Relaxation processes in the excited state of C_{60}–*o*-quinodimethane adducts

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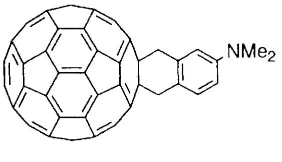
Intramolecular electron transfer and exciplex formation in a C_{60} adduct possessing an *N*,*N*-dimethylaniline (DMA) moiety, C_{60}–DMA, in cyclohexane and benzonitrile have been investigated in comparison with the intermolecular reactions between C_{60}–*o*-quinodimethane (OQD) and DMA. The fluorescence of C_{60}–DMA in cyclohexane was little quenched by the DMA moiety and was almost the same as that of C_{60}–OQD, in contrast with the decrease and red shift in the fluorescence of C_{60}–OQD in the presence of excess DMA in cyclohexane, mainly resulting from exciplex formation. The difficulties in the intramolecular exciplex formation of C_{60}–DMA in cyclohexane are considered to result from its unfavourable molecular structure, which also affects charge-transfer complex formation. On the other hand, in benzonitrile the fluorescence of C_{60}–DMA was significantly quenched and red shifted. The quenching is due to the intramolecular electron transfer from the DMA moiety to the S_1 state of the C_{60} moiety, where the rate constant was estimated as 1.5×10^{10} s^{-1}. The red shift is brought about by the charge-transfer character in the S_1 state, resulting from the through-bond interaction between the two chromophores. The transient absorption spectra of C_{60}–DMA in cyclohexane exhibited the $T_n \leftarrow T_1$ bands, in good agreement with those of C_{60}–OQD without a dimethylamino group. In benzonitrile, however, the $T_n \leftarrow T_1$ bands were considerably weakened by the decrease in the triplet population, and the lifetime (7 μs) of T_1 was reduced relative to that in cyclohexane (28 μs). The decrease in the lifetime in benzonitrile can be ascribed to the weak charge-transfer interaction between the T_1 of the C_{60} moiety and the S_0 of the DMA moiety.

Fullerene C_{60} is an electron acceptor and its photoinduced electron transfer with electron donors[1] has been thoroughly investigated in connection with its photophysical properties[2] since the successful preparation and isolation of C_{60} on a large scale.[3] Not only the S_1 but also the T_1 state of C_{60} is known to be efficiently quenched by appropriate donors, such as *N*,*N*-dimethylaniline (DMA) or diethylaniline (DEA), although the formation of charge-transfer (CT) complexes is rather depressed in the ground state (for example, the equilibrium constant $K = 0.1$–0.3 dm^3 mol^{-1} for C_{60}–DEA, depending on the solvent).[1d] Together with such properties, the reactivities of C_{60} with various reagents have been presented, and a large number of its derivatives extensively synthesized.[4] While the electrochemical properties[5] and the absorption and fluorescence spectra[6] of C_{60} derivatives have been disclosed, their photophysical properties have not been studied sufficiently. Recently, Anderson *et al.*[7] reported the transient absorption spectra of the excited triplet species of a dihydro-C_{60} derivative and the anion radical generated by intermolecular electron transfer with DMA for the first time as C_{60} derivatives. They found that the photophysical processes are not appreciably affected by the functionalization of C_{60}, though the S_1 (40.2 kcal mol^{-1}) and T_1 (33.5 ± 0.6 kcal mol^{-1}) energies are slightly lower than those of C_{60} itself (46.1 and 36.3 kcal mol^{-1}, respectively).[7] The influence of the intramolecular additional chromophore on the photophysical properties of C_{60}, however, remains unknown.

Thus the electronic and photophysical properties of C_{60}–*o*-quinodimethane (OQD) adducts having various aromatic rings (benzene, naphthalene, phenanthrene and pyrene) in the vicinity of the C_{60} core have been examined.[8] These properties were found to be virtually independent of the attached aromatic rings, according to the measurements of the redox potentials, the absorption spectra, the fluorescence spectra and transient absorption spectra; there is only a little through-bond or through-space electronic interaction between the C_{60} moiety and the aromatic rings. Interestingly, in the C_{60}–pyrene adduct, energy transfer from the S_1 of pyrene to the C_{60} moiety was observed. No electron transfer process, however, could be detected within these adducts, owing to insufficient electron-donating properties of the attached aromatic rings.

Thus we were prompted to synthesize adduct **1** (see below) having a dimethylamino group on the benzene ring of adduct **2**,[9] to enable the intramolecular electron transfer and the exciplex formation which have rarely been examined owing to difficulty in the synthesis of such C_{60} derivatives. Such studies are of great interest and importance, since the two chromophores can be sterically fixed to some extent, unlike the intermolecular case, and the effect of the geometry on the electron-transfer process may be clarified. Imahori *et al.* synthesized a porphyrin-linked C_{60} and observed the intramolecular electron transfer from S_1 of porphyrin to C_{60}.[10] During the course of our study, Williams *et al.* synthesized a C_{60} derivative containing a DMA moiety,[11] which is bridged through a pyrrolidine ring and located at a distance of *ca.* 5 Å from the C_{60} surface. They found quenching of the S_1 state in polar solvents owing to the intramolecular electron transfer.



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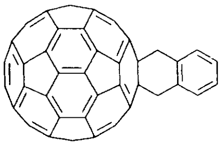

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In this paper, we discuss not only the intramolecular electron transfer process but also exciplex formation in **1**, in comparison with the intermolecular ones between **2** and DMA. For comparison with **1**, it is appropriate to use **2** rather than C_{60} itself, since the electronic properties of the C_{60} moiety of **1** are considered to be more similar to those of **2** than to those of C_{60}. Such comparison between the intra- and intermolecular cases is necessary for clarification of the photophysical processes of C_{60} derivatives generally. The DMA moiety in **1** is linked to the C_{60} moiety through a cyclohexene ring, which seems to be most stable in the half-boat conformation, as in the other C_{60}–OQD adduct.[8,9] Thus it can be located closer to the C_{60} surface than in the adduct described by Williams *et al.*[11] It is possible that such a conformation and position of the DMA moiety should influence the electron-transfer process and exciplex formation.

Results and Discussion

Synthesis

C_{60} adduct **1** possessing a DMA moiety was synthesized as shown in Scheme 1. 4-Aminobenzocyclobutene (**4**) was readily prepared from the corresponding nitro compound **3**, by slightly modifying the method reported previously.[12] The primary amine **4** was methylated with trimethyl phosphate to give **5**, which is expected to undergo the thermally allowed conrotatory electrocyclic ring opening and give an *o*-quinodimethane derivative. Treatment of **5** with C_{60} in refluxed 1,2,4-trichlorobenzene for 6 h gave the desired monoadduct **1**, along with an isomeric mixture of diadducts and other by-products. Monoadduct **1** was separated by column chromatography on alumina, and further purified by reprecipitation (isolated yield: 19%).

The ^1H NMR signals for the methylene protons were observed in the range $\delta = 4$–5 as two sets of AB quartet with considerable broadening at room temperature, attributable to the flipping of the cyclohexene ring.[8,9] These signals were found to coalesce completely above 50 °C, similar to those in adduct **2** without a DMA moiety.[8b] The dimethylamino group on the benzene ring is considered to have little effect on the ring inversion, indicating that the electronic interaction is not as large between the C_{60} and DMA moieties.

Electrochemical properties

The redox potentials of **1** were measured by cyclic voltammetry (CV) in benzonitrile at room temperature. Three reversible waves due to the reduction of the C_{60} moiety were observed at -1.06, -1.46 and -2.02 V *vs.* Fc/Fc$^+$ (ferrocene/ferrocenium). These values are in good agreement with those of **2** without a DMA moiety (-1.04, -1.45 and -2.01 V),[8b] although slightly negative shifted compared with those of C_{60} itself (-0.93, -1.35 and -1.83 V).[8b] The electronic property of the C_{60} moiety is little perturbed by the dimethylamino group. The oxidation of the DMA moiety was detected as a pseudo-reversible wave at +0.40 V.

Absorption spectra

The absorption spectrum of **1** in cyclohexane at room temperature is shown in Fig. 1. The spectrum, exhibiting a broad $S_1 \leftarrow S_0$ band with vibrational structures around 700 nm and a sharp band at 433 nm, is in good agreement with that of **2**. No distinct CT band was observed in **1**, suggesting that the formation of intramolecular CT complexes is negligible in the ground state, although a DMA moiety is located in the vicinity of the C_{60} core in **1**. These circumstances are considered to correspond with those in which *ca.* 2 mol dm^{-3} DMA is present around C_{60}. The absorption spectrum of **1** in benzonitrile was also similar to that in cyclohexane. These results are in remarkable contrast with those in the intermolecular case, as described below.

Fig. 2 illustrates the absorption spectra of **2** in the absence and presence of DMA in cyclohexane. With an increase in the DMA concentration, the absorbance in the region of 400–650 nm monotonically increased, in a manner similar to that reported for C_{60} itself and DEA.[1d] This increased band obviously suggests the formation of CT complexes. The equilibrium constant (K) was determined as 0.2 dm^3 mol^{-1}, by employing a modified Benesi–Hildebrand equation, on the

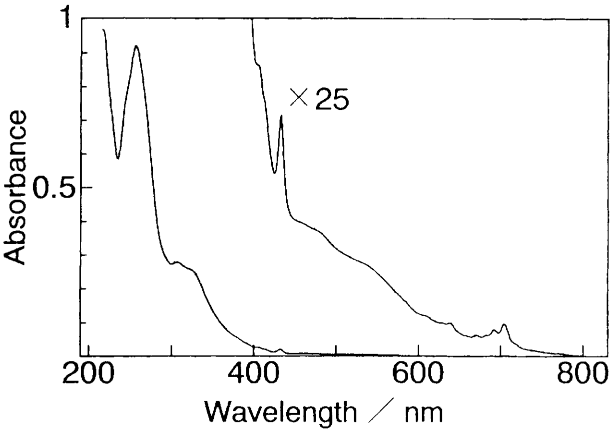


Fig. 1 Absorption spectra of **1** in cyclohexane at room temperature

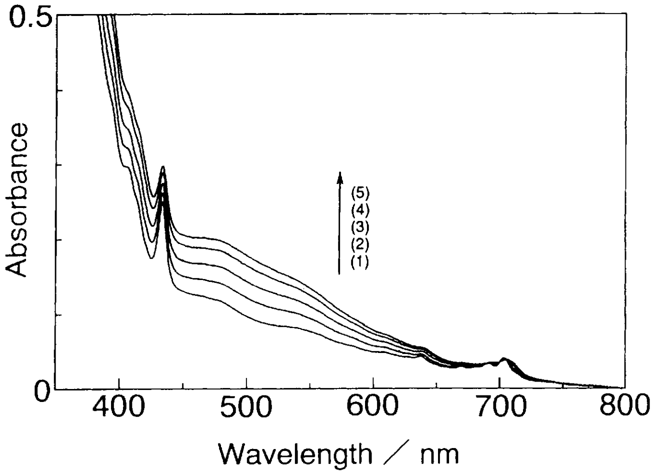
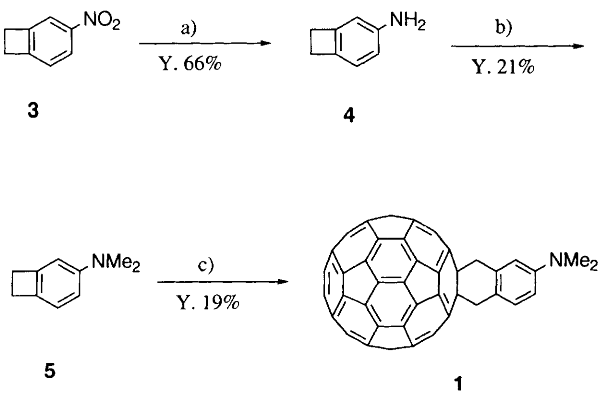


Fig. 2 Absorption spectra of **2** (8×10^{-5} mol dm^{-3}) in the absence and presence of DMA in cyclohexane at room temperature: [DMA] = (1) 0, (2), 0.4 (3) 0.8, (4) 1.2 (5) 1.6 mol dm^{-3}



Scheme 1 Synthesis of C_{60} adduct **1**

assumption of a 1 : 1 complex. This value is also comparable to that in C_{60} and DEA;[1d,e] the ability to form CT complexes is little disturbed by the functionalization of C_{60}, despite the lower oxidizability of **2** than of C_{60}.

The failure to form intramolecular CT complexes in **1** must be related to the arrangement of the DMA moiety, which is more or less fixed by the cyclohexene ring. The MM2 calculations show that the most stable conformation of the cyclohexene ring is the half-boat, as shown in Fig. 3. In this conformation, where the DMA and C_{60} moieties are nearest to each other, the benzene ring of the DMA moiety is located so that it can slightly deviate from the C_{60} surface, although the distance between the centre of the benzene ring and the C_{60} surface is within 4 Å. In such a conformation, the two chromophores are considered to be unable to produce CT complexes efficiently, despite their relative closeness. In the transition state during the ring inversion, the formation of CT complexes becomes much more difficult.

On the other hand, in the intermolecular case, DMA molecules can move freely in solvent, and preferentially overlap the C_{60} surface of **2**, leading to CT complexes. As the K value demonstrates, however, the contribution of the CT complex is not so significant, since the difference between the reduction potential of **2** and the oxidation potential of DMA (0.41 V *vs.* Fc/Fc^+)† is too large [$E(D^+/D) - E(A^-/A) = 0.41 - (-1.04) = 1.45$ (V)].

Fluorescence spectra

The fluorescence spectrum of **1** was measured in both cyclohexane and benzonitrile upon 433 nm excitation at room temperature. At this excitation wavelength, only the C_{60} moiety of **1** can be excited; the locally excited singlet state of the C_{60} moiety [$S_1(C_{60})$] is accessible. As Fig. 4(a) demonstrates, the fluorescence with vibrational structures observed in cyclohexane was essentially identical with that of **2** in cyclohexane,[8b] including the maximum position (707 nm). When a solution of **1** with the same absorbance as that of **2** at 433 nm was employed, the fluorescence intensity was also comparable to that of **2**, indicating that both quantum yields (Φ_f) are almost equal.

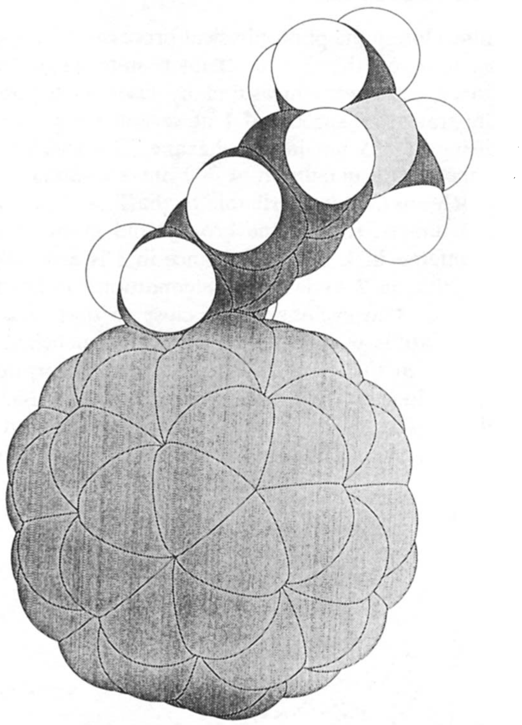


Fig. 3 Most stable conformation of **1** on the basis of the MM2 calculations

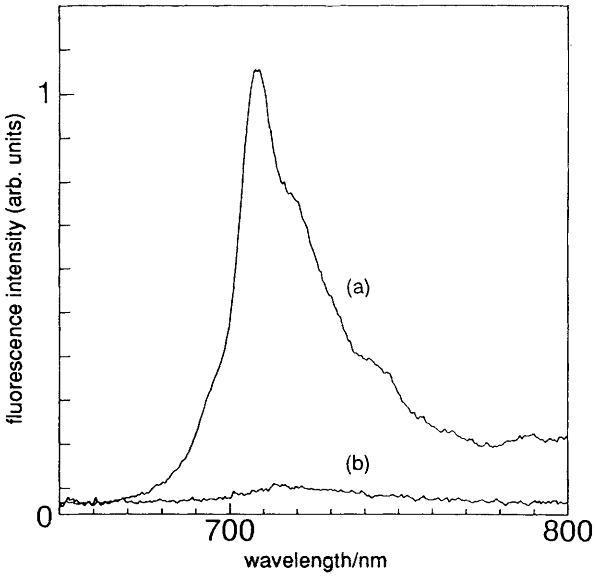


Fig. 4 Fluorescence spectra of **1** upon 433 nm excitation in (a) cyclohexane and (b) benzonitrile at room temperature

The fluorescence decay function of **1** in cyclohexane was measured by means of the picosecond single-photon-counting method. Fig. 5 shows the observed and calculated decay functions, along with the excitation lamp function (N_2 laser). Although the counts were low, this decay profile was successfully analysed by the deconvolution method as a single-exponential function with a lifetime of 1.19 ns. This value is comparable to that of **2** in cyclohexane (1.25 ns) under similar conditions. Therefore $S_1(C_{60})$ in **1** is concluded to be little quenched by the DMA moiety in cyclohexane; $S_1(C_{60})$ in both **1** and **2** behaves in the same way in cyclohexane.

On the other hand, as shown in Fig. 4(b), the fluorescence intensity in benzonitrile was drastically reduced to about 1/20 of that in cyclohexane, and the maximum was slightly red shifted, though the position is not clear owing to its weakness and broadening. Such quenching and red shift in benzonitrile were not observed for **2** without a DMA moiety. The Gibbs energy changes (ΔG) in the intramolecular electron transfer process from S_0 of DMA to S_1 of the C_{60} moiety,

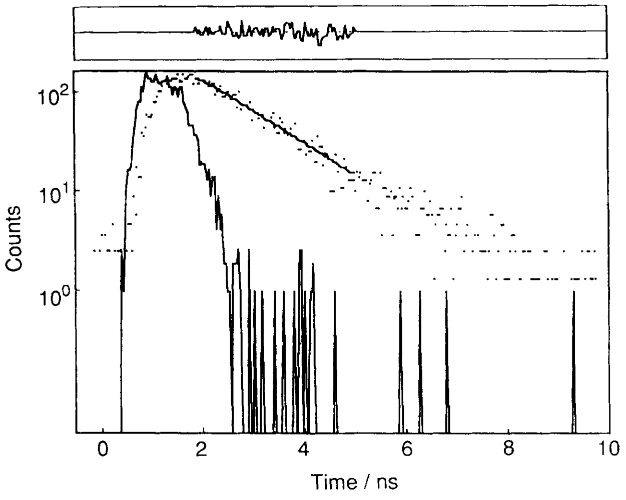


Fig. 5 Fluorescence decay function of **1** upon 337 nm excitation in cyclohexane at room temperature

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† Measured in benzonitrile under conditions similar to those for **1** and **2**.

$S_0(DMA)$–$S_1(C_{60})$, in **1** can be estimated using the method of Rehm and Weller:[13]

$$\Delta G = E_{ox}(DMA) - E_{red}(C_{60}) - {}^1\Delta E_{00} - e^2/\varepsilon R - \Delta G_{solv} \qquad (1)$$

where R is the centre-to-centre distance between the donor and acceptor and $E_{ox}(DMA)$, $E_{red}(C_{60})$, ${}^1\Delta E_{00}$, $e^2/\varepsilon R$ and ΔG_{solv} denote the oxidation potential of the DMA moiety (0.40 V), the first reduction potential of the C_{60} moiety (−1.06 V), the $S_1 \leftarrow S_0$ 0–0 transition energy (1.75 eV) of **1**, the Coulombic attraction energy and the correction term for the solvation Gibbs energy,[14] respectively. Since the ΔG values were calculated as −0.36 eV in benzonitrile (exothermic) and +0.29 eV in cyclohexane (endothermic),† the quenching in benzonitrile is reasonably attributable to the intramolecular electron transfer, $S_0(DMA)$–$S_1(C_{60})$. This quenching behaviour is analogous to that in the C_{60} adduct described by Williams *et al.*[11] The red shift in benzonitrile, which was not mentioned in that study,[11] suggests that the S_1 state of **1** has a CT character in benzonitrile, in contrast with that in cyclohexane. This CT character may be produced by the through-bond rather than through-space interaction between $S_1(C_{60})$ and $S_0(DMA)$ in benzonitrile, as is obvious from the conformation in **1**. Therefore the observed intramolecular electron transfer is also considered to take place *via* the through-bond interaction, as is reported in the similar intramolecular donor–acceptor cases.[14]

It was difficult to measure the fluorescence lifetime of **1** in benzonitrile [$\tau_{f(BN)}$], because the fluorescence was extremely weak. Thus, the lifetime was estimated using the lifetime in cyclohexane [$\tau_{f(CH)}$]. The ratio of the lifetimes in cyclohexane and benzonitrile can be expressed as

$$\tau_{f(BN)}/\tau_{f(CH)} = [\Phi_{f(BN)}/\Phi_{f(CH)}][k_{f(CH)}/k_{f(BN)}] \qquad (2)$$

The value $\Phi_{f(BN)}/\Phi_{f(CH)}$ was calculated as 0.053 from the area of the fluorescence spectra and the absorbance at the excitation wavelength.‡ On the assumption that the fluorescence radiative rate constants in cyclohexane [$k_{f(CH)}$] and benzonitrile [$k_{f(BN)}$] are equal, the value $\tau_{f(BN)}$ was determined as 63 ps. On the basis of the lifetimes, the rate constant of the intramolecular electron transfer in **1** in benzonitrile was estimated as 1.5×10^{10} s^{-1}. This value is slightly larger than that in the C_{60} adduct by Williams *et al.*[11] (1.3×10^9–1.2×10^{10} s^{-1}), probably because the DMA moiety in **1** is closer to the C_{60} moiety than in their adduct.

The fluorescence spectrum of **1** in cyclohexane is in contrast with that of **2** in the presence of DMA in cyclohexane. Fig. 6 demonstrates the fluorescence spectra of **2** in the absence and presence of DMA. With the progressive addition of DMA, the fluorescence of **2** was gradually decreased and slightly red shifted. The fluorescence intensity in the presence of 1.6 mol dm^{-3} DMA is about 1/5 of that in the absence of DMA. The extent of the red shift is comparable to that of **1** in benzonitrile. These results, also reported in the case of C_{60} and DEA in methylcyclohexane,[1d] may be interpreted in terms of the two pathways: (1) the electron transfer between S_1 of **2** and S_0 of DMA, or that *via* the direct excitation of the CT complexes in the ground state, and (2) the exciplex formation between S_1 of **2** and S_0 of DMA. The former pathway seems to be less significant, because this process is considered to be endothermic, as no intramolecular electron transfer, $S_0(DMA)$–$S_1(C_{60})$, was detected for **1** in cyclohexane. Since the red shift obviously suggests the exciplex fluorescence, the latter pathway seems to be more probable. In addition, the decrease in the concentration of the uncomplexed **2** in the ground state is also concerned with the decrease in the fluorescence intensity to some extent.

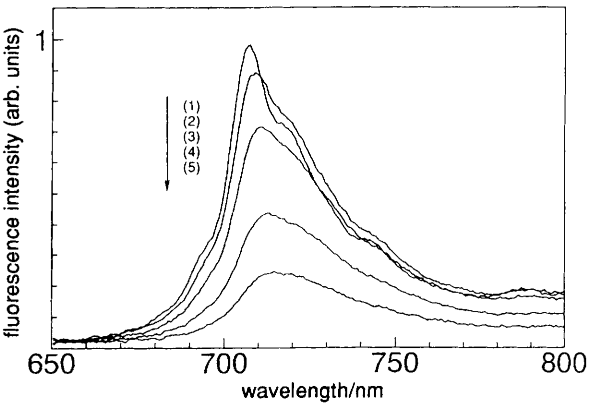

Fig. 6 Fluorescence spectra of **2** (8×10^{-5} mol dm^{-3} in the absence and presence of DMA upon 433 nm excitation in cyclohexane at room temperature: [DMA] = (1) 0, (2), 0.4, (3) 0.8, (4) 1.2, (5) 1.6 mol dm^{-3}

The absence of the intramolecular exciplex fluorescence in **1** in cyclohexane can be explained in the same way as that in the CT complexes in the ground state. Similar results were obtained by Mataga *et al.* for compounds in which the pyrene and DMA moieties are linked with a polymethylene [$-(CH_2)_n-$] unit; they could detect the exciplex fluorescence when $n = 3$, but not when $n = 1$ or 2 in non-polar solvents.[15] On the basis of these results, they suggested that, in such solvents, the exciplex formation requires the conformation in which the donor and acceptor moieties overlap in a sandwich-like arrangement. These results appear to hold for the case of the C_{60} derivatives satisfactorily.

Transient absorption spectra

To examine closely the photophysical processes of **1**, including the behaviour of the excited triplet state (T_1), transient absorption spectra were measured by laser flash photolysis. Fig. 7 illustrates the spectra of **1** at several delay times after laser pulsing at 355 nm in cyclohexane. The spectra of **1** in cyclohexane with a maximum at 700 nm are similar to those of **2**,[8b] which are mainly ascribable to the $T_n \leftarrow T_1$ absorption of the C_{60} moiety, though the broad band at *ca.* 800 nm is relatively intense in **1**. The absorbance in **1** is generally comparable to that in **2** under similar conditions, indicating the triplet yield of **1** in cyclohexane is close to that of **2** (*ca.* 1). This is compatible with S_1 of **1** being little quenched by the DMA moiety in this solvent. The transient absorption of **1** decays according to first-order kinetics with a lifetime of about 28 µs, except for that at *ca.* 800 nm mentioned above. The lifetime is almost equal to that in **2** (32 µs).[8b] Therefore

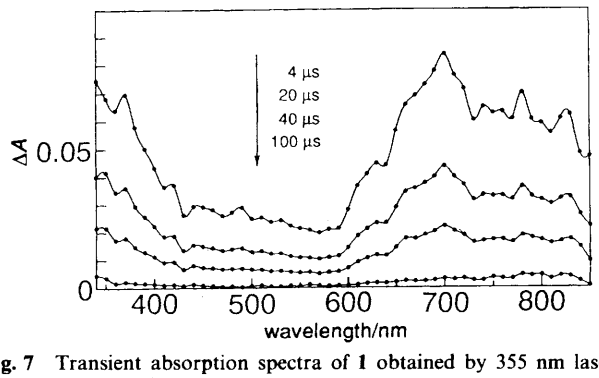

Fig. 7 Transient absorption spectra of **1** obtained by 355 nm laser photolysis in cyclohexane at room temperature

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† For R, 8 Å was used. The ε values for benzonitrile and cyclohexane are 25.2 and 2.02, respectively.

‡ $\Phi_{f(BN)}/\Phi_{f(CH)} = (A_{CH}/A_{BN})(K_{BN}/K_{CH})(n_{CH}^2/n_{BN}^2)$, where A, K and n denote the area of the fluorescence spectra, the absorbance at the excitation wavelength and the refractive index, respectively, of benzonitrile (BN) and cyclohexane (CH).

the T_1 state of the C_{60} moiety in **1** in cyclohexane is concluded to behave in virtually the same manner as that of **2**, as in the case of the S_1 state in cyclohexane; $T_1(C_{60})$ in **1** is not disturbed by the DMA moiety in cyclohexane. The band at *ca.* 800 nm, for which decay is slower than for other bands, may be due to a kind of photoreaction product, although the detail is currently obscure.

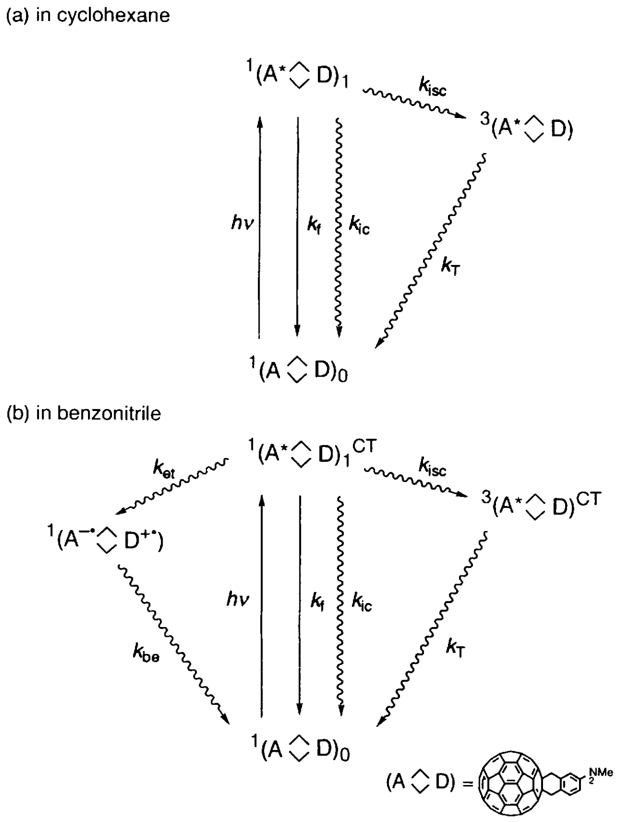
On the other hand, in benzonitrile, the $T_n \leftarrow T_1$ absorption of **1** was greatly quenched up to about 1/10 of that in cyclohexane to give a considerably unresolved spectrum, while that of **2** without a dimethylamino group was almost independent of the solvents. The quenching of the $T_n \leftarrow T_1$ bands of **1** in benzonitrile is derived from the decrease in Φ_{ISC} (intersystem crossing) due to the intramolecular electron transfer between S_0(DMA) and $S_1(C_{60})$. The shape of the spectrum, including the broad band at *ca.* 800 nm, was similar to that in cyclohexane. The transient absorption of the singlet radical ion pairs resulting from the intramolecular electron transfer between S_0(DMA) and $S_1(C_{60})$ could not be observed in the present measurement system. This result is apparently brought about by the rapid back electron transfer in the radical ion pairs; the rate constant was estimated to be of the order of 10^{10} s^{-1} on the basis of the Marcus theory.[16]

The lifetime of T_1 in **1** in benzonitrile was obviously reduced (about 7 μs) compared with that in cyclohexane, while that of **2** is almost independent of solvent. The decrease of the lifetime in benzonitrile is reasonably explained by the weak CT interaction between $T_1(C_{60})$ and S_0(DMA) in the T_1 state of **1** in benzonitrile, since the lifetime of the excited triplet states with a CT character is generally known to be shorter than that without a CT character.[17] Such interaction is quite probable in polar solvents such as benzonitrile but negligible in non-polar solvents such as cyclohexane. The possibility of the intramolecular electron transfer, $S_0(DMA)$–$T_1(C_{60})$, seems to be negligible, since the ΔG value in $S_0(DMA)$–$T_1(C_{60})$ is slightly negative (−0.11 eV).† This is also supported by the fact that the transient absorption of the triplet radical ion pair could not be detected, although the lifetimes should be long enough to be observed in the measurement system.

Conclusion

The photophysical processes of the C_{60}–DMA adduct **1**, including the intramolecular electron transfer, are summarized in Scheme 2, in which A* is the locally excited state of the C_{60} moiety, $S_1(C_{60})$ or $T_1(C_{60})$ in **1**.

In cyclohexane [(Scheme 2(a)], the behaviour of $S_1(C_{60})$ in **1** is essentially identical with that in **2** without a dimethylamino group. The $S_1(C_{60})$ state is converted into $T_1(C_{60})$ *via* the ISC with $\Phi_{ISC} \approx 1$. The photophysical process of $T_1(C_{60})$ in **1** is also similar to that in **2** in cyclohexane. These results indicate that the electronic properties of $S_1(C_{60})$ and $T_1(C_{60})$ are little disturbed by the DMA moiety in non-polar solvents such as cyclohexane. There is almost no intramolecular CT interaction between the C_{60} and DMA moieties, even in the excited states. The absence of the interaction in cyclohexane is mainly caused by the undesirable situation between the two chromophores rather than the insufficient electron-donating property of the DMA moiety, since the intermolecular exciplex fluorescence was observed in **2** in the presence of DMA. The formation of the exciplex is considered to be considerably influenced by the conformation, as Mataga and Ottolenghi had pointed out,[15] although more work with well designed model compounds is needed.



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Scheme 2 Relaxation process in the excited state of 1 in (*a*) cyclohexane and (*b*) benzonitrite (CT denotes a charge-transfer character in the excited state)

On the other hand, $S_1(C_{60})$ of **1** in benzonitrile has a CT interaction with the DMA moiety, as is obvious from the red-shifted fluorescence. This interaction is produced through the cyclohexene ring between the two chromophores. The intramolecular electron transfer from S_0(DMA) to $S_1(C_{60})$ was accomplished to give a singlet radical ion pair, in contrast with the case in cyclohexane, as also supported by the ΔG values for the intramolecular electron transfer. Since the electron transfer is quite rapid ($k_{et} = 1.5 \times 10^{10}$ s^{-1}), the ISC process into the T_1 state was considerably reduced compared with that in cyclohexane. Also in the triplet state, $T_1(C_{60})$ and S_0(DMA) seem to interact with each other in a weak CT manner, since the lifetime of $T_1(C_{60})$ was shorter than that in cyclohexane. The singlet ion pair resulting from the intramolecular electron transfer reverts rapidly to the ground state through the back electron transfer. Such behaviour was almost unobserved in **2** without a dimethylamino group, even in benzonitrile. Hence, the intramolecular CT interaction can be realized in the polar solvent when the adduct has a moiety with sufficient electron-donating property, even though the conformation is undesirable.

Experimental

General

^{1}H and ^{13}C NMR spectra were measured on a JEOL α-500 FT NMR spectrometer. Absorption spectra were recorded on a JASCO Ubest-50 spectrophotometer. Fluorescence spectra were measured on a Hitachi-4010 spectrofluorimeter. These spectra were obtained in cyclohexane (spectroscopic grade) or benzonitrile (distilled over P_2O_5 under reduced pressure) with a silica cell of 10 mm optical path at room temperature. The sample concentration is in the range 10^{-5}–10^{-4} mol dm^{-3}. The fluorescence decay functions were measured by a picosecond fluorescence lifetime measurement system C4780 (Hamamatsu Photonics).

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† The ΔG value in the intramolecular electron transfer, $S_0(DMA)$–$T_1(C_{60})$, can be readily calculated by replacing the term $^1\Delta E_{00}$ in eqn 1 by $^3\Delta E_{00}$. It was estimated to be −0.11 eV, by regarding the $^3\Delta E_{00}$ value as 1.50 eV by analogy with the adduct reported in ref. 11.

Electrochemical Measurements

CV was performed on a Hokuto HAB-151 potentiostat/galvanostat with a function generator. The working electrode was a platinum disc and the counter electrode a platinum wire. The reference electrode was an Ag/0.01 mol dm^{-3} AgNO$_3$ electrode filled with 0.1 mol dm^{-3} Bu$_4^n$NPF$_6$ in benzonitrile (BN). Measurements were run at room temperature on a 1 mmol dm^{-3} solution of the sample in BN containing 0.1 mol dm^{-3} Bu$_4^n$NPF$_6$ as a supporting electrolyte, after the solution was deaerated by bubbling argon gas. Voltammograms were recorded on a Graphtec WX-1100 *X–Y* recorder at a sweep rate of 200 mV s^{-1}. All the potentials were referenced to the Fc/Fc$^+$ redox couple observed at + 0.07 V *vs.* Ag/AgNO$_3$.

Transient absorption spectra

Transient absorption spectra were measured by nanosecond time-resolved laser photolysis with an Nd^{3+} : YAG laser (Spectra-Physics GCR-130, the third harmonics, 355 nm, pulse width 6 ns) or an XeCl excimer laser (Lambda Physik LEXTRA 50, 308 nm, pulse width 17 ns). A 150 W xenon flash lamp (Ushio UXL 151D) was used as a probe light for the detection of the transients. The monitoring light passing through a monochromator (Ritsu MC-20N) was detected by a photomultiplier tube (Hamamatsu R928) and recorded on a digitizing oscilloscope (Tektronix TDS 540). The time profiles were analysed by a personal computer (NEC PC-9821 Ap). The sample solution was degassed by at least three freeze–thaw cycles on a high-vacuum line. The absorbance of the solutions was adjusted to *ca.* 0.7 at the excitation wavelength.

4-Aminobenzocyclobutene(4)[12]

To a solution of 4-nitrobenzocyclobutene[12,18] (290 mg, 1.9 mmol) and tin(II) chloride dihydride (2.14 g, 9.5 mmol) in ethanol (38 cm^3) sodium borohydride (36.1 mg, 0.95 mmol) was added in ethanol (38 cm^3) with stirring over a period of 30 min. After being stirred for 1 h, the reaction mixture was cooled to 5–10 °C, and cold water (40 cm^3) was added. The ethanol solution was neutralized with a cold 3.5 mmol dm^{-3} NaOH aqueous solution to pH 7, concentrated, and extracted with diethyl ether. The extracts were washed with H$_2$O, dried over Mg$_2$SO$_4$, and evaporated. The residue was purified by column chromatography (Al$_2$O$_3$, benzene–ethyl acetate) to give **4** as a brown oil (150 mg, 1.26 mmol, yield 66%).

4-(Dimethylamino)benzocyclobutene (5)

A mixture of 4-aminobenzocyclobutene (390 mg, 3.3 mmol) and trimethyl phosphate (468 mg, 3.3 mmol) was gradually heated to 150 °C with stirring. After being refluxed for 1.5 h, the reaction mixture was cooled to room temperature. A 3.8 mol dm^{-3} NaOH aqueous solution was added, and the mixture was stirred vigorously for 1.5 h to hydrolyse the phosphate ester. After the addition of water (200 cm^3), the solution was extracted with diethyl ether three times. The extracts were washed with H$_2$O and dried over Mg$_2$SO$_4$. The evaporation of the solvent resulted in a brown oil product, **5** (101 mg, 3.4 mmol, 21%). ^{1}H NMR δ_H (500 MHz; CDCl$_3$; standard Me$_4$Si 2.89 (6 H, s), 3.10 (4 H, s), 6.58 (1 H, s), 6.64 (1 H, d, *J* 8.0 Hz), 6.92 (H, d, *J* 8.0 Hz).

C$_{60}$–4-(dimethylamino)benzocyclobutene adduct (1)

C$_{60}$ (100 mg, 0.14 mmol) and 4-(dimethylamino)benzocyclobutene (30.7 mg, 0.20 mmol) dissolved in 1,2,4- trichlorobenzene (16.6 cm^3) were allowed to remain at the reflux temperature for 8 h, and the solvent was removed *in vacuo*. The residue was chromatographed on alumina to give the desired monoadduct **1** as a brown solid, the diadducts (composed of some isomers), and the recovery of C$_{60}$. The monoadduct **1** was further purified by reprecipitation from toluene and methanol (22 mg, 0.027 mmol, 19%). ^{1}H NMR δ_H [500 MHz; CDCl$_3$: CS$_2$ (1 : 1); standard Me$_4$Si 3.09 (6 H, s), 4.31 (2 H, br m), 4.75 (2 H, br m), 6.84 (1 H, br d, *J* 6.9 Hz), 7.01 (1 H, s), 7.43 (1 H, d, *J* 6.9 Hz). ^{13}C NMR δ_c [125 MHz; CDCl$_3$: CS$_2$ (1 : 1); standard Me$_4$Si; 40.70 (N*Me*$_2$), 44.30, 45.67 (benzylic), 66.07, 65.65 (aliphatic quaternary carbon of C$_{60}$), 112.02, 128.34 (aromatic *C*—H); the other aromatic carbons and the sp^2 carbons of the C$_{60}$ moiety could not be discerned clearly, since the latter 58 carbons are all unequivalent owing to the low symmetry.

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