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

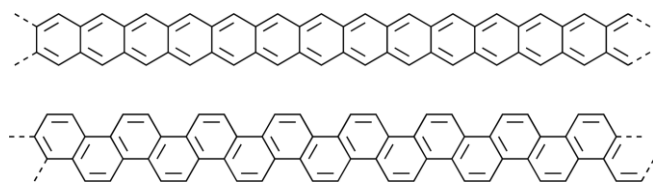
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Abstract: Mono- and diglyoxylation of chrysene and naphthalene leads to Perkin reactants that yield bismaleates, which efficiently photocyclize to elongated phenacenetetracarboxylic esters. Their band gaps remain significantly larger than the value postulated for polyphenacene. The 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.

Introduction

The two conceptually simplest and thinnest hypothetical graphene nanoribbons are polyacene and polyphenacene. Whilst higher acenes, i.e., longer than heptacene, are too unstable to be isolated due to their only minimal sextet stabilization, and whilst 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 (i.e., fulminene) have been isolated from coal tar,^[4] and alkyl-substituted [7]- and [11]phenacenes have been synthesized by Mallory and coworkers through Wittig condensations and photocyclisations of alkyl-substituted mono- and bifunctional phenanthrene precursors.^[5]



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

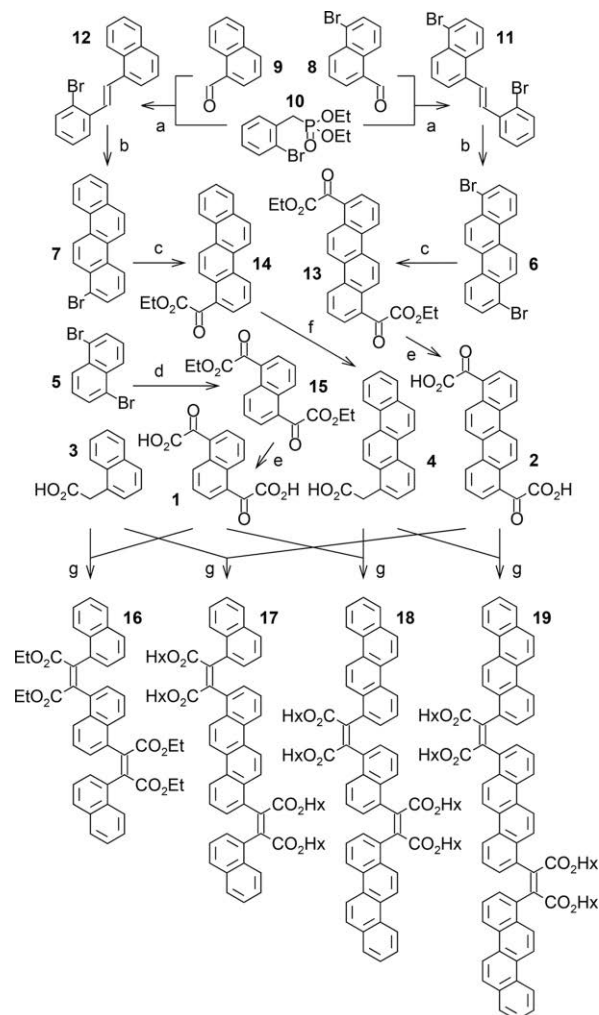
The Perkin condensation of arylenediglyoxylic acids with arylacetic acids followed by same-pot esterification smoothly

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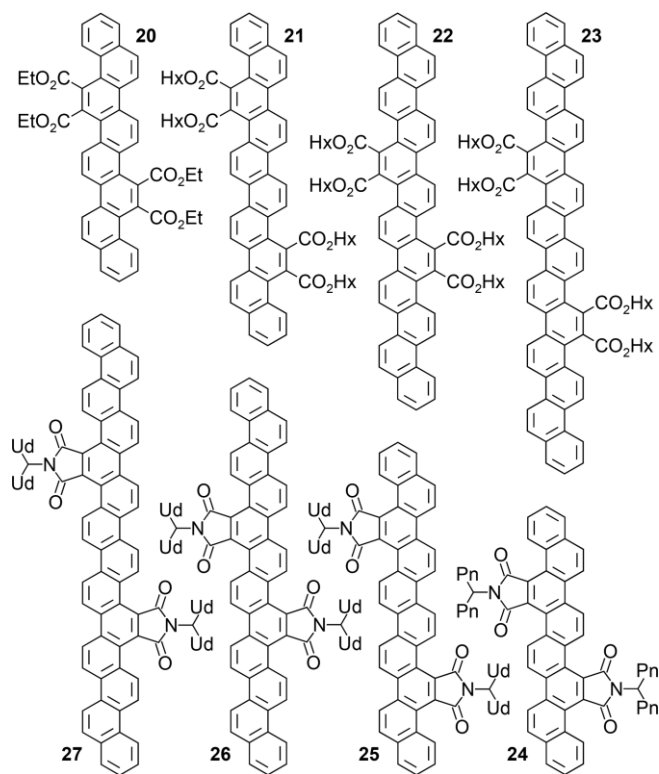
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Scheme 2. Synthesis of naphthalene- and chrysene-based bismaleates **16–19** as precursors of phenacenetetracarboxylic esters **20–23**. (a) NaH, THF, 51–73 %; (b) $h\nu$, I₂, O₂, EtOAc, 75–78 %; (c) 1. THF, *n*BuLi, 2. EtO₂CCO₂Et, 76–84 %; (d) 1. 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.

leads to arylenebis(arylmaleates),^[6] and such bismaleates may be oxidatively photocyclized to yield extended arenetetracarboxylic esters.^[7] This approach, if pursued with bifunctional phenacene fragments such as 1,5-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). Terminal arylacetic acid building blocks, such as 1-naphthylacetic 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]phenacenetetracarboxydiimide has been obtained recently in a similar fashion from 1,5-naphthylenediacetic acid and phenylglyoxylic acid,^[8] and similar elongated dinaphtho[1,2-*a*;1',2'-*h*]anthracenetetracarboxylic derivatives have been obtained previously by palladium-catalyzed double dehydrobrominations.^[9]



Scheme 3. [8]-, [10]-, [12]-, and [14]phenacenetetracarboxylic esters **20–23** and -tetracarboxydiimides **24–27** obtained from bismaleates **16–19** by oxidative photocyclization ($h\nu$, I₂, O₂, EtOAc, 63–80 %) and subsequent imidification (R₂CHNH₂Cl, imidazole, *o*-C₆H₄Cl₂, 65–90 %). Pn = *n*-pentyl, Hx = *n*-hexyl, Ud = *n*-undecyl.

Results and Discussion

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 1-bromochrysene **7** from 5-bromo-1-naphthaldehyde **8**^[12] and 1-naphthaldehyde **9**, respectively, in a Horner reaction with di-

ethyl (2-bromobenzyl)phosphonate **10** 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 concentration-independent, presumably because the rather voluminous naphthyl and 2-bromophenyl moieties hinder intermolecular sidephotoreactions 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 precipitated during the reaction. The photocyclization of **12** to **7** has previously been reported at high dilution – 1 mmol/L (0.3 g/L) – in a similar yield (74 %).^[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 larger dibromoarenes, **5** cannot be substituted twice to give **15** by using *n*BuLi and diethyl oxalate. The main compound obtained by such a procedure is ethyl 5-butylnaphthyl-1-glyoxylate, because naphthylene-1,5-dilithium reacts once through nucleophilic substitution with bromobutane, which is formed as a side product of the bromine–lithium exchange. To avoid this unwanted reaction, we used two equivalents of *t*BuLi, since the 2-bromo-2-methylpropane formed by the bromine–lithium exchange reaction immediately reacts with another *t*BuLi molecule to give inert 2-methylpropene and 2-methylpropane through β -elimination.

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

The double Perkin condensations of either of the diglyoxylic acids **1** or **2** with either of the acetic acids **3** or **4**, followed by in situ esterification, led to the bismaleates **16–19** in 40–66 % yield. 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 the targeted phenacenetetracarboxylates **20–23** in 63–80 % yield, which, with the exception of **22**, precipitated conveniently from the reaction medium in pure form. 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 melting temperatures observed 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 approximately 240 °C, while **23** melts at approximately 300 °C.

The four phenacenetetracarboxylates were transformed directly 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 in 65–90 % yield. The structures of the four phenacenediimides 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, which results in correspondingly complex peaks for the two neighboring hydrogen atoms and four doublets for the non-terminal aromatic hydrogen atoms. This confirms that neither the fourfold photocyclization of the bismaleates to give phenacenetetracarboxylates **20–23** nor the high-temperature transformations of the latter to give the final diimides **24–27** are impeded by unexpected rearrangements.

The optical absorption spectra of dilute chloroform solutions (Figure 1) surprisingly show that both in the ester and in the imide series, the longest-wavelength absorption edges of the two shorter homologues are nearly identical (415 nm [corresponding to an optical band gap of 2.99 eV] for the esters **20** and **21**, 505 nm [2.46 eV] for the imides **24** and **25**), and occur at about 15 nm 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 position 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 dinaphtho-anthracenes, 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 herein described 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.

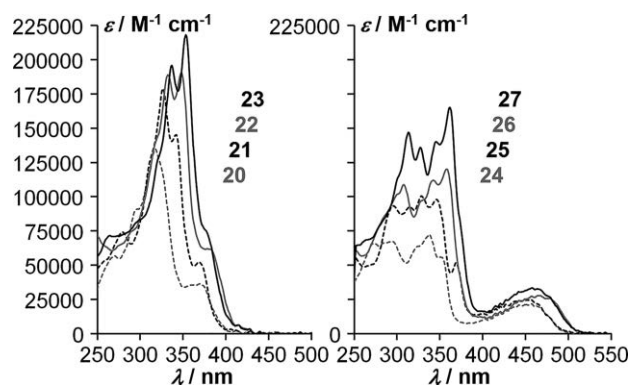


Figure 1. Absorption spectra of [8]-, [10]-, [12]-, and [14]phenacenetetracarboxylic esters **20–23** and -tetracarboxydiimides **24–27** (2.5 $\mu\text{mol L}^{-1}$ in chloroform).

For 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 for the esters is discernible only as a shoulder (Figure 1).

To quantify the absolute donor/acceptor character of the esters and imides, we also performed differential pulse and cyclic voltammetry of dichloromethane solutions with ferrocene as the 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 is 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-accepting character of such imides. Due to the irreversible redox transitions and to the limited solubility, especially of the longer imides in dichloromethane, 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 $-5.9 \text{ eV} \pm 0.15$ 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 of the phenacene and the HOMO energies are only weakly dependent on the substituents, the difference in LUMO energies between esters and imides is striking. As expected, the

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

Phenacene	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] Vs. ferrocene (Fc) in DCM. [b] From Fc/Fc⁺ at 4.80 eV below vacuum.

latter are considerably better electron acceptors than the former. As the first oxidation potentials (and HOMO energies) are quasi-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 upon oxidation is localized on the polycyclic aromatic core, whereas the negative charge injected upon 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 polyphenacene^[3] indicates that unsubstituted phenacenes might have to be considerably longer than the phenacenes investigated here to be electronically quasi-identical with polyphenacene.

Conclusion

In summary, following the elaboration of appropriate mono- and difunctionalized chrysene and naphthalene precursors, the 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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- [1] S. Kivelson, O. L. Chapman, *Phys. Rev. B* **1983**, *28*, 7236.
- [2] a) A. Ciesielski, T. M. Krygowski, M. K. Cyrański, *Symmetry* **2010**, *2*, 1390; b) A. Graovac, I. Gutman, M. Randić, N. Trinajstić, *J. Am. Chem. Soc.* **1973**, *95*, 6267; c) K. Fries, *Liebigs Ann. Chem.* **1927**, *454*, 121.
- [3] Y.-W. Son, M. L. Cohen, S. G. Louie, *Phys. Rev. Lett.* **2006**, *97*, 216803.
- [4] K. F. Lang, H. Buffleb, J. Kalowy, *Chem. Ber.* **1964**, *97*, 494.
- [5] a) F. B. Mallory, K. E. Butler, A. Bérubé, E. D. Luzik, C. W. Mallory, E. J. Brondyke, R. Hiremath, P. Ngo, P. J. Carroll, *Tetrahedron* **2001**, *57*, 3715; b) F. B. Mallory, K. E. Butler, A. C. Evans, E. J. Brondyke, C. W. Mallory, C. Yang, A. Ellenstein, *J. Am. Chem. Soc.* **1997**, *119*, 2119; c) F. B. Mallory, K. E. Butler, A. C. Evans, C. W. Mallory, *Tetrahedron Lett.* **1996**, *37*, 7173.
- [6] a) M. Ferreira, E. Giroto, A. Bentaleb, E. A. Hillard, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2015**, *21*, 4391; b) E. Giroto, M. Ferreira, P. Sarkar, A. Bentaleb, E. A. Hillard, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2015**, *21*, 7603.
- [7] a) M. G. B. Cabral, D. M. Pereira de Oliveira Santos, A. Bentaleb, E. A. Hillard, R. Cristiano, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2016**, *22*, 8043; b) M. Ferreira, G. Naulet, H. Gallardo, P. Dechambenoit, H. Bock, F. Durola, *Angew. Chem. Int. Ed.* **2017**, *56*, 3379; *Angew. Chem.* **2017**, *129*, 3428; c) M. G. Belarmino Cabral, D. M. Pereira de Oliveira Santos, R. Cristiano, H. Gallardo, A. Bentaleb, E. A. Hillard, F. Durola, H. Bock, *ChemPlus-Chem* **2017**, *82*, 342.
- [8] R. Wang, K. Shi, K. Cai, Y. Guo, X. Yang, J.-Y. Wang, J. Pei, D. Zhao, *New J. Chem.* **2016**, *40*, 113.
- [9] H. Bock, P. Carré, E. A. Hillard, F. Durola, *Eur. J. Org. Chem.* **2015**, 1028.
- [10] O. Cakmak, I. Demirtas, H. T. Balaydin, *Tetrahedron* **2002**, *58*, 5603.
- [11] a) M. Sarobe, H. C. Kwint, T. Fleer, R. W. A. Havenith, L. W. Jenneskens, E. J. Vlietstra, J. H. van Lenthe, J. Wesseling, *Eur. J. Org. Chem.* **1999**, 1191; b) H. Bock, S. Huet, P. Dechambenoit, E. A. Hillard, F. Durola, *Eur. J. Org. Chem.* **2015**, 1033.
- [12] P. Ruggli, R. Preuss, *Helv. Chim. Acta* **1941**, *24*, 1345.
- [13] F. B. Mallory, C. W. Mallory, *Org. React.* **1984**, *30*, 1.
- [14] W. J. Archer, R. Taylor, P. H. Gore, F. S. Kamounah, *J. Chem. Soc. Perkin Trans. 2* **1980**, 1828.