Conversion of donor-substituted homonaphthoquinones to indenonaphthoquinones *via* intramolecular photoinduced electron-transfer

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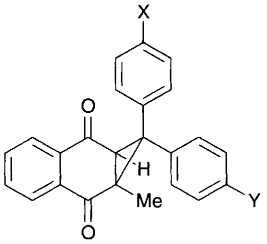
Irradiation of bis(*p*-anisyl)- or *p*-anisylphenyl-homonaphthoquinones 1a,b in the presence of $Mg(ClO_4)_2$ results in the formation of indenonaphthoquinones 2a,b *via* intramolecular photoinduced electron-transfer.

Intramolecular photoinduced electron-transfer (PET) systems[1] are useful and important in artificial photosynthesis[2] and molecular-level optoelectronics.[3] A variety of covalently-linked donor–acceptor (D–A) molecules have been extensively studied to try to understand the structural and photophysical factors governing electron-transfer *i.e.* the D–A distance and orientation, the free energy of reaction, and the electronic coupling.[4] However, there are only a few examples of dynamic electron-transfer reactions involving bond-cleavage and bond-forming processes.[5,6]

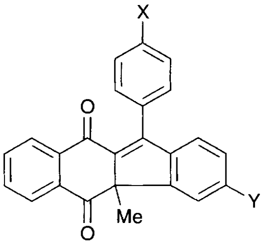
Recently, we have found the mechanism for intermolecular PET reactions of diphenyl-substituted homonaphthoquinones with various donors.[7,8]

Here we report a new photoreaction of homonaphthoquinones *via* intramolecular PET. For this purpose we used the anisyl-linked homonaphthoquinones **1a,b**.

Irradiation of bis(*p*-anisyl)homonaphthoquinone **1a** (50 mg) with 0.1 or 5 equiv. of $Mg(ClO_4)_2$ (140 mg) in acetonitrile (20 ml) through a Pyrex filter (>330 nm) with a high pressure mercury lamp for 1 day gave indenonaphthoquinone **2a** in almost quantitative yield (Table 1).



1a X = Y = OMe
endo-**1b** X = OMe, Y = H
exo-**1b** X = H, Y = OMe
1c X = Y = Me
1d X = Y = H



2a X = Y = OMe
b X = OMe, Y = H
c X = H, Y = OMe

Similar treatment of *p*-anisylphenylhomonaphthoquinones (*endo*- and *exo*-**1b**) gave indenonaphthoquinone **2b** as the sole product accompanied by the *endo–exo* photoisomerization of **1b** (entries 4,5). The possible constitutional isomer **2c** could not be detected by ^1H NMR analysis. The structures of **2a,b** were deduced by IR, ^1H NMR, ^{13}C NMR and mass spectra as well as X-ray crystal analysis for **2b**†,‡ (Fig. 1).

These reactions did not occur in the absence of $Mg(ClO_4)_2$ or in the dark at ordinary temperature (entries 3,6). Furthermore, it was noted that the replacement of the anisyl group of **1a** by a tolyl or phenyl group increased its photoreactivity as demonstrated by bis(*p*-tolyl)- and diphenyl-homonaphthoquinones **1c** and **1d** (entries 7,8).

The absorption spectrum of the methoxy-substituted **1a** was very similar to that of the unsubstituted **1d**, and appreciable intramolecular charge transfer absorption was not observed. Fluorescence of **1a** and **1d** were observed in acetonitrile with irradiation light of 300 nm at which **1a** and **1d** have almost the same logarithmic molar absorptivity, 3.26 and 3.24 respectively. Homonaphthoquinone **1a** showed a strong fluorescence (λ_{max} = 502.6 nm), but the fluorescence of **1d** was negligible. The emission maximum of **1a** shifted to shorter wavelength with decreasing solvent polarity *i.e.* 453.8 (THF) and 413.4 nm (benzene). The fluorescence of **1a** is due to the formation of the intramolecular exciplex of **1a**.[6] Therefore, the present reaction can be envisaged as involving an intramolecular PET from the anisyl group to the naphthoquinone moiety under the influence of $Mg(ClO_4)_2$.

With these observations in mind, it is proposed that the present photoreaction proceeds through a mechanism outlined for **1a** in Scheme 1. The first step is the photoexcitation of **1a** followed by intramolecular electron transfer. The generated radical ion **I** undergoes ring-opening resulting in a zwitterion **II**. Here, the role of added $Mg(ClO_4)_2$ is probably the suppression of the intramolecular back-electron transfer as well as stabilization of **I**. Such additive effects of metal ions to enhance the PET reaction is well-known.[9,10] The next step is an intramolecular cyclization of **II** as rationalized by the nucleophilic attack of the

Table 1 Photoreaction of homonaphthoquinones **1** in the presence of $Mg(ClO_4)_2$ in acetonitrile

Entry	Homonaphtho-quinone	Additive (equiv.)	Irradiation time	conv.(%)[a]	Yield (%)[a] 2a	2b
1	**1a**	$Mg(ClO_4)_2(5)$	1	100	~100	—
2	**1a**	$Mg(ClO_4)_2(0.1)$	3	100	~100	—
3	**1a**	none	1	0	0	—
4	*endo*-**1b**	$Mg(ClO_4)_2(5)$	3	45.0[b]	—	93.5
5	*exo*-**1b**	$Mg(ClO_4)_2(5)$	3	37.2[c]	—	83.1
6	*endo*-**1b**	none	3	0[d]	—	0
7	**1c**	$Mg(ClO_4)_2(5)$	3	0	—	—
8	**1d**	$Mg(ClO_4)_2(5)$	3	0	—	—

[a] Measured from NMR peak areas of methyl protons of the remaining of **1b** and **2b** to the methylene peak of 4-chloromethylbiphenyl used as an interna standard. [b] Unconsumed **1b** consist of 78 : 22 (*endo* : *exo*) mixture. [c] Unconsumed **1b** consists of 25 : 75 (*endo* : *exo*) mixture. [d] Unconsumed **1b** consists of 81 : 19 (*endo* : *exo*) mixture.

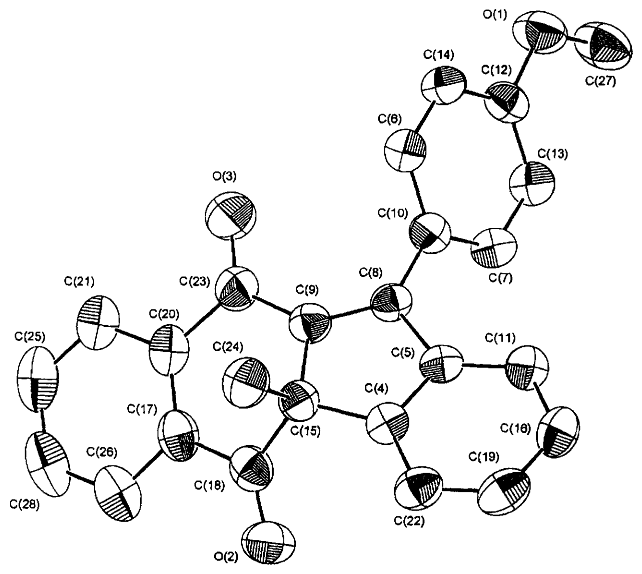
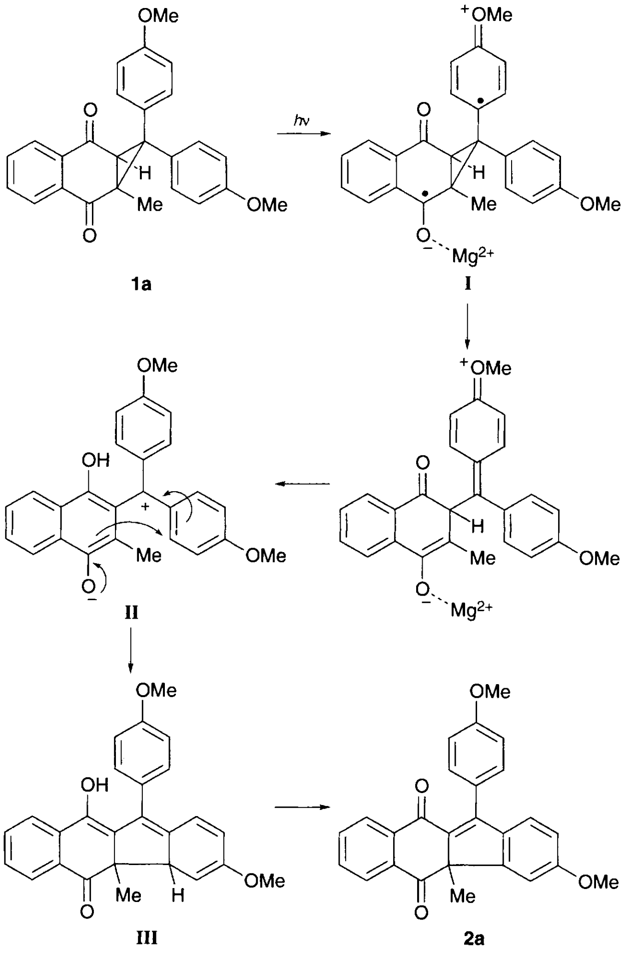


Fig. 1 Molecular structure of **2b** (hydrogen atoms omitted). Selected bond lengths (pm) and angles (°): C(4)–C(5) 139.6(5), C(4)–C(15) 150.4(5), C(5)–C(8) 147.4(5), C(8)–C(9) 134.9(5), C(9)–C(15) 151.6(5), C(4)–C(5)–C(8) 108.7(3), C(5)–C(4)–C(15) 109.1(3), C(5)–C(8)–C(9) 108.8(3), C(8)–C(9)–C(15) 110.9(3), C(8)–C(9)–C(23) 129.6(3), C(9)–C(15)–C(18) 109.8(3), C(15)–C(9)–C(23) 119.0(3), C(9)–C(15)–C(4) 102.5(3), C(4)–C(15)–C(18) 114.6(3) (Thermal ellipsoids are at 50% probability).

enolate ion moiety to the *ortho*-position of the benzyl cation to afford the tetracyclic quinol **III**. Furthermore, the resulting **III** may be oxidised to the aromatized indenonaphthoquinone **2a**. The absence of possible **2c** in the photoreaction of **1b** is due to the unfavourable electron accumulation on the anisyl ring. Thus, the chemoselective formation of **2b** both for *endo*- and *exo*-**1b** is not surprising since the stereochemistry of **1b** would be completely lost in the zwitterion intermediate like **II**. It is noteworthy that the conversion of *endo*-**1b** was higher than that of *exo*-**1b** (entries 4,5). This is due to the more enhanced intramolecular Coulomb interaction for the *endo*-radical ion **I**.[11]

An attempt to photoreact diphenyl substituted **1d** with donor anisole or 1,3,5-trimethoxybenzene failed even in the presence of excess $Mg(ClO_4)_2$, although the intermolecular PET is expected to be feasible from the ΔG value for anisole (-112 kJ mol^{-1} according to the Rehm–Weller equation[12]) as well as fluorescence quenching experiment with anisole.§

We thank Dr T. Kawamoto (Osaka University) for his generous help with the X-ray crystal structure analysis of **2b**.



Scheme 1

Footnotes

† *Spectroscopic data* for **2a**: Yellow prisms (from hexane–benzene). Mp 112–113 °C; IR(KBr) cm^{-1} 1029, 1294, 1331, 1510 and 1670; δ_H ($CDCl_3$): 1.77 (s, 3 H), 3.89 (s, 3 H), 3.96 (s, 3 H), 6.95 (dd, J_1 2.64, J_2 8.58 Hz, 1 H), 7.02 (d, J 8.58 Hz, 2 H), 7.39 (d, J 8.58 Hz, 1 H), 7.48 (d, J 2.64 Hz, 1 H), 7.68–7.74 (m, 4 H) and 8.09–8.23 (m, 2 H); δ_C ($CDCl_3$) 27.1, 55.3, 55.8, 64.0, 111.2, 113.2, 114.6, 124.3, 125.5, 127.4, 127.6, 128.3, 131.9, 133.2, 134.2, 134.6, 135.5, 137.5, 148.8, 150.7, 160.8, 161.2, 183.3 and 195.7; *m/z* 396(M^+). Other new products also provided satisfactory analytical and spectroscopic data.

‡ *Crystal data* for $C_{25}H_{18}O_3$ **2b**; M_w 366.00, monoclinic, space group $P2_1/c$, a = 1687.4(9), b = 1510.8(7), c = 750.0(6) pm, β = 101.83(6)°, V = 1871(2) × 10^6 pm^3, Z = 4, Dc = 1.26 g cm^{-3}, $F(000)$ = 743, l(Mo-Kα) = 0.71073. All crystallographic measurements were made using a MAC science MXC3 diffractometer. The structure was solved by direct methods(SIR) and refined by full-matrix least squares analysis using 4273 unique reflections to final R factor = 0.0471, R_w = 0.0434. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Fluorescence of **1d** was quenched by anisole. Stern–Volmer plots of the fluorescence quenching were linear for anisole concentration, indicating the electron transfer to the singlet excited state of **1d**.

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