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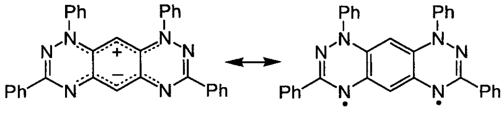
3,5,7,9-Tetraphenylhexaazaacridine: A Highly Stable, Weakly Antiaromatic Species with 16 π Electrons**

Peter Langer, Anja Bodtke, Nehad N. R. Saleh, Helmar Görls, and Peter R. Schreiner**

The efficiency of electrical, magnetic, and optical devices based on organic materials is closely related to their HOMO–LUMO energy gap.[1] The structure of tetraphenylhexaazaanthracene (TPH-anthracene, **1**), first prepared in 1908 as a stable, highly fluorescent compound,[2] was recently studied by Wudl and Houk et al.; **1** exists as a zwitterionic cyanine (resonance structure **1a**) that undergoes photoinduced intramolecular electron transfer to give a radical pair.[3,4] Wudl and



1a (TPH-anthracene) **1b**

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[*] Prof. Dr. P. Langer
Institut für Chemie, Universität Rostock
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
Fax: (+49) 381-498-6412
E-mail: peter.langer@uni-rostock.de
and
Leibniz-Institut für Organische Katalyse (IfOK)
an der Universität Rostock e.V.
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Prof. Dr. P. R. Schreiner
Institut für Organische Chemie, Justus-Liebig-Universität
Heinrich-Buff-Ring 58, 35392 Giessen (Germany)
Fax: (+49) 641-99-34309
E-mail: prs@chem.uga.edu
and
The University of Georgia, Department of Chemistry
Athens, GA (USA)
E-mail: prs@chem.uga.edu
Dr. A. Bodtke, Dr. N. N. R. Saleh
Institut für Chemie und Biochemie
Ernst-Moritz-Arndt Universität Greifswald
Soldmannstrasse 16, 17487 Greifswald (Germany)
Dr. H. Görls
Institut für Anorganische und Analytische Chemie
Universität Jena
August-Bebel-Strasse 2, 07740 Jena (Germany)

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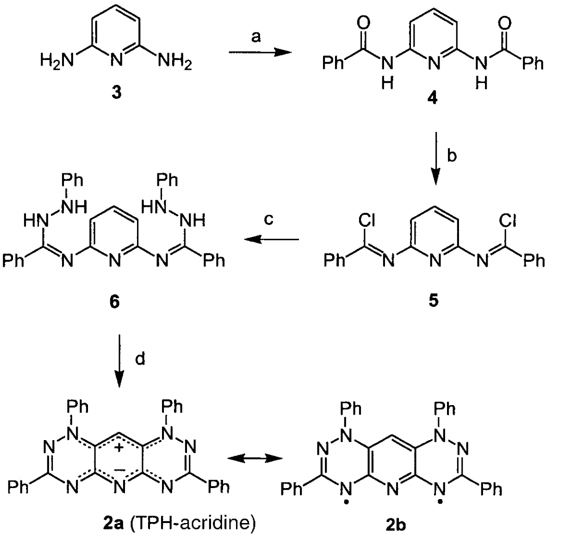
Houk et al. concluded that the apparent antiaromaticity of **1** is overwhelmed by the dominance of cyanine ion stabilization. However, the aromatic properties, which can be assessed in a straightforward manner by, for instance, nucleus-independent chemical shifts (NICS),[5] were not analyzed further.

Herein, we report the synthesis of what is, to the best of our knowledge, the first example of a hexaazaacridine, namely 3,5,7,9-tetraphenylhexaazaacridine (TPH-acridine, **2**). By means of a combination of experimental and computational results, we show that **1** and **2** can be viewed as stable, 16-π-electron, weakly antiaromatic highly zwitterionic structures with very low lying triplet states. As neutral molecules are usually less polarized than their excited states, **2**, along with its carbon analogue **1**, is the exception where the state polarity is reversed so that photoexcitation leads to a less polarized excited state. As a consequence, normally much higher lying triplet and singlet states are much closer in energy. It is conceivable that appropriately substituted acridines can have open-shell ground states and would be excellent candidates for organic magnets and data storage.[1]

The synthesis of TPH-acridine (**2**) essentially follows the strategy reported for the synthesis of **1** (Scheme 1).[2,3]



Scheme 1. Synthesis of TPH-acridine (**2a**): a) PhCOCl (2 equiv), NEt_3 (2 equiv), CH_2Cl_2, 14 h, 0–20°C, 48%; b) PCl_5 (2.9 equiv), toluene, 1.5 h, 20°C, then 2 h, reflux, 88%; c) $PhNHNH_2$ (2.7 equiv), *n*-hexane, 14 h, 0–20°C, 90%; d) air, DBU (2.8 equiv), MeOH, 4 d, 20°C, 10%. DBU = diazabicyclo[5.4.0]undec-7-ene.

However, the oxidative cyclization of **6** as the key step proved to be very sluggish and afforded **2** in only 3% yield. After much experimentation, we found that **2** can be obtained reproducibly in 10% yield. Both the workup of the final product and the quality of **6** proved to be important parameters. In this context, the preparation of (rather unstable) bis(imidoyl) dichloride **5** in high purity was crucial and required careful handling.

The deep purple hexaazaacridine **2** is air stable, thermally stable up to 400°C, and poorly soluble in most organic solvents. Particularly noteworthy is its strong solvatochromic character (Table 1): a solution of **2** in DMF is orange colored ($\lambda_{max} = 547$ nm) and, despite the low solubility of **2**, highly fluorescent at $F(\lambda_{max}) = 585$ nm. In TFA (CF_3CO_2H), however, the solubility of **2** is higher owing to protonation to give cationic **2**-H$^+$ (deep purple solution). Therefore, most NMR spectra were recorded in [D$_1$]TFA. Compound **2** is somewhat soluble in glacial acetic acid, concentrated nitric acid, phosphoric acid, and perchloric acid to give orange, red, bluish purple, and green solutions, respectively. Excellent solubility and strong bathochromism were observed in concentrated sulfuric acid ($\lambda_{max} = 662$ nm, deep green solution). Successive dilution of this solution with water or acetone changes the color from green to blue and purple and finally to pink and orange (see Supporting Information for quantitative measurements); this process is reversible. In addition to the acidity and concentration, the counterion also affects the absorption of the solution, which suggests the formation of aggregates.

Table 1: Solvatochromic properties of **2**.

Solvent	λ_{max} [nm] (log ε)	Color of solution
DMF	547 (4.51)	orange, strongly fluorescent, poorly soluble
CH_3CO_2H	535 (4.57)	orange, fluorescent, poorly soluble
conc. HNO_3	–	red, very poorly soluble
conc. H_3PO_4	540 (4.29)	bluish purple, poorly soluble
conc. $HClO_4$	–	green, very poorly soluble
CF_3CO_2H	–	deep purple, reasonably soluble
conc. H_2SO_4	662 (4.34)	deep green, highly soluble

The structure of TPH-acridine (**2**) was independently confirmed through a crystal structure analysis of the cation **2**-H$^+$, which was prepared by protonation of **2** with hydrochloric and glacial acetic acids (Figures 1 and 2). Protonated TPH-acridine is a symmetric molecule that is protonated at the central nitrogen atom. Analysis of the bond lengths of THP-acridine indicates that the ionic resonance structure **2a**-H$^+$ is more important than the diradical contributor **2b**-H$^+$; this compares well with **1**.

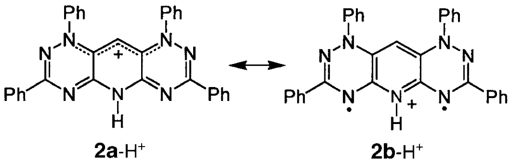


Figure 1. Resonance structures of protonated TPH-acridine, **2**-H$^+$.

For a better understanding of the electronic nature of **2**, we also computed its properties and compared those to **1**. As Wudl and Houk et al. successfully employed density functional theory (DFT) to examine the structures and energies of **1**, we adopted the same approach (B3LYP)[6] but expanded the basis set from 6-31G* to 6-311+G** for the energies on the B3LYP/6-31G*-optimized geometries because we noted a marked basis set dependence of the singlet–triplet energy separation (ΔE_{ST}); this is not unexpected for species with

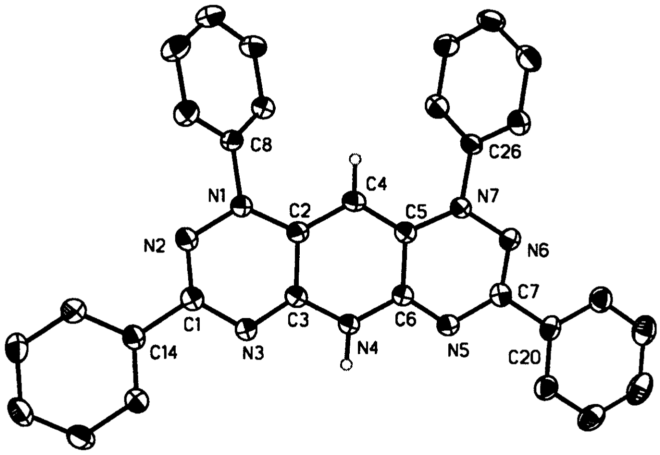


Figure 2. ORTEP plot of protonated TPH-acridine, **2**-H$^+$. Bond lengths [Å] and angles [°]: N1-C2 1.353(3), N1-N2 1.368(3), N2-C1 1.307(3), N3-C3 1.304(3), N3-C1 1.368(3), N4-C3 1.359(3), N4-C6 1.359(3), C2-C4 1.390(3), C2-C3 1.441(3); C2-N1-N2 123.28(19), C1-N2-N1 116.34(19), C3-N3-C1 115.8(2), C3-N4-C6 123.7(2), N2-C1-N3 126.2(2), N1-C2-C4 125.4(2), N1-C2-C3 114.46(19), C4-C2-C3 120.2(2), N3-C3-C2 123.3(2). CCDC 255822 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

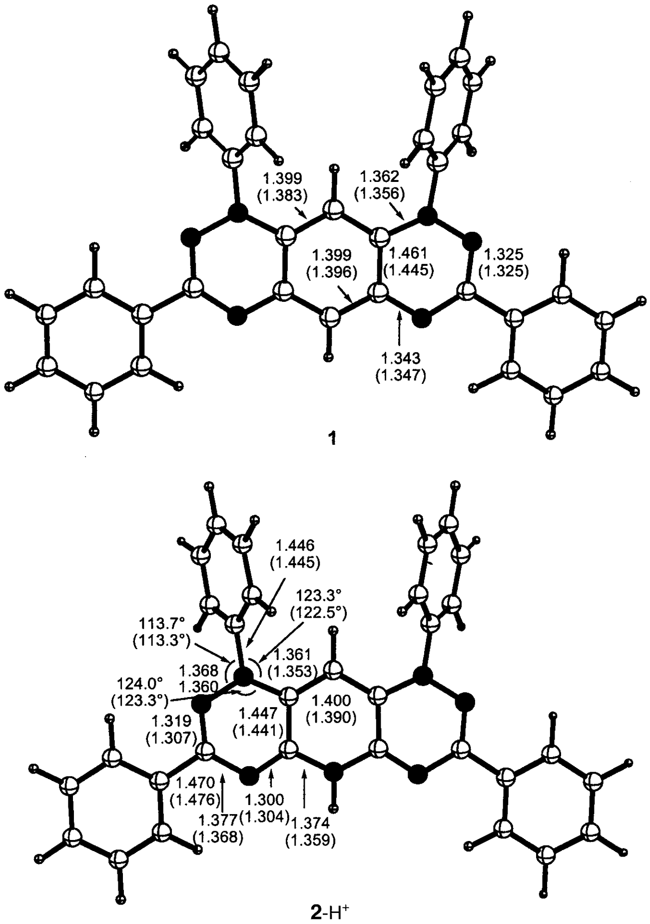


Figure 3. TPH-anthracene (**1**) and protonated TPH-acridine, **2**-H$^+$: comparison of selected bond lengths [Å] of the computed structure (B3LYP/6-31G*) and the crystal structure (in parentheses).

highly polarized ground and close-lying excited states. Our final level is therefore B3LYP/6-311+G**//B3LYP/6-31G*; zero-point vibrational energy (ZPVE) differences are marginal and are therefore not applied (the ZPVEs are reported in the Supporting Information). For the computation of UV spectra, we utilized time-dependent DFT (TD-B3LYP/6-311+G**), which is capable of describing vertical excited states more reliably than, for example, configuration interaction with single excitations (CIS).[7]

Since the crystal structure of TPH-anthracene (**1**) is known and the structure of the complete molecule had not been computed (the phenyl groups had been replaced by hydrogen atoms in the original publication),[3] we first optimized the structure of **1** to establish whether our computational approach would reproduce the structural details within acceptable errors. We computed **1** in C_s and C_2 symmetry (rotation of one of the *N*-phenyl groups relates these two structures) and found the C_s form to be very slightly preferred (0.3 kcal mol^{-1}); the X-ray crystal structure is asymmetric (C_1) as a result of packing effects. The key structural parameters agree quite well (Figure 3), and we expect our approach also to give good structural data for TPH-acridine (**2**). The phenyl groups in **1** lower ΔE_{ST} by 2.4 kcal mol^{-1} (at B3LYP/6-31G*), but this separation (16.3 kcal mol^{-1} for the preferred C_s structure) increases to 17.1 kcal mol^{-1} when we employ a more polarizable and diffuse basis set at our reference level. For proper comparison, we also computed protonated TPH-acridine, **2**-H$^+$, at B3LYP/6-31G*; the key structural parameters are in excellent agreement with the crystal structure data (Figure 3).

A comparison of the measured and computed ^{13}C NMR data of protonated **2** (the spectrum was recorded in [D$_1$]TFA) also is favorable (Table 2); the average deviation of the computed data to lower fields is only about 5 ppm and can be explained by neglect of solvent effects.

The UV/Vis spectrum is also well reproduced computationally with a maximum absorption at 506 nm (experimentally at 535 nm in AcOH), which is assigned to an excited state that corresponds qualitatively to the lowest triplet state (as in **1**).[3] By analogy to **1**, the fluorescence spectrum is not a mirror image of the UV/Vis absorption spectrum; the Stoke's

Table 2: Experimental and computed (B3LYP/6-311+G**//B3LYP/6-31G*) ^{13}C NMR chemical shifts (δ [ppm], relative to TMS as internal standard) for **2**-H$^+$.

Type	CH	CH	CH	CH	C	CH	CH	CH	C	C	C	C
exptl	91.1	126.3	129.4	131.2	132.1	132.5	134.0	135.4	141.2	141.5	158.3	158.6
theor	89.2	133.5	134.8	136.7	136.2	139.0	139.8	143.1	143.0	147.3	159.1	166.0
$\Delta\delta$	1.9	7.2	5.4	5.5	4.1	6.5	5.8	7.7	1.8	5.8	0.8	7.4

shift of **2** is about 26000 cm^{-1}, even larger than that of **1** (15000 cm^{-1}) and hence about 5 to 40 times the typical Stoke's shift of typical laser dyes.[8]

Azaacridine **2** also has a C_s singlet ground state with a ΔE_{ST} of 15.1 kcal mol^{-1}; note that this gap is significantly larger at B3LYP/6-31G* (21.1 kcal mol^{-1}). The C_2 singlet state lies 7.9 kcal mol^{-1} higher in energy and displays an even larger basis set effect on the ΔE_{ST} (20.8 at B3LYP/6-31G* and only 6.2 kcal mol^{-1} at our reference level). Stability tests showed no instabilities in the wavefunctions of the singlet states; in other words, the small ΔE_{ST} can be interpreted on the basis of aromaticity/antiaromaticity (see below). Like anthracene **1**, acridine **2** is highly polar (dipole moment: 8.2 D) and displays pronounced charge separation. The nitrogen atom in the central ring is the most negatively polarized (−0.53 according to a natural bond orbital (NBO) analysis) and is also the preferred site of protonation (in either the C_s or C_2 form); protonation at N3 and N2 is 3.8 and 18.4 kcal mol^{-1} less favorable, respectively. This is nicely confirmed by the crystal structure of **2**-H^+.

Table 3: NICS values (B3LYP/6-311+G**//B3LYP/6-31G*) of **1**, **2**, and **2**-H^+.

NICS value relative to ring center	**1** inner	**1** outer	**2** inner	**2** outer	**2**-H^+ inner	**2**-H^+ outer	Cyclobutadiene (D_{4h})
0.0	+0.6	+7.9	+3.5	+6.3	+3.1	+4.1	+27.1
0.5	−1.1	+5.6	+0.9	+4.0	+1.5	+1.9	+27.9
1.0	−2.0	+2.6	−1.1	+1.4	+0.3	−0.1	+19.0
2.0	−0.2	+0.7	−0.5	+0.1	+0.2	−0.3	+4.5
3.0	+0.2	+0.2	−0.2	−0.1	0.0	−0.2	+1.2
4.0	+0.2	+0.1	−0.2	−0.2	−0.1	−0.2	+0.4

The computed NICS values in the ring centers (Table 3) reveal that all three rings of acridine **2** are antiaromatic. The same is true for **1** although the degree of antiaromaticity varies more strongly. As NICS values in the ring centers often are affected by the σ electrons of neighboring bonds, we also computed the NICS values above the ring centers and compare these with the extreme case of an antiaromatic species, namely D_{4h} cyclobutadiene.[9] This analysis shows that the outer rings of **1**, **2**, and **2**-H^+ at 0.5 Å above the ring of the plane are, with the exception of the inner ring of **1**, weakly antiaromatic. NICS points that are further away from the ring centers demonstrate that the antiaromatic character decreases rapidly, in particular for the inner rings; these NICS values are typical for nonaromatic structures. The decrease in antiaromaticity, which is much more pronounced than for cyclobutadiene, can be rationalized by differences in the ring size and the high polarity of the heterocycles in **1** and **2**.

Hence, **1** and **2** must be considered to be stable, weakly antiaromatic molecules with highly polar singlet ground states. Our conclusions are further supported by visual inspection of the HOMO of **2** (C_s; Figure 4), which is symmetrically π-antibonding. This is in analogy to the simplest neutral antiaromatic singlet, the highly unstable D_{4h}-symmetric cyclobutadiene (it is common knowledge that it has a triplet ground state). Remarkably, the ΔE_{ST} for cyclobutadiene is in the same range (5.9 kcal mol^{-1} at B3LYP/6-311+G** and 11.5 kcal mol^{-1} at CCSD(T)/cc-pVDZ//B3LYP/6-311+G**)[10] as that of **1** and **2**, which lends further support to the proposal that these polycyclic structures are indeed stable antiaromatic entities. Although this formally contradicts the conclusions of Wudl und Houk et al.[3] for TPH-anthracene that double cyanine ion stabilization of zwitterion **1a** is preferred over the formal 16-π antiaromaticity (**1b**),[11] we remark that the earlier study computationally examined a smaller model system with a smaller basis set, which has a large effect on the energies (see above). However, the two conclusions are not necessarily mutually exclusive because the systems under consideration are only weakly antiaromatic and partially avoid this unfavorable situation through strong polarization.

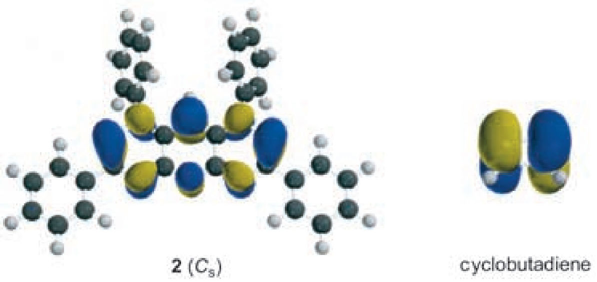


Figure 4. HOMOs of **2** and cyclobutadiene (only one of the two degenerate HOMOs is shown).

In conclusion, TPH-acridine, which we have synthesized and characterized, represents the first hexaazaacridine. The structure and spectroscopic properties of TPH-acridine and TPH-anthracene were studied by DFT computations and NICS analysis. TPH-acridine and TPH-anthracene represent highly zwitterionic structures with very low-lying triplet states. Both polycyclic structures can be considered to be stable 16-π-electron, weakly antiaromatic entities. TPH-acridine and TPH-anthracene are of great theoretical and structural interest and exhibit exciting physical properties that may be utilized in organomagnetic applications.

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