Photochemistry of 9-vinyl substituted anthracenes, of their reduced derivatives and of Diels Alder type adducts of 9-vinylanthracenes with activated dienophiles

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Abstract

The photochemistry of the vinyl substituted (*E*)-3-(anthran-9-yl)propenoates and (*E*)-9-(aroylethenyl)anthracenes as well of their reduced derivatives has been studied at λ = 254 nm and at λ = 352 nm. At λ = 254 nm and λ = 352 nm, the 9-vinyl substituted anthracenes undergo *E*/*Z*-isomerization, while their reduced derivatives undergo [4+4]-dimerisation reactions at λ = 352 nm. An X-ray crystal structure shows the [4+4]-photoadducts to be head-to-tail.

The photochemistry of cycloadducts of (*E*)-3-(anthran-9-yl)propenoates and (*E*)-9-(aroylethenyl)anthracenes with maleimides and other activated dienophiles mainly show E/Z-isomerisation.

Keywords: 9-substituted anthracenes, photochemistry, [4+4]-cycloaddition

Introduction

Previously, the authors have communicated a facile access to (*E*)-3-(anthran-9-yl)propenoates and (*E*)-9-(aroylethenyl)anthracenes via solventless Wittig-olefination of the commercially available 9-formylanthracene.[1] These together with aryl-substituted anthracenes[2] make for interesting anthranyl-based photoelectronic materials. Some use of these has been found in molecular wires,[3] in light-regulated semiconducting materials and as potential constituent molecules in light-harvesting devices for organic solar cell applications (Figure 1).[4,5] Here, however, the photochemical stability of such compound is of importance. On the other hand, one can view these molecules as possible starting materials to larger molecules formed by C-C bond linking transformations utilizing the reactivity of the *π*-system of these conjugated anthracenes, where photochemical reactions may be the strategy of choice.

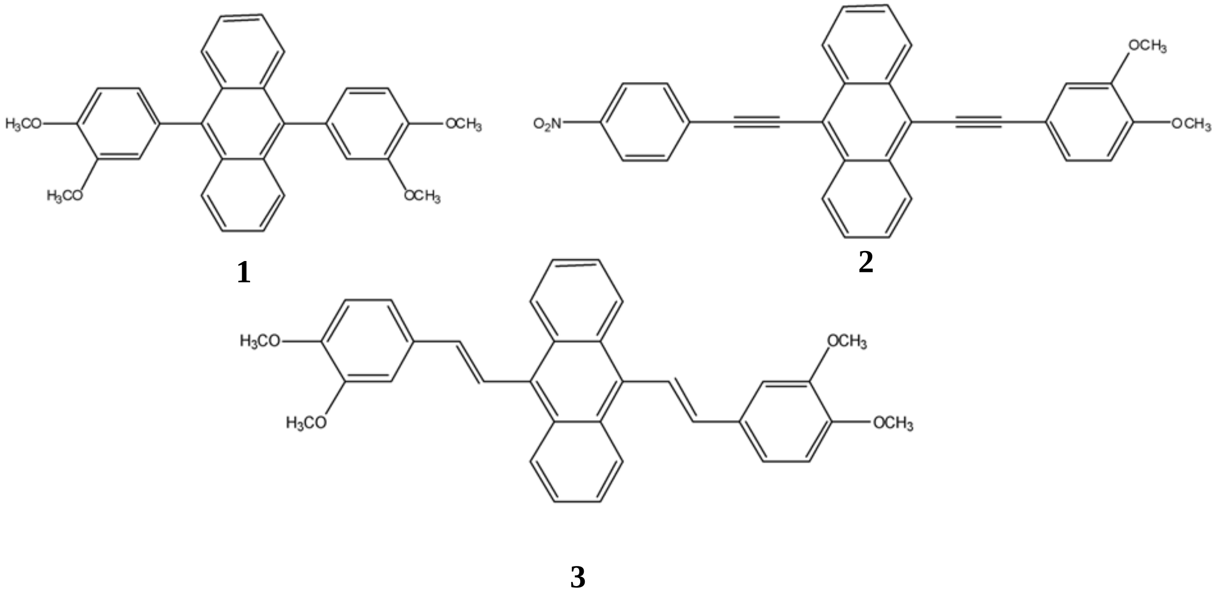
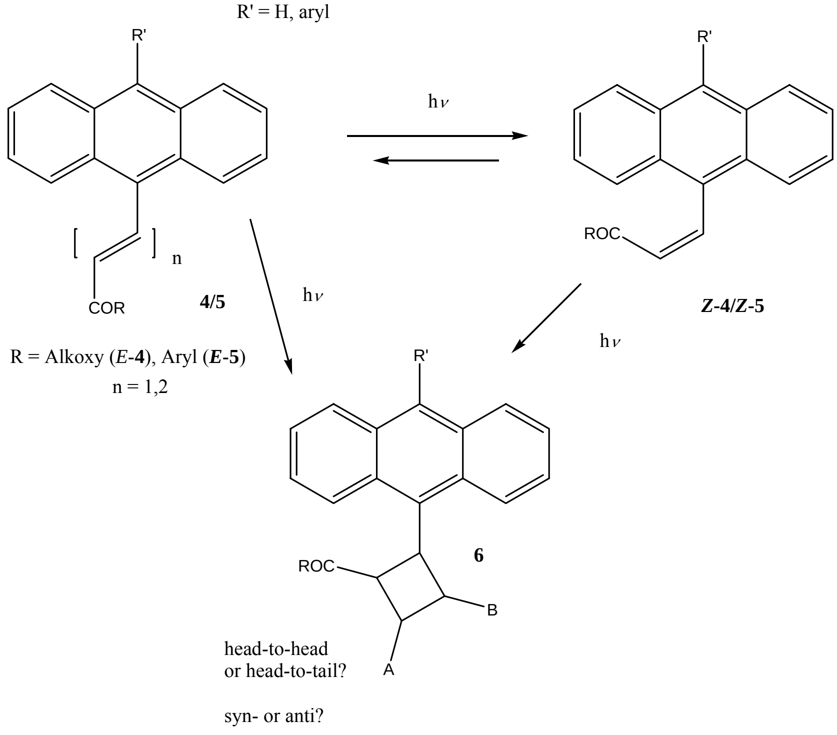


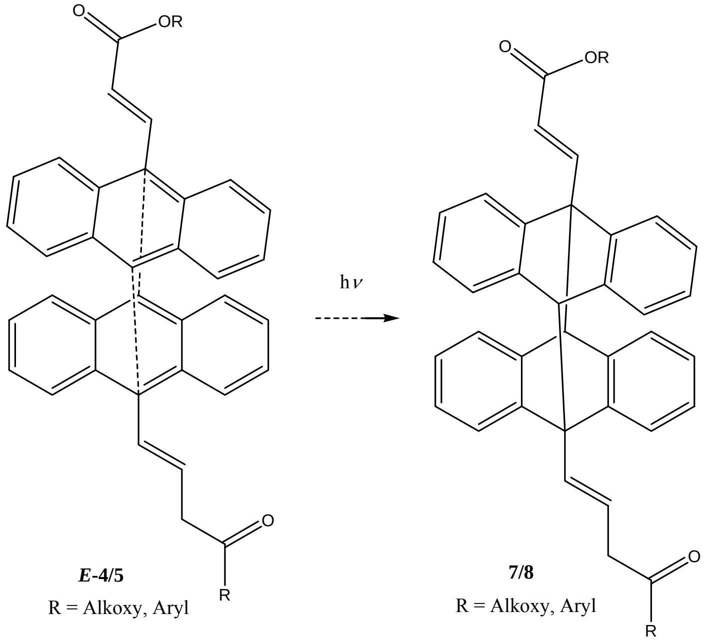
Figure 1. Pi-extended anthracenes as components for organic solar cell applications.

To our knowledge, little information has been obtained of the photochemical behavior of 9-ethenyl or 9-ethynyl substituted anthracenes,[4-7] especially where the other terminus of the double bond or triple bond is substituted by an electron withdrawing substituent. There is one example of a report of the behavior of benzoylethenylanthracenes, which was shown to give *E*/*Z*-isomerisation upon photoirradiation, coupled with a novel rearrangement.[6,7] As dominant photochemical transformations of these molecules in general, one can view the *E*-/*Z*-isomerisation of the double bond (Scheme 1), a possible [2+2]-cycloaddition of the double bond (Scheme 1) and a [4+4]-cycloaddition of the anthranyl unit (Scheme 2).



Scheme 1. Conceivable photochemical reactions of anthranylacrylates ***E*-4** and aroyl-ethenylanthracenes ***E*-5**.

In the following, our results on the photochemical reactivity of (*E*)-3-(anthran-9-yl)propenoates and (*E*)-9-(aroylethenyl)anthracenes is shown with an emphasis of the behavior under relatively short irradiation times in view of a potential synthetic viability of the reactions as well as the behavior under long irradiation times in view of the life-time of such molecules under photoirradiation. In addition, the short-time results induced the authors to study the photochemical reactivity of cycloadducts of the anthracenes above with maleimides as well as the photochemical reactivity of the hydrogenated derivatives of (*E*)-3-(anthran-9-yl)propenoates and (*E*)-9-(aroylethenyl)anthracenes.



***E*-4/5**
R = Alkoxy, Aryl

7/8
R = Alkoxy, Aryl

Scheme 2. Conceivable photochemical reactions of anthranylacrylates ***E*-4** and aroyl-ethenylanthracenes ***E*-5** (continued).

Experimental

Melting points were measured with a Stuart SMP10 melting point apparatus and are uncorrected. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100.5 MHz) spectra were taken on a Varian 400 MHz spectrometer. Infrared spectra were taken on a spectrometer (solid samples as KBr pellets, liquid samples using NaCl plates). Column chromatography was carried out on silica gel S (0.2 – 0.5 mm and 0.063 – 0.1 mm, Riedel de Haen) and with Sigma Aldrich 60 Å (230 – 400 mesh, Merck grade 9385). Analytical thin layer chromatography (TLC) was carried out on silica on TLC Alu foils from Fluka (with fluorescent indicator at λ = 254 nm). For detection a UVGL-58 lamp was used from UYP (Upland, CA, USA). UV-VIS spectra were obtained from a Varian Cary 50 conc UV-VIS spectrophotometer, with CH_2Cl_2 [Sigma Aldrich, purris. p.a., ≥ 99.9% (GC)] and acetonitrile [Panreac, HPLC grade and Romil Chemical, Far-UV grade 190, pur. 99.9%] as solvent. For the photoirradiation, a Luzchem LZC 4V photoreactor was used with 13 USHIO G8T5 lamps (7.2 W low pressure mercury arc lamp with a radiation peak at λ = 253.7 nm) and with 14 Hitachi FL8BL-B (0.75 W, UV irradiance 8.0 $(\mu/\mathrm{cm})^2$, with a radiation peak at λ = 352 nm). CH_2Cl_2 [Sigma Aldrich, purris. p.a., ≥ 99.9% (GC)] and benzene were taken as solvents in the photoirradiation experiments.

The anthranylacrylates ***E*-4** and 9-aroylethenylanthracenes ***E*-5** were photoirradiated in a Luzchem LZC 4V photoreactor using USHIO G8T5 lamps (at λ = 253.7 nm) and with Hitachi FL8BL-B (at λ = 352 nm [peak output]). The photolysis reactions were monitored by ^{1}H NMR spectroscopy. If the reactions seemed promising, the reaction mixtures were separated by column chromatography on silica gel, and the products were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), IR and melting point, where applicable.

Also, the *N*-aryl-9-substituted-9,10-dihydro-9,10(4,'5')-succinimido)anthracenes as the cycloadducts between the anthranylacrylates/aroylethenylanthracenes and N-arylmaleimides were submitted to photoirradiation with USHIO G8T5 lamps (at λ = 253.7 nm). The photolysis reactions were monitored by ^{1}H NMR spectroscopy. If the reactions seemed promising, the reaction mixtures were separated by column chromatography on silica gel, and the products were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), IR and melting point, where applicable.

Photoreaction of 9-(*E*)-4-methylbenzoylethenylanthracene (***E*-5-Me**) – general procedure of the photoirradiation of 9-(*E*)-aroylethenylanthracenes ***E*-5** at λ = 253.7 nm. - 9-(*E*)-4-Methylbenzoylethenylanthacene (***E*-5-Me**, 50 mg, 0.16 mmol) in CH_2Cl_2 (2.2 mL) was photoirradiated at λ = 254 nm (peak output) for 24 h. The photoreaction was monitored by ^1H NMR spectroscopy. Afterwards, the cooled reaction mixture was submitted directly to column chromatography on silica gel (benzene) to give starting material and 9-(*Z*)-4-methylbenzoylethenylanthracene (***Z*-5-Me**, 18 mg), eluting after the starting material, as a yellow-orange solid, mp. 144 °C; ν_{max} (KBr/cm^{-1}) 3043, 1664, 1608, 1426, 1232, 885, 840, 778, 731; δ_H (400 MHz, $CDCl_3$) 2.24 (3H, s, CH_3), 6.94 (2H, d, ^3J = 7.2 Hz), 7.40 – 7.45 (5H, m), 7.57 (2H, d, ^3J = 7.2 Hz), 7.85 (1H, d, ^3J = 11.6 Hz), 7.92 – 7.95 (2H, m), 8.08 – 8.10 (2H, m), 8.32 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 125.0 (2C, CH), 125.5 (2C, CH), 125.7 (2C, CH), 127.0 (CH), 128.3 (2C, CH), 128.6[8] (2C, CH), 128.7 (2C, CH), 128.7(5) (CH), 130.5 (C_{quat}, 2C), 130.9 (C_{quat}), 131.0 (C_{quat}, 2C), 134.9 (C_{quat}), 139.1 (CH), 143.3 (C_{quat}), 191.5 (C_{quat}, CO).

Photoreaction of *N*-(4-methoxyphenyl)-9-(*E*)-benzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (***E*-26-OMe,** Scheme 13, X=OMe, Y=H). - ***E*-26-OMe** (100 mg, 0.19[5] mmol) was photoirradiated at λ = 254 nm (peak output) in CH_2Cl_2 (3.5 mL) for 60h. The reaction mixture was subjected directly to column chromatography on silica gel (CH_2Cl_2) to give *N*-(4-methoxyphenyl)-9-(*Z*)-benzoylethylene-9,10-dihydro-9,10(4,'5')-succinimido)anthracene (***Z*-26-OMe**, 43 mg) as an oil; ν_{max} (neat/cm^{-1}) 3064, 2838, 1775 (w), 1721, 1669, 1597, 1457, 1389, 1300, 1177, 1029, 1003, 909, 830, 732, 695, 551; δ_H (400 MHz, $CDCl_3$) 3.41 (bd, *J* = 3.2 Hz), 3.71 (3H, s, OCH_3), 4.88 (1H, d, *J* = 3.2 Hz), 6.32 (2H, d, ^3J = 8.8 Hz), 6.74 (2H, d, ^3J = 8.8 Hz), 7.14 – 7.56 (12H, m), 7.70 (1H, bs), 8.00 (bd, 2H, ^3J = 8.8 Hz)*; δ_C (100.5 MHz, $CDCl_3$) 46.0, 48.3, 55.4, 114.3 (2C, CH), 123.9, 124.2 (CH), 124.4 (broad), 125.5 (CH), 126.7 (broad), 126.8, 127.0 (CH), 127.0(5) (CH), 127.6 (2C, CH), 128.6 (2C, CH), 128.7(5) (broad), 133.0 (CH), 137.9 (CH), 140.0 (broad), 159.5(C_{quat}), 175.7 (C_{quat}, NCO), 176.2 (C_{quat}, NCO), and starting material.

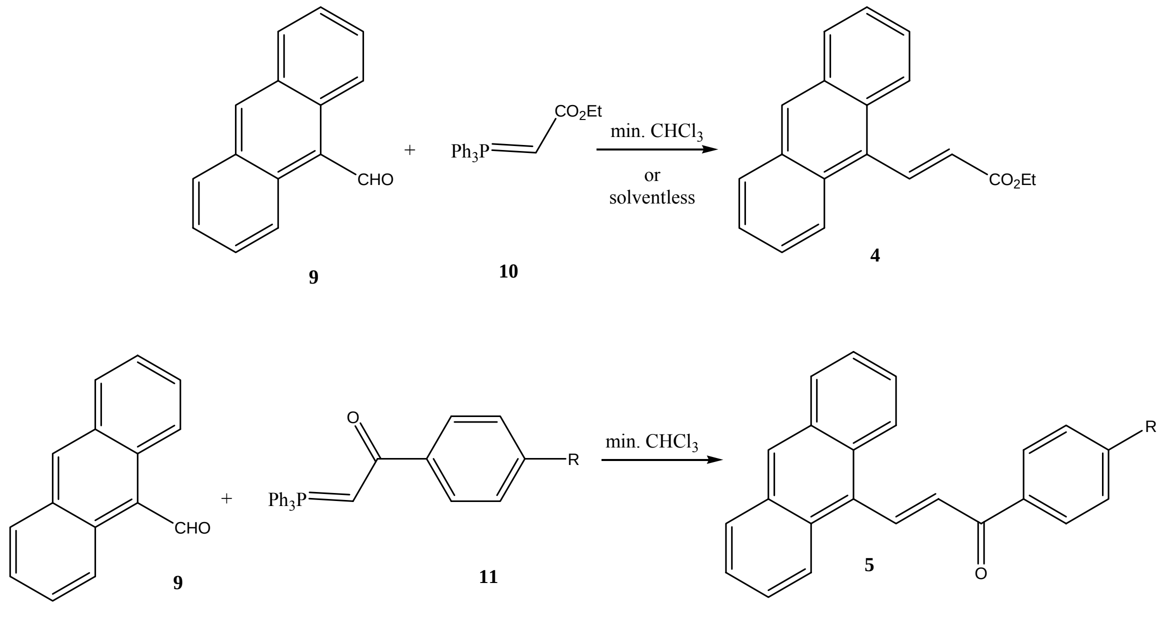
*some H and ^{13}C NMR absorptions may be so broad at rt that they could not be detected.

Preparation of ethyl 3-anthran-9-ylpropionate (**20**). – To ethyl 3-anthran-9-ylacrylate (***E*-4**, 276 mg, 1.0 mmol) in toluene (5 mL) is given Pd/C (5 wt%, 80 mg) and acetic acid (142 mg). Thereafter is added $NaBH_4$ (182 mg). After stirring the mixture for a day at rt, further acetic acid (71 mg) and $NaBH_4$ (91 mg) are added. The reaction takes time to complete, and the progress is monitored by TLC (toluene), where the starting material shows yellow fluorescence and the product light blue fluorescence. After the reaction is complete, half conc. aq. HCl (1 mL) and water (15 mL) are added to hydrolyse excess $NaBH_4$. The mixture is extracted with CH_2Cl_2 (3 X 25 mL) and the organic phase is dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (CH_2Cl_2) gives **20** (230 mg, 85%) as a pale yellow viscous oil*; ν_{max} (neat/cm^{-1}) 1729, 1623, 1446, 1372, 1182, 1158, 1045, 834, 733, 602; δ_H (400 MHz, $CDCl_3$) 1.29 (3H, t, ^3J = 7.6 Hz, CH_3), 2.80 (2H, t, ^3J = 8.4 Hz), 3.97 (2H, t, ^3J = 8.4 Hz), 4.22 (2H, q, OCH_2), 7.48 (2H, m), 7.55 (2H, m), 8.02 (2H, d, ^3J = 8.4 Hz), 8.30 (2H, d, ^3J = 9.2 Hz), 8.37 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 14.3 (CH_3), 23.3 (CH_2), 35.4 (CH_2), 60.7 (OCH_2), 124.0 (2C, CH), 125.0 (2C, CH), 125.9 (2C, CH), 126.4 (CH), 129.3 (2C, CH), 129.5 (2C, C_{quat}), 131.6 (2C, C_{quat}), 132.5 (C_{quat}). *with a slight impurity of ethyl 3-(9,10-dihydroanthran-9-yl)propionate (**21**).

Photoirradiation of ethyl 3-anthran-9-ylpropionate (**20**). - Ethyl 3-anthran-9-ylpropionate (**20**, 200 mg, 0.72 mmol) in benzene (4 mL) was photoirradiated at λ = 352 nm for 22h. After 22h, colorless crystals had precipitated and were hanging on the reaction tube's walls. The overstanding solution was decanted and the crystals were washed with hexane to give dimer **22** (110 mg, 55%) as a colorless solid; ν_{max} (KBr/cm^{-1}) 3066, 2978, 2924, 1728, 1474, 1449, 1424, 1374, 1301, 1260, 1181, 1082, 1019, 860, 792, 768, 697, 676, 642; δ_H (400 MHz, CDCl$_3$) 1.27 (6H, t, ^3J = 7.2 Hz, 2 CH$_3$), 2.36 (4H, t, ^3J = 7.6 Hz), 3.05 (4H, t, ^3J = 7.6 Hz), 3.92 (2H, s, CH), 4.19 (4H, q, ^3J = 7.2 Hz, 2 OCH$_2$), 6.80 – 6.88 (8H, m), 6.90 (4H, d, ^3J = 7.2 Hz, ^4J = 1.6 Hz), 6.94 (4H, d, ^3J = 7.2 Hz, ^4J = 1.2 Hz); δ_C (100.5 MHz, CDCl$_3$) 14.3 (2C, CH$_3$), 30.6 (2C, CH$_2$), 31.4 (2C, CH$_2$), 55.9 (2C, CH), 60.6 (2C, OCH$_2$), 64.2 (2C, C$_{quat}$), 125.4(5) (4C, CH), 125.5 (4C, CH), 125.7 (4C, CH), 127.6 (4C, CH), 142.1 (4C, C$_{quat}$), 143.5 (4C, C$_{quat}$), 174.0 (2C, CO).

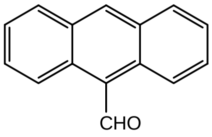
Results and Discussion

(*E*)-3-(Anthran-9-yl)propenoates (***E*-4**) and (*E*)-9-(aroylethenyl)anthracenes (***E*-5**) could be prepared easily by Wittig reaction of 9-formylanthracene with the respective conjugated phosphorane, as communicated earlier (Scheme 3).[1]



Scheme 3. Preparation of anthranylacrylates ***E*-4** and aroyl-ethenylanthracenes ***E*-5.**

The UV-Vis spectra of compounds **4** and **5** were measured, both in dichoromethane (CH_2Cl_2) and in acetonitrile (CH_3CN) (Table 1). The UV spectra were not affected noticeably by the nature of the solvent and corresponded, where known, with the literature data.[8]



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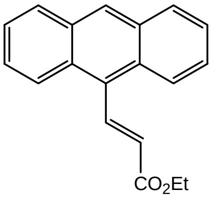
λ_{max} [nm] (ε $mol^{-1}cm^{-1}$)

354 (3620) 370 (6080) 400 (6680) 405 (6700)	352 (3300) 370 (6135) 400 (6670)
(CH_2Cl_2)	(CH_3CN)

λ_{max} [nm] (ε $mol^{-1}cm^{-1}$)

351 (5545) 366 (8400) 385 (10370)	358 (4415) 379 (7410) 385 (9010)
(CH_3CN)	



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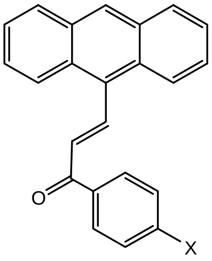
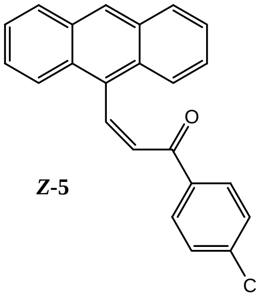


***E*-5**

λ_{max} [nm] (ε $mol^{-1}cm^{-1}$)

X = CH_3	X = OCH_3	X = H	X = Cl	X = Br
351 (4700) 370 (6688) 391 (8500) 405 (8719)	300 (15333) 305 (15305) 352 (5350) 371 (7180) 391 (9440) 405 (9660)	330 (2750) 355 (4430) 371 (6090) 391 (8330) 410 (9225)	350 (4740) 371 (6160) 390 (7240) 410 (7310)	354 (5160) 370 (6440) 391 (8100) 415 (9395)
(CH_2Cl_2)	(CH_2Cl_2)	(CH_2Cl_2)	(CH_2Cl_2)	(CH_2Cl_2)

X = F	X = CH_3	X = 3-NO_2
351 (4095) 369 (5810) 391 (8190) 410 (9490)	352 (4100) 371 (6170) 405 (8510)	352 (4435) 387 (5760) 425(7690)
(CH_2Cl_2)	(CH_3CN)	(CH_2Cl_2)

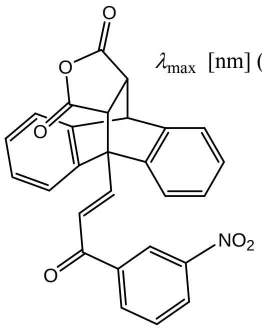


***Z*-5**

λ_{max} [nm] (ε $mol^{-1}cm^{-1}$)

336 (3900)
351 (5700)
370 (7300)
390 (6900)

(CH_2Cl_2)



λ_{max} [nm] (ε $mol^{-1}cm^{-1}$)

340 (560)

***E*-12-NO$_2$**

Table 1. UV band maxima of selected compounds in CH_2Cl_2 and CH_3CN.

Of the anthranylacrylates **4** and **13** single crystals were grown, and X-ray crystal structure analyses were carried out (Figures 2 and 3).[9] In both cases, it was noted that intermolecular distances were too large for photochemical dimerisation reactions in the crystal.

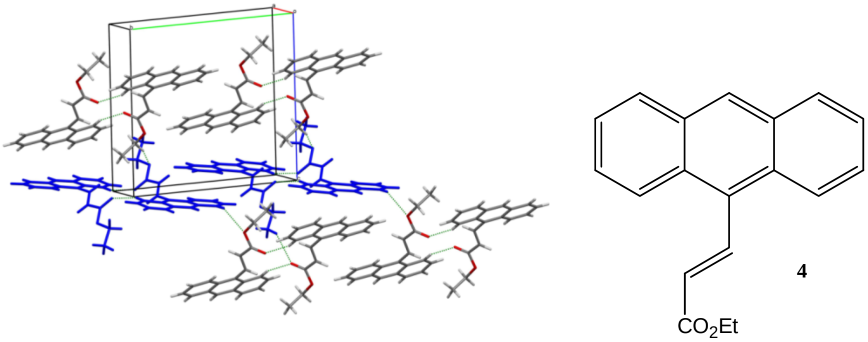

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Figure 2. Crystal packing of ethyl 3-(anthran-9-yl)acrylate (**4**).

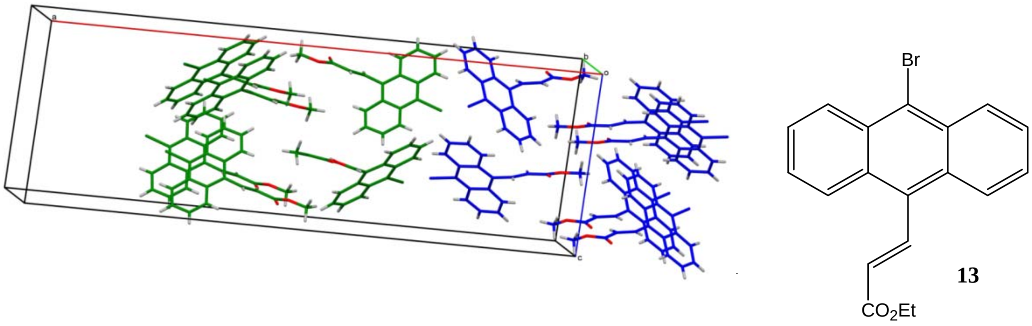
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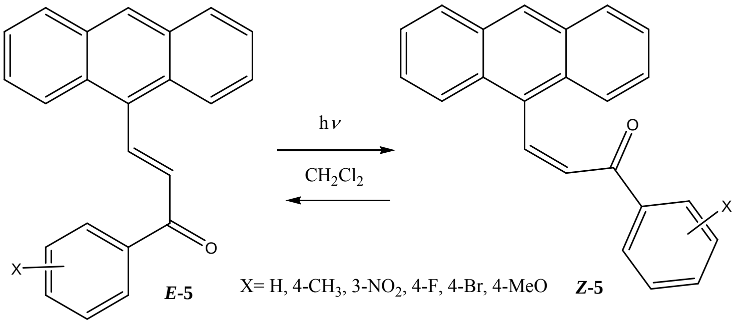
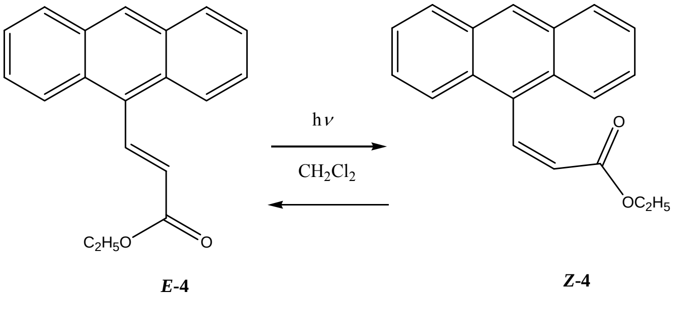
Figure 3. Crystal packing of ethyl 3-(9-bromoanthran-10-yl)acrylate (**13**).

Next, (*E*)-3-(anthran-9-yl)propenoates (***E*-4**) and (*E*)-9-(aroylethenyl)anthracenes ***E*-5** were photoirradiated in CH_2Cl_2 at $\lambda \geq 254$ nm. It was noted that the *E*-aroylethenylanthracenes ***E*-5** upon photoirradiation formed mixtures of close to 1:1 *E*- and *Z*-aroylethenylanthracenes after 24h (Scheme 4). Also, ethyl *E*-anthranylacrylate (***E*-4**) isomerized under photoirradiation

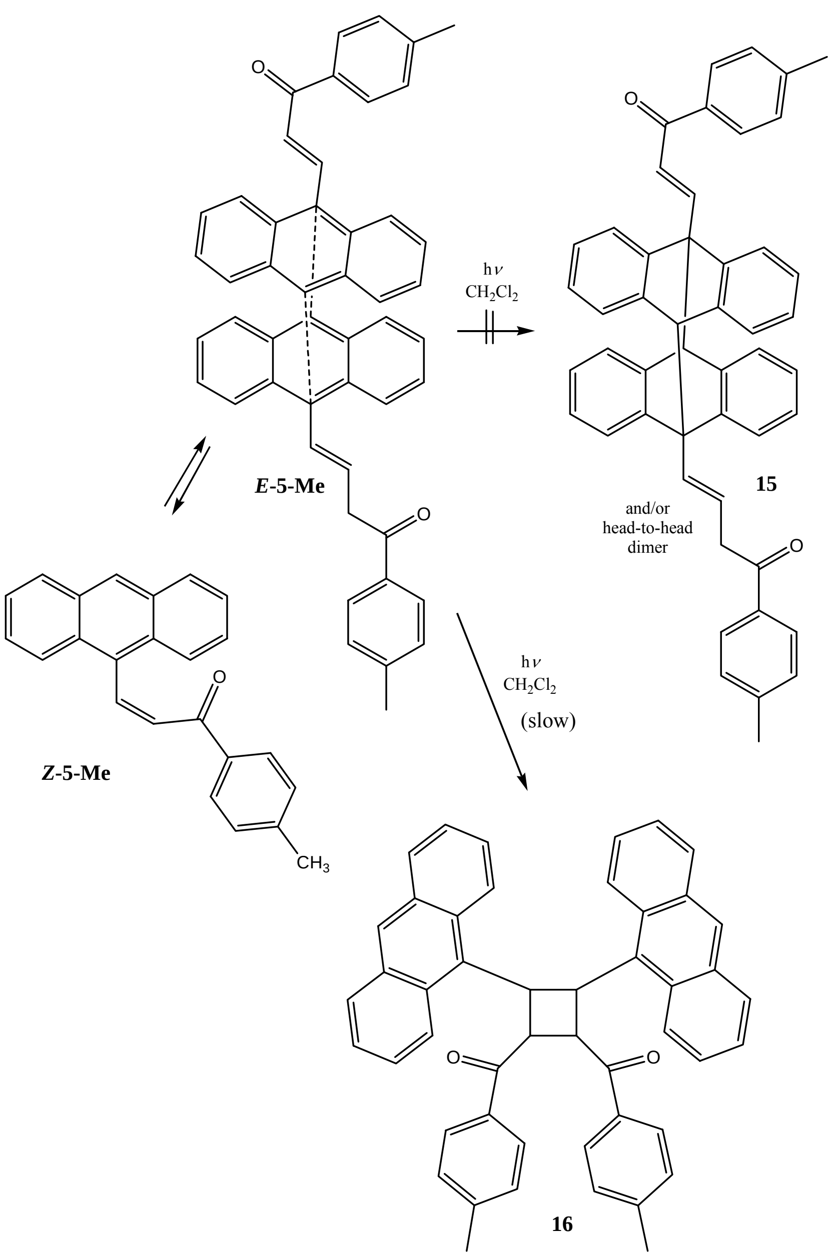
(Scheme 5), however, the acrylate showed some polymerization over time. Also, the photoreaction mixtures of the aroylethenylanthracenes ***E*-5** were appreciably dark so that some oligomerisation was occurring. The *Z*-isomers as photoproducts could be isolated by column chromatography and obtained in a pure state, except for the (*Z*)-4-methoxybenzoylethenylanthracene (**Z-5-OMe**). Interestingly, the *Z*-isomers **Z-5** elute from the column after than *E*-isomers ***E*-5**, which is unusual. The *Z*-isomers **Z-5** were photoirradiated, and again a mixture of *E*-/*Z*-isomers was noted. No rearrangement products as described by Becker et al.[7] were noted at this wavelength. Also, at this short wavelength, no [4+4]-cycloaddition would have been expected, but a [2+2]-cycloaddition could have been possible.[10]



Scheme 4. *E*-/*Z*-isomerisation of the (*E*)-aroylethyleneanthracene ***E*-5** at $\lambda = 253.7$ nm.

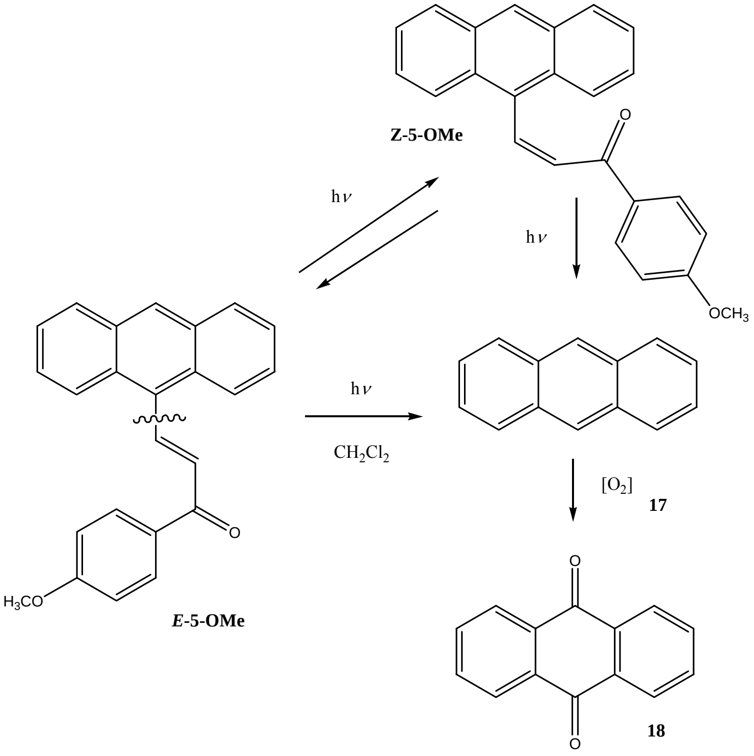


Scheme 5. *E*-/*Z*-isomerisation of ethyl (*E*)-9-anthranylacrylate ***E*-4** at $\lambda = 253.7$ nm.



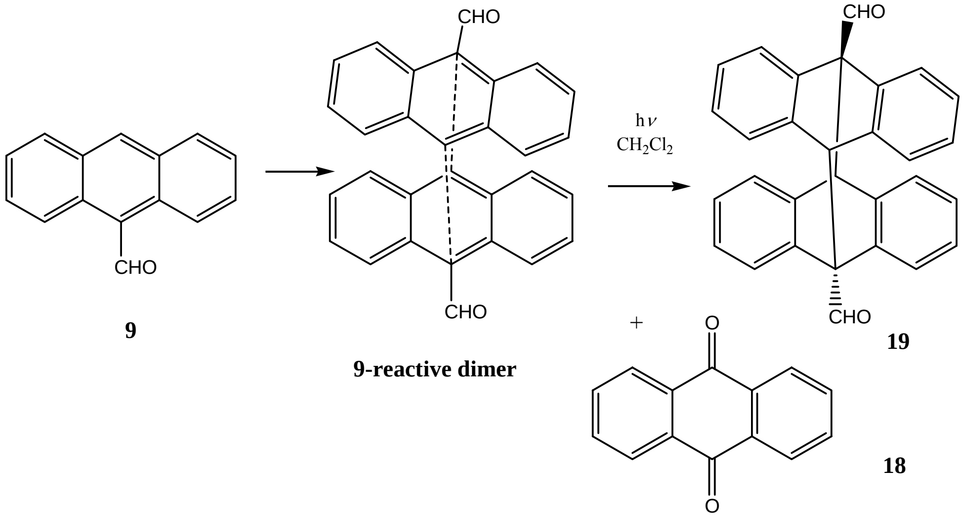
Scheme 6. Slow build-up of two isomers of HH-[2+2]-cycloadduct **16** in photoirradiation of aroylethenylanthracene (***E*-5-Me**). The main reaction is shown in Scheme 4.

Next, 9-(*E*)-aroylethenylanthracenes ***E*-5** were photoirradiated with blacklight UV radiation (λ = 352 nm peak output). In CH_2Cl_2, again a rapid conversion to an equilibrium of 9-(*E*)- and 9-(Z)-aroylethenylanthracenes was observed. Additionally, over days, a build-up of two other products was observed. These were characterized by two doublets each in the aliphatic region of the NMR spectrum. Due to their coupling contants, they were attributed to the *cis*- and *trans*-isomers of the head-to-head [2+2]-cycloadduct **16** (Scheme 6). In benzene, for non-deaerated solutions of ***E*-5-OMe**, the main product in a 3-day photoirradiation in blacklight UV ($\lambda = 352$ nm peak output) is anthraquinone (**18**) (Scheme 7).



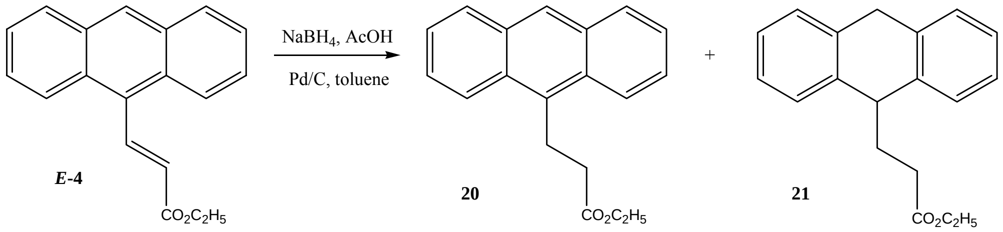
Scheme 7. Photoirradiation of aroylethenylanthracene (***E*-40-OMe**) in benzene under blacklight UV ($\lambda = 352$ nm peak output).

In order to see whether the conditions used above are suitable in general to even reported photo-induced [$4\pi + 4\pi$] cycloaddition reactions, the known photochemical reaction of 9-formylanthracene (**9**) was investigated both in CH_2Cl_2 and in benzene. The photochemical dimerisation proceeds more quickly in benzene than in CH_2Cl_2. It had been reported previously that halogenated solvents such as CCl_4 and bromobenzene[11] are detrimental to the photochemical dimerisation in comparison to THF, ether or toluene. In the present case, in a 0.16 M solution of 9-formylanthracene (**9**) in non-deaerated benzene, 50% of dimerizes photolytically within 24h, while under otherwise the same conditions only 25% of 9-formylanthracene (**9**) dimerizes to **19** in non-deaerated CH_2Cl_2 within 48h (Scheme 8). In either case, anthraquinone (**18**) was also produced. The product mixture was separated by column chromatography on silica gel (hexane – CH_2Cl_2: 1.5/1). The colorless dimer eluted first, followed by the yellow starting material and anthraquinone. Only one isomer of the photo-dimer was obtained, both in CH_2Cl_2 and in benzene. This had already been found by Applequist et al.[12] in the photoirradiation of 9-formylanthracene (**9**).



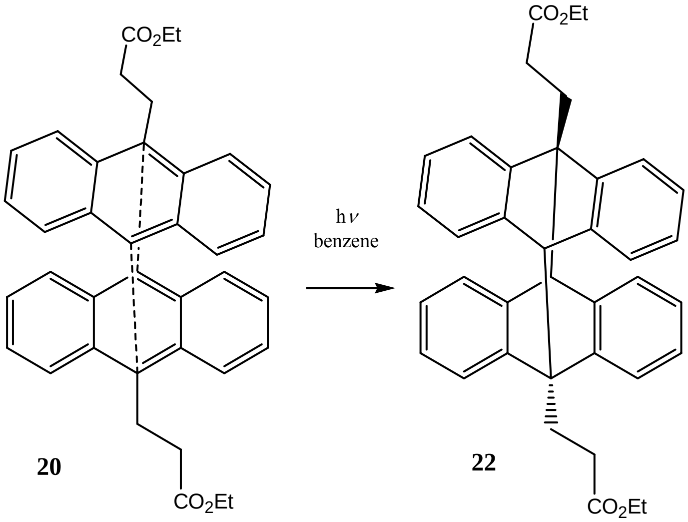
Scheme 8. Photodimerisation of 9-formylanthracene (**9**) in non-deaerated CH_2Cl_2 under blacklight UV light (λ = 352 nm peak output).

Lastly, ethyl (*E*)-9-anthranylacrylate (***E*-4**) was hydrogenated to give ethyl 9-anthranylpropionate (**20**). Normal hydrogenation using H_2 gas under Pd/C was not used as this was thought to be too dangerous as there had been a previous, small laboratory fire using H_2 in presence of Pd/C. Here, it was tried to produce hydrogen *in situ* by reacting $NaBH_4$ with AcOH in the presence of Pd/C.[13-15] The double bond hydrogenation took a long time, and partially the anthracene core was also hydrogenated to produce ethyl 9,10-dihydroanthranylpropionate (**21**) as side product (Scheme 9). The hydrogenation of the central ring system of the anthracene with hydrogen in presence of a Pd-catalyst had been reported previously, with 9,10-diphenylanthracene being reduced over Pd/C.[16] Driving force of the hydrogenation of the anthranyl moiety is the stability of the two isolated benzo groups, which are found to be more aromatic than the anthranyl unit.



Scheme 9. Hydrogenation of ethyl anthranylacrylate (**39-Et**) to ethyl anthranyl-propionate (**67**) using $NaBH_4$, AcOH, Pd/C as a reagent substitute for H_2, Pd/C.

The photolysis of ethyl anthranylpropionate (**20**) in benzene using blacklight UV (λ = 352 nm peak output) radiation gave the [4+4]-dimer **22** rapidly (Scheme 10), which crystallized from the solution. A single crystal of the molecule is being prepared.

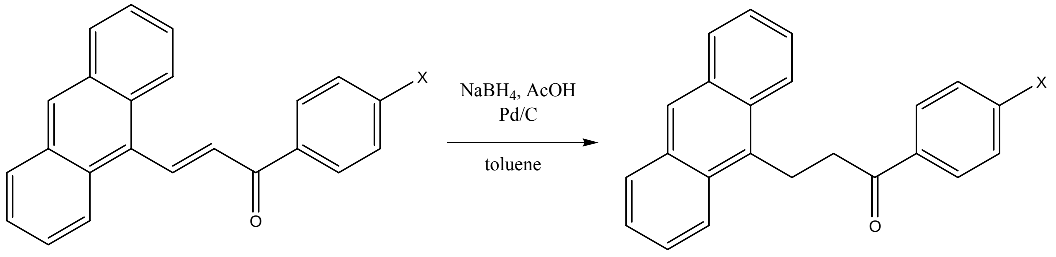


20 **22**

Scheme 10. Photochemical [4+4]-dimerisation of ethyl 9-anthranylpropionate (**20**) using blacklight UV (λ = 352 nm peak output).

So, the exchange of an ethenyl substituent to a ethyl substituent changes the photochemical pathway from a purely *E*-/*Z*- isomerisation and [2+2]-cycloaddition to a [4+4]-cycloaddition, see also ref. 8,17.

Similarly, the aroylethenylanthracenes ***E*-5** were hydrogenated to aroylethylanthracenes **23** (Scheme 11).

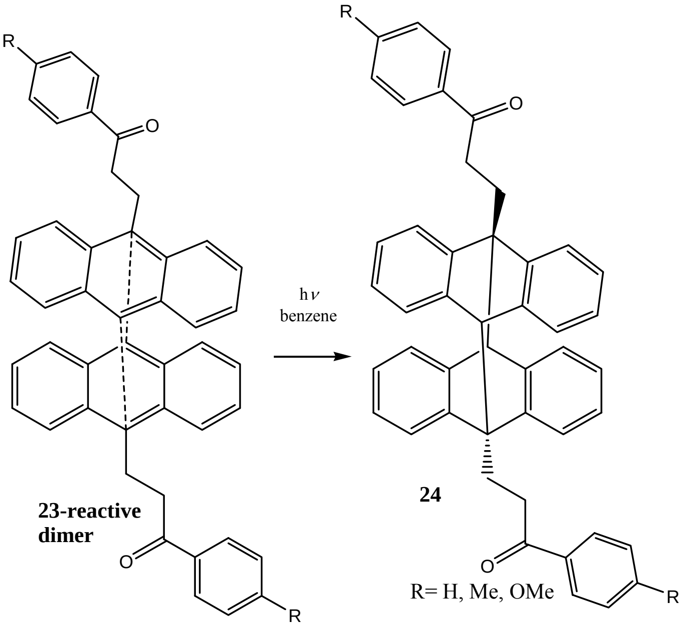


***E*-5** **23**

R= H, Me, OMe

Scheme 11. Hydrogenation of (*E*)-9-(2-phenacylethenyl)anthracenes (***E*-40**) to 9-(2-phenacylethyl)anthracenes using NaBH$_4$, AcOH, Pd/C as a reagent substitute for H_2, Pd/C.

Photoirradiation of the aroylethylanthracenes **23** in benzene at λ = 352 nm led rapidly to the [4+4] photoadducts **24**. A single crystal of **24-OMe** could be obtained, albeit with inclusion benzene, which was used as a solvent during the chromatographic purification of **24-OMe**.



Scheme 12. Photochemical [4+4]-dimerisation of 9-aroylethylanthracenes (**23**) using blacklight UV (peak output λ = 352 nm).

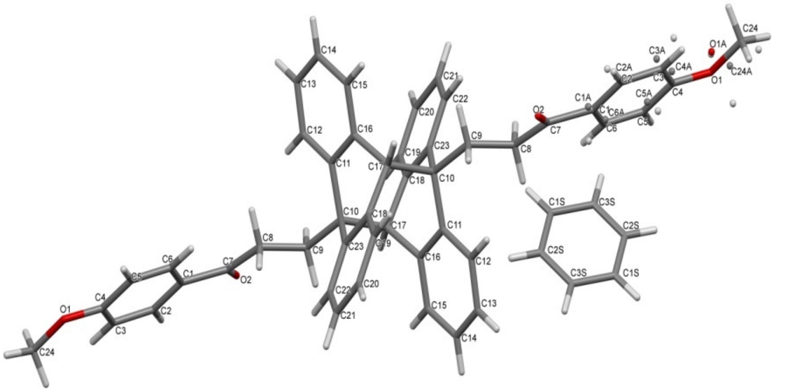
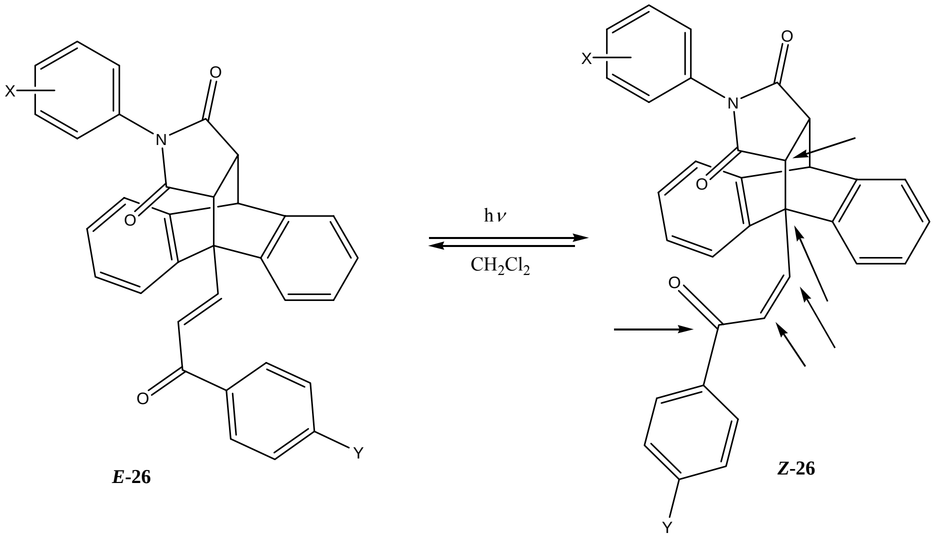


Figure 4. A view of the molecular structure of the molecule **24-OMe**. Disorder of one methoxyphenyl group can be noted.

At last, in an effort to force the making of the [2+2]-cycloadducts of anthranylacrylates ***E*-4** and aroyl-ethenylanthracenes ***E*-5**, these were subjected to a Diels-Alder reaction with maleimides. It was planned to study the photoreactivity of the cycloadducts with the idea that should they produce [2+2]-cycloadducts, these would be subjected to retro-Diels Alder reactions.

The synthesis of the cycloadducts of anthranylacrylates ***E*-4** and aroyl-ethenylanthracenes ***E*-5** has been discussed previously.[1] Photoreactions of the cycloadducts ***E*-25** and ***E*-26** in CH_2Cl_2 at $\lambda \geq 254$ nm gave exclusively the *Z*-isomers as a mixture of *E*- and *Z*-isomers. The *Z*-isomers could be separated by column chromatography.



Scheme 13. *E*-/*Z*-isomerisation of ***E*-26** in CH_2Cl_2 upon photoirradiation at $\lambda = 254$ nm. Arrows indicate disappearing ^{1}H and ^{13}C NMR peaks due extreme broadening.

In conclusion, under photoirradiation at $\lambda = 254$ nm, 9-anthranylacrylates **4** *E*/*Z*-isomerize. Over longer periods of irradiation, oligomers form. Also, 9-benzoylethenylanthracenes **5** *E*/*Z*-isomerize, but the reactions are much cleaner. The cycloadducts of 9-aroylethenylanthracenes with maleimides, **26**, undergo facile *E*-/*Z*-

isomerisation. According to the ^{1}H and ^{13}C NMR spectra of the compounds ***Z*-26**, the aroylethenyl substituent performs a rotation in NMR time that broadens peaks of the substituent and of neighboring Cs and Hs considerably.

Using blacklight UV (peak output at λ = 352 nm), 9-aroylethenylanthracenes **5** again undergo *E*-/*Z*-isomerisation. Small amounts of [2+2]-cycloadducts of type **16** are formed in CH_2Cl_2. Under the same conditions, 9-formylanthracene (**9**) was shown to undergo the known [4+4]-cycloadditive dimerisation to **19**. When anthranylacrylate **4** and aroylethenylanthracenes **5** are reduced to anthranylpropionate **20** and aroylethylanthracene **23**, respectively, these can be used in photochemical [4+4]-cycloadditive dimerisations, reacting to **22** and **24**.

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