Pergamon

Tetrahedron, Vol. 52, No. 3, pp. 935-940, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)00933-7

Photoisomerisation of 9-Anthrylsubstituted Pyridyl Enones

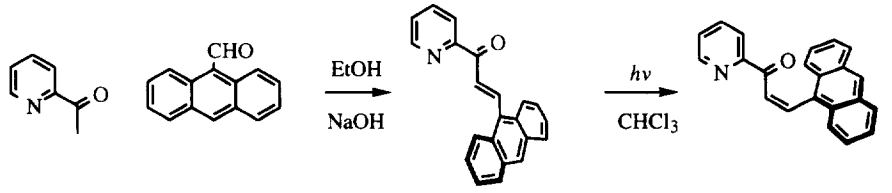
Edwin C. Constable* and Diane R. Smith

Institut für Anorganische Chemie, Universität Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland.

Abstract. The enone 3-(9-anthryl)-1-(2-pyridyl)-2-propenone undergoes a facile photochemical *E* to *Z* isomerisation. Studies of related enones indicate that the photochemical properties are controlled by subtle changes in the structure of the molecule.

There has been much interest in controlled photoinduced electron transfer (PET) within supramolecular systems. [1] Anthracene is popular as the fluorophore in such systems as its photochemistry and photophysics are well-understood. [2,3] We recently reported the synthesis and coordination behaviour of a 2,2':6',2"-terpyridine bearing a photoactive anthracene unit. [4] In addition to the potential interactions between metal ions and the anthracene group in the complexes of this ligand, we now report that there are also interactions between the olefinic C=C bond and the anthracene unit in the ligand precursor, the enone, **1**.

The condensation reaction of 2-acetylpyridine with one equivalent of 9-anthrylaldehyde in ethanol in basic conditions afforded *E* -**1** as an orange solid in a yield of 93% after recrystallisation from methanol in the dark. [4]



E - **1** *Z* - **1**

Scheme 1. Synthesis of the *E* and *Z* enones.

This compound was characterised as the *E* isomer on the basis of the ^{1}H NMR spectrum which showed $^3J_{HH}$ between the olefinic protons of 16 Hz. Irradiation of a chloroform solution with a mercury lamp fitted with a 330nm cut-off filter for 5 min, or upon standing in sunlight, resulted in a slight paling in colour and complete isomerisation to the *Z* isomer as evident from NMR spectroscopy (Figure 1). [5] The resonances corresponding to the olefinic protons had shifted upfield to δ 8.27 and 8.65 (as compared

with δ 8.49 and 8.94) and the coupling between these protons was reduced to 12 Hz (Table). In the solid state the *E* isomer is photochemically stable and solutions maintained in the dark are stable to isomerism. No reverse (*Z* -*E*) isomerisation was observed either under thermal or photochemical conditions. This lack of photochemical reversibility is not surprising when the electronic spectra are considered. The broadness of the π–π* absorption bands in *E*-**1** means that it is not possible to selectively irradiate those of the *Z*-**1** isomer and so any irradiation results in the formation of the more photo-stable isomer, *E*-**1**. Under similar conditions, solutions of the analogous phenyl and naphthyl substituted 2-pyridyl enones showed no similar photochemical behaviour. However, the pyridyl moiety is not a prerequisite for the olefinic isomerisation in anthryl-substituted enones to occur, since 3-(9-anthryl)-1-(2-phenyl)-2-propenone and 3,4-bis(9-anthrylmethylene)tetrahydrofuran-2,5-dione have also been shown to undergo photoisomerisation. [6,7]

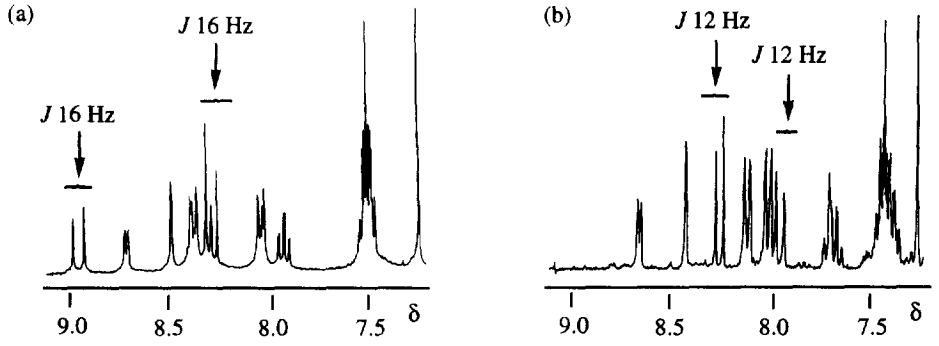
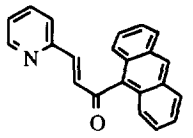


Figure 1. ^{1}H NMR spectra of (a) *E*-**1** and (b) *Z*-**1**

In contrast to the above, the reversed enone *E*-**2** (prepared from the condensation reaction of 9-acetylanthracene with 2-pyridinecarboxaldehyde) did not undergo photochemical isomerisation in solution. However, its fluorescence properties were virtually identical to those of *E*-**1**. This is in contrast to the general behaviour of 9-carbonyl-substituted anthracenes which are usually non-fluorescent as a result of the anthracene excited state being quenched by the transfer of electrons to the triplet nπ* level [8]

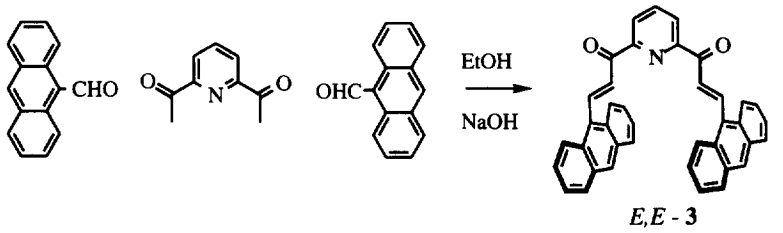


E - **2**

The above observations indicate that the requirement for isomerisation is an anthracene conjugated to the olefinic bond of an enone.

The bischalcone **3** was prepared in an analogous manner to **1** by the condensation of 2,6-diacetylpyridine with 2 equivalents of 9-anthrylaldehyde in the presence of base (Scheme 2). The orange

precipitate formed consisted of only one product, as evident from tlc, and was recrystallised from toluene in the dark. The ^{1}H NMR spectrum showed only one set of olefinic protons with a coupling constant of 16 Hz consistent with the *E,E* isomer (Table). Furthermore, the anthracene protons come into resonance upfield of the more usual values. This is consistent with the two anthracene moieties adopting an intramolecular stacked arrangement in solution. [9] The symmetrical nature of the product was confirmed by the observation of 14 carbon environments in its ^{13}C NMR spectrum.



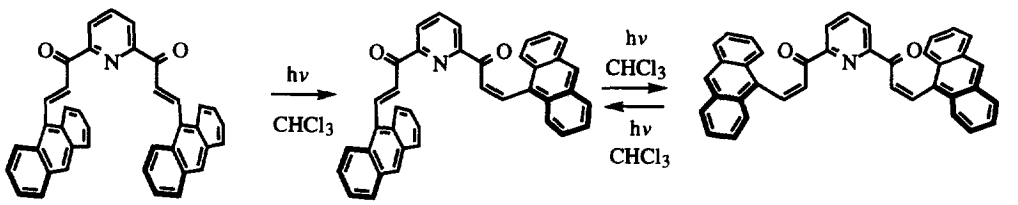
E,E - **3**

Scheme 2. Synthesis of the bischalcone *E,E*-**3**.

Recrystallisation of this product from toluene in the light allowed yellow crystals corresponding to the *E,Z* isomer to be isolated. This compound was characterised in the first instance as an isomer of **3** by the presence of the same molecular ion at *m/z* 539 in the EIMS spectrum. However, both the ^{1}H NMR and ^{13}C NMR spectra showed a doubling of signals compared with the *E,E* isomer, and hence the product was not the symmetric *Z,Z* isomer. The spectrum showed the anthracene protons at more typical values (Table) hence suggesting that there was no π–π stacking interactions in this isomer. This was confirmed by a preliminary crystallographic analysis of this compound which clearly showed one olefinic bond in the *Z* arrangement and the other in the *E* conformation. [10] Although the solid state structure revealed some intermolecular stacking, the separation between the molecules is significantly greater than the expected for a strong π–π stacking interaction.

Irradiation of a chloroform solution of *E,E*-**3** with a mercury lamp fitted with a 330 nm cut-off filter resulted in isomerisation; first to *E,Z*-**3** and then to *Z,Z*-**3** (Scheme 3). This process was followed by the shifts of the resonances corresponding to the olefinic and the anthracene protons in the ^{1}H NMR spectrum. Complete conversion to the *Z,Z* isomer was never achieved, *i.e.* a photostationary state was obtained with a 10:1 ratio of the *E,Z* and *Z,Z* isomers. However, since the three isomers had different mobilities on silica gel, sufficient of the *Z,Z* isomer was isolated from the equilibrium mixture by preparative thin layer chromatography for analysis. The ^{1}H NMR spectrum (Table) was relatively simple, with one set of olefinic protons having a coupling constant of 12 Hz. In comparison to *E,E*-**3**, the protons on the pyridine ring in *Z,Z*-**3** are more strongly shielded ($\Delta\delta$ ~0.6) by the anthracene systems now surrounding the pyridine ring. On standing in sunlight a solution of the *Z,Z* isomer underwent isomerisation to give the photostationary state. Attempts to convert *Z,E*-**3** to *E,E*-**1** by thermal or photochemical methods have proved unsuccessful. Molecular modelling studies have shown the *Z,Z* isomer to be of higher energy compared with either the *Z,E* or the *E,E* isomers (120.1, 114.7, 105.2

kcalmol^{-1}, respectively). [11]



E,E - **3** *E,Z* - **3** *Z,Z* - **3**

Scheme 3. Photoinduced isomerisation of the bischalcone **3**.

Table. ^{1}H NMR data ($CDCl_3$, 300 MHz)

H	*E*-**1**	*Z*-**1**	*E*-**2**	*E,E* -**3**	*E,Z* -**3**	*Z,Z*-**3**
3	m, 8.28-8.34	m, 7.63-7.75	d *J* 7.6 Hz, 7.36	d, *J* 8Hz, 8.27	m, 7.85-7.92	d, *J* 8Hz, 7.68
4	m, 7.89-7.97	m, 7.63-7.75	td 7.63-7.70	t, *J* 8Hz, 8.18	m, 8.32-8.41	m, 7.48-7.57
5	m, 7.48-7.58	m, 7.36-7.51	m, 7.22-7.28	d, *J* 8Hz, 8.52	m, 7.85-7.90	d, *J* 8Hz, 7.68
6	d, *J* 7.6Hz, 8.72	d *J* 7.6Hz, 8.65	d *J* 7.6Hz,8.62	----------	----------	----------
a'	d, *J* 16 Hz,8.28	----------	d *J* 16 Hz, 7.21	d, *J* 16 Hz, 8.27	d, *J* 16 Hz, 8.38	----------
b'	d, *J* 16 Hz,8.94	----------	d *J* 16 Hz, 7.70	d, *J* 16 Hz, 8.94	d, *J* 16 Hz, 9.00	----------
1',8'	m, 8.35-8.42	----------	m, 8.04-8.10	m, 8.50-8.55	d, *J* 8Hz, 8.50	----------
2',7'	m, 7.48-7.58	----------	m, 7.44-7.53	m, 7.12-7.28	m, 7.54-7.70	----------
3',6'	m, 7.48-7.58	----------	m, 7.44-7.53	m, 7.02-7.10	m, 7.28-7.43	----------
4',5'	m, 8.01-8.08	----------	m, 7.88-7.94	d, *J* 8Hz, 7.92	m, 7.95-8.03	----------
10'	s, 8.49	----------	s, 8.55	s, 8.40	s, 8.58	----------
a''	----------	d, *J* 12Hz, 7.95	----------	----------	d, *J* 12Hz, 7.88	d, *J* 12Hz, 8.05
b''	----------	d, *J* 12Hz, 8.27	----------	----------	d, *J* 12Hz, 8.18	d, *J* 12Hz, 8.22
1'',8''	----------	m, 8.09-8.15	----------	----------	d, *J* 8Hz, 8.12	m, 8.12-8.18
2'',7''	----------	m, 7.36-7.51	----------	----------	m, 7.54-7.70	m, 7.45-7.51
3'',6''	----------	m, 7.36-7.51	----------	----------	m, 7.28-7.43	m, 7.45-7.51
4'',5''	----------	m, 7.99-8.04	----------	----------	m, 7.95-8.03	m, 8.99-8.04
10''	----------	s, 8.42	----------	----------	m, 8.32-8.41	s, 8.42

Further evidence for the face to face stacked arrangement of the anthracene rings in the *E,E* isomer came from the comparison of the fluorescence spectra. Whereas *E*-**1**[12] and *Z*-**1** were equally fluorescent, the *E,E* isomer exhibited only half the fluorescence intensity of the *E,Z* isomer but equal to the *Z,Z* isomer (Figure 2). This quenching of fluoresence intensity in *E,E*-**3** is characteristic of intramolecular quenching of the anthracene triplet excited state by the π–π interaction of the proximate anthracene rings. In the case of *Z,Z*-**3**, quenching of the fluorescence may be achieved by the pyridine ring "sandwiched" between the two anthracene moieties.

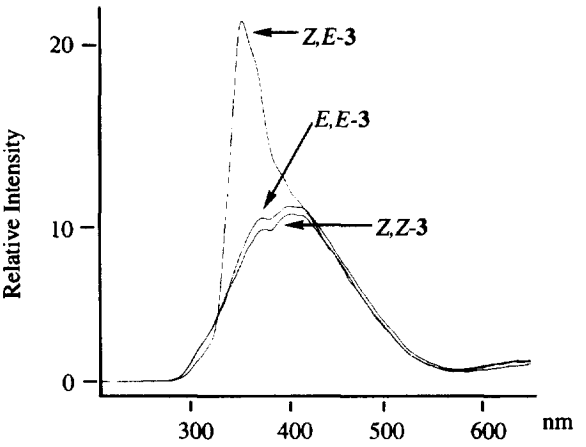


Figure 2. Fluorescence spectra of the bischalcone isomers (7.42×10^{-7} M in $CHCl_3$, λ_{ex} = 230 nm).

Experimental

E-1-(9-Anthryl)-3-(2-pyridyl)-2-propenone (*E*-**2**): A warm solution of 9-acetylanthracene (0.50 g, 2.3 mmol) in ethanol (10 ml) was added to a stirred solution of 2-pyridinecarboxaldehyde (0.24 g, 2.3 mmol) and aqueous sodium hydroxide (2 ml of a 1.5 M solution) in ethanol (20 ml). After 2 h the orange precipitate was collected by filteration and recrystallised from ethanol (0.62 g, 89%). EIMS 309 $[M]^+$. ν_{CO} 1667 cm^{-1}, $\lambda_{max}(CHCl_3)$ 229 nm (2.59×10^{-6} M, ε, 10.3×10^5), 359 (6.47×10^{-5} M, ε, 6.7×10^3), 373 (6.47×10^{-5} M, ε, 6.7×10^3), λ_{em} 406 nm.

E,E-2,6-Di(3-(9-anthryl)-1-oxo-2-propenyl)pyridine (*E,E*-**3**): Aqueous sodium hydroxide (15 mmol) was added to a warm solution of 9-anthrylaldehyde (2.06 g, 10 mmol) in ethanol (20 ml). After stirring for 15 min 2,6-diacetylpyridine (0.81 g, 2 ml of a 1.5 M solution)was added and the solution stirred at room temperature for 4 h. The orange precipitate was collected by filtration and recrystallised from toluene in the dark to afford the *E,E* isomer as orange needles (2.13 g, 79%). EIMS 539 $[M]^+$, ^1H (300 MHz, $CDCl_3$) Table . ^{13}C NMR (75 MHz, $CDCl_3$) 125.0, 125.3, 126.3, 126.3, 128.6, 128.7, 129.4, 129.7, 129.8, 131.2, 138.5, 142.2, 153.4, 188.4. ν_{CO} 1665 cm^{-1}, λ_{max} ($CHCl_3$) 228 nm (7.42×10^{-7} M, ε, 4×10^6), 435 nm (3.71×10^{-5} M, ε, 1.3×10^4), λ_{em} ($CHCl_3$) 405 nm. Calc for $C_{39}H_{25}NO_2$, C, 86.80; H, 4.68; N, 2.60 %. Found C, 86.66; H, 4.48; N, 2.33 %.

E,Z-2,6-Di(3-(9-anthryl)-1-oxo-2-propenyl)pyridine (*E,Z*-**3**):: EIMS 539 $[M]^+$, ^1H (300 MHz, $CDCl_3$) Table . ^{13}C NMR (75 MHz, $CDCl_3$) 125.1, 125.4, 125.5 (x2) , 125.7, 125.7, 126.5, 127.1, 128.0 (x2), 128.5, 128.7, 128.8 (x2), 129.0, 129.8 (x2), 130.3, 131.0, 131.4, 137.9, 142.0, 142.3, 152.8, 153.4, 188.4 189.1. ν_{CO} 1672 cm^{-1}, λ_{max} ($CHCl_3$) 233 nm (7.42×10^{-7} M, ε, 4×10^6), 435 nm (3.71×10^{-5} M, ε, 1.2×10^4), λ_{em} ($CHCl_3$) 359 nm. Calc for $C_{39}H_{25}NO_2$, C, 86.80; H, 4.68; N, 2.60 %. Found C, 86.55; H, 4.58; N, 2.53 %.

Z,Z-2,6-Di(3-(9-anthryl)-1-oxo-2-propenyl)pyridine (Z,Z-**3**):: EIMS 539 $[M]^+$, ^1H (300 MHz, $CDCl_3$) Table . ^{13}C NMR (75 MHz, $CDCl_3$) 125.2, 125.4, 125.5, 125.8, 127.2, 128.1, 128.6, 128.9, 131.1, 131.3, 137.4, 141.9, 152.9, 189.2. ν_{CO} 1676 cm^{-1}, λ_{max} ($CHCl_3$) 231 nm (7.42×10^{-7} M, ε, 3×10^6), 377 nm (3.71×10^{-5} M, ε, 1.3×10^4), λ_{em} ($CHCl_3$) 409 nm.

Acknowledgements

We gratefully acknowledge the SERC and the Schweizerischer Nationalfonds zur Förderung der wissenenschaftlichen Forschung for financial support; This work has been in part supported by the European Community Human Capital and Mobility Program - Contract no. ERBCHRXCT 94-0492.

References and Footnotes

1. See for example, Denti, G.; Serroni, S.; Sampagna, S.; Juris, S. A.; Ciano, M; Balzani, V. in *Perspectives in Coordination Chemistry*, eds Williams, A.F.; Floriani, C.; Mernach, A.E. VCHA, Basel, 1992.
2. Becker, H.-D. *Chem. Rev.*, **1993**, *93*, 145-172 and references therein.
3. Bissel, R.; de Silva, A.P.; Gunaratna, H.Q.N.; Lynch, P.L.M.; Maguire, G.E.M.; Sandanayake, K.R.A.S. *Chem. Soc. Rev.*, **1992**, *21*, 187-195 and references therein. James, T.D.; Sandanyake, K.R.A.S.; Shinkai, S. *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 2207-2209. Murru, M.; Parker, D.; Williams, G; Beeby, A. *J. Chem. Soc., Chem. Commun.*, **1993**, 1116-1118. Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.;. Sacchi, D. *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 1975-1977. Fages, F.; Desvergne, J.-P.; Kampke, K.; Bouas-Laurent, H.; Lehn, J.-M.; Meyer, M.; Albrecht-Gary, A.-M. *J. Am. Chem. Soc.*, **1993**, *115*, 3658-3664.
4. Constable, E.C.; Smith, D.R. *Supramol. Chem.*, **1994**, *4*, 5-7.
5. λ_{max} ($CHCl_3$) 229 nm (ε, 9×10^5), 379 nm (ε, 5.7×10^3), λ_{em} ($CHCl_3$) 406 nm.
6. Becker, H.-D.; Becker, H.-C.; Sandros, K.; Andersson, K. *Tetrahedron Lett.*, **1985**, *26*, 1589-1592. Becker; H.-D.; Andersson, K. *J. Org. Chem.*, **1983**, *48*, 4542-4549.
7. Heller, H.G.; Ottaway, M.J. *J. Chem. Soc. Chem. Commun.*, **1995**, 479-480.
8. Hirayama, S. *J. Chem. Soc., Faraday Trans. 1*, **1982**, *78*, 2411-2421.
9. Benniston, A.C.; Harriman, A.; Lynch,V.M. *Tetrahedron Lett.*, **1994**, *35*, 1473-1476. Benniston, A.C.; Harriman, A.; Lynch,V.M. *J. Am. Chem. Soc.*, **1995**, *117*, 5275-5291.
10. The crystals were fine needles and the crystal structure could not be fully refined below R=10%.
11. Calculations were performed using Molecular Simulations Cerius^2 TM software.
12. λ_{max} ($CHCl_3$) 227 nm (2.5×10^{-6} M, ε, 9×10^5), 428 nm (6.47×10^{-5} M, ε, 3.6×10^3), λ_{em} ($CHCl_3$) 405 nm.

(*Received in Germany* 17 *July* 1995; *revised* 11 *October* 1995; *accepted* 19 *October* 1995)