SHORT PAPER

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Formation and crystal structures of 9-methylanthracene photodimer and lepidopterene[†]

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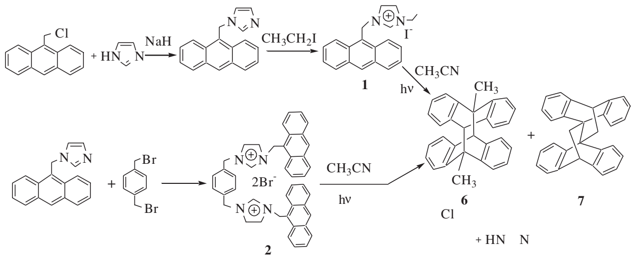
The 9-methylanthracene photodimer (**6**) and lepidopterene (**7**) were prepared by a photo-dimerisation reaction of 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) or α, α′-di[1-(9-anthracenylmethyl) imidazolium]-*p*-xylene dibromide (**2**). Compound **6** is derived from the head-tail [4+4] cycloaddition of two molecular 9-methylanthracenes, and the butterfly-shaped compound **7** is formed via the 9-methyleneanthracene radical in a two steps precess. The single crystal structure of **6** was determined by X-ray diffraction analysis. The changes of luminescent intensities of compounds **1**, **2** and **7** are reported.

Keywords: crystal structure, 9- methylanthracene photodimer, lepidopterene

The conversion of anthracene derivatives to photodimers by the action of sunlight has been known for a long time.[1] Many photodimers derived from substituted anthracenes in solution and in the solid state have been reported.[2] Considerable interest is now focused on the development of multifunctional spin systems with synergetic properties, and successful studies have recently been reported with regard to photofunctional magnetic materials derived from some inorganic compounds[3] and metal complexes.[4] Several organic spin systems with photo-functionality[5] and organo-magnetic materials have also been developed.[6] The chromophoric system of anthracene is a promising system for investigating the change of magnetic properties in a spin system arising from the structural change upon irradiation. Photodimerizations of 9-substituted anthracenes in solution are efficient, usually giving rise to head-to-tail dimers.[7] Anthracene derivatives having various linkages have been shown to undergo intramolecular [4+4] or [4+2] cycloaddition (cyclomerisation) and to exhibit emission from the intramolecular excimer state.[8] In spite of the potential reactivity to cyclodimerisation, studies on bichromophoric compounds having 9-anthryl group are very limited.[9] Herein we wish to report a new method of the preparation of known 9- methylanthracene dimer (**6**) and lepidopterene (**7**) from 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) or α, α’-di[1-(9-anthracenylmethyl) imidazolium]-*p*-xylene dibromide (**2**).

1-(9-Anthracenylmethyl)-3-ethylimidazolium iodide (**1**) was prepared from imidazole by stepwise alkylation with 9-chloromethylanthracene followed by ethyl iodide, and obtained as yellow crystals by analogy with a reported process.[10] α, α’-di[1-(9-anthracenylmethyl) imidazolium]-*p*-xylene dibromide (**2**) was prepared by reaction of 1-(9-anthracenylmethyl) imidazole and α, α’-dibromo-*p*-xylene[11] (Scheme 1). Known compounds of 9-methylanthracene photodimer **6**[12] and lepidopterene **7**[13, 14] were prepared by a new method from **1** or **2** in acetonitrile and methanol solution by irradiation. Photodimer **6** is slightly soluble in DMSO and insoluble in dichloromethane. Lepidopterene **7** is soluble in dichloromethane and slightly soluble in methanol.

The crystal structures of **6** and **7** are shown in Fig. 1. The former has not been reported previously, and the latter has been verified by X-ray diffraction method[14].



Scheme 1 Preparation of compounds 6 and 7.

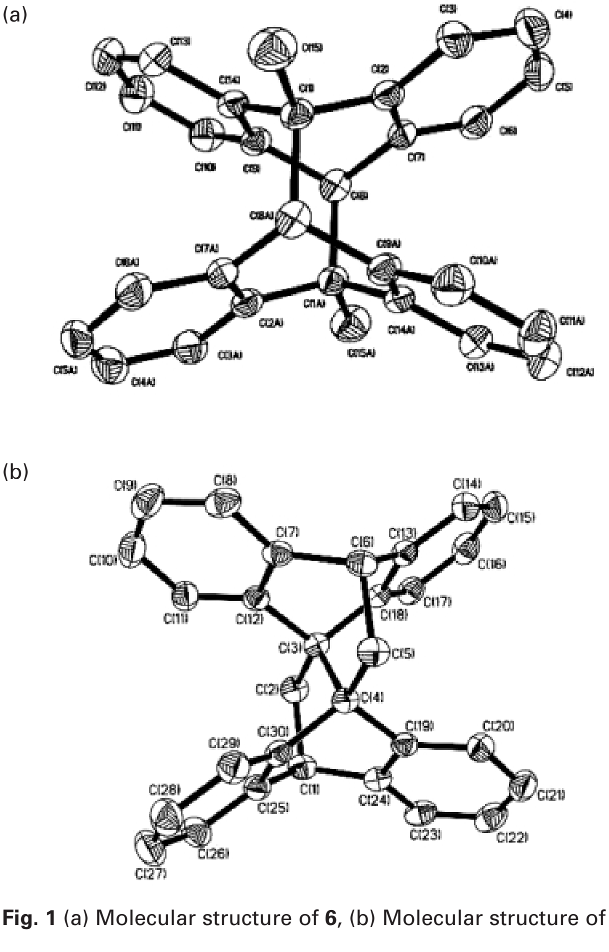


Fig. 1 (a) Molecular structure of **6**, (b) Molecular structure of **7**.

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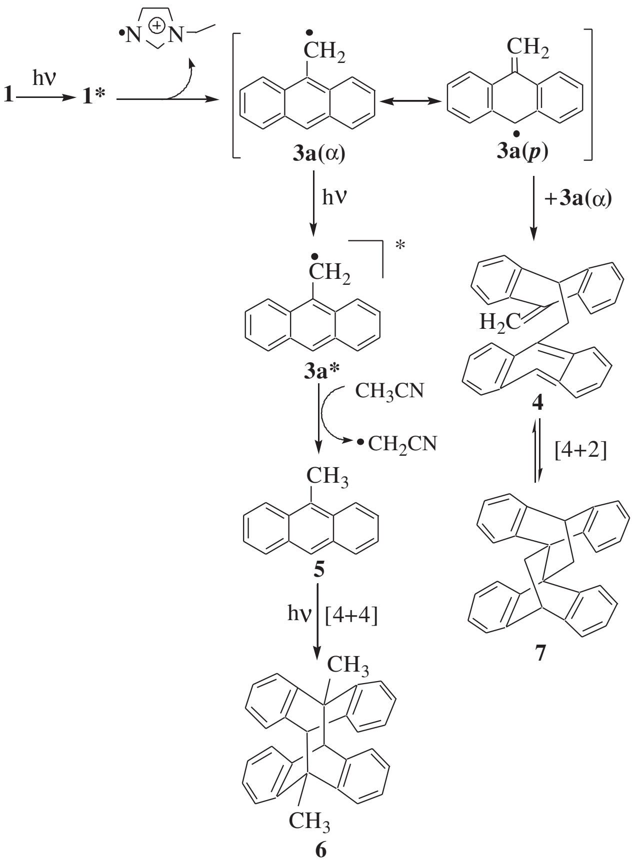
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 2 Mechanism of formation of compounds **6** and **7**.

The pathways for the formation of **6** and **7** are shown in Scheme 2. The cleavage of C–N bond of **1** under irradiation took place by a multiple-photon process,[15] *i.e.* two photons for C–N bond cleavage and a photon for resulting 9-anthracenylmethyl radical **3a** to form the excited 9-anthracenylmethyl radical **3a***. Intermediates **3a** (α) and **3a** (*para*) can inter convert. **3a*** may capture a hydrogen atom from the solvent acetonitrile[16] to form 9-methylanthracene **5.** Then [4+4] cycloaddition of two molecules **5** occurred to give heat-to-tail product **6** under irradiation. The formation of **7** resulted from a two-step reaction, in which the first step was the dimerisation of the radical **3a** (α) and **3a** (*para*) to form **4,** and the second step was the conversion of **4** via thermal intramolecular Diels–Alder reaction to form **7**. The AM1 calculations[17] for the ground state of radical **3a** revealed a *ca* 3-fold higher spin density in the *para* than in the α position and this accounts for the preferred δ/*para* rather than α/α coupling. Steric factors are presumably the reason why the *para*/*para* dimer is not formed. The ground state radical **3a** is the likely precursor to the coupling products **7** rather than its excited state **3a*** because of the reversal in the spin densities for these two electronic configurations.[18] In addition, the equilibrum between **4** and **7** was observed[13, 19] in the solution, but it is shifted far to the side of **7**, and it can be detected by ^{1}H NMR spectrum and fluorescence emission spectrum.

Similarly, compound **2** in acetonitrile/methanol also underwent the cleavage of C–N bond to give **6** and **7** only to liberate a different radical, namely, α, α'-diimidazole-*p*-xylene diradical.

The luminescent emission spectra of **1, 2, 7** and anthracene are shown in Fig. 2. In dichloromethane **1** and **2** shown anthracene type fluorescence emission, but weaker than that of anthracene. This can be attributed to the presence of the photoinduced electron transfer (PET) process of the lone pair electrons of the nitrogen atom to anthracene ring.[20] In compounds **6** and **7**, the aromaic structures are lost in the central ring, and therefore, **6** does not give noticeable fluorescence emission. However, compound **7** has a weak anthracene type fluorescence emission at *ca* 380–500 nm arising from **4**, due to the equilibrum between **4** and **7** in solution (Scheme 2), and it exhibits exciplex fluorescence near 600 nm.[13]

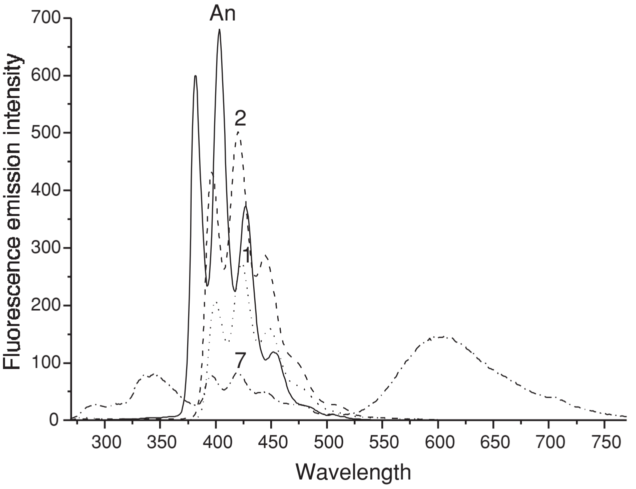


Fig. 3 Emission spectra of compound **1** (...), **2** (----), **7** (-·-·-) and anthracene (—) at 298 K upon excitation at 256 nm in CH_2Cl_2 (**1**: 5.0×10^{-6} mol/l, **2**: 2.5×10^{-6} mol/l, **7**: 5.0×10^{-6} mol/l and anthracene: 5.0×10^{-6} mol/l).

Experimental

Synthesis of α, α'*-di[1-(9-anthracenylmethyl) imidazolium]-p-xylene dibromide* (**2**): An acetonitrile (100 ml) solution of 1-(9-anthracenylmethyl) imidazole (2.800 g, 10.852 mmol) and α, α'-dibromo-*p*-xylene (1.452 g, 5.500mmol) was refluxed for 3 days and a yellow precipitate was formed. The product was filtered and washed with acetonitrile and ethyl ether to afford a yellow powder. Yield: 4.730 g, 83.5%. m.p.184–186°C. Anal. Calcd for: C, 67.70; H, 4.65; N, 7.18. Found: C, 67.38; H, 4.82; N, 7.49. ^{1}H NMR (DMSO-d$_6$, 300 MH$_Z$): δ 5.33 (s, 4H, CH_2Ph), 6.53 (s, 4H, CH_2An) (An: anthracene), 7.32 (s, 4H, PhH), 7.62 (t, *J* = 8.2, 4H, AnH), 7.65 and 7.76 (s, 2 × 2H, 4, 5-imiH) (imi: imidazole), 7.70 (t, *J* = 8.2, 4H, AnH), 8.24 (d, *J* = 8.2, 4H, AnH), 8.48 (d, *J* = 8.2, 4H, AnH), 8.87 (s, 2H, AnH), 9.19 (s, 2H, 2-imiH). ^{13}C NMR (DMSO-d$_6$, 75 MH$_Z$): δ 45.0 (CH_2Ph), 51.2 (CH_2An), 122.4, 123.0, 123.3, 125.6, 127.7, 128.5, 129.3, 130.1, 130.6, 131.0, 135.3, 135.8 (PhC, imiC and AnC). IR (KBr) δ: 3025(w), 2969(w), 2875(w), 1623(m), 1556(m), 1447(s), 742(m).

Formation of 9-methylanthracene photodimer (**6**) *and lepidopterene* (**7**): *Method 1*: An acetonitrile (20 ml) solution of 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) (0.400 g, 0.984 mmol) was irradiated with a high-pressure Hg lamp (400 W) under nitrogen at 70°C for 24 h, and a yellow precipitate was formed. The precipitate was filtered and washed with methanol and ethyl ether to give a pale yellow powder. The powder was extracted with CH_2Cl_2 (3 × 10 ml), The insoluble residue was **6** (0.017 g, 9%), and the soluble product solid in CH_2Cl_2 was compound **7** (0.024g, 13%).

Method 2: An acetonitrile (20 ml) solution of 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) (0.400 g, 0.984 mmol) was exposed to sunlight for 15 days at room temperature to give two colourless crystalline solids, among which **6** was insoluble in CH_2Cl_2 (0.013 g, 7%) and **7** was soluble in CH_2Cl_2 (0.020 g, 11%).

Method 3: 9-Methylanthracene photodimer (**6**) and lepidopterene (**7**) were also prepared with α, α'-di[1-(9-anthracenylmethyl) imidazolium]-*p*-xylene dibromide (**2**) (0.400g, 0.512 mmol) as starting materal in acetonitrile and methanol solution following methods 1 or 2 (0.028 g, 14%).

6: m.p. 236–238°C (lit.,[12] m.p. 238°C). IE/MS: *m*/*z* 384 (M$^+$)(9%). Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.44; H, 6.12. ^{1}H NMR (DMSO-d$_6$, 300MHz) δ: 2.19 (s, 6H, CH_3), 4.06 (s, 2H, CH), 6.78 (m, 8H, ArH), 7.01 (t, *J* = 7.2 Hz, 4H, ArH), 7.40 (d, *J* = 7.2 Hz, 4H, ArH).

Table 1 Crystal data and details of refinement for compound **6** and **7**

	Compound **6**	Compound **7**
Empirical formula	C_{30} H_{24}	C_{30} H_{22}
Formular weight	384.49	382.48
Crystal system	Monoclinic	Monoclinic
space group	*P2(1)/c*	*P2(1)/n*
a (Å)	9.906(3)	7.719(3)
b (Å)	12.634(6)	14.229(5)
c (Å)	13.498(4)	17.925(6)
β(°)	114.116(5)	96.150(7)
V(Å^3)	998.2(5)	1957.6(12)
D_c(g/cm^3)	1.279	1.298
Z	2	4
μ (mm^{-1})	7.2	7.3
T (K)	293(2)	293(2)
θ_{range} (°)	2.25–3.98	1.83–25.03
Ind reflections	1566 [*R*(int)= 0.0543]	3446 [*R*(int)= 0.0367]
R_1	0.0617	0.0409
wR_2	0.1467	0.0890

Table 2 Selected bond lengths(Å) and bond angles(°) for compound **6** and **7**

Compound **6**		Compound **7**	
C(1)–C(2)	1.516(4)	C(1)–C(25)	1.496(3)
C(1)–C(14)	1.526(4)	C(1)–C(24)	1.503(2)
C(1)–C(15)	1.531(5)	C(1)–C(2)	1.549(3)
C(1)–C(8)#1	1.615(4)	C(2)–C(3)	1.540(2)
C(7)–C(8)	1.514(4)	C(3)–C(4)	1.648(2)
C(8)–C(9)	1.509(4)	C(4)–C(30)	1.524(2)
		C(4)–C(19)	1.528(2)
C(2)–C(1)–C(14)	106.7(2)	C(25)–C(1)–C(24)	109.1(16)
C(2)–C(1)–C(15)	113.1(3)	C(25)–C(1)–C(2)	106.6(15)
C(14)–C(1)–C(15)	112.7(3)	C(24)–C(1)–C(2)	105.8(15)
C(2)–C(1)–C(8)#1	110.2(2)	C(3)–C(2)–C(1)	110.6(15)
C(14)–C(1)–C(8)#1	110.0(2)	C(30)–C(4)–C(19)	107.8(15)
C(15)–C(1)–C(8)#1	104.2(3)	C(30)–C(4)–C(5)	115.2(15)
C(7)–C(2)–C(1)	117.2(3)	C(19)–C(4)–C(5)	115.4(15)
C(2)–C(7)–C(8)	117.8(3)	C(30)–C(4)–C(3)	104.5(14)
C(9)–C(8)–C(7)	107.9(3)	C(19)–C(4)–C(3)	103.9(14)
C(9)–C(8)–C(1)#1	113.5(2)	C(5)–C(4)–C(3)	108.9(13)
C(7)–C(8)–C(1)#1	113.1(2)		

7: m.p. 320–322°C (lit.,[13] m.p. 317–323°C). IE/MS: *m/z* 382 (M^+) (7%). Anal. Calcd for $C_{30}H_{22}$: C, 94.21; H, 5.80. Found: C, 93.84; H, 5.44. ^{1}H NMR (DMSO-$d_{6,}$ 300MHz) δ: 2.86 (d, *J* = 2.4 Hz, 4H, CH_2), 4.72 (t, *J* = 2.4 Hz, 2H, CH), 6,77(d, *J* = 7.2 Hz, 2H, ArH), 6.79 (t, *J* = 7.2 Hz, 2H, ArH), 6.97 (t, *J* = 7.2 Hz, 2H, ArH), 7.38(d, *J* = 7.2 Hz, 2H, ArH). ^{13}C NMR (DMSO-d_6, 75 MH_Z): 27.9 (CH_2). 44.1 (CH), 122.4, 123.2, 124.8, 125.2 and 143.3 (PhC).

Crystal structure determination: X-ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer equipped with a graphic crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ=0.071073 nm). The unit cell dimensions were obtained with least-squares refinements and the structure was solved by direct methods using the SHELXTL-97 program.[21] Crystalographic data were summarised in Table 1 and selected bond lengths and bond angles were showed in Table 3 for **6** and **7**.

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