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Explorations of the solubilizing effectiveness of $CH_3OCH_2CH_2O$ substituents in the photocyclizations of some 1,2-diarylethylenes to [*n*]phenacenes

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ABSTRACT

We have previously published many photocyclizations of 1,2-diarylethylenes to produce zig-zag aromatic ring systems with $n = 5$, 7, and 11 fused benzene rings. We invented the name [*n*]phenacenes for these compounds. To increase their solubilities we attached either various alkyl or phenyl substituents. We present here our recent explorations of the effectiveness of $CH_3OCH_2CH_2O$ substituents as solubilizing groups in three examples of diarylethylene photocyclizations that produced one [5]phenacene and two [7]phenacene systems.

In a series of earlier publications[1a–d] we have reported the photocyclizations of a number of 1,2-diarylethylenes to produce [*n*]phenacenes having $n = 5$, 7, or 11 benzene rings fused in an extended zig-zag pattern. In these previous studies we attached several alkyl or phenyl substituents along the aromatic ring skeletons of the diarylethylenes in order to provide adequate solubilization for both the diarylethylenes and their [*n*]phenacene photoproducts. These solubilizing substituents were very useful for the recrystallizations as well as for the spectral analyses of these compounds.

In our choice of effective solubilizing groups there had to be a compromise that allowed sufficient solubility to permit further functionalization and elongation as well as ease of purification through recrystallization. Some earlier attempts using long-chain tertiary alkyl substituents gave oils throughout the synthetic schemes, and the resulting difficulties in purification contributed to failures in the subsequent chemistry attempted. Unfortunately the ability of the side chains to adequately solubilize large [*n*]phenacenes is not known until well into the synthetic scheme. However, an advantage of employing polyether groups rather than alkyl side chains is that they can be exchanged[2] with either longer or shorter ether groups as needed along the synthetic pathway. In this way one can more easily adjust the solubility of the molecule to make it either more soluble or less soluble.

We report here our preliminary investigations to explore the solubilizing ability of pairs of $CH_3OCH_2CH_2O$ substituent groups (which we have abbreviated in Schemes 1–4 as RO groups) in the photochemical syntheses of the three [*n*]phenacene compounds **1**, **2**, and **3** shown in Scheme 1. The syntheses of these three compounds are presented in Schemes 2–4.

Schemes 2–4 indicate that modifications of the chemistry used for the syntheses of the polyether-substituted phenacenes were necessary as compared with the syntheses of the alkyl- and phenyl-substituted phenacenes.[1] One complication arose with the free-radical bromination reactions using *N*-bromosuccinimide in carbon tetrachloride because the competing electrophilic aromatic brominations on the phenacene rings were sometimes significant competing reactions. Conditions were optimized for free-radical chemistry using an external light source and a free-radical initiator, and this succeeded in eliminating (or at least minimizing) the substitution pathways for some reactions (e.g., **7** → **8** and **18** → **19**). In other cases, especially in the [5]phenacene and [7]phenacene systems, these competing substitution reactions persisted which is likely a result of the fact that polyether substitution on an aromatic ring results in a more electron-rich system that will be more susceptible to ring bromination. However, there was good improvement in several of these cases when the free-radical bromination was carried out using α,α,α-trifluorotoluene as solvent.[3]

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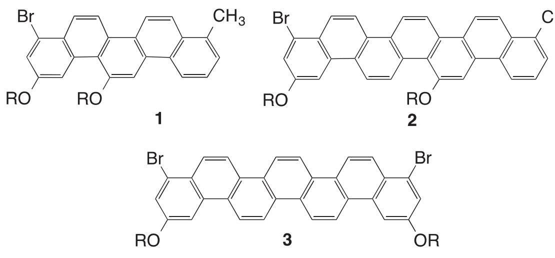
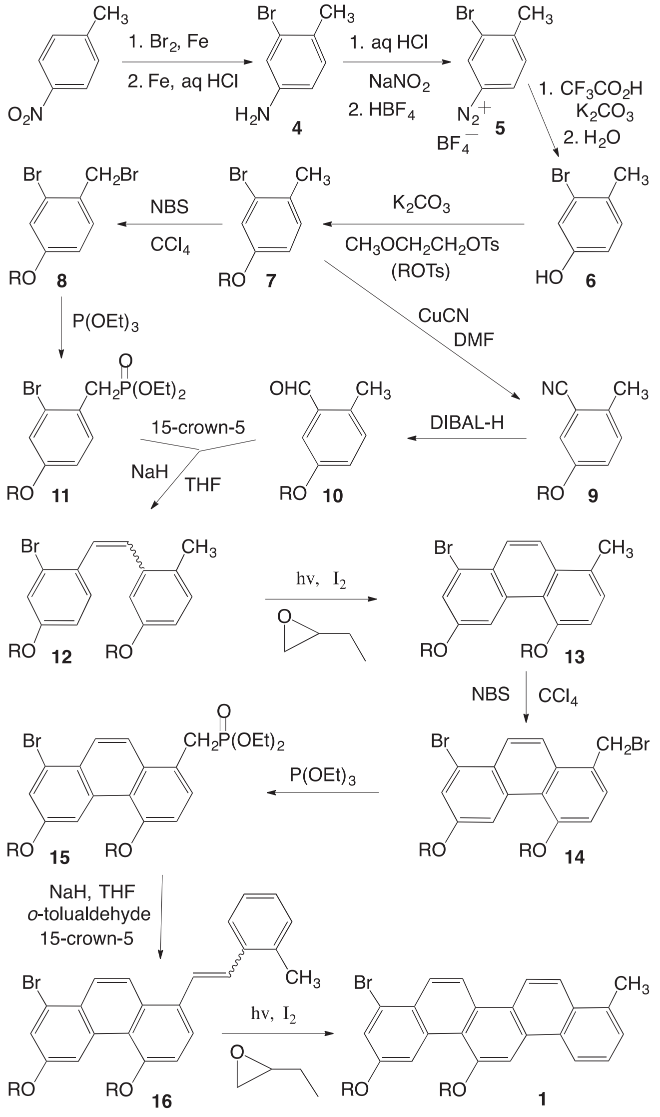
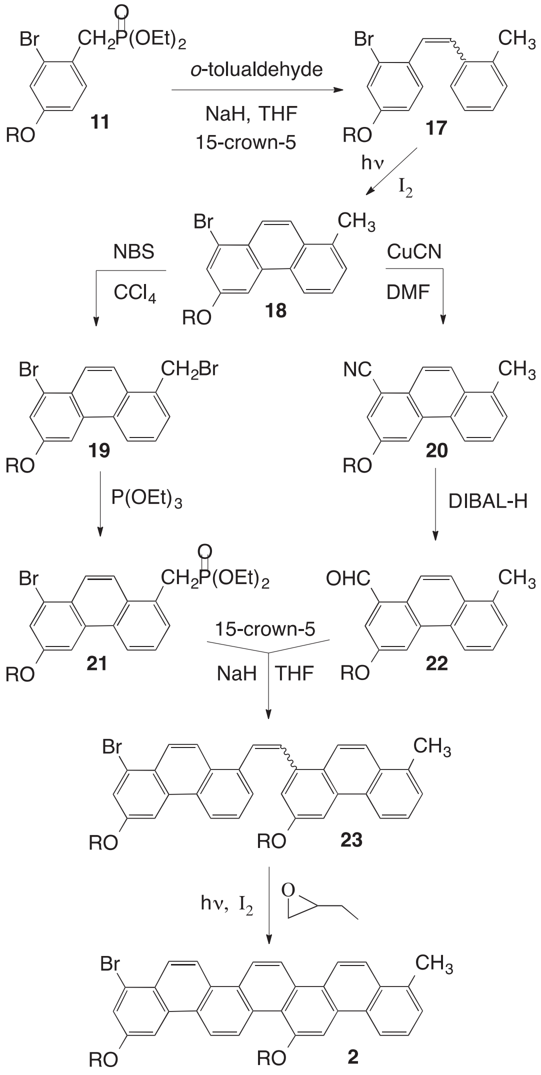


Scheme 1.

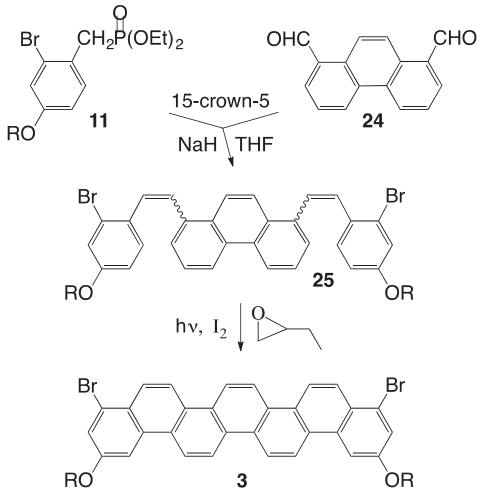


Scheme 2. Synthesis of [5]phenacene **1**.

Further evidence of more reactive aromatic rings was observed in compounds **7** and **18** in our unsuccessful attempts to transform a bromo substituent on an aromatic ring bearing a polyether group to an aldehyde using the standard butyllithium and DMF procedure. In the syntheses described in Schemes 2 and 3 it was necessary to use a two-step procedure where the aromatic bromo compound was reacted first with cuprous cyanide and the resulting nitrile was then converted to the aldehyde by treatment with DIBAL (e.g., **7** → **9** → **10** in Scheme 2, and **18** → **20** → **22** in Scheme 3).



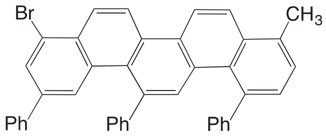
Scheme 3. Synthesis of [7]phenacene **2**.



Scheme 4. Synthesis of [7]phenacene **3**.

This work was begun with the assumption that the polyether substituents would be more effective at solubilizing the phenacenes and their precursors than had been found for the alkyl- and

Table 1
Solubility measurements in benzene at room temperature



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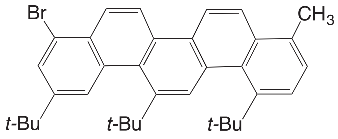

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Compound	Sample amt		Benzene amt		mol/L
	mg	mmol	g	mL	
26	4.0	0.0067	0.8229	0.939	0.0071[1d]
26	4.0	0.0067	0.8366	0.954	0.0070[1d]
27	4.0	0.0074	0.0935	0.107	0.069[1d]
27	4.0	0.0074	0.0926	0.106	0.070[1d]
1	4.0	0.0077	3.9375	4.492	0.0017
1	4.0	0.0077	3.9785	4.539	0.0017
2	4.0	0.0064	44.9570	51.2915	0.00012
2	4.0	0.0064	44.6863	50.9826	0.00013
3	4.0	0.0059	17.0489	19.4511	0.00030
3	4.0	0.0059	17.1450	19.5608	0.00030

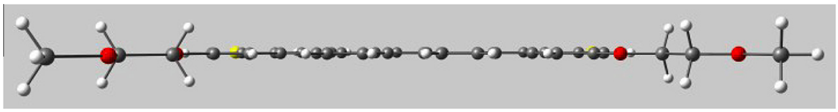

Figure 1. Optimized geometry of compound **3**, sideview.

phenyl-substituted compounds. A comparison of the solubilities of *tert*-butyl and phenyl substitution was reported earlier.[1d] As listed in Table 1, in the two [5]phenacenes **26** and **27** shown above, the phenyl substituents in compound **26** were less effective solubilizing groups than were the *tert*-butyl substituents in compound **27**. This had not been anticipated and our intuition failed us once again for the case of the polyether-substituted [5]phenacene **1** which we found to be about 4 times less soluble in benzene than its *tert*-butyl counterpart! (The comparison is not exact because the *tert*-butyl- and phenyl-substituted compounds **26** and **27** each have three solubilizing groups attached to the [5]phenacene backbone whereas the polyether derivative **1** has only two solubilizing groups.)

Two direct solubility comparisons were possible with the polyether-substituted [5]phenacene and [7]phenacenes as shown in Table 1. First, in comparing the mol/L solubilities of the two [7]phenacenes **2** and **3**, another solubility pattern emerges. Compound **3**, the symmetrically substituted [7]phenacene, is slightly more than twice as soluble in benzene at room temperature than the unsymmetrically substituted [7]phenacene **2**. Second, both the [5]phenacene **1** and the [7]phenacene **2** have unsymmetric substitution patterns and two polyether solubilizing groups. Solubility measurements on **1** and **2** showed that the addition of the two extra aromatic rings in the [7]phenacene **2** decreased its solubility in benzene by more than a factor of ten as compared with that of the [5]phenacene **1**. This behavior may help explain why subsequent chemistry that was attempted to elongate compound **1** to produce an [11]phenacene was unsuccessful as low solubility became a major factor.

It is believed that crystal packing of the phenacene molecules in the solid state contributes to their overall solubility. The less-soluble phenyl-substituted phenacenes were found by X-ray crystallography to pack much more closely in the crystal lattice than did their more soluble *tert*-butyl-substituted counterparts.[1d] A similar effect might be occurring with the polyether groups. Unfortunately, we have not been successful in growing an X-ray quality crystal of any polyether-substituted phenacene, but we have carried out a calculation for compound **3** using Gaussian 09 Revision D.01[4] with the B3LYP hybrid DFT method and the 6-31G* basis set.[5] This calculation confirms our suggestion that the linear nature of the polyether chains should not interfere with the close and effective packing of the phenacene rings in the crystal lattice as do the *tert*-butyl groups. This is illustrated dramatically in the sideview representation of the compound **3** molecule shown above in Figure 1 that emerges from the calculation.

A logical extension of the current work could be to use either longer polyether groups as solubilizing substituents or more of them to achieve the appropriate solubility for the synthesis of longer [*n*]phenacene derivatives.

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Supplementary data

Supplementary data (experimental procedures, characterizations and spectroscopic data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.02.124.

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