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Weak Fluorescence from [2.2]Metacyclophane

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Synopsis. Weak fluorescences from [2.2]metacyclophane (MCP) were observed: the normal and intramolecular excimer fluorescences were at 305 and 361 nm respectively. It has been shown that a rapid radiationless deactivation due to the interaction between the two benzene rings in MCP occurs preferentially and the excimer formation responsible for the photocyclization takes place to a small extent.

Recently, the transannular π-electronic interaction in [2.2]metacyclophane (MCP) has come to be of interest.[1-3] In contrast to that in [2.2]paracyclophane,[4] the assumption of the interaction in MCP was denied in both the ground[1] and the excited states.[2]

However, the transannular interaction between the two benzene rings in the excited state of MCP has been recently suggested from the abnormal photochemical behaviors: the small reaction quantum yields (less than 0.01), the large quantum yield for the radiationless deactivation process (0.99), and the lack of emission.[3]

The reason why the two central hydrogen atoms in the intermediate M resulting in the photocyclization should be *cis*-form[3] has not been given. In order to elucidate further the photochemical and photophysical behaviors in MCP, we have made measurements on the emission from MCP, using a highly sensitive single photon counter.

Experimental

The chemical reagents and procedures were essentially as previously described.[3] Samples were degassed by a freeze-pump-thaw method.

The fluorescence from MCP was measured by a single photon counter similar to that reported by Hikida *et al.*[5] It was possible to measure the fluorescence quantum yields up to $\sim 10^{-6}$. The yields for normal and excimer fluorescences of MCP at 270 nm were measured by comparison with quinine bisulfate 0.1 N H_2SO_4 at 366 nm. The absolute yield at 366 nm was determined to be 0.54 by Melhuish.[6] The light intensities at 270 and 366 nm were also measured using a quantum counter (an 8 g/l solution of rhodamine B).[7]

Results and Discussion

Figure 1 shows the fluorescence from MCP in degassed cyclohexane at room temperature. The fluorescence spectrum comprises two bands at 305 and 361 nm. From the mirror image in Fig. 1, the band at 305 nm was assigned to the normal fluorescence from MCP. The band at 361 nm was assigned to the intramolecular excimer fluorescence[8] judging from the broad and structureless fluorescence band which was shifted by 5100 cm^{-1} to lower frequencies relative to the normal fluorescence. The quantum yields for the normal and the excimer fluorescences in degassed cyclohexane at 270 nm and 15° were 2 $(\pm 0.1)\times 10^{-5}$ and $5._6(\pm 0.5)\times 10^{-6}$, respectively. The lifetime τ_{s1} of the lowest excited singlet state S_1, which corresponds to the $^1B_2$ state of the locally excited state of benzene, was estimated to be *ca.* 10 ps, from the values of the fluorescence quantum yield (2×10^{-5}) and the rate constant of k_f $(\sim 2.5\times 10^6\ s^{-1})$ for the radiative transition from S_1 to S_0. No phosphorescence from MCP could be observed in MP at 77 K.

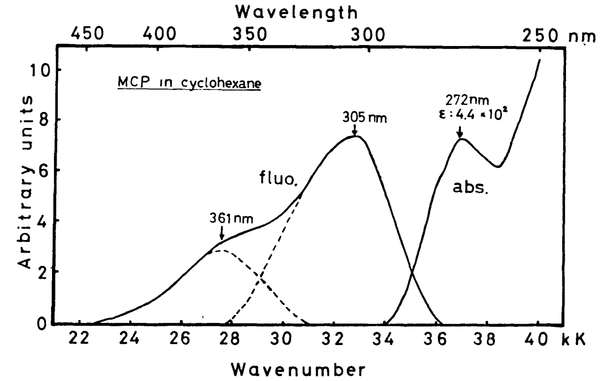

Fig. 1. Absorption and fluorescence spectra of 1.6×10^{-3} M cyclohexane solution of MCP.

From these results, a rapid radiationless deactivation process k_d (see Fig. 2) should be involved in the S_1 state of MCP. A possible explanation for the large k_d is that rotational motions of the two benzene rings in S_1 may facilitate the internal conversion. It is well known that the deactivation process in the excited state of some dyes, such as auramine O and crystal violet, is enhanced by the rotational motion.[9-11]

Although the interacting chromophores in MCP are not separated by three carbon atoms ($n=3$ rule),[12] the sandwich configuration of MCP can be attained by rotating the benzene rings around the central carbon atoms. It is known that in the ground state this rotation with a large activation energy (>27 kcal/mol) is very difficult to take place.[13-15] This may be due to the fact that the transannular interaction[16] in the excited state gives an attractive force between them, resulting in the formation of MCP excimer. The excimer formation

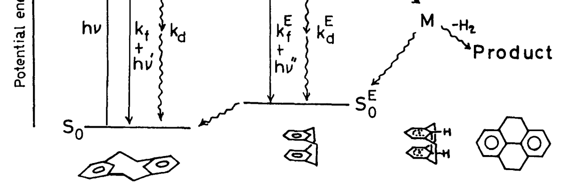

Fig. 2. Schematic energy state diagram for the photochemical processes in MCP.

of MCP has a very close relation with the intermediate M in the photochemical cyclization of MCP.[3] The "sandwich" excimer structure is responsible for the M formation, followed by the thermal reaction to give the products (4,5,9,10-tetrahydropyrene plus a hydrogen molecule) or the starting material.[3] The behavior in the excited state of MCP can be accounted for by the scheme shown in Fig. 2. Thus, the reason why the central hydrogen atoms in M should be in a *cis*-configuration can be well understood. The efficiency for the intramolecular excimer formation becomes small because of the rapid deactivation competing with the excimer formation.

In conclusion, it is obvious that the transannular interaction due to the proximity of two benzene rings exists in the excited MCP.

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