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On the Saddle-Shaped Nature of 14,15-Dimethylbenzo[*s*]picene

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Introduction

Recently, a convenient synthesis of benzo[*s*]picene was given,[1] in the hope that this would aid in shedding some more light onto the nature of this and similar molecules in terms of their structural chemistry and relation to carcinogeneity. Polycyclic hydrocarbons with the so-called bay regions are potent carcinogens. This structural feature is also believed to cause deviation from planarity.[1] An X-ray structure of this type of molecule should therefore be of interest in relation to the biological properties. The little-investigated nature of these molecules becomes clear when realizing that no crystal structure information has been published on this molecule, as evidenced by searching the CCDC database.[2] The only similar system that could be found was that of β-tribenzopyrene,[3] which is nonplanar but more rigid than benzo[*s*]picene. Our interests in this and similar systems are the molecular structure and configuration of nonplanar polyaromatic[4,5,6] molecules and their relation to the often atropisomeric precursors, as indeed is the case here.

Results and Discussion

We have prepared 14,15-dimethylbenzo[*s*]picene (**2**) by a route similar to the one given in ref 1 but found the use of a Suzuki coupling reaction more convenient than the Kumada couplings (Scheme 1).[1,7] Furthermore, the ^{1}H NMR spectrum of the 1,1′-bis(4,5-dimethyl-1,2-phenylene)naphthalene (**1**) is explained through the existence of atropisomers. It was found that of the three atropisomers observed in solution (*R*(trans), *S*(trans), and meso-cis) only two were observed in the solid state (*R*(trans) and *S*(trans), one of which is shown in Figure 1a). It was further shown, by letting a solution known to contain the cis form crystallize fully, that the cis form did not crystallize. A comparison of the observed powder diffractogram for the fully crystallized sample with the calculated powder diffractogram based on the model obtained from the single-crystal structure of **1** proved this. Thus, under the conditions given, the cis form does not crystallize to any significant extent but converts through rotation of a naphthyl substituent to the *R*(trans) or *S*(trans), which then is incorporated into the crystal.

The 14,15-dimethylbenzo[*s*]picene was found to exist in only one form in solution as established by ^{1}H NMR. The molecular structure as determined by X-ray crystallography showed the molecule as being quite distorted from planarity and saddle shaped (Figure 1b). A comparison with the β-tribenzopyrene,[3] the only other structurally similar molecule with a known structure, showed that both share a similar and quite strained conformation. While the molecular conformation of β-tribenzopyrene is constrained by a crystallographic mirror plane passing through the molecule compound **2** is not subject to such a constraint and is thus slightly more distorted. On the basis of this fact, it is difficult to envisage that the benzo[*s*]picene system should be able to exhibit atropisomerism as the optically active counterpart to the observed would be exceptionally strained.

Experimental Section

Synthetic Methods and Materials. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 250 MHz instrument with TMS as internal reference at 300 K. All the NMR spectra were recorded in $CDCl_3$ unless otherwise stated. In the ^{13}C NMR spectrum of compound **2**, the signal from one carbon atom could not be observed; this is ascribed to accidental isochrony. All reagents used were reagent grade and used without further purification. The temperatures given are internal temperatures. Chromatographic separations were performed on silica gel 60 (SiO_2, 0.040−0.063 mm, 230−240 mesh). TLC was carried out on SiO_2. The crystals used for X-ray crystallography were obtained from HPLC-grade solvents. Elemental analyses (C, H, N) were performed at DB Lab, Stenhuggervej 9, DK-5230 Odense M, Denmark. The samples were dried in a vacuum oven at 80 °C for 24 h prior the analysis.

1,1′-Bis(4,5-dimethyl-1,2-phenylene)naphthalene (1). 1-Naphthylboronic acid (15.5 g, 90 mmol), 1,2-dibromo-4,5-dimethylbenzene (10.6 g, 40 mmol), and $Pd(PPh_3)_2Cl_2$ (1.2 g, 2.0 mmol, 5 mol %) were refluxed in toluene (150 mL, degassed) and 3 M Na_2CO_3 (aqueous, 60 mL, degassed) under vigorous stirring for 18 h under an argon atmosphere. The dark mixture was cooled to 20 °C, diluted with toluene (200 mL), and filtered through a pad of Celite. The aqueous phase was separated, the organic phase was washed with 1 M NaOH (100 mL), hydrochloric acid (1 M, 50 mL), and brine (50 mL) and dried (Na_2SO_4), and the solvent was removed under reduced pressure. The orange residue was redissolved in CH_2Cl_2 (100 mL), and SiO_2 (70 g) was added. The solvent was removed, and the coated SiO_2 was placed in a Soxhlet thimble and extracted continuously with *n*-hexane for at least 24 h. The *n*-hexane was evaporated, leaving almost pure **1**. Recrystallization from 96% EtOH gave **1** as colorless crystals in 86% yield (12.3 g): mp 181−182 °C; $R_f \approx$ 0.42 (*n*-hexane/$CHCl_3$, 2:1, v/v); ^{1}H NMR δ 7.91−6.85 (m, 16H), 2.39 (s, 2.66H_{cis}), 2.38 (s, 3.34H_{trans}); ^{13}C NMR δ 139.1, 138.9, 137.7, 137.6, 135.5, 135.2, 133.3, 133.2, 132.9, 132.7, 132.6, 131.8, 128.2, 128.0, 127.7, 126.9, 126.8, 126.7, 126.5, 126.4, 125.5, 125.3, 125.1, 124.8, 124.5, 19.5; MS (EI, 70 eV) *m*/*z* 358 (100), 343 (50), 327 (27), 163 (68). Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.55; H, 6.39.

14,15-Dimethylbenzo[*s*]picene (2). A stirred degassed solution of **1** (2.15 g, 6.0 mmol), iodine (1.78 g, 7.0 mmol), and 1,2-epoxybutane (8 mL) in benzene (1 L) was irradiated with unfiltered UV light from a 400 W medium-pressure mercury lamp. The reaction was monitored by means of GC−MS, since the starting material and the product had the same R_f values in different TLC eluents. The organic phase was washed with

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(1) Tang, X.-Q.; Harvey, R. G *J. Org. Chem.* **1995**, *60*, 3568.

(2) Cambridge Crystallographic Data Centre database, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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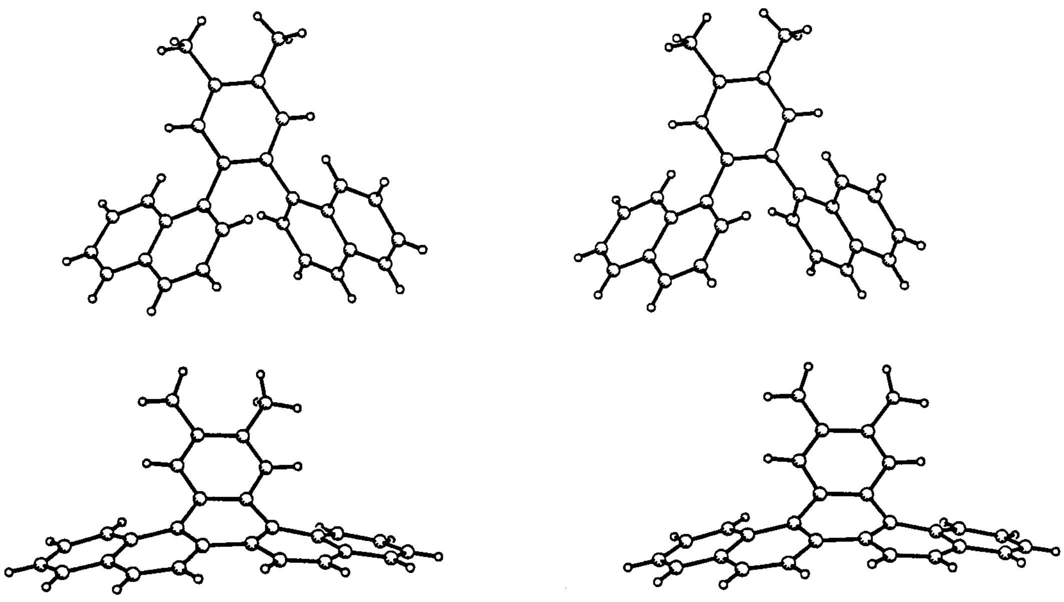
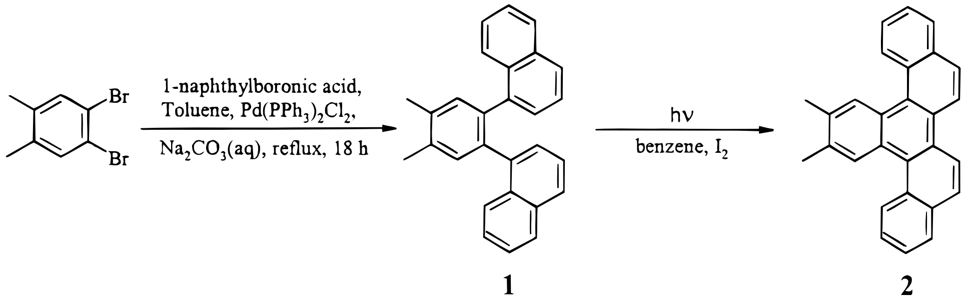


Figure 1. (a) Top: stereoview of the trans form of the 1,1′-bis(4,5-dimethyl-1,2-phenylene)naphthalene (only one form of the disordered methyl groups shown for clarity). (b) Bottom: stereoview of the saddle-shaped and quite distorted 14,15-dimethylbenzo-[*s*]picene. Notice that the molecule does not exhibit mirror symmetry as there is a noticeable steric demand between the two hydrogen atoms in the middle of the molecule resulting in a slight twisting of the molecule.

Scheme 1



NaHSO$_3$ (5%, 50 mL) and dried (Na$_2$SO$_4$). Evaporation of the solvent left crude product. Recrystallization from *n*-hexane/CHCl$_3$ gave **2** (1.97 g, 92%) as colorless crystals: mp 262−263 °C; ^{1}H NMR δ 9.05 (d, 2H, $J = 8$ Hz), 8.76 (s, 2H), 8.63 (d, 2H, $J = 9$ Hz), 8.04 (t, 4H, $J = 7$ Hz), 7.67 (m, 4H), 2.55 (s, 6H); ^{13}C NMR δ 135.7, 133.9, 130.2, 129.8, 129.1, 128.8, 128.5, 127.8, 127.6, 126.3, 126.2, 121.2, 20.7; MS (EI, 70 eV) *m*/*z* 356 (100), 339 (16), 326 (18), 163 (77). Anal. Calcd for C$_{28}$H$_{20}$: C, 94.34; H, 5.66. Found: C, 93.39; H, 5.89.

NMR. The low-field region in the ^{1}H NMR spectrum of compound **1** recorded in 1,1,2,2-tetrachloro-1,2-dideuterioethane at 300 K was well resolved and could be assigned using a COSY spectrum. Two sets of signals were observed in the ratio of 0.8:1 and tentatively assigned to the cis and trans atropisomers, respectively. A ratio of 1:2 would be expected if the meso-cis and the *R*(trans) and *S*(trans) forms have the same energy and therefore are present in solution in equal amounts. At higher temperatures, most of the signals broadened, especially those assigned to the ABC system of the naphthyl groups. A definite coalescence temperature was not observed, but maximum broadening occurred near 380 K. In contrast, the ^{1}H NMR spectrum of **2** in CDCl$_3$ showed no evidence of exchange between isomers. The absence of isomers and high symmetry of **2** made the assignment of signals rather straightforward. A singlet at 8.76 ppm is due to the proton in the bay region ortho to a methyl group. The AB systems created in the molecule give rise to two dublets at 9.05 and 8.63 ppm while the AA′XX′ systems is seen as a triplet at 8.04 and a multiplet centered at 7.67 ppm in the 250 MHz spectrum. Higher resolution was obtained in a 500 MHz spectrum where the multiplet is separated into two triplets at 7.68 and 7.62 ppm originating form the protons ortho to the peri positions. The triplet seen at 8.04 ppm can therefore be assigned to the protons in the peri positions and must consist of two overlapping doublets.

Table 1. Crystallographic Data

compd	1	2
formula	C$_{28}$H$_{22}$	C$_{28}$H$_{20}$
formula wt	358.46	356.44
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
Z	4	4
a, Å	11.037(2)	12.024(2)
b, Å	18.978(4)	7.5310(15)
c, Å	10.602(2)	19.962(4)
α, deg	90	90
β, deg	117.17(3)	99.62(3)
γ, deg	90	90
V, Å^3	1975.7(7)	1782.2(6)
ρ, g cm^3	1.205	1.328
crystal dimens, mm	0.37 × 0.35 × 0.25	0.30 × 0.20 × 0.05
type of radiation	Mo Kα	Mo Kα
μ, cm^{-1}	0.068	0.075
T, K	120(2)	120(2)
no. of reflns	20 363	18 257
unique reflections (with $I > 2\sigma$)	3188	2501
R_{int}	0.0305	0.0584
$R(F)$, $R_w(F^2)$ all data	0.0419, 0.1157	0.0484, 0.1278

Crystallography Methods. See Table 1 for general details. Crystals of **1** and **2** were drawn directly from the mother liquor, coated with a thin layer of oil, mounted on a glass capillary using grease (Apiezon), and transferred quickly into the cold nitrogen stream on the diffractometer. Data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. Absorption corrections were made using SADABS[8] Direct methods for the structure solution and full-matrix least-squares refinements were used. For compound **1**, hydrogen atoms were included in calculated positions; the methyl groups, however, were found to be disordered. This was modeled as two mutually exclusive groups and refined with respect to the sof, which was found to be 0.606 and 0.394, respectively. For compound **2**, hydrogen atoms were observed close to the expected positions and included in the refinement. Programs used were SMART, SAINT and SHELXTL from Siemens.[9,10] The structures were checked for overlooked symmetry using MISSYM and for voids in PLATON.[11] Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

Supporting Information Available: Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths and bond angles, powder diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Emperical absorption program (SADABS) written by George Sheldrick for the Siemens SMART platform.

[9] Sheldrick, G. M. *SHELXTL95;*. Siemens Analytical X-ray Instruments Inc.: Madison WI, 1995.

[10] Siemens. *SMART* and *SAINT*. *Area-Detector Control and Integration Software*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

[11] Spek, A. L. *Acta Crystallogr*. **1990**, *A46*, C-31.