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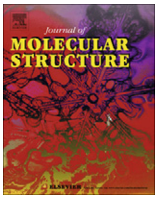

Crystal structures and conformational behavior in solution of two isomeric dicyanobiphenyls

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ABSTRACT

Two dicyanobiphenyls, 3-phenylphtalodinitrile (**1**) and 4-phenylphtalodinitrile (**2**) were synthesized by Pd(II)-catalyzed cyanation of relevant dichlorobiphenyls (PCB5 and PCB12), and their structures were determined by single crystal X-ray diffraction. The dihedral angle between the phenyl rings is equal to 51.50° in *o*-substituted molecule **1** and 30.76° in **2**. To rationalize the conformational differences between two molecules the optimized geometries and potential energy curves (relative energy *vs.* torsion angle) were calculated at the B3LYP/6-31+G(d) level of theory using the PCM solvation model. The electronic properties of substituents were found to affect slightly on the conformational characteristics of the substituted biphenyls in solution.

1. Introduction

The structure of different substituted biphenyls has become an object of research for many scientific groups so far. There are two main reasons for this interest. The first one is the use of the biaryl (and in particular biphenyl) derivatives as liquid crystals and electro-optical materials [1]. The macroscopic electro-optic activity of organic materials depends upon the molecular hyperpolarizability of individual organic chromophores and noncentrosymmetric order of the chromophores in a hardened polymer lattice [1c]. It is evident that these properties strongly depend on spatial structure of biphenyls and their geometric parameters in the crystals [1a,2]. The other aspect of interest is the study on polychlorinated biphenyls (PCBs) as pollutants. Being a major class of man-made persistent organic pollutants these compounds are of environmental and health concern due to their toxicity and resistance to biodegradation [3,4]. With the aim to understand how the pattern and degree of chlorination influence the properties of PCBs, the numerous computational studies on biphenyl and all the chlorinated biphenyls (from 1 to 10 chlorine atoms, 209 congeners) have been undertaken [5]. The dihedral angle between the benzene rings in biphenyls was found to be one of the most important parameters that influence the toxicity of PCBs. For example, Chana et al. reported that the toxic congeners possess conformations with low dipole moments, a fact that may be linked to the ready accumulation on the adipose tissue [5h]. Also the dihedral angle is important in chemical reprocessing of PCBs into environmentally safe products. Among the others we demonstrated that PCBs undergo catalytic carbonylation under mild conditions in the presence of cobalt carbonyl catalyst modified by epoxy derivatives [6] and the congener's structure drastically influences on its reactivity and selectivity [7].

It has been shown [8] that the dihedral angle between the planes of benzene rings in the biphenyl derivatives depends on the steric properties of substituents. At the same time, the influence of the electronic factors on this parameter has not been systematically studied (excluding cases when the substituents strongly conjugate to each other [1a,2]). Therefore, we investigated the structure and conformational behavior of two dicyanobiphenyls, 3-phenylphtalodinitrile (**1**) and 4-phenylphtalodinitrile (**2**) (Scheme 1).

These compounds were chosen as research objects because the cyano-group has a significant electronic effect, while possessing relatively small volume. This combination of properties seems to be interesting from the viewpoint of the substituents influence on structure and conformational properties of biphenyl derivatives. Moreover, the crystal structures for these two compounds have not been reported so far.

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2. Experimental

2.1. Synthesis

Compounds **1** and **2** were synthesized via Pd(II)-catalyzed cyanation of relevant dichlorobiphenyls (PCB5 and PCB12) as reported in [9].

2.2. General procedure

Under inert conditions Na_2CO_3 (10 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (4.2 mmol), the corresponding dichlorobiphenyl (2.0 mmol), and DMF (5.0 mL) were placed into a Schlenk flask. Then degassed solution of $Pd(OAc)_2$ (0.09 mmol) and PPh3 (0.3 mmol) in DMF (2.0 mL) was added. The flask was heated at 130 °C for 20 h. After cooling to room temperature dichloromethane (2 mL) and *n*-hexane (2 mL) were added, the reaction mixture was washed with water and the organic phase was dried over Na_2SO_4. After evaporation of the solvents the residue is subjected to column chromatography (silica, hexane–ethyl acetate). (**1**): m. p. 136–137 °C (lit. [10] 137–138 °C); (2): m. p. 158–159 °C (lit. [11] 156–157 °C).

2.3. X-ray study

X-ray data for **1** and **2** were collected at 100 K with Bruker APEX-II CCD diffractometer by φ and ω-scan mode using Mo Kα radiation (λ = 0.71073 Å). No absorption correction was applied to the experimental diffraction data. Structures were solved by direct methods with *SHELXS*–97 and refined by full–matrix least–squares methods on F^2 with *SHELXL*–97 [12]. All H atoms were placed in idealized positions and refined with constrained C–H distances and *U*iso(H) values set to 1.2*U*eq of the attached C atom. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Numbers CCDC 812947 and 812948. Copies of these data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Crystal data and details on the structure refinement are given in Table 1. The geometric parameters for **1**–**2** are given in Table 1S in Supporting Information.

2.4. Computational details

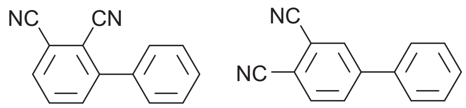
All computations were performed by using *GAUSSIAN 2003* programs at the B3LYP/6-31+G(d) level of theory [13]. The DFT approach was found to give reliable values of torsional barriers of PCBs [8d]. **1** and **2** alongside with the parent PCB5 and PCB12 were optimized by using Becke's three-parameter hybrid density functional, which includes a mixture of Hartree–Fock exchange and DFT exchange correlation. Potential energy curves (PEC) (relative energy *vs.* torsion angle θ from $\theta = 0$ to $\theta = 180°$ in step of 10°) were calculated. Frequency calculations show that all estimated PEC minima have no imagine frequencies and therefore are actual minima on potential energy surface. The all PEC maxima are *bona fide* transition states because all of them have only one imagine frequency, and the normal coordinate of this imagine frequency vibration corresponds to torsion angle deformation in all cases.

3. Results and discussion

Compounds **1** and **2** were synthesized by Pd(II)-catalyzed cyanation of relevant dichlorobiphenyls (Scheme 2):

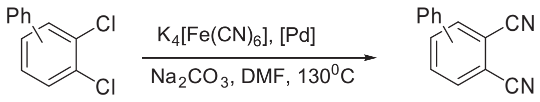
Table 1
Crystal data and structure refinement parameters for **1** and **2**.

Compound	1	2
Empirical formula	$C_{14}H_8N_2$	$C_{14}H_8N_2$
Formula weight	204.22	204.22
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pbca
Unit cell dimensions		
a (Å)	10.8588(6)	12.597(2)
b (Å)	7.6967(4)	7.3386(11)
c (Å)	12.3246(7)	22.785(3)
β (°)	99.835(1)	90
V (Å^3)	1014.9(1)	2106.4(5)
Z	4	8
D (calc) (Mg/m^3)	1.337	1.288
Absorption coefficient (mm^{-1})	0.081	0.078
F(0 0 0)	424	848
Reflections collected	7292	12,265
Independent reflections	2410 [*R*(int) = 0.0229]	2057 [*R*(int) = 0.1186]
Reflections with [*I* > 2(*I*)]	2031	1208
Data/restraints/parameters	2410/0/145	2057/0/145
Goodness-of-fit on *F*2	1.056	1.018
Final *R* indices [*I* > 2(*I*)]		
R_1 wR_2	0.0387, 0.1044	0.0482, 0.0956
R indices (all data)	0.0464, 0.1103	0.1037, 0.1180
Largest diff. peak and hole, e.Å^{-3}	0.326 and −0.207	0.231 and −0.224



1 **2**

Scheme 1.



Scheme 2.

Molecular structures of **1** and **2** are shown in Fig. 1. Two compounds crystallize in the monoclinic *P*2_1/*n* (**1**) and orthorhombic *Pbca* (**2**) space groups with one molecule per asymmetric unit.

The two molecules have similar geometries (Table 1S). The impact of *ortho*- *vs. meta*-cyano groups does not indicate any change in the bridging C—C distance, being 1.4865(14) Å in **1** against 1.485(3) Å in **2**. The absence of bulky substituent in *ortho*-positions in **2** explains the smaller value of the dihedral angle between two benzene rings being 30.76° in **2** against 51.50° in **1**, respectively. For comparison, the same dihedral angle is 48.7° in *ortho*-substituted 2-chloro-3-phenyl benzoic acid [14], and 47.34(5) and 46.72(6)° in methyl 2-chloro-3-(4-chlorophenyl)benzoate and methyl 4-chloro-2-(4-chlorophenyl)benzoate, respectively [7b]. Using the facilities of CSD (Version 5.31, November 2009, 4 updates) [15] we fulfilled the comparative analysis of the impact of the cyano- against chloro-substituents placed at the same *ortho*- or *meta*-positions in the biphenyl moiety on the C–C–C–C torsion angle. The entries used in this study were restricted by the metal-free structures without disordering and containing the biphenyl fragments with the following sets of substituents: (a) *ortho*-substituents: CN, H, H, H; (b) *ortho*-substituents: Cl, H, H, H; (c) *ortho*-substituents: H, H, H, H, *meta*-substituent: CN; (d) *ortho*-substituents: H, H, H, H, *meta*-substituent: Cl. The corresponding histograms (Fig. 1S in SI) reveal definite similarities: