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

Hasnaa Sadeq, Thies Thiemann*, John P. Graham, Yosef Al Jasem, Bernhard Bugenhagen, Nathir al Rawashdeh, Mazen al Sulaibi

1 Department of Chemistry, Faculty of Science, UAE University, PO Box 15551, Al Ain, Abu Dhabi, United Arab Emirates
2 Department of Chemical Engineering, Faculty of Engineering, UAE University, Al Ain, United Arab Emirates
3 Institute of Inorganic Chemistry, University of Hamburg, Martin-Luther-King Platz 6, D-20146 Hamburg, Germany
4 Department of Applied Chemical Sciences, Jordan University of Science & Technology, P.O. Box 3030, Irbid-22110, Jordan
9,10-Disubstituted anthracenes have interesting electro-optical applications and usage as sensor materials. These include polymers with 9,10-disubstituted anthranyl subunits.

Figure 1. Disubstituted anthracene with carbon-numbering
In our endeavor to produce interlinked 9,10-disubstituted anthranyl-containing materials photochemically, be it by photochemical dimerisation or photochemical polymerization, the photochemistry of 3-(anthran-9-yl)acrylates was studied. Possible photochemical pathways for these molecules were envisaged to be E-/Z-isomerisation of the acrylate moiety and photodimerisation of the acrylate moiety.

Scheme 1. Possible photodimerisation products of anthranylacrylates
as well as a possible competing $[4+4]$-photodimerisation of the anthranyl unit.

Scheme 2. Possible competing $[4+4]$-photodimerisation of anthranylacrylates
Figure 2. Crystal packing of ethyl 3-(anthran-9-yl)acrylate showing intermolecular distances that are too large for photochemical dimerisation reactions in the crystal.
This would mean that a photochemical dimerisation of molecules in the crystal would be unlikely. In solution, however, the photochemistry of the molecules is very complex. Therefore, it was decided to cycloadd enes across the anthranyl units, carry out the photochemistry of the vinyl group, and subsequently subject the molecules to a Retro-Diels Alder reaction.

In the following, the authors show the preparation of the anthranylacrylates and aroylethenylantracenes and their Diels–Alder reactivity.
Scheme 3. Solventless Wittig-olefination reactions to anthranylacrylate 2 and aroylethenyl-anthracenes 8
Scheme 4. Bromination of anthranylacrylate 2a and anthranylcarbaldehyde 5

Bromination of anthranylacrylates of type 2 leads mainly to bromination of the central ring system of the anthracene.
**Scheme 5.** Pi-extension of anthranylacrylate 9a by Suzuki-Miyaura cross-coupling reaction.
Scheme 6. Solventless cycloaddition of 9-anthranylcarbaldehyde 5 to maleimides 16

\[ 5 + 16 \xrightarrow{115 \degree C \text{ neat}} 17 \]

\( X = 4\text{-Br}, 4\text{-CH}_3, 4\text{-OCH}_3, \text{H} \)
Scheme 7. [4+2]-Cycloaddition of anthranylacrylates 2a/2b with maleimides and maleic anhydride
Scheme 8. Cycloaddition reactions of pi-extended anthracenes 12 with maleimides 16.
Scheme 9. Cycloaddition reactions of arylethenylanthracenes 8 with maleimides 16
Scheme 10. Cycloaddition reactions of aroylethenylanthracenes 8 and maleic anhydride (14) and diethyl maleate (23a).
Scheme 11. Cycloaddition of anthranylcarbaldehyde (5) and benzoquinone (25) with subsequent photochemically aided oxidative dehydrogenation of the cycloadduct.
Conclusions:

3-(Anthran-9-yl)acrylates and 9-aroylethenylanthracenes can be produced facilely by solventless Wittig reaction.

3-(Anthran-9-yl)acrylates can be brominated selectively to produce 3-(9-bromoanthran-10-yl)acrylates, which can be used as substrates to produce pi-extended anthracenes by Suzuki-Miyaura cross-coupling reaction.

3-(Anthran-9-yl)acrylates, 9-anthranylcarbaldehyde and 9-aroylethenylanthracenes easily undergo Diels Alder type cycloaddition reactions with a variety of bisactivated enes. Of these, 3-(anthran-9-yl)acrylates and 9-anthranylcarbaldehyde undergo solventless Diels-Alder reactions with maleimides.
Thank you very much for your kind interest!

For questions or comments, please contact: thies@uaeu.ac.ae or thiesthiemann@yahoo.de