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Restricted Rotation in 9-Phenyl-anthracenes: A Prediction Fulfilled

Kirill Nikitin,* Helge Müller-Bunz, Yannick Ortin, Jimmy Muldoon, and Michael J. McGlinchey*

*School of Chemistry and Chemical Biology, University College Dublin,
Belfield, Dublin 4, Ireland*

kirill.nikitin@ucd.ie; michael.mcglinchey@ucd.ie

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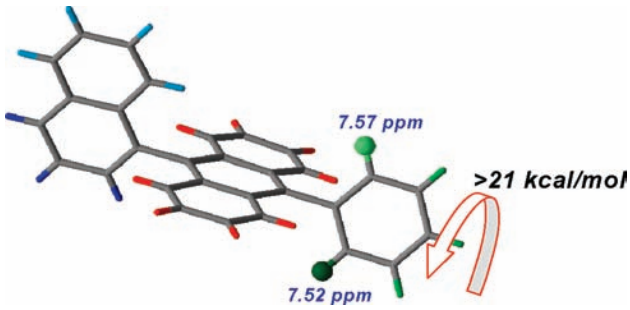
ABSTRACT



The calculated phenyl rotation barrier in 9-phenylanthracene has been reported as ∼21 kcal mol^{-1}, but experimental verification of this barrier is limited by its intrinsic symmetry. V-T NMR indicated the barrier to interconversion of the *syn* (C_{2v}) and *anti* (C_{2h}) rotamers of 9,10-bis(3-fluorophenyl)anthracene to be ∼21 kcal mol^{-1}. Likewise, the V-T NMR spectra of 9-(1-naphthyl)-10-phenylanthracene reveal that the rotational barrier of the unsubstituted phenyl ring is at least 21 kcal mol^{-1}.

The phenomenon of atropisomerism, whereby slowed rotation about carbon−carbon single bonds can give rise to separable different structures, has a long and distinguished history. The first successful isolation of enantiomeric 2,2′,6,6′-tetrasubstituted biphenyls was reported by Christie and Kenner in 1922,[1a] and the field was developed significantly in now classic studies from the groups of Adams[1b,c] and of Oki.[1d] As emphasized by Mislow, for rotations in 2,2′-disubstituted biphenyls the transoid transition state is markedly favored relative to its cisoid analogue.[2a,b] Moreover, very considerable salt effects have been reported for the racemization of biphenyls having cationic groups in the 2,2′-positions.[2c]

It soon became evident that the barrier height was heavily dependent on the steric bulk of the substituents, with hydrogen, of course, being the least demanding. The comprehensive pioneering study by Bott, Field, and Sternhell of a wide range of 2,2′-disubstituted biaryls revealed quantitative correlations between the rotational barriers and the van der Waals radii of the relevant substituents.[3] Moreover, it was proposed that pairwise contributions to the rotational barriers were additive; however, this suggestion has recently been refuted.[4]

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Concomitantly, it was demonstrated that interconnected, fused unsubstituted aromatic systems, e.g. binaphthyls, are atropisomeric thus opening up routes to chiral catalysts and switches.[5] In many cases the barrier exceeds 25 kcal mol^{-1} and the atropisomers are separable on the laboratory time scale. Slowed rotation of substituted phenyl groups attached to an aliphatic or aromatic framework is well-known.[6a] Although reports of restricted rotation of unsubstituted phenyls are scarce, they have been observed in 1,4-adducts of 9-phenylanthracene.[6b]

Furthermore, we have very recently shown that phenyl rotation is only minimally restricted in the 9,10-diphenyl-dibenzo-dihydrobarrelene, **1**, and cannot be readily observed by variable-temperature NMR spectroscopy; in contrast, when the bridge length is increased to four atoms, as in the 9,10-diphenylbicyclo[4.2.2]dioxadecadiene, **2**, this barrier exceeds 23 kcal mol^{-1}.[7] In the latter case, both *ortho*-hydrogens of the potentially rotating phenyls would engage in simultaneous steric repulsion with the peripheral benzo rings. In **1** the dihedral angle between the exterior benzo blades is 134°, whereas it increases to 166° in **2**.[7] This raises the question as to whether rotation of an unsubstituted phenyl group in 9-phenylanthracene, **3**, would be significantly hampered in the case where the interplanar angle of the peripheral blades has increased to 180° (Figure 1).

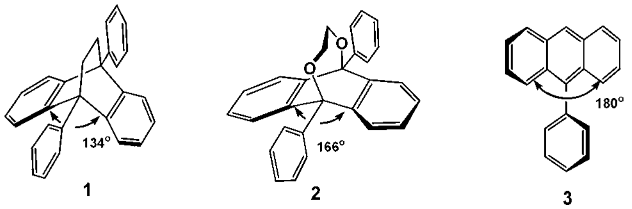

Figure 1. Rotational barriers in molecules **1**−**3** are markedly dependent on the interplanar angle between the exterior blades: <8 kcal mol^{-1} (**1**), >23 kcal mol^{-1} (**2**), and (calculated) ∼21 kcal mol^{-1} (**3**).

The barrier to phenyl rotation in 9-phenylanthracene, **3**, has been computed at the DFT level, and it was shown that rotation of the phenyl group would require a substantial energy cost of 20.2−20.8 kcal mol^{-1}, dependent on the basis set used.[8] Moreover, these data also indicated that, in the ground state, the phenyl would be oriented orthogonal to the anthracene ring plane, whereas in the transition state the phenyl and anthracenyl fragments would adopt a nonplanar, stepped, ladder-like arrangement, as in Figure 2.

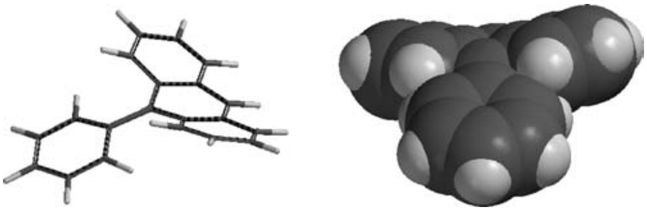

Figure 2. Views of the DFT-calculated transition state for phenyl rotation in 9-phenylanthracene, **3**.

The intrinsic C_{2v} or D_{2h} symmetry of 9-phenylanthracene, **3**, or 9,10-diphenylanthracene, **4**, respectively, renders the pairs of *ortho* and *meta* CH positions equivalent and so does not allow the rotational process to be monitored by variable-temperature NMR spectroscopy. Hence, it is necessary to break the symmetry, but to do so in such a fashion so as not to perturb the molecular geometry significantly. In previous work, we have used this approach to study the independent rotation of ethyl or phenyl substituents as well as of the tripods in $[C_6Et_5C(O)Me)]Cr(CO)_3$, $[C_6Et_6]Cr(CO)(CS)(NO)]^+$, or $(C_5Ph_5)Fe(CO)(CHO)PR_3$, respectively.[9]

To this end, we here report the syntheses, structures, and dynamic behavior of 9,10-bis(3-chlorophenyl)anthracene, **5a**, 9,10-bis(3-fluorophenyl)anthracene, **5b**, and 9-(1-naphthyl)-10-phenylanthracene, **6**. Diphenylanthracenes **5**, previously reported in conjunction with their photophysical properties, can be conveniently prepared by palladium-catalyzed cross-coupling of 9,10-dibromoanthracene and the corresponding arylboronic acids.[10] Although we are unaware of any direct claims of atropisomerism in molecules such as **5**, there are cases in which more than ten aromatic resonances are present in their ^{13}C spectra, indicating restricted rotation on the NMR time-scale.[11]

The 125 MHz ^{13}C NMR spectrum of 9,10-bis(3-chlorophenyl)anthracene, **5a**, at 298 K exhibited more than ten individual resonances. Full assignment of all peaks revealed that, as expected, the peaks of C(12), C(13), C(15), and C(16) were in fact narrowly spaced twin signals, with separations of 4, 4, 2, and 5 Hz, respectively. Moreover, as the temperature was gradually raised to 363 K, the peaks did not broaden or coalesce. These observations not only suggest

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the concurrent existence of *syn* (C_{2v}) and *anti* (C_{2h}) isomers of **5a** (Figure 3) but also indicate an aryl rotation barrier greater than 21 kcal mol^{-1}. DFT optimization of the energy profile of **5a** at the B3LYP level furnished a barrier of ~22 kcal mol^{-1}; in addition, it revealed that **5a** adopts a ladder-like conformation in the transition state, as previously reported for the unsubstituted parent molecule, **3**. Interestingly, attempts to separate the *syn* and *anti* isomers of **5a** by chromatographic or crystallization techniques failed, perhaps suggesting that the barrier is unlikely to exceed 24 kcal mol^{-1}.

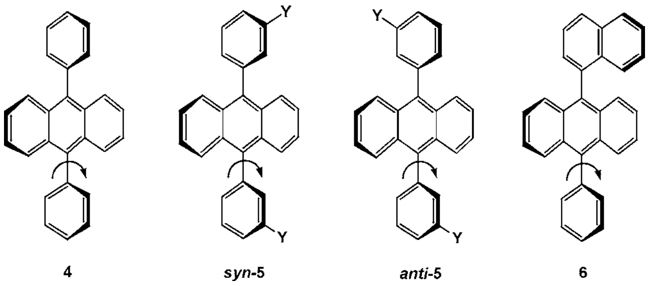

Figure 3. Slowed rotation of the phenyls cannot be observed experimentally in the D_{2h}-symmetric system **4**; however, the symmetry can be lowered, to C_{2v} in *syn*-**5**, to C_{2h} in *anti*-**5**, and to C_s in **6**.

This work was extended to include 9,10-bis(3-fluorophenyl)anthracene, **5b**, in which the smaller steric size of fluorine relative to chlorine might lead to a somewhat lower rotational barrier if buttressing effects play a significant role.[12] Fortunately, the fluoro-compound **5b** furnished X-ray quality crystals, and the structure of the *anti* isomer appears in Figure 4. It transpired that, in the solid state, *syn*- and *anti*-atropisomers are present in equal amounts, and the fluorine occupancies of both *meta*-positions of the phenyl rings are 50%. The fluorophenyls adopt an angle of 85° with the plane of the anthracene thus deviating only slightly from the perpendicular orientation. Nonoptimized virtual rotation of the phenyls indicates that very significant steric strain would occur in the planar conformation as the nominal closest approach distance (CAD) of H(1) and H(12) would be only 0.72 A. As for **3**,[8a] DFT optimization at the B3LYP level indicated a nonplanar transition state and indicated that rotation of one of the fluorophenyl moieties would evoke an energy penalty of ~22 kcal mol^{-1}.

The 125 MHz ^{13}C NMR spectrum of **5b** was recorded at 298 K without fluorine decoupling (Figure 4); complete assignment of all peaks revealed that C(12), C(15), and C(16) gave rise to twin signals separated by 3.6, 2.0, and 2.5 Hz, respectively. As the temperature was allowed to rise, the twinned peaks of C(12) and C(16) gradually broaden but do not reach coalescence, while the peaks of C(15) coalesce at 353 K. An intermediate rate analysis of this exchange process indicated an exchange rate of 2 s^{-1} and a rotational barrier of ~21 kcal mol^{-1} for the 3-fluorophenyl moiety, in reasonably good agreement with the DFT results.

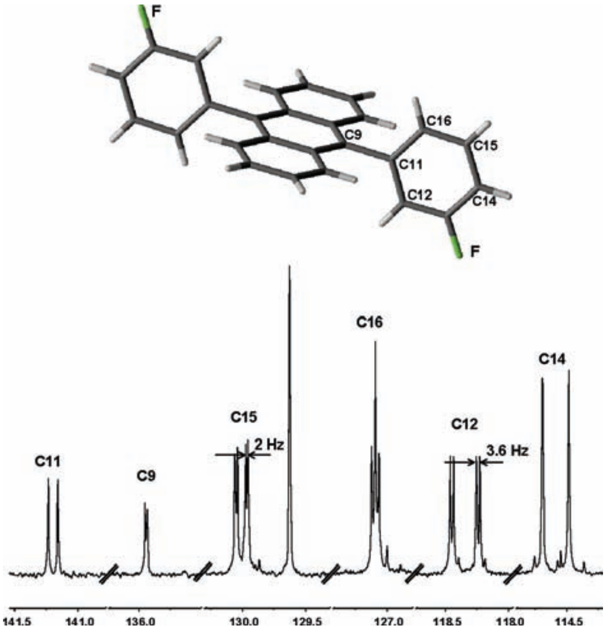

Figure 4. Molecular structure of 9,10-di(3-fluorophenyl)anthracene, **5b** (*anti* isomer shown), and sections of the 125 MHz ^{13}C NMR spectrum of *syn*/*anti*-**5b**.

Having obtained both theoretical and experimental evidence that the rotation of a *meta*-substituted phenyl linked to the 9-position of anthracene is slow on the NMR time scale, and may be somewhat sensitive to the buttressing effect of the *meta*-substituent, it was deemed appropriate to investigate the rotational barrier of an unsubstituted phenyl. This requires that the symmetry of the *environment* of the phenyl has to be broken rather than the symmetry of the phenyl itself. To this end, 9-(1-naphthyl)-10-phenylanthracene, **6**, was prepared and characterized by X-ray crystallography. A previous DFT computation on 1,9′-naphthylanthracene predicted a structure in which the two aromatic moieties would be orthogonal with a naphthyl rotation barrier of 38 kcal mol^{-1}.[8a] As shown in Figure 5, the phenyl and naphthyl fragments in **6** adopt dihedral angles of 80° and 88°, respectively, with the plane of the anthracene and a dihedral angle between themselves of 12°. Assuming time-averaged mirror symmetry in solution, and a very high barrier to naphthyl rotation, the *ortho* and *meta* positions of the phenyl ring should be nonequivalent unless rotation about the C(9)−C(11) bond were to become rapid on the NMR time scale.

The 600 MHz ^{1}H NMR spectrum of **6** at 303 K is shown in Figure 5. The anthracene protons H(1)/H(8) were unambiguously distinguished from H(4)/H(5) by their NOE interactions with the *ortho* phenyl protons H(12)/H(16) which appear at 7.57 and 7.52 ppm, once again revealing restricted rotation of the phenyl ring. The peak at 7.51 ppm corresponds to that of the *ortho* phenyl protons in 9,10-diphenylan-

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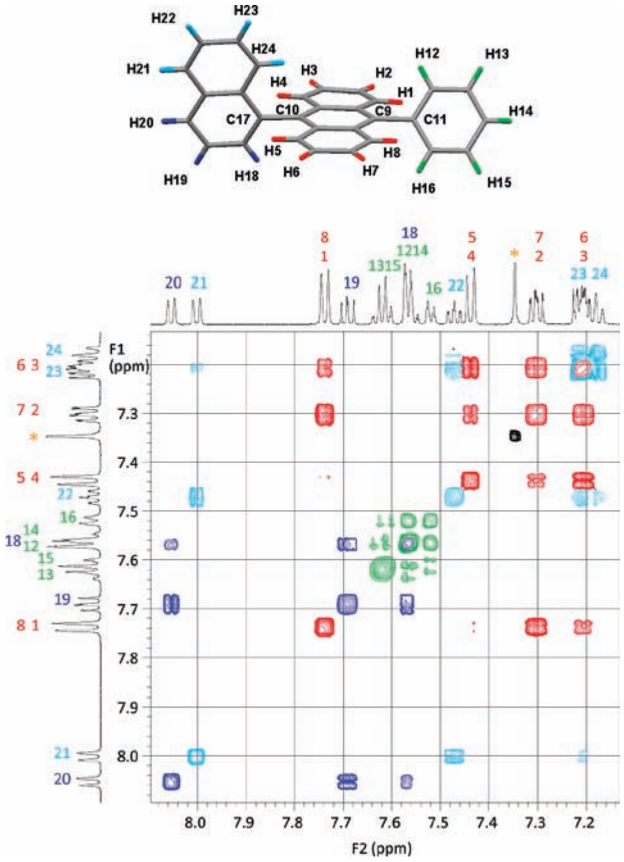

Figure 5. Molecular structure of 9-(1-naphthyl)-10-phenylanthracene, **6**, and its 2D ^{1}H−^{1}H 600 MHz COSY spectrum showing four individual color-coded spin systems; benzene is marked with an asterisk (*).

thracene and so is assigned to H(16). The other *ortho* phenyl proton, H(12) which is proximate to the benzo ring of the naphthalene moiety, experiences a slightly different environment and is somewhat deshielded. However, these peaks begin to broaden at 363 K demonstrating that the unsubstituted phenyl moiety exhibits slow rotation on the NMR time scale even at this temperature. One can therefore justify a minimum barrier of ~21 kcal mol^{-1}, in agreement with the previously reported theoretical value for phenylanthracene, **3**, (20.8 kcal/mol^{-1}) and our own DFT B3LYP level calculations for **6** (~22 kcal mol^{-1}).

To conclude, the previously calculated prediction of a rotational barrier of ~21 kcal mol^{-1} for 9-phenylanthracene has been fulfilled experimentally by examining a close structural analogue in which the symmetry has been lowered from C_{2v} to C_s, thus rendering the edges of the unsubstituted phenyl moiety nonequivalent. While the magnitude of this rotational barrier might not have been anticipated intuitively, it provides an archetypical example whereby it may be rationalized on the basis of simultaneous double repulsions experienced by the two *ortho*-positions of the phenyl ring with hydrogens on the anthracene. Although the barrier of ~21 kcal mol^{-1} is not quite large enough to engender conformationally stable and separable isomers at room temperature, the angular rigidity of the 9-phenylanthracene system has important stereochemical consequences. These factors may be usefully considered when designing new generations of enantioselective catalysts that contain biaryl and, in particular, phenylanthracene fragments.[13]

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Supporting Information Available: Experimental procedures and NMR characterization for compounds **5a**, **5b**, and **6** (COSY, TOCSY, HSQC, HMBC, NOE), as well as X-ray crystallographic collection, refinement details, and cifs. This material is available free of charge via the Internet at http://pubs.acs.org.

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