) and 40% aqueous Bu₄NOH (2 drops) were refluxed together for 18 h. After cooling, water (10 ml) and ethyl acetate (20 ml) were added, the layers separated, and the aqueous layer washed with ethyl acetate (2 × 20 ml). The combined organic fractions were washed with brine (10 ml) and dried over MgSO₄. The solvents were evaporated to give a brown oil which was purified on a silica-gel column [ethyl acetate/petroleum ether (50–70) 1:1]. Recrystallization from ethanol/petroleum ether (50–70) gave the product as yellow crystals (yield 54 mg, 51%).

Crystal data

C₄₄H₄₀N₁₆·C₂H₆O
M_r = 838.99
 Triclinic, *P* $\bar{1}$
a = 12.937 (5) Å
b = 13.186 (5) Å
c = 13.815 (6) Å
 α = 87.300 (5)°
 β = 70.756 (5)°

γ = 68.719 (5)°
V = 2066.2 (14) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.09 mm⁻¹
T = 168 (2) K
 0.50 × 0.50 × 0.40 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
T_{min} = 0.870, *T_{max}* = 0.967

24130 measured reflections
 7196 independent reflections
 5180 reflections with *I* > 2σ(*I*)
R_{int} = 0.045

Refinement

R[*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.126
S = 1.03
 7196 reflections
 569 parameters

1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.27 e Å⁻³
 $\Delta\rho_{\min}$ = -0.32 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1—C6	1.367 (3)	C1'—C6'	1.363 (3)
C1—C2	1.424 (3)	C1'—C2'	1.415 (3)
C2—C3	1.383 (3)	C2'—C3'	1.386 (3)
C3—C4	1.426 (3)	C3'—C4'	1.425 (3)
C4—C5	1.367 (3)	C4'—C5'	1.355 (3)
C5—C6	1.387 (3)	C5'—C6'	1.394 (3)
C5—C6 ⁱ	1.507 (3)	C5'—C6' ⁱⁱ	1.499 (3)
N11—C15	1.329 (3)	N51—C55	1.339 (3)
N11—N12	1.348 (2)	N51—N52	1.340 (3)
N21—C25	1.333 (3)	N61—C65	1.322 (3)
N21—N22	1.336 (3)	N61—N62	1.348 (3)
N31—C35	1.334 (3)	N71—N72	1.338 (2)
N31—N32	1.344 (3)	N71—C75	1.341 (3)
N41—C45	1.328 (3)	N81—C85	1.332 (3)
N41—N42	1.343 (3)	N81—N82	1.339 (3)
C6—C1—C2	115.0 (2)	C6'—C1'—C2'	115.0 (2)
C3—C2—C1	121.74 (19)	C3'—C2'—C1'	121.44 (19)
C2—C3—C4	121.86 (19)	C2'—C3'—C4'	122.03 (19)
C5—C4—C3	114.8 (2)	C5'—C4'—C3'	114.9 (2)
C4—C5—C6	123.3 (2)	C4'—C5'—C6'	122.8 (2)
C4—C5—C6 ⁱ	146.7 (2)	C4'—C5'—C6' ⁱⁱ	147.1 (2)
C6—C5—C6 ⁱ	89.97 (17)	C6'—C5'—C6' ⁱⁱ	90.11 (17)
C1—C6—C5	123.1 (2)	C1'—C6'—C5'	123.5 (2)

Symmetry codes: (i) -*x* + 2, -*y* + 1, -*z*; (ii) -*x* + 1, -*y* + 2, -*z* + 1.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O90—H90A...N62	0.84	2.02	2.828 (3)	162

Crystal decay was monitored by the measurement of duplicate reflections and was found to be negligible. The OH hydrogen was located in a difference Fourier synthesis and constrained to that position [*U*_{iso}(H) = 1.5*U*_{eq}(O)]. C-bound H atoms were placed in calculated positions, with C—H distances set at 0.95–0.99 Å, and refined as riding [*U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(C)]. Distinction between atoms N2 and C5 within the pyrazole rings was made on the basis of alternative refinements and the fact that the N1—N2 bonds are longer than the N1—C5 bonds (Table 1).

Table 3

Conformational arrangements of substituents in octasubstituted biphenylenes and naphthalenes.

Substituent	CSD refcode	Conformation (MacNicol <i>et al.</i> , 1985)
Biphenylenes		
Ethyl ^a	CEVDAX	<i>ababbaba</i>
2-Pyridylsulfanylmethyl ^b	UKOZEZ	<i>abababab</i>
Pyrazol-1-ylmethyl	This work	<i>aababbab</i>
	This work	<i>abbabaab</i>
Naphthalenes		
Phenylsulfanyl (yellow form) ^c	BOWWOZ	<i>aabbaabb</i>
Phenylsulfanyl (red form) ^{c,d}	BOWWOZ01	<i>aabbaabb</i>
3-Methylphenylsulfanyl ^e	DEFCAS	<i>aabbaabb</i>
4-Methylphenylsulfanyl ^e	DEFCAIA	<i>abbabaab</i>
4-(2-Phenylprop-2-yl)phenylsulfanyl ^f	FAJDEZ	<i>aaabaaab</i>
3,5-Dimethylphenylsulfanyl ^g	TELXEN	<i>abababba</i>
3,4-Dimethylphenylsulfanyl ^h	TODMAA	<i>aabbaabb</i>
Cyclohexylsulfanyl ⁱ	KOLXAK	<i>abbabaab</i>
Phenylselenyl ^j	JOTHIJ	<i>abaababb</i>
3-Methylphenoxy ^k	JEFDAZ	<i>abbabaab</i>
2-Naphthoxy ^k	JEFCUS	<i>ababbaba</i>
Bromomethyl ^l	WUTRAE	<i>abababab</i>
3,3-Dimethylbut-1-enyl ^m	FEWHIZ	<i>abbabaab</i>

Notes: (a) Taha *et al.* (2000); (b) McMorran & Steel (2003); (c) Barbour *et al.* (1983); (d) Suenaga *et al.* (2003); (e) MacNicol *et al.* (1985); (f) Downing *et al.* (1998); (g) Downing, MacNicol *et al.* (1996); (h) Downing, Frampton *et al.* (1996); (i) MacNicol *et al.* (1991); (j) MacNicol *et al.* (1992); (k) Freer *et al.* (1989); (l) Simaan *et al.* (2003); (m) Stulgies *et al.* (2005).

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3053). Services for accessing these data are described at the back of the journal.

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