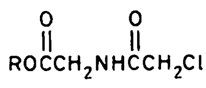
Photochemical Properties of Dibenzo-18-crown-6 in the Presence of a Guest Cation[1]

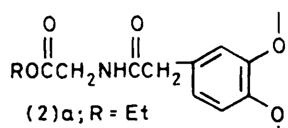
By MASARU TADA,* ATSUSHI SUZUKI, and HIDEKI HIRANO
(*Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku, Tokyo* 160, *Japan*)

Summary Photochemical condensation between dibenzo-18-crown-6 and ethyl *N*-chloroacetylglycinate (**1a**) was depressed by the presence of potassium ion; this behaviour is considered to originate from an increase in the ionisation potential of the crown ether on complexation.

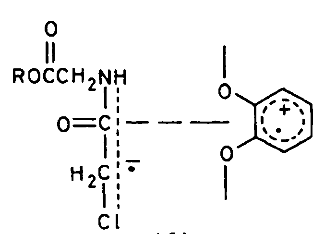
FORMATION of host–guest complexes may alter the photoreactivity of excited molecules.[1,2] We have been studying the photochemistry of crown ethers to test the effect of complexation and to introduce functional groups to crown ethers and now report the photochemical behaviour of dibenzo-18-crown-6 (DB18C6). A mixture of ethyl *N*-chloroacetylglycinate (**1a**) ($1·8 \times 10^{-2}$ M) and DB18C6 ($6·0 \times 10^{-3}$ M) was irradiated in MeCN–H_2O (1 : 1) for 29 h under N_2 using a 450 W high pressure Hg lamp mounted in a rotatory irradiation apparatus. The distance between the lamp and the quartz sample tubes was *ca.* 5 cm. The product mixture was separated by preparative t.l.c. (SiO_2, EtOAc–EtOH, 10 : 1) to give (**2a**) [m.p. 138 °C; mass spectrum *m/e* 504 ($M^+ + 1$), 503 (M^+); i.r. ($CHCl_3$) 1742, 1675, 1261, and 1133 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1·18 (3H, t), 3·52 (2H, s), 3·70—4·20 (20H), 6·8 (7H, m), and 7·2 br (NH)] in >16% yield as the only isolated product in addition to the recovered DB18C6 (>80%). This photoreaction was depressed by the addition of potassium chloride ($6·0 \times 10^{-3}$ M) and gave (**2a**) in 8% yield.



(1) a; R = Et
b; R = K



(2) a; R = Et
b; R = Me



(3)

Potassium *N*-chloroacetylglycinate (**1b**) and DB18C6 were irradiated under similar conditions and similar work up, and after neutralisation with dil. HCl and esterification with diazomethane, gave (**2b**) [m.p. 120—121 °C; mass spectrum *m/e* 490 ($M^+ + 1$), 489 (M^+); i.r. ($CHCl_3$) 1740, 1668, 1260, and 1135 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 3·52 (2H, s), 3·58 (3H, s), 3·78—4·15 (18H), 6·8 (7H, m), and 7·2 br (NH)] in <10% yield and recovered DB18C6 (*ca.* 90%).

The proposed structures of these products are in good agreement with spectral data. The site of condensation on the benzene ring was tentatively assigned (although it cannot be specified from spectroscopic data) from steric reasons and because 1,2-dimethoxybenzene reacts preferentially at the 4-position in a similar photocondensation.[3,4] The DB18C6 u.v. absorptions ($3·33 \times 10^{-4}$ M in $MeCN–H_2O$, 1 : 1) appear in the range 250—290 nm and are changed only slightly (λ_{max} 275 → 273 nm; ϵ, 5900 → 5600) on addition of potassium chloride ($1·67 \times 10^{-2}$ M). The concentration of DB18C6 used for the photoreaction ($6·0 \times 10^{-3}$ M) is high enough to absorb, almost completely, the emission from the lamp within this range of wavelengths, and hence the effect of the salt on the reactivity of DB18C6 cannot originate from a lowering of the number of excited molecules.

Yonemitsu *et al.* have studied extensively this type of reaction and have established a mechanism involving electron transfer to give the intermediate (**3**) which contains radical ion pairs,[5] followed by the loss of chloride ion and radical coupling. Complexation of the potassium ion (formation constant *K ca.* 180 mol^{-1})[6] raises the ionisation potential of DB18C6 and hence electron transfer must be depressed.

The wavelength [λ_{max} (emission) 305 nm] and intensity of the fluorescence of DB18C6 ($3·33 \times 10^{-4}$ M in $MeCN–H_2O$, 1 : 1) were essentially not affected by the addition of potassium chloride under the conditions used. The efficiency of fluorescence quenching by ethyl *N*-chloroacetylglycinate (**1a**), however, was diminished in the presence of potassium chloride. The slopes ($k_q\tau_0$) of Stern–Volmer plots for the fluorescence quenching of DB18C6 ($3·33 \times 10^{-4}$ M in $MeCN–H_2O$, 1 : 1) at various concentrations of potassium chloride are 70·5 (no KCl), 57·0 ($1·65 \times 10^{-4}$ M), 45·0 ($3·33 \times 10^{-4}$ M), and 39·8 ($6·65 \times 10^{-4}$ M). The fluorescence quenching of 1,2-dimethoxybenzene was not affected by potassium chloride, however.

Tetracyanoethylene (TCNE) forms charge-transfer (CT) complexes with various donor molecules, the CT-absorption of complexes varying with the ionisation potential of the donor molecule.[7] The Table shows the effect of potassium chloride on the CT-absorptions of TCNE complexes of DB18C6 and 1,2-dimethoxybenzene.

TABLE. CT-Absorptions of the complexes of dibenzo-18-crown-6 ($2·5 \times 10^{-2}$ M) and 1,2-dimethoxybenzene ($2·5 \times 10^{-2}$ M) with TCNE ($7·7 \times 10^{-2}$ M) in $MeCN–H_2O$ (5 : 1).

	Dibenzo-18-crown-6		1,2-Dimethoxybenzene	
Amount KCl used	—	1 equiv.	—	1 equiv.
λ_{max}/nm	565	545	550	550
Absorbance	0·54	0·38	0·45	0·43

Potassium chloride affects the photochemistry of DB18C6 as shown by its influence on the following: (a) photocondensation involving an electron transfer process; (b) fluorescence quenching[8,9] by ethyl *N*-chloroacetylglycinate; and (c) the CT-absorption of the TCNE-complex.[7] These effects may be understood by considering the increase in ionisation potential of the crown ether upon complexation of the potassium cation in its cavity.

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[1] For previous part in the series 'Photochemistry of Host-Guest Complexes' see M. Tada and H. Hirano, *Tetrahedron Letters*, 1978, 5111.
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