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Tetracarboxy-functionalized [8], [10], [12] and [14]Phenacenes

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Abstract: Mono- and diglyoxylation of chrysene and naphthalene leads to Perkin reactants that yield bismaleates which efficiently photocyclize to elongated phenacene-tetracarboxylic esters. Their band gaps remain significantly larger than the value postulated for polyphenacene. Reaction with α -branched amines gives the corresponding imides, which are significantly stronger electron acceptors than the esters. The obtained [12] and [14]phenacenes are the longest [*n*]phenacenes that have been synthesized to date.

The two conceptually simplest and thinnest hypothetical graphene nanoribbons are polyacene and polyphenacene. Whilst higher acenes longer than heptacene are too unstable to be isolated due to their only minimal sextet stabilization and hypothetical polyacene is postulated to be a metal,¹ polyphenacene (Scheme 1) is fully Fries-stabilized (i.e. it allows a Kekulé formula where all hexagons are made of three double and three single bonds),² with a predicted band gap of about 2.5 eV.³ Phenacenes up to [6]phenacene (a.k.a. fulminene) have been isolated from coal tar,⁴ and alkyl-substituted [7] and [11]phenacenes have been synthesized by Mallory and coworkers by Wittig condensations plus photocyclisations of alkyl-substituted mono- and bifunctional phenanthrene precursors.⁵



Scheme 1. The two hypothetical polymers polyacene (top) and polyphenacene (bottom).

The Perkin condensation of arylenediglyoxylic acids with arylacetic acids followed by same-pot esterification smoothly leads to arylenebis(arylmaleates),⁶ and such bismaleates may be oxidatively photocyclized to yield extended arenetetracarboxylic tetraesters.⁷ This approach, if pursued with

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such 1,5bifunctional phenacene fragments as naphthylenediglyoxylic acid 1 and 1,7-chrysenylenediglyoxylic acid 2 as central building blocks (Scheme 2), should lead to long phenacenes substituted with four solubilizing alkylester substituents that allow modification of the chromophore by transformation into the corresponding bis(alkylimides). As terminal arylacetic acid building blocks, 1-naphtylacetic acid 3 and 1-chrysenylacetic acid 4 may be used, to lead to tetracarboxylic derivatives of [8], [10], [12] and [14]phenacene (Scheme 3). A [6]phenacene-tetracarboxdiimide has been obtained recently in similar fashion from 1,5-naphthylenediacetic acid and phenylglyoxylic acid,8 and similar elongated dinaphtho[1,2-a;1',2'-h]anthracene-tetracarboxylic derivatives have been obtained previously by palladium-catalyzed double dehydrobrominations.9

We prepared 1, 2 and 4 from the corresponding bromoarenes. 1,5-dibromonaphthalene 5 is most conveniently obtained by regioselective photobromination of 1-bromonaphthalene in CCl₄,¹⁰ whereas bromination of chrysene leads to 6,12- but not 1,7-dibromochrysene 6.11 We therefore synthesized 6 and 1bromochrysene 7 from 5-bromo-1-naphthaldehyde 8¹² or 1naphthaldehyde 9 and diethyl (2-bromobenzyl)phosphonate 10 by a Horner reaction followed by oxidative photocyclization of the intermittent naphthylstyrenes 11 and 12 in ethyl acetate at room temperature in the presence of iodine and air. These photocyclizations proved to be surprisingly concentrationindependent, presumably because the rather voluminous naphthyl and 2-bromophenyl moieties hinder intermolecular side-photoreactions such as 2+2 cyclizations to tetraarylcyclobutanes.¹³ The bromochrysenes 6 and 7 were thus obtained on a 14-20 mM (4-7 g/L) scale in 78% and 75% yield by simple filtration from the reaction medium, from which they precipitate during the reaction. The photocyclization of 12 to 7 has previously been reported at high dilution - 1 mmol/L (0.3 g/L) – in similar (74%) yield.¹⁴ Treatment of **6** and **7** with *n*-BuLi followed by diethyl oxalate yielded the glyoxylic esters 13 and 14. Dibromonaphthalene 5 was transformed similarly into the diglyoxylic ester 15, but t-BuLi had to be used in this case to avoid butylation. Contrary to what has been observed with bigger dibromoarenes, 5 cannot be substituted twice to 15 by the usual action of n-BuLi and diethyl oxalate. The main compound obtained by such a procedure is ethyl 5butyInaphthyl-1-glyoxylate, because naphthylene-1,5-dilithium reacts once by nucleophilic substitution on bromobutane, which is formed as a side product of the bromine-lithium exchange reaction. To avoid this unwanted reaction, we used two equivalents of t-BuLi per function, since the 2-bromo-2methylpropane formed by the bromine-lithium exchange reaction immediately reacts with another t-BuLi molecule to give inert 2methylpropene and 2-methylpropane by β -elimination.

Diesters 13 and 15 were hydrolyzed to the corresponding diglyoxylic acids 1 and 2, whereas monoester 14 was reduced with concomitant hydrolysis to the monoacetic acid 4.

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Scheme 2. Synthesis of naphthalene- and chrysene-based bismaleates **16-19** as precursors of phenacene-tetracarboxylic esters **20-23**. (a) NaH, THF, 51-73%; (b) hv, l₂, O₂, EtOAc, 75-78%; (c) 1. THF, *n*-BuLi, 2. EtO₂CCO₂Et, 76-84%; (d) 1. THF, *t*-BuLi, 2. EtO₂CCO₂Et, 85%; (e) NaHCO₃, EtOH-H₂O, 100%; (f) 1. NaI, H₃PO₂, H₂O, AcOH, 2. MeSO₃H, 81%; (g) 1. NEt₃, Ac₂O, THF, 2. ROH, RBr, DBU, 40-66%. Hx = *n*-hexyl.

The double Perkin condensations of either of the diglyoxylic acids 1 and 2 with either of the acetic acids 3 and 4, followed by in-situ esterification, led in 40-66% yield to the bismaleates 16-19. Due to the low solubility and thus low reactivity of the initially formed bismaleic dianhydride, the final esterification step leading to the longest homologue 19 necessitated a prolonged reaction time of five days. Photoreaction of the bismaleates in ethyl acetate in the presence of iodine and oxygen under borosilicate-filtered irradiation by a medium-pressure mercury immersion lamp gave in 63-80% yield the targeted phenacenetetracarboxylates 20-23, which, with the exception of 22, conveniently precipitated pure from the reaction medium. The higher solubility of 22, with respect to its homologues 21 and 23 with identical solubilizing alkyl groups, may be imparted to the

much stronger aggregation tendency of the central unsubstituted chrysene segments in **21** and **23** compared to the shorter and thus sterically more shielded central unsubstituted naphthalene segment in **22**. The evolution of the melting temperature with increasing molecular length confirms the relatively weak aggregation tendency of **22**: Albeit a linear increase of melting temperature from **21** via **22** to **23** would be in line with the growth of the arene system, **21** and **22** both melt at ca. 240°C, whereas no melting is observed with **23** up to 300°C.

The four phenacene-tetracarboxylates were transformed directly in 65-90% yield into the homologous swallow-tailed N,N'dialkylimides 24-27 by condensation with an appropriate symmetrical (dialkylmethyl)amine in the presence of imidazole in refluxing o-dichlorobenzene. The structures of the four phenacene-diimides are unambiguously confirmed by their highly symmetric and sufficiently deconvoluted aromatic regions of their ¹H NMR spectra that show only two aromatic triplets and 8. 10 or 12 doublets (in the notable absence of any singlets) for 25, 26 and 27, respectively, whilst for the shortest homologue 24 the two would-be triplets convolute, resulting in correspondingly complex peaks for the two neighboring hydrogens, plus 4 doublets for the non-terminal aromatic hydrogens. This confirms that neither the four-fold photocyclizations of the bismaleates to the phenacene-tetracarboxylates 20-23 to nor the hightemperature transformations of the latter to the final diimides 24-27 are impeded by unexpected rearrangements.



Scheme 3. [8]-, [10]-, [12]- and [14]phenacene-tetracarboxylic esters **20-23** and -tetracarboxdiimides **24-27** obtained from bismaleates **16-19** by oxidative photocyclization (h_{v} , l_{z} , O_{z} , EtOAc, 63-80%) and subsequent imidification ($R_{2}CHNH_{3}CI$, imidazole, *o*-C₆H₄Cl₂, 65-90%). Pn = *n*-pentyl, Hx = *n*-hexyl, Ud = *n*-undecyl.

The optical absorption spectra in dilute chloroform solution (Figure 1) surprisingly show that both in the ester and in the imide series, the long wavelength absorption edges of the two shorter homologues are nearly identical (415 nm [corresponding to an optical band gap of 2.99 eV] for for the esters 20 and 21, 505 nm [2.46 eV] for the imides 24 and 25), and occur at about 15nm shorter wavelength than the absorption edges of the two longer homologues, which are also nearly identical (430 nm [2.88 eV] for the esters 22 and 23, 520 nm [2.38 eV] for the imides 26 and 27). This suggests that the positioning of the substituents is of non-negligible influence on the optical band gap, as we have observed previously in tetracarboxy-substituted dinaphtho[1,2-a;1',2'-h]anthracenes.9 In these dinaphthoanthracenes, the band gap was found to be smaller when the substituents are closer to the middle of the arene system, i.e. when they are more closely conjugated with each other. A similar behavior is apparent in the phenacenes: The optical band gap diminishes when the arene is lengthened at the ends (when passing from peripheral naphthalenes to peripheral chrysenes. i.e. from 21 to 22 or from 25 to 26), but remains constant if the arene is lengthened by insertion in the center (when passing from central naphthalene to central chrysene, i.e. from 20 to 21, or 22 to 23, or 24 to 25, or 26 to 27). In the latter case, the influence of the overall lengthening of the chromophore on the optical band gap is thus compensated as the substituents are simultaneously moved further apart.

At all four phenacene lengths, the absorption edge of the imide is at 90 nm longer wavelength than that of the corresponding ester, due to the appearance of a broad long wavelength absorption peak in the imides, whose equivalent is discernible only as a shoulder in the esters (Figure 1).



Figure 1. Absorption spectra of [8]-, [10]-, [12]- and [14]phenacene-tetracarboxylic esters 20-23 and -tetracarboxdiimides 24-27 (2.5 μ mol L⁻¹ in chloroform).

To quantify the absolute donor/acceptor character of the esters and imides, we also performed differential pulse and cyclic voltammetry in DCM solution with ferrocene as internal standard. In all cases, the first oxidation proved to be irreversible, and the first reduction of the esters was found to be irreversible as well under these conditions, only the first reduction of the imides being quasi-reversible. This irreversibility is not surprising given the characteristically large band gaps and thus rather outlying oxidation and reduction potentials of these fully Fries-stabilized systems. The reversibility of the reduction potentials of the diimides is in agreement with the established electron acceptor character of such imides. Due to the irreversible redox transitions and to the limited solubility especially of the longer imides in DCM, the obtained HOMO and LUMO values and the resulting electrochemical band gaps are less precise than the optical band gaps obtained from the absorption spectra. The observed first oxidation and reduction potentials yield HOMO and LUMO energies of -5.85±0.15 eV and -2.7±0.1 eV for the four esters and of -5.9eV±0.15 eV and -3.2±0.1 eV for the four imides (Table 1). Thus whilst both the HOMO and the LUMO energies are only weakly dependent on length and the HOMO energies are only weakly dependent on substitution, the difference in LUMO energies between esters and imides is striking, the latter thus being, as expected, considerably better electron acceptors than the former. As the first oxidation potentials (and HOMO energies) are guasi-independent of substitution, whereas the first reduction potentials (and LUMO energies) differ considerably between esters and imides, it may be assumed that the positive charge injected on oxidation is localized on the polycyclic aromatic core, whereas the negative charge injected on reduction tends to be localized on the carboxylic substituents. The observed differences between the optical and electrochemical band gaps of 0.1-0.4 eV correspond to the exciton binding energies and are similar to the values of 0.15-0.35 eV observed with the aforementioned dinaphthoanthracenes.9

As the electrochemical band gaps of unsubstituted phenacenes are expected to be larger than those of esters **20-23** (3.15 ± 0.15 eV) and imides **24-27** (2.7 ± 0.15 eV) with their conjugated carboxylic substituents, the observation of band gaps in the esters that are well above the value of 2.5 eV predicted for unsubstituted polyphenacene³ indicates that unsubstituted phenacenes might have to be considerably longer than the phenacenes investigated here to be electronically quasi-identical with polyphenacene.

 Table 1. Observed first oxidation and reduction potentials, HOMO and LUMO energies, electrochemical and optical band gaps, and exciton binding energies

Phen- acene	1 st ox. (eV) ^[a]	1 st red. (eV) ^[a]	E _{HOMO} (eV) ^[b]	E _{LUMO} (eV) ^[b]	redox gap (eV)	opt. gap (nm)	opt. gap (eV)
20	+1.16	-2.09	-5.96	-2.71	3.25	415	2.99
21	+0.96	-2.13	-5.76	-2.67	3.09	415	2.99
22	+0.96	-2.07	-5.76	-2.73	3.03	430	2.88
23	+0.92	-2.17	-5.72	-2.63	3.09	430	2.88
24	+1.24	-1.61	-6.04	-3.19	2.85	505	2.46
25	+1.08	-1.66	-5.88	-3.14	2.74	505	2.46
26	+1.06	-1.57	-5.86	-3.23	2.63	520	2.38
27	+0.96	-1.62	-5.76	-3.18	2.58	520	2.38

[a] versus ferrocene (Fc) in DCM. [b] from Fc/Fc⁺ at 4.80eV below vacuum

In summary, following the elaboration of appropriate mono- and difunctionalized chrysene and naphthalene precursors, the

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combination of Perkin condensations with oxidative photocyclizations provided a simple and straightforward access to phenacenes of unprecedented length. Whilst the respective tetraesters and diimides differ considerably in band gap, the evolution of the band gap with molecular length is only weakly discernible. It remains to be seen whether even longer phenacenes with similar substitution patterns will slowly converge towards a significantly smaller gap than the [12] and [14]phenacenes presented here.

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The longest known phenacenes so far are constructed efficiently from chrysene and naphthalene diglyoxylic and monoacetic acids by Perkin condensations and photocyclizations. T. dos Santos Moreira, M. Ferreira, A. Dall'armellina, R. Cristiano, H. Gallardo, E. A. Hillard, H. Bock*, F. Durola*

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RO₂C

RO₂C . Ac₂O, <u>NEt₃</u>

2. Esteril 3. hv, l₂

.CO₂R

CO₂R

HO₂C HO₂C

4 steps

Tetracarboxy-functionalized [8], [10], [12] and [14]Phenacenes