

Extended anthracenes and their use as dienes in Diels-Alder reactions

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Introduction

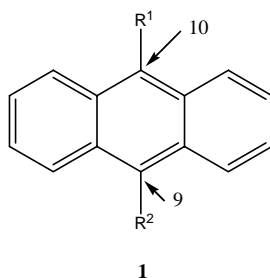
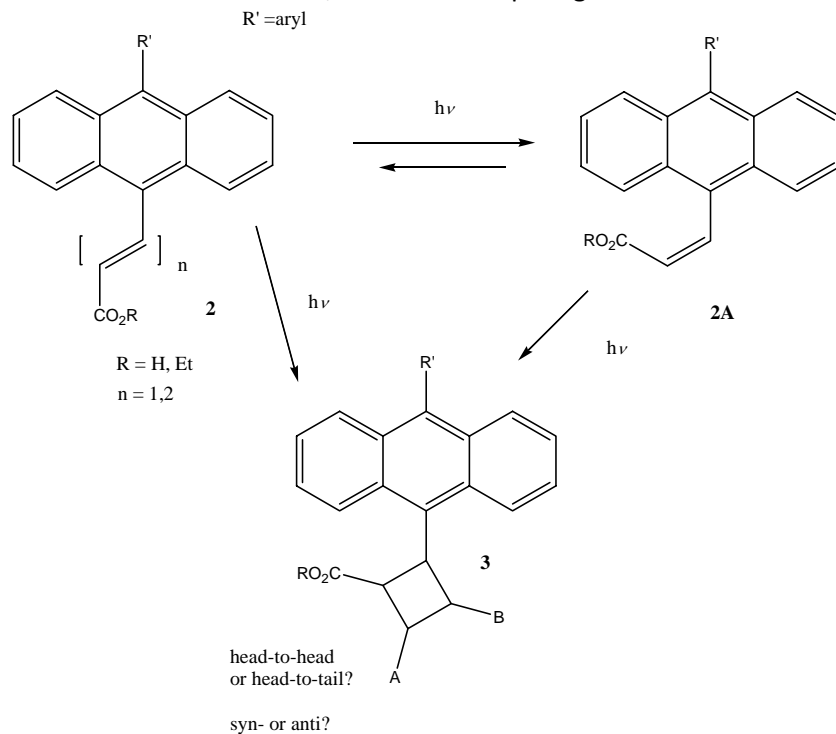


Figure 1. Disubstituted anthracene with carbon-numbering

Anthracenes have interesting electrooptical properties. 9,10-Disubstituted anthracenes have been forwarded as blue light emitting molecules in organic light emitting diodes.¹ Also, anthracenes as subunits in polymers have elicited interest such as as material in the emitting layer of OLEDs.² Additionally, anthracenes, and especially 9,10-disubstituted derivatives **1**, have been used as sensors.³ The authors have interest to use 3-(anthran-9-yl)acrylates as building blocks for anthracene-containing polymers as well as for dimeric anthracenes of type **3** connected with a cyclobutyl unit as potential sensors that can be connected to surfaces by manipulation of the ester functions in **3**. Polymerisation was envisaged to be possible by photochemically initiated radicals⁴ and dimer formation was envisaged to be proceeding photochemically. Now, the photochemistry of anthracenes themselves has been investigated in great detail,^{5,6} and it has been found that the outcome of the reaction depends on the substituents. Anthranylacrylates (**9**) have not been studied photochemically, to our knowledge. So, apart from the

acrylate unit in the anthracenes **2**, the anthracenes themselves are known to undergo photochemical [4 + 4]-cycloadditions under certain conditions,⁷ and thus competing reactions can be foreseen.



Scheme 1. Possible photodimerisation products of anthranylacrylates

Initially, the anthranylacrylates were grown in a crystal with the aim of photolysing in the crystal. The structures of representative anthranylacrylates in the crystal have been measured by us, with an X-ray crystallographic determination of ethyl (*E*)-3-(anthran-9-yl)propenoate ethyl and of (*E*)-3-[9-bromoanthran-10-yl]propenoate.⁸ In the crystal of ethyl (*E*)-3-[9-bromoanthran-10-yl]propenoate (Figure 3), the closest distance between double bonds of two molecules, which are molecules in one strand, is 5.321 (3) Å.^{8b} Although this distance is smaller than the smallest distance found in the non-brominated parent compound (5.549 (3) Å) (Figure 2),^{8a} it is still larger than in many of those found for aryl-enes that undergo [2 + 2]-photodimerization readily.^{9,10} The anthranyl units themselves, while aligned parallel to each other in one strand, are off-set to each other and are much further apart (5.321 (3) Å for C1—C1 and C8—C8) than in anthracenes (less than 4.2 Å) that have been reported to undergo [4 + 4]-photodimerization in the crystal.^{11,12} This makes a photodimerisation in the crystal highly unlikely. Also, initial results from photoreactions of the anthranylacrylates in solutions have found the photochemistry of the anthranylacrylates to be complex.

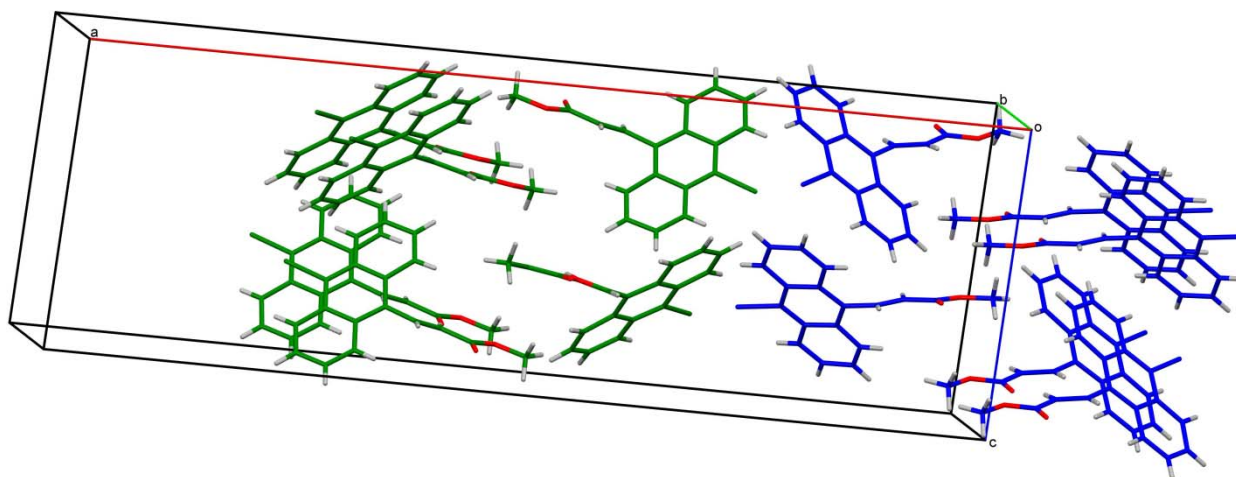


Figure 3. Crystal packing of ethyl 3-(9-bromoanthran-10-yl)acrylate showing intermolecular distances that are too large for photochemical dimerisation reactions in the crystal.^{8b}

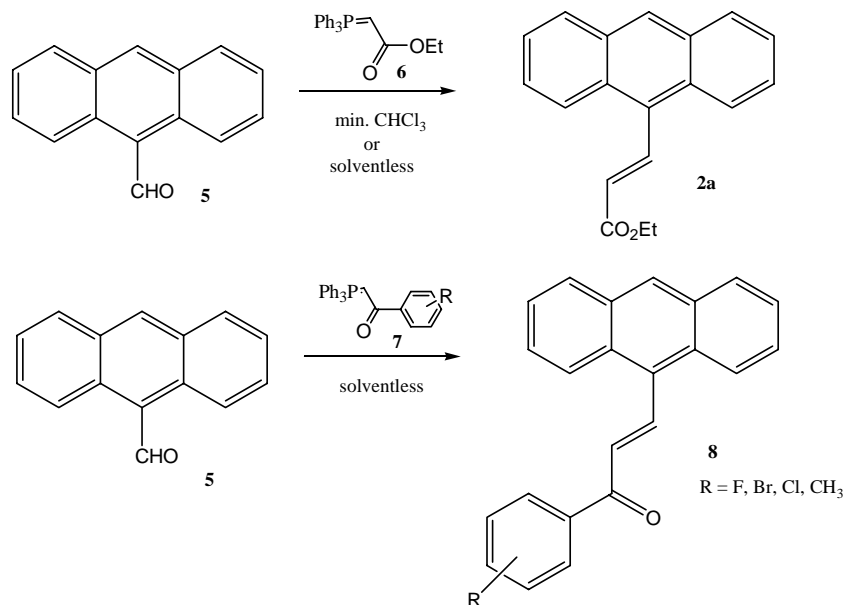
For this reason, it was decided to attempt to “protect” the anthran-10-yl unit first by cycloaddition reaction, subsequently carry out the photochemical reaction, and thereafter liberate the anthran-10-yl unit by retro-Diels-Alder reaction. In the present communication, the authors detail the preparation of a variety of anthran-10-ylacrylates and aroylethenylanthracenes and discuss their cycloaddition behavior versus a number of common deactivated enes. The photochemical behavior of the products and their subsequent manipulation will be communicated later.

Results and discussion

i. Preparation of anthran-10-ylacrylates and aroylethenylanthracenes

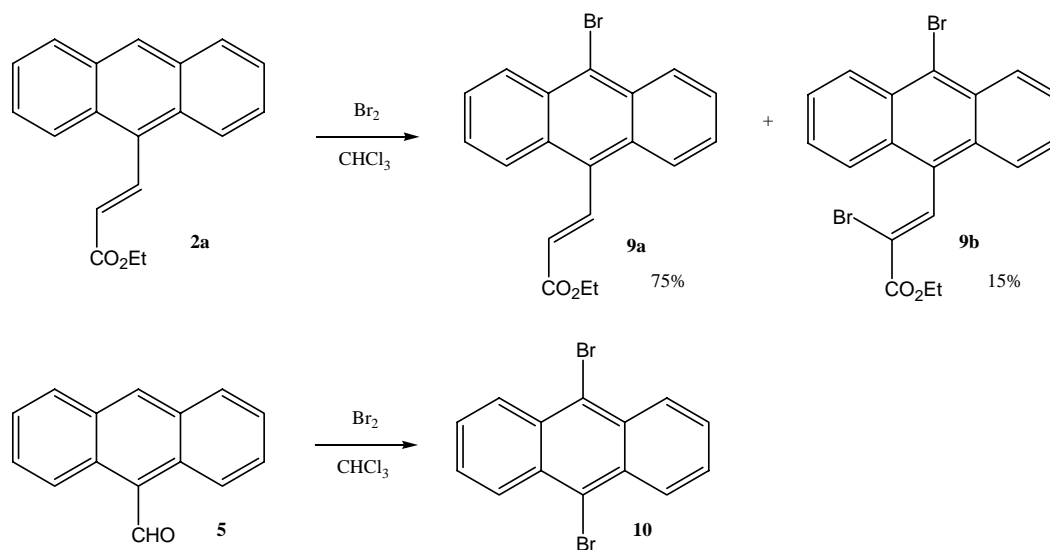
Commercially available 9-anthran-10-ylcarbaldehyde (**5**) should lend itself to Wittig olefination with conjugated phosphoranes such as alkoxycarbonylmethylidenetriphenylphosphoranes **6** or substituted aroylmethylidenetriphenylphosphorane **7**. However, first reaction of **5** with formylmethylidenetriphenylphosphorane showed that 9-anthran-10-ylcarbaldehyde (**5**) does not react with ease, where here the temperature needed for any reaction to occur resulted in decomposition of the phosphorane, even when the reaction was carried out under nitrogen. Also, the Wittig reaction of 9-anthran-10-ylcarbaldehyde (**5**) with fluorophenylcarbonylmethylidenetriphenylphosphorane (**8-F**), run in refluxing xylene at 125 °C, was not yet complete after 24h. It is believed that it is the steric hindrance exerted by the two ancillary benzo groups of the anthracene that leads to sluggish reactions. In former times, the authors have studied Wittig olefinations in solventless and under solvent-reduced systems.¹³⁻¹⁵ When **5** is reacted with ethoxycarbonylmethylidenetriphenylphosphorane (**6**) in very small amounts of CHCl₃ at 110 °C, the reaction to the Wittig-product is complete after 90 min (Scheme 3). In later experiments **5** and **6** were reacted solventless, where a magnetically stirred mixture of **5** and **6** was heated to 130 °C. At 130 °C, the mixture produces a melt, and this liquid undergoes Wittig olefination rapidly. No inert atmosphere is

used when running the experiment. While such reaction conditions may be seen as a contribution to green chemistry, the easiest way of separating the product from the phosphorane, used in slight excess, and the triphenylphosphine oxide is by column chromatography with benzene as eluent. Also, the aroylmethylenetriphenylphosphoranes **7** react with **5** under solventless conditions at 140 °C, albeit in reaction times of 3-4h (Scheme 3). Again, these reactions are run in air.

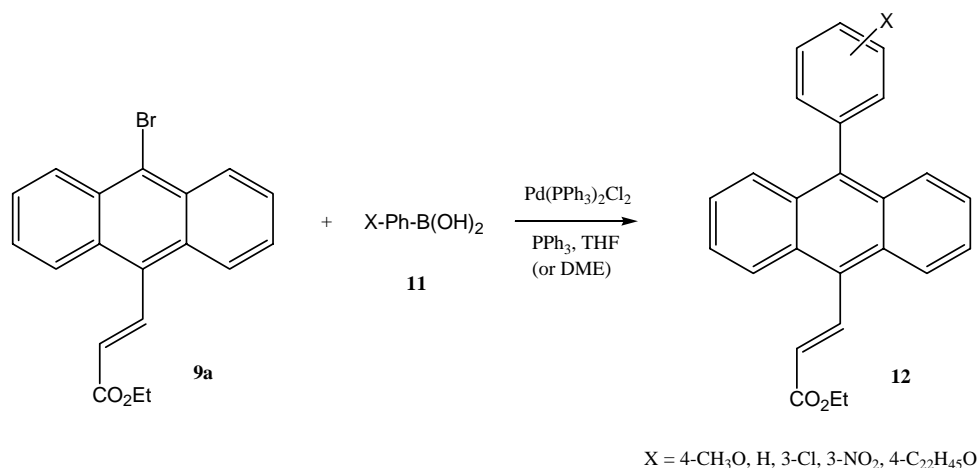


Scheme 3. Solventless Wittig-olefination reactions to anthranylacrylate **2** and aroylethenyl-anthracenes **8**

2a was subjected to bromination (Br_2 , CHCl_3 , rt). Little addition to the acrylate system was observed, although a small amount (15%) of (*Z*)-3-[10-bromoanthran-9-yl]-2-bromopropenoate (**9b**) was formed. Bromination took place at the central ring of the anthracene to give ethyl (*E*)-3-[9-bromoanthran-10-yl]propenoate (**9a**, 75%) (Scheme 4). Reaction of 9-anthranylcarbaldehyde (**5**) with bromine under analogous conditions (Br_2 , CHCl_3) does not furnish the corresponding bromoanthranylcarbaldehyde but 9,10-dibromoanthracene (**10**), formally a decarbonylative bromination (Scheme 4). Ethyl (*E*)-3-[9-bromoanthran-10-yl]propenoate (**9a**) lends itself to arylation through Suzuki cross-coupling reactions at C9. These were easily performed with 4-methoxy-, 3-nitro-, and 3-chlorophenylboronic acids **11** and phenylboronic acid itself [**11**, $\text{X}=\text{H}$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, aq. Na_2CO_3 , dioxane] to furnish the pi-extended systems **12** (Scheme 5). For further use (not shown) such as anchoring to a surface, **12** could be hydrolyzed to the respective acrylic acids.



Scheme 4. Bromination of anthranilacrylate **2a** and anthranilcarbaldehyde **5**.

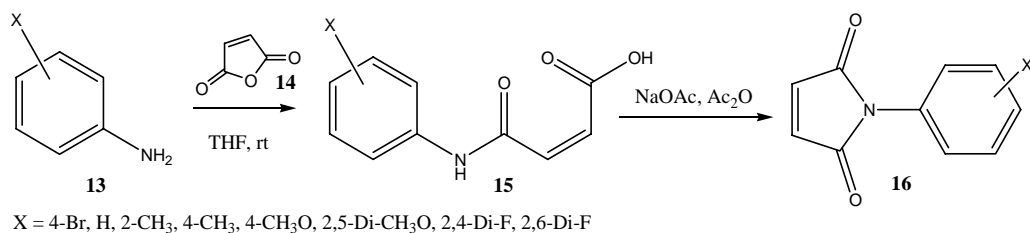


Scheme 5. Pi-extension of anthranilacrylate **9a** by Suzuki-Miyaura cross-coupling reaction.

ii. Diels-Alder reactions of the pi-extended anthracenes

ii.a. Preparation of the dienophiles

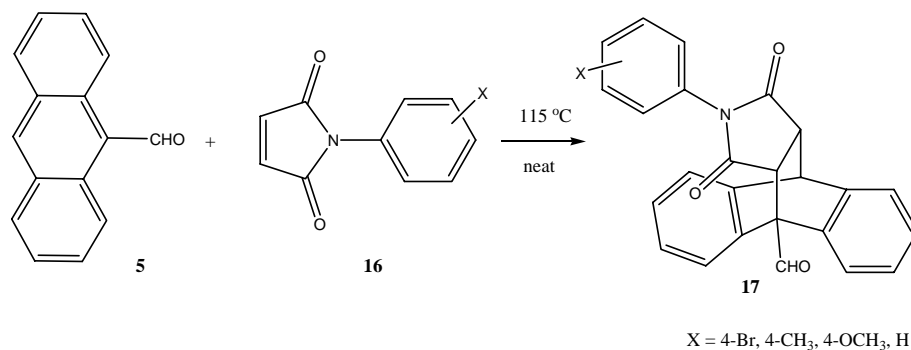
Maleic anhydride (**14**) and diethyl fumarate were acquired commercially. *N*-Aryl maleimides **16** were produced analogous to known literature procedures.¹⁶ Substituted anilines **13** were reacted with maleic anhydride (MSA, **14**) to give the corresponding maleic acid monophenylamides **15**. The reactions were carried out in THF at rt. While most anilines **13** reacted within 90 min., anilines with electron-withdrawing substituents were more sluggish to react. Thus, while 2,4-difluoroaniline (**13** X=2,4-Di-F) still reacted within 90 min. to give the ring opened amide in acceptable yield, 2,6-difluoroaniline (**13** X=2,6-Di-F) did not. Diethyl maleate was produced by reaction of MSA with ethanol (EtOH, Na₂CO₃ [solid], rt).



Scheme 6. Preparation of substituted maleimides (analogous to ref. 16).

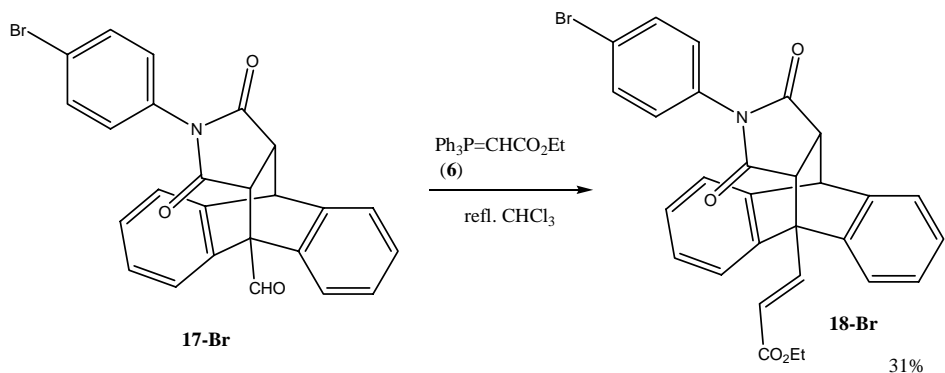
ii.b. [4+2]-Cycloaddition reaction of 9-anthranilcarbaldehyde, alkyl anthranilacrylates, and aroylethenylanthracenes

[4+2]-Cycloaddition with substituted anthracenes have been studied.¹⁷ As it was not certain whether the vinyl substituent on C9 of the anthracene would have a detrimental effect or would participate in the cycloaddition reaction of the anthracene, at first it was attempted to carry out the Diels-Alder reaction of the anthracene at the stage of the 9-anthranilcarbaldehyde (**5**), followed by a Wittig reaction of the carbaldehyde containing cycloadduct **17** (Scheme 7). 9-Anthranilcarbaldehyde (**5**) has been submitted to [4+2]-cycloaddition reactions previously,¹⁸ although not to cycloaddition reactions with maleimides **16**. In our studies, 9-anthranilcarbaldehyde was subjected to solventless Diels Alder reactions at 110 – 115 °C with a number of maleimides. After 13h, the reaction mixtures were cooled and diluted with ether/hexane, whereupon the cycloadducts crystallized. The reactions gave appreciable yields (78% - quant.), and in no instance could a concomitant decarbonylation be observed. Solventless reactions have been used previously in the cycloaddition of anthracenes with liquid mono-activated alkenes such as with alkyl acrylates or propiolates,^{17,18} but not with maleimides.



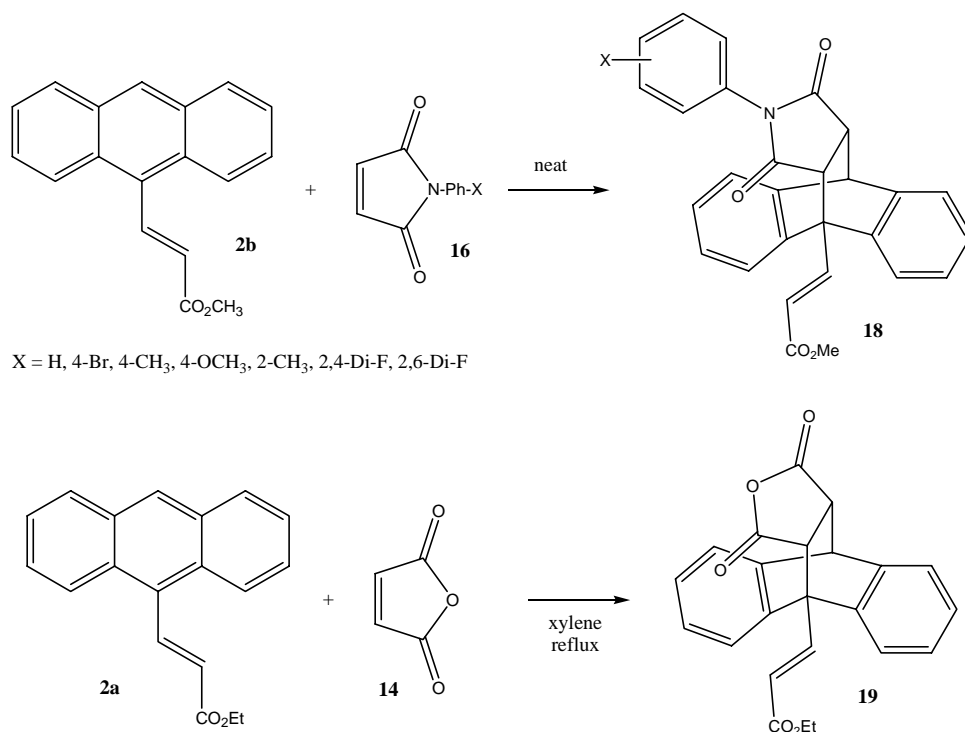
Scheme 7. Solventless cycloaddition of 9-anthranilcarbaldehyde **5** to maleimides **16**.

The subsequent step of the Wittig reaction of the cycloadduct carbaldehyde was found to be more difficult, most likely due to the steric crowding in the transition state. Thus, in refluxing CHCl₃, **17-Br** with **6** produced the Wittig product **18-Br** in only 31% yield after 90 min (Scheme 8). Neither additional reaction time nor a second addition of the phosphorane to the reaction mixture gave satisfactory results. Also, the separation of the product from the starting material proved not to be easy.

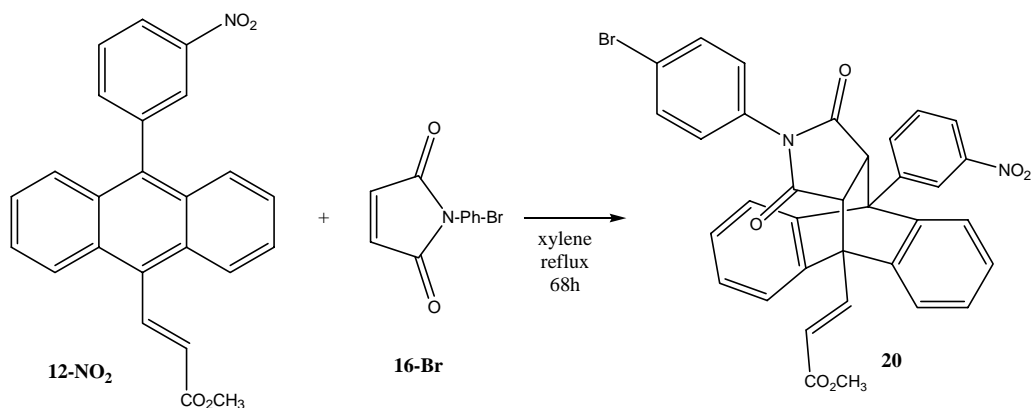


Scheme 8. Wittig olefination of cycloadduct **17-Br** with conjugated phosphorane **6**.

Therefore, it was decided to carry out the Wittig-olefination with the 9-anthranilcarbaldehyde first and subsequently subject the acrylates (**2a**: alkyl = ethyl; **2b**: alkyl = methyl) thus obtained to Diels Alder type reactions. This worked well, where diene and dienophile were heated, again under solventless conditions for the Diels Alder reaction to proceed. The mixture provided a melt at the reaction temperature of 120 °C, which started to solidify as the reaction proceeded. Although the melting – solidification behavior indicates that the reaction may be completed after 15-20 min., this type of reaction was run for 3-4 h.



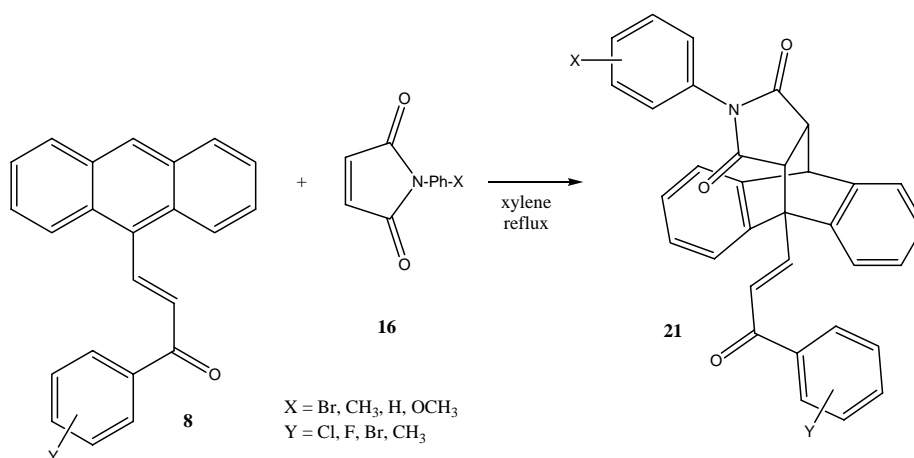
Scheme 9. [4+2]-Cycloaddition of anthranilacrylates **2a/2b** with maleimides and maleic anhydride.



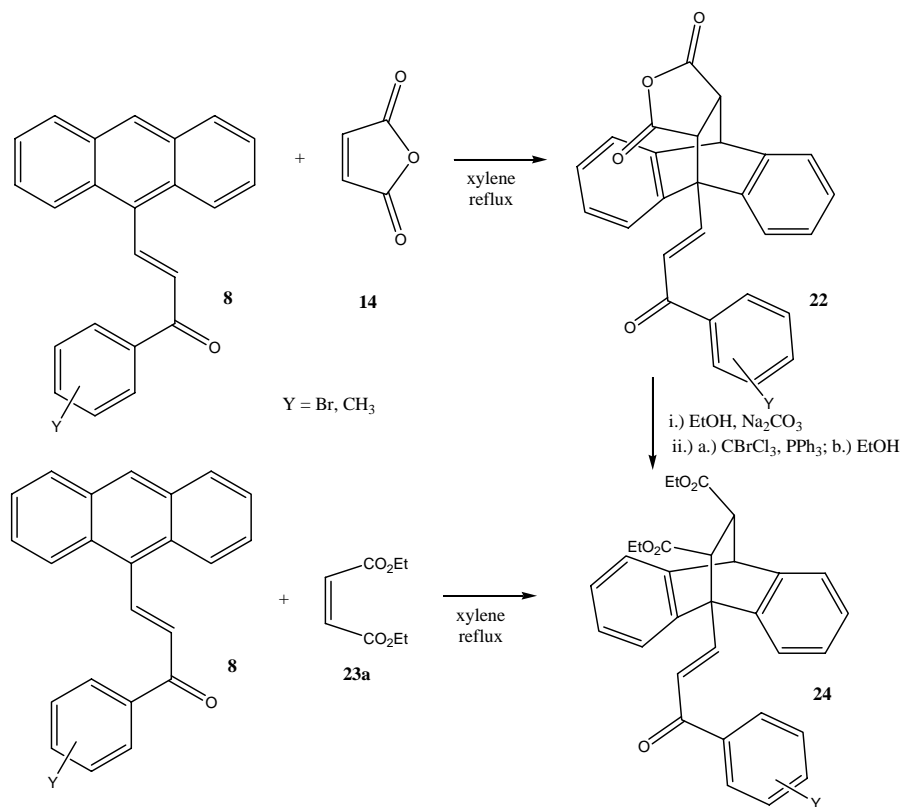
Scheme 10. Cycloaddition reactions of pi-extended anthracenes **12** with maleimides **16**.

The pi-extended anthranylacrylates **12** undergo cycloaddition with maleimides, also. In this case the reaction times are longer (Scheme 10). The acrylates **12** melt at temperatures higher than 140 °C, and thus the reactions have to be run in refluxing xylene. The longer reaction times do not indicate overriding electronic differences (see below) in **12** as compared to **2**, but may find their reason in stereochemical considerations, taking into account a rotating aryl group at C9.

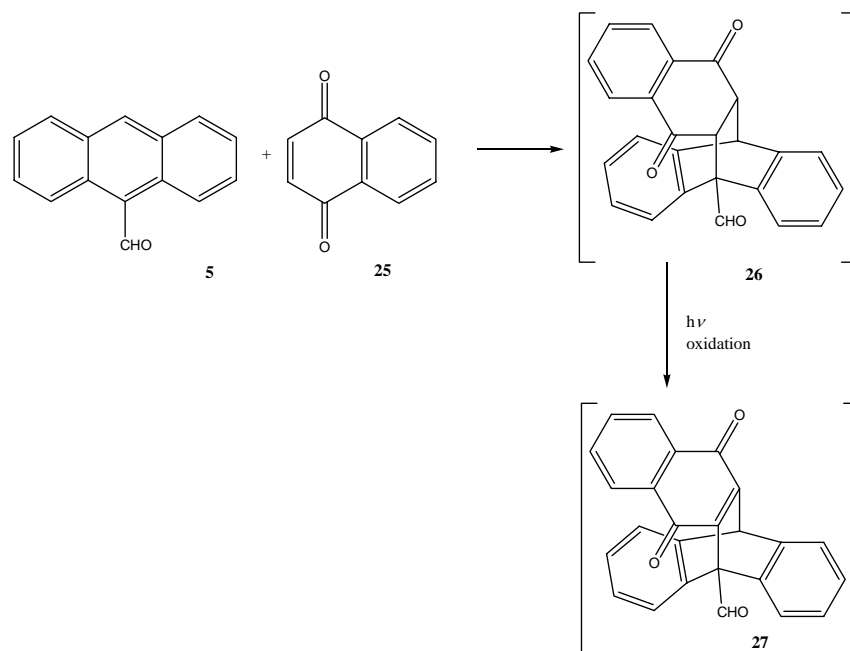
For cycloaddition reactions of arylolethynylantracenes **8** with maleimides **16** (Scheme 11) solutions of **8** and **16** in xylene were heated at reflux as again also arylolethynylantracenes **8** have high melting points and even in mixtures with maleimides **16** do not produce melts at 130 °C. As dienophiles not only maleimides **16** were utilized, but also maleic anhydride **14** and diethyl maleate and fumarate produced the respective cycloadducts. Reactions with diethyl maleate (**23a**) and diethyl fumarate (**23b**) proceeded much more slowly than reactions with maleimides **16** and with maleic anhydride (**14**) (Scheme 12). To gain cycloadducts **24** in higher yield it was found beneficial to ring open the anhydride functionality of the respective cycloadducts of **8** with MSA (**14**), **22**, by reaction with ethanol (EtOH, Na₂CO₃ [solid]), followed by esterification (CBrCl₃, PPh₃; ii. EtOH, Scheme 12).



Scheme 11. Cycloaddition reactions of arylolethynylantracenes **8** with maleimides **16**.

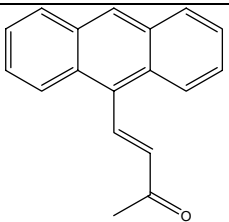
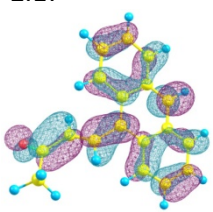
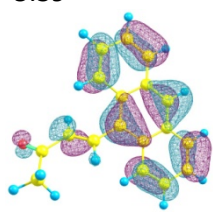
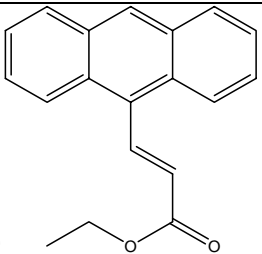
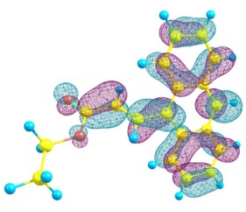
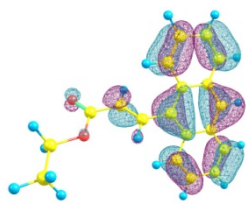
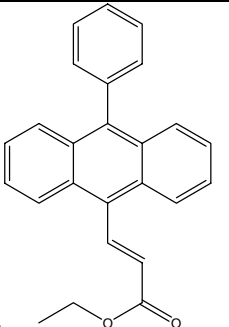
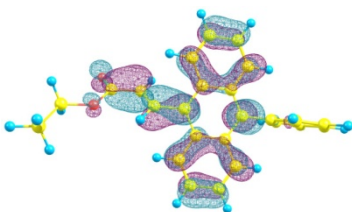
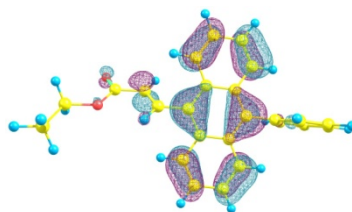
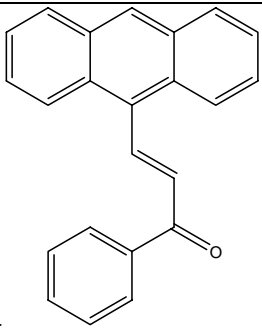
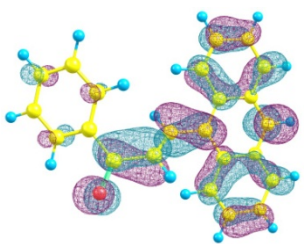
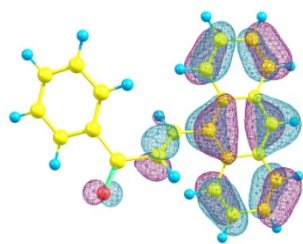


Scheme 12. Cycloaddition reactions of aroylethenylantracenes **8** and maleic anhydride (**14**) and diethyl maleate (**23a**).



Scheme 13. Cycloaddition of anthranilcarbaldehyde (**5**) and benzoquinone (**25**) with subsequent photochemically aided oxidative dehydrogenation of the cycloadduct.

Figure 4. Spatial distribution and energies of HOMO – LUMO for representative anthranlylacrylates and aroyl and acetylenylantracenes. It can be seen that the HOMOs and the LUMOs, respectively, for the compounds are similar in energy and spatial distribution. All calculations were performed using the Gaussian 09W C01 program.¹⁹ Geometry optimizations for the each molecule were performed without symmetry constraints in the gas-phase using the B3LYP^{20,21} hybrid functional and 6-31G(d) basis set. Optimized structures were confirmed to be energy minima through vibrational frequency calculations. Orbital energies and isosurfaces were calculated using the same functional and basis set.

	LUMO (eV)	HOMO (eV)
Str1 	-2.17 	-5.39 
Str2 	-2.05 	-5.32 
Str3 	-2.02 	-5.25 
Str4 	-2.12 	-5.33 

Anthranlylacrylates and aroylethenylantracenes seem to react equally well, the major difference in the reaction being associated with the physical property of the melting point of the starting materials rather than with significantly different electronic characteristics of the starting materials. This can also be

viewed from the computational data of HOMO-LUMO of selected vinylanthracenes, where no significant differences in HOMO – LUMO data is discernable, when comparing the compounds (Figure 4).

Lastly, the reaction of benzoquinone **25** with 9-formylanthracene **5** leads to the primary cycloadduct **26** which is oxidatively dehydrogenated to **27** (Scheme 13). The dehydrogenation can be accelerated significantly by photoirradiation of **26** adsorbed to silica gel. For **26**, with an easily enolizable structure lastly leading to quinone system, this may not be surprising. Momentarily, studies are underway to see whether other cycloadducts show a similar behavior as a further possible reaction pathway in the photoirradiation of the cycloadducts.

Experimental

General

The phosphoranes were prepared by reaction of the phenacyl bromides and of alkyl bromoacetates with triphenylphosphine and subsequent dehydrobromination of the phosphonium bromides with aq. Na_2CO_3 , analogous to ref. 22. For the general preparation of **2a**, see ref. 8a.

Preparation of selected compounds:

Methyl 9-anthranilacrylate (**2b**). - To a solution of triphenylphosphine (PPh_3 , 1.82 g, 6.94 mmol) in CH_2Cl_2 (20 mL) was added dropwise bromotrichloromethane (CBrCl_3 , 1.42 g, 7.17 mmol), and the resulting solution was stirred at rt for 40 min, whereupon it turns orange-brown. Then, 9-anthranilacrylic acid (**2-OH**, 1.5 g, 6.05 mmol) was added, and the suspension was stirred under reflux for 90 min. Thereafter, methanol (3 mL) was added dropwise, and the reddish solution is stirred under reflux for 10h. The cooled solution is concentrated *in vacuo* and the residue is subjected to column chromatography on silica gel (eluent: CH_2Cl_2) to give **2b** (913 mg, 58%) as bright yellow needles (hexane), mp. 120 – 122 °C; ν_{max} ($\text{KBr}/\text{cm}^{-1}$) 1717, 1638, 1168, 1155, 735; δ_{H} (400 MHz, CDCl_3) 3.92 (3H, s, OCH_3), 6.44 (1H, d, $^3J = 16.4$ Hz), 7.46 – 7.51 (4H, m), 8.00 (2H, d, $^3J = 8.4$ Hz), 8.22 (2H, d, $^3J = 8.4$ Hz), 8.45 (1H, s), 8.65 (1H, d, $^3J = 16.4$ Hz); δ_{C} (100.5 MHz, CDCl_3) 52.0 (OCH_3), 125.2 (2C, CH), 125.4 (2C, CH), 126.3 (2C, CH), 126.8 (CH), 128.3 (CH), 128.8 (2C, CH), 129.0 (C_{quat}), 129.3 (C_{quat}), 131.2 (C_{quat}), 142.3 (CH), 166.9 (C_{quat} , CO). Found: C, 82.49; H, 5.47%. Calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_2$ (262.30) C, 82.42; H, 5.38%.

9-[2-(4-Fluorophenylcarbonyl)ethenyl]anthracene (**8-F**). - A solventless mixture of anthranilcarbaldehyde (**5**, 100 mg, 0.48 mmol) and 4-fluorobenzoylmethylidetriphenylphosphorane (**7-F**, 400 mg, 1.0 mmol) was heated at 140 °C for 18h. The cooled reaction mixture was subjected directly to column chromatography on silica gel (eluent: benzene) and gave **8-F** (111 mg, 71%) as a yellow solid, mp. 145 - 148 °C; ν_{max} ($\text{KBr}/\text{cm}^{-1}$) 3046, 1659, 1597 (s), 1504, 1410, 1355, 1267, 1208, 1152, 1010, 979, 850, 733; δ_{H} (400 MHz, CDCl_3) 7.18 (2H, dd, $^3J = 8.4$ Hz, $^3J = 8.4$ Hz), 7.49 – 7.54 (5H, m), 8.01 – 8.04 (2H, m), 8.11 (2H, dd, $^3J = 9.2$ Hz, $^4J = 5.6$ Hz), 8.27 – 8.30 (2H, m), 8.47 (1H, s), 8.79 (1H, d, $^3J = 15.6$ Hz), δ_{C} (100.5 MHz, CDCl_3) 115.9 (2C, CH, $^2J_{\text{CF}} = 22.5$ Hz), 125.2 (2C, CH), 125.5 (2C, CH), 126.5 (2C, CH), 128.6 (CH), 129.0 (2C, CH), 129.6 (2C, C_{quat}), 130.5 (2C, C_{quat}), 131.3 (3C, CH, and 2CH, $^3J_{\text{CF}} = 11.1$ Hz), 134.2 (C_{quat} , $^4J_{\text{CF}} = 3.0$ Hz), 142.2 (CH), 165.8 (C_{quat} , $^1J_{\text{CF}} = 255.1$ Hz), 188.0 (C_{quat} , CO).

Ethyl (*E*)-3[9-bromoanthran-10-yl]propenoate (**9a**). - To a solution of ethyl (*E*)-3[anthran-9-yl]propenoate (1.17 g, 4.24 mmol) in chloroform (10 mL) was added dropwise bromine (780 mg, 4.96 mmol) in chloroform (5 mL). The solution was stirred at rt and discolored immediately. The solution was concentrated *in vacuo*. Then, dichloromethane (10 mL) and triethylamine (505 mg, 5.0 mmol) were added, and the resulting solution was heated to reflux for 15 min. The cooled mixture was extracted with water, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Column chromatography of the residue on silica gel (benzene-hexane 1:1) gave **9a** as a yellow solid (1.12 g, 3.18 mmol, 75%); IR (KBr/cm⁻¹) ν_{\max} 2979, 1716, 1634, 1438, 1176, 907, 748, 718; δ_{H} (400 MHz, CDCl₃) 1.41 (3H, t, ³*J* = 7.2 Hz, CH₃), 4.38 (2H, q, ³*J* = 7.2 Hz, OCH₂), 6.37 (1H, d, ³*J* = 16.4 Hz), 7.53 – 7.55 (2H, m), 7.60 – 7.62 (2H, m), 8.22 (2H, d, ³*J* = 10.2 Hz), 8.54 (1H, d, ³*J* = 16.4 Hz), 8.58 (2H, d, ³*J* = 10.2 Hz); δ_{C} (100.5 MHz, CDCl₃) 14.4 (CH₃), 61.0 (OCH₂), 125.8 (2C, CH), 126.3 (C_{quat}), 126.4 (2C, CH), 127.2 (2C, CH), 128.1 (CH), 128.4 (2C, CH), 129.9 (C_{quat}), 130.2 (C_{quat}), 130.3 (C_{quat}), 141.7 (CH), 166.2 (C_{quat}, CO); and ethyl (*Z*)-3-[10-bromoanthran-9-yl]-2-bromopropenoate (**9b**, 206 mg, 15%) as a yellow solid; mp. 133 – 134 °C; IR (KBr/cm⁻¹) ν_{\max} 3011, 2980, 1727, 1616, 1259, 1235, 1033, 906, 755; δ_{H} (400 MHz, CDCl₃) 1.48 (3H, t, ³*J* = 7.2 Hz, CH₃), 4.48 (2H, q, ³*J* = 7.2 Hz, OCH₂), 7.52 – 7.56 (2H, m), 7.60 – 7.64 (2H, m), 7.94 (2H, d, ³*J* = 8.0 Hz), 8.59 (2H, d, ³*J* = 8.8 Hz), 8.89 (1H, s); δ_{C} (100.5 MHz, CDCl₃) 14.3 (CH₃), 63.2 (OCH₂), 123.0 (C_{quat}), 124.6 (C_{quat}), 125.7 (2C, CH), 126.6 (2C, CH), 127.3 (2C, CH), 128.5 (2C, CH), 128.6 (2C, C_{quat}), 128.9 (C_{quat}), 130.2 (2C, C_{quat}), 140.7 (CH), 162.3 (C_{quat}, CO).

Cycloadduct **18 (X=OMe)** of methyl 9-anthranylacrylate (**2b**) and 4-methoxyphenylmaleimide (**16-OMe**). - A mixture of methyl 9-anthranylacrylate (**2b**, 186 mg, 0.71 mmol) and 4-methoxyphenylmaleimide (**16-OMe**, 144 mg, 0.71 mmol) were reacted at 115 °C for 3h. The mixture initially produced a melt, which then solidified. The mixture was cooled, and the solid was taken up in diethyl ether (15 mL) and filtered. The filter cake was washed with diethyl ether (2 X 10 mL) to give **18-OMe** as a pale yellow solid (294 mg, 89 %); ν_{\max} (KBr/cm⁻¹) 2959, 2839, 1713, 1514, 1458, 1395, 1252, 1200, 1178, 1033, 775, 761; δ_{H} (400 MHz, CDCl₃) 3.42 (1H, dd, ³*J* = 8.4 Hz, ³*J* = 3.2 Hz), 3.51 (1H, d, ³*J* = 8.4 Hz), 3.72 (3H, s, OCH₃), 3.88 (3H, s, OCH₃), 4.90 (1H, d, ³*J* = 3.2 Hz), 6.37 (2H, d, ³*J* = 8.8 Hz), 6.69 (1H, d, ³*J* = 16.4 Hz), 6.77 (2H, d, ³*J* = 8.8 Hz), 7.18 – 7.39 (7H, m), 7.44 (1H, d, ³*J* = 6.8 Hz), 7.97 (1H, d, ³*J* = 16.4 Hz); δ_{C} (100.5 MHz, CDCl₃) 45.9 (CH), 48.0 (CH), 48.2 (CH), 51.9 (OCH₃), 52.0 (C_{quat}), 55.4 (OCH₃), 114.3 (2C, CH), 123.5 (CH), 123.7 (C_{quat}), 123.8 (CH), 124.2 (CH), 125.5 (CH), 126.7 (CH), 127.2 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.6 (2C, CH), 129.7 (2C, CH), 138.2 (C_{quat}), 139.2 (C_{quat}), 140.8 (C_{quat}), 141.9 (C_{quat}), 142.8 (CH), 159.8 (C_{quat}), 166.6 (C_{quat}, CO₂CH₃), 174.5 (C_{quat}, CNO), 175.5 (C_{quat}, CNO). Found: C, 75.26; H, 4.97; N, 3.00%. Calcd. for C₂₉H₂₃NO₅ (465.50) C, 74.83; H, 4.98; N, 3.01%.

Conclusions

Anthranylacrylates **2** and phenylacylethenylantracenes **8** can be easily produced by solventless Wittig olefination of anthranylcarbaldehyde **5**. Anthranylacrylates **2** can be easily brominated in the central aromatic ring system to bromoanthranylacrylates **9a**, which can be transformed by Suzuki-Miyaura cross-coupling reaction to the pi-extended anthranylacrylates **12**. **2** (and **5**) lend themselves to solventless cycloaddition reactions with maleimides **16**. Cycloaddition reactions can be performed with the arylethenylantracenes **8**, albeit in refluxing xylene. Cycloaddition reactions with the extended anthranylacrylates **12** are possible, also, but the molecules are less reactive.

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