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 \(\lambda = 254\) nm and at \(\lambda = 352\) nm. At \(\lambda = 254\) nm and \(\lambda = 352\) nm, the 9-vinyl substituted anthracenes undergo \(E/Z\)-isomerization, while their reduced derivatives undergo \([4+4]\)-dimerisation reactions at \(\lambda = 352\) 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 \(\pi\)-system of these conjugated anthracenes, where photochemical reactions may be the strategy of choice.

![Figure 1](image_url)  
**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 benzoylethenylantracenes, 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).

\[
\begin{align*}
\text{R'} & = \text{H, aryl} \\
\text{R} & = \text{Alkoxy (E-4), Aryl (E-5)} \\
n & = 1,2
\end{align*}
\]

**Scheme 1.** Conceivable photochemical reactions of anthranylacrylates \(E-4\) and aroyl-ethenylantracenes \(E-5\).

In the following, our results on the photochemical reactivity of \((E)-3-\text{(anthran-9-yl)}\)propenoates and \((E)-9-\text{(aroylthlenyl)}\)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 \((E)-3-(\text{anthran-9-yl})\text{propenoates}\) and \((E)-9-(\text{aroylthene})\text{anthracenes}\).

![Diagram of conceivable photochemical reactions of anthranylacrylates E-4 and aroyl-ethenylanthracenes E-5](image)

**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. \(^1\text{H}\) NMR (at 400 MHz) and \(^{13}\text{C}\) 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 $\lambda = 254$ 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$_2$Cl$_2$ [Sigma Aldrich, purris. p.a., $\geq 99.9\%$ (GC)] and acetonitrile [Panreac, HPLC grade and Romil Chemical, Far-UV grade 190, pur. 99.9%] as solvent. For the photoirradiation, a Luzchem LZR 4V photoreactor was used with 13 USHIO G8T5 lamps (7.2 W low pressure mercury arc lamp with a radiation peak at $\lambda = 253.7$ nm) and with 14 Hitachi FL8BL-B (0.75 W, UV irradiance 8.0 ($\mu$/cm$^2$, with a radiation peak at $\lambda = 352$ nm). CH$_2$Cl$_2$ [Sigma Aldrich, purris. p.a., $\geq 99.9\%$ (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 $\lambda = 253.7$ nm) and with Hitachi FL8BL-B (at $\lambda = 352$ 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’)-succinimidoanthracenes as the cycloadducts between the anthranylacrylates/aroylethenylanthracenes and N-arylmaleimides were submitted to photoirradiation with USHIO G8T5 lamps (at $\lambda = 253.7$ 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 $\lambda = 253.7$ nm. - 9-(E)-4-Methylbenzoylethenylanthracene (E-5-Me, 50 mg, 0.16 mmol) in CH$_2$Cl$_2$ (2.2 mL) was photoirradiated at $\lambda = 254$ nm (peak output) for 24 h. The photoreaction was monitored by $^1$H 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; $\nu_{\text{max}}$ (KBr/cm$^{-1}$) 3043, 1664, 1608, 1426, 1232, 885, 840, 778, 731; $\delta_{\text{H}}$ (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); $\delta_{\text{C}}$ (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$_{\text{quat}}$, 2C), 130.9 (C$_{\text{quat}}$), 131.0 (C$_{\text{quat}}$), 134.9 (C$_{\text{quat}}$), 139.1 (CH), 143.3 (C$_{\text{quat}}$), 191.5 (C$_{\text{quat}}$, 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 $\lambda = 254$ nm (peak output) in CH$_2$Cl$_2$ (3.5 mL) for 60h. The reaction mixture was subjected directly to column chromatography on silica gel (CH$_2$Cl$_2$) 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; $\nu_{\text{max}}$ (neat/cm$^{-1}$) 3064, 2838, 1775 (w), 1721, 1669, 1597, 1457, 1389, 1300, 1177, 1029, 1003, 909, 830, 732, 695, 551; $\delta_{\text{H}}$ (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)*; $\delta_{\text{C}}$ (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),
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 NaBH₄ (182 mg). After stirring the mixture for a day at rt, further acetic acid (71 mg) and NaBH₄ (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 NaBH₄. The mixture is extracted with CH₂Cl₂ (3 X 25 mL) and the organic phase is dried over anhydrous MgSO₄ and concentrated in vacuo. Column chromatography of the residue on silica gel (CH₂Cl₂) gives 20 (230 mg, 85%) as a pale yellow viscous oil*; \( \nu_{\text{max}} \) (neat/cm⁻¹) 1729, 1623, 1446, 1372, 1182, 1158, 1045, 834, 733, 602; \( \delta_{\text{H}} \) (400 MHz, CDCl₃) 1.29 (3H, t, \( ^3J = 7.6 \) Hz, CH₃), 2.80 (2H, t, \( ^3J = 8.4 \) Hz), 3.97 (2H, t, \( ^3J = 8.4 \) Hz), 4.22 (2H, q, OCH₂), 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); \( \delta_{\text{C}} \) (100.5 MHz, CDCl₃) 14.3 (CH₃), 23.3 (CH₂), 35.4 (CH₂), 60.7 (OCH₂), 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 \( \lambda = 352 \) 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; $\nu_{\text{max}}$ (KBr/cm$^{-1}$) 3066, 2978, 2924, 1728, 1474, 1449, 1424, 1374, 1301, 1260, 1181, 1082, 1019, 860, 792, 768, 697, 676, 642; $\delta$ (400 MHz, CDCl$_3$) 1.27 (6H, t, $^{3}J = 7.2$ Hz, 2 CH$_3$), 2.36 (4H, t, $^{3}J = 7.6$ Hz), 3.05 (4H, t, $^{3}J = 7.6$ Hz), 3.92 (2H, s, CH), 4.19 (4H, q, $^{3}J = 7.2$ Hz, 2 OCH$_2$), 6.80 – 6.88 (8H, m), 6.90 (4H, d, $^{3}J = 7.2$ Hz, $^{4}J = 1.6$ Hz), 6.94 (4H, d, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz); $\delta$ (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$_{\text{quat}}$), 125.4 (5) (4C, CH), 125.5 (4C, CH), 125.7 (4C, CH), 127.6 (4C, CH), 142.1 (4C, C$_{\text{quat}}$), 143.5 (4C, C$_{\text{quat}}$), 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 dichloromethane (\( \text{CH}_2\text{Cl}_2 \)) and in acetonitrile (\( \text{CH}_3\text{CN} \)) (Table 1). The UV spectra were not affected noticeably by the nature of the solvent and corresponded, where known, with the literature data.\(^8\)
Table 1. UV band maxima of selected compounds in CH$_2$Cl$_2$ and CH$_3$CN.

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

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

**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$_2$Cl$_2$ 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 aroylethenylantracenes \( E-5 \) 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 \((Z)-4\)-methoxybenzoylthenylanthracene \((Z-5-\text{OMe})\). 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-anthrylacrylate \( E-4 \) at \( \lambda = 253.7 \) nm.
Scheme 6. Slow build-up of two isomers of HH-[2+2]-cycloadduct 16 in photoirradiation of aroylenanthracene (E-5-Me). The main reaction is shown in Scheme 4.

Next, 9-(E)-arylenanthracenes E-5 were photoirradiated with blacklight UV radiation ($\lambda = 352\,\text{nm}$ peak output). In CH$_2$Cl$_2$, again a rapid conversion to an equilibrium of 9-(E)- and 9-(Z)-arylenanthracenes 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 constants, 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 aroylenylanthracene (**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\(_2\)Cl\(_2\) and in benzene. The photochemical dimerisation proceeds more quickly in benzene than in CH\(_2\)Cl\(_2\). 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 CH₂Cl₂ within 48h (Scheme 8). In either case, anthraquinone (18) was also produced. The product mixture was separated by column chromatography on silica gel (hexane – CH₂Cl₂: 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 CH₂Cl₂ 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 CH₂Cl₂ 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 H₂ 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 H₂ in presence of Pd/C. Here, it was tried to produce hydrogen in situ by reacting NaBH₄ with AcOH
in the presence of Pd/C.\textsuperscript{13-15} The double bond hydrogenation took a long time, and partially the anthracene core was also hydrogenated to produce ethyl 9,10-dihydroanthrylpropionate (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.\textsuperscript{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 NaBH₄, AcOH, Pd/C as a reagent substitute for H₂, Pd/C.

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

Scheme 11. Hydrogenation of (E)-9-(2-phenacylethenyl)anthracenes (E-40) to 9-(2-phenacylethyl)anthracenes using NaBH₄, AcOH, Pd/C as a reagent substitute for H₂, Pd/C.
Photoirradiation of the aroylethylanthracenes 23 in benzene at $\lambda = 352$ 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 $\lambda = 352$ 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 \textit{E-4} and aroyl-ethenylanthracenes \textit{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 \textit{E-4} and aroyl-ethenylanthracenes \textit{E-5} has been discussed previously.\textsuperscript{1} Photoreactions of the cycloadducts \textit{E-25} and \textit{E-26} in CH\textsubscript{2}Cl\textsubscript{2} at $\lambda \geq 254$ nm gave exclusively the Z-isomers as a mixture of \textit{E-} and \textit{Z-}isomers. The \textit{Z-}isomers could be separated by column chromatography.

\begin{center}
\textbf{Scheme 13.} \textit{E-}/\textit{Z-}isomerisation of \textit{E-26} in CH\textsubscript{2}Cl\textsubscript{2} upon photoirradiation at $\lambda = 254$ nm.
\end{center}

Arrows indicate disappearing $^1$H and $^{13}$C NMR peaks due extreme broadening.

In conclusion, under photoirradiation at $\lambda = 254$ nm, 9-anthranylacrylates \textit{4} \textit{E}/\textit{Z-}isomerize. Over longer periods of irradiation, oligomers form. Also, 9-benzoylethenylanthracenes \textit{5} \textit{E}/\textit{Z-}isomerize, but the reactions are much cleaner. The cycloadducts of 9-aroylethenylanthracenes with maleimides, \textit{26}, undergo facile \textit{E-}/\textit{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 $\lambda = 352$ nm), 9-aroylethenylantracenes 5 again undergo $E$-/Z-isomerisation. Small amounts of [2+2]-cycloadducts of type 16 are formed in CH$_2$Cl$_2$. Under the same conditions, 9-formylanthracene (9) was shown to undergo the known [4+4]-cycloadditive dimerisation to 19. When anthranylacrylate 4 and aroylethenylantracenes 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.

References


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