

potential of the fullerene adduct is thus estimated to be ca. -0.57 V vs SCE, i.e. in good agreement with literature reports for other fullerene adducts¹¹. A model of the donor (4-(dimethylamino)benzylamine from Aldrich) shows an irreversible oxidation wave of +0.74 V vs SCE in acetonitrile leading to an estimated midpoint potential +0.71 V vs SCE (i.e. comparable to N,N- dimethylparatoluidine)¹².

The structure of the adduct **C₆₀[3]DMA**, obtained by minimization with semi-empirical AM1 calculations is shown in Figure 4.6. The aromatic ring of the donor is in an orthogonal relation to the plane that bisects the two sp³ carbons of the fullerene. Although the center to center distance of the two chromophores is estimated to be ca. 9 Å, the edge to edge distance is only ca. 5 Å.

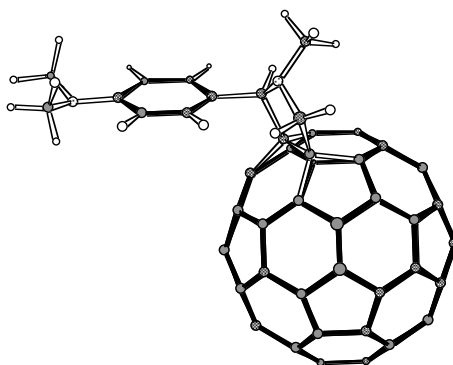


Fig. 4.6. Structure of compound **C₆₀[3]DMA** obtained with AM1.

4.3.2 Energetic Considerations

An estimate of the driving force for photoinduced charge separation ($-\Delta G_{cs}$) in compound **C₆₀[3]DMA** was made using the standard Weller-type approach^{13, #}:

$$\Delta G_{cs} = e(E_{ox}(D) - E_{red}(A)) - E_{00} - \frac{e^2}{4\pi\epsilon_0\epsilon_s R_c} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-} \right) \left(\frac{1}{37.5} - \frac{1}{\epsilon_s} \right)$$

This requires, in addition to the donor and acceptor redox potentials (+0.71 V and -0.57 V vs SCE, see above) and the singlet or triplet state energy ($^1E_{00} = 1.76$ eV and $^3E_{00} = 1.50$ eV, see above), substitution of the center to center distance (R_c) and of the effective ionic radii of the donor and acceptor radical cation and anion (r^+ respectively r^-). For R_c a value of 9 Å was estimated from our modeling results (Fig. 4.6). The r^+ and r^- values were calculated from the

Note that $\frac{e^2}{4\pi\epsilon_0} = 14.4$ eV Å

apparent molar volumes of N,N-dimethylaniline (density = $\rho = 0.956$) and of C₆₀ (density 1.65)¹⁴ using a spherical approach ^{5c}.

$$4/3 \pi r^3 = M/N\rho$$

Here M is the molecular weight and N is Avogadro's number. This gives $r^+ = 3.7 \text{ \AA}$ and $r^- = 5.6 \text{ \AA}$. Resulting ΔG_{cs} values in various solvents are listed in Table 4.3, where furthermore values are given for the barrier to charge separation ($\Delta G^\#$) as estimated via the classical Marcus equation:

$$\Delta G^\# = (\Delta G + \lambda)^2 / 4\lambda \quad \text{with} \quad \lambda = \lambda_i + \lambda_s$$

$$\lambda_s = e^2 / 4\pi\epsilon_0 (1/r - 1/R_c)(1/n^2 - 1/\epsilon_s)$$

For this estimation the solvent reorganization term (λ_s) was calculated using the Born-Hush approach ^{5c} and the internal reorganisation energy (λ_i) was set at 0.3 eV. The latter value was estimated using the charge transfer absorption maximum of C₆₀ in pure diethylaniline (550 nm)¹⁵ and the charge transfer emission maximum of C₆₀ in methylcyclohexane containing 0.1 M diethylaniline (740 nm) ^{2d, h}. The energy difference between these two maxima equals $2\lambda_i$, resulting in $\lambda_i \approx 0.3 \text{ eV}$. An estimate of the Gibbs free energy change for charge recombination ($\Delta G_{cr} = -\Delta G_{cs} - {}^1E_{00}$) in compound **C₆₀[3]DMA** is also given in table 4.3.

$$\Delta G_{cr} = e(-E_{ox}(D) + E_{red}(A)) + e^2/4\pi\epsilon_0 \epsilon_s R_c + e^2/8\pi\epsilon_0 (1/r^+ + 1/r^-)(1/37.5 - 1/\epsilon_s)$$

For the triplet state, only the Gibbs free energy change ($\Delta G_{cs}(T)$) and the barrier for electron transfer ($\Delta G^\#(T)$) differ from the values for the singlet state.

Important conclusions from the data collected in Table 4.3 are as follows: (i) The driving force for charge separation ($-\Delta G_{cs}$) from the fullerene S₁ state becomes positive in solvents more polar than toluene, in good agreement with the fluorescence data, and from the T₁ state it requires solvents more polar than chloroform. The relatively high triplet yield and the absence of fluorescence of **C₆₀[3]DMA** in dichloromethane (see Table 4.2) indicates that in this solvent of medium polarity charge recombination to the local triplet is a major decay path of the charge transfer state. (ii) Charge separation is in the normal region ($-\Delta G_{cs} < \lambda$) for every solvent. (iii) The barrier for electron transfer from S₁ is always at least 0.08 eV lower than from T₁ (the difference in the barrier is 0.23 eV (5.4 kcal/mol) in methylcyclohexane and 0.08 eV (1.9 kcal/mol) in benzonitrile). This indicates that electron transfer rates from the triplet should always be slower than from the singlet state, and this effect should be strongest in non-polar solvents, in agreement with the results of Caspar and Wang ²ⁱ. It has to be

realised that in our system the difference in rate between the two theoretically possible paths implies that electron transfer will only occur via the singlet state, and not via the triplet.

Table 4.3. *Gibbs free energy change for charge separation (ΔG_{cs}), barrier to charge separation ($\Delta G^\#$) and Gibbs free energy change for charge recombination (ΔG_{cr}) and the reorganisation energy (λ) in different solvents (given with dielectric constants (ϵ) and refractive indices (n)) for both the singlet and triplet (T) state, obtained for compound **C₆₀[3]DMA** with $R_c = 9 \text{ \AA}$, $r^+ = 3.7 \text{ \AA}$, $r^- = 5.6 \text{ \AA}$, internal reorganisation energy (λ_i) is 0.3 eV.*

solvent	ϵ	n	ΔG_{cs} (eV)	λ (eV)	$\Delta G^\#$ (eV)	ΔG_{cr} (eV)	ΔG_{cs} (T) (eV)	$\Delta G^\#$ (T) (eV)
methycyclohexane	2.07	1.423	0.22	0.32	0.22	-1.98	0.48	0.50
toluene	2.38	1.497	0.12	0.34	0.16	-1.88	0.38	0.38
chloroform	4.70	1.446	-0.22	0.70	0.08	-1.54	0.04	0.20
dichloromethane	8.93	1.424	-0.38	0.87	0.07	-1.38	-0.12	0.16
1,2-dichlorobenzene	9.93	1.552	-0.40	0.78	0.04	-1.36	-0.14	0.12
benzonitrile	25.20	1.528	-0.50	0.88	0.04	-1.26	-0.24	0.12

4.5 Conclusions

The solvent dependence of the fluorescence and triplet-triplet absorption of **C₆₀[3]DMA** indicates that in polar solvents an extra deactivation path of the excited states (S_1 or T_1) of **C₆₀[3]DMA** becomes available. As the population of a charge transfer state is exergonic in polar solvents (according to the Weller equation) we attribute this quenching path to an intramolecular electron transfer that deactivates the locally excited states.

Fluorescence decay data indicate that the singlet state electron transfer quenching process in benzonitrile takes place with a rate between 1.3×10^9 and $1.2 \times 10^{10} \text{ s}^{-1}$.

Because, even at the relatively small edge-to-edge donor-acceptor distance present in **C₆₀[3]DMA**, the charge transfer state can only be populated in rather polar solvents, our results also imply that fullerenes are not very well suited for use as electron accepting chromophores for long range electron transfer in bichromophoric donor-bridge-acceptor systems, unless a significantly stronger donor than N,N-dimethylaniline (e.g. N,N,N',N'-tetramethyl-*p*-phenylenediamine) is used. One of our previous studies on the solvent dependence of intramolecular charge separation has already shown that optimal (in a Marcus sense) electron transfer interactions (at a given distance) can only be accomplished if already in a nonpolar solvent electron transfer is energetically favourable: ^{5d} i.e. by applying polar solvents one can gain driving force (and make electron transfer energetically possible) but one will never obtain the highest electron transfer rates. Our results thus suggest that high rate photoinduced intramolecular electron transfer in the systems described in ref 4b, c and 5e will

not be possible due to the large separation distance or the small driving force, although the different spatial orientation of the donor and acceptor in these systems may be of influence (In Chapter 5 it is shown that the different spatial orientation is indeed of great influence for one of these systems).

Furthermore our results indicate that functionalization of C₆₀ is accompanied by a decrease of the ¹E₀₀ with ca. 0.23 eV and a shift to a more negative first reduction potential of ca. 0.17 V. Thus, under the same conditions (i.e. donor, distance and solvent), the driving force for charge separation for an adduct of C₆₀, compared to "native" C₆₀, would be ca. 0.40 eV less exergonic. This would mean that C₆₀ adducts are less suited for photoinduced electron transfer systems than "native" C₆₀. It thus would seem preferable to incorporate a C₆₀ unit into an electron transfer system by a supramolecular method, such as complexation by calix[8]arenes ¹⁶ or γ-cyclodextrins ¹⁷, leaving the C₆₀ unit intact.

4.6 Final remarks

4.6.1 New literature

After the submission and publication of the manuscript on which this chapter is based a number of publications have appeared that describe the synthesis and the photophysical properties of fullerene adducts that incorporate an electron donating group. These publications are reported in chapter 5.

4.6.2 Reaction pathways

We can visualise the data presented in table 4.3 by making use of potential energy curves. In Fig. 4.7. it is illustrated that in methylcyclohexane the charge transfer state is in-accessible. In the polar solvent benzonitrile, the charge transfer state can be populated from the S₁ state via a small barrier (and theoretically from the triplet state via a larger barrier). If we go to the bottom of the potential energy curve that represents the charge transfer state we see that it is strongly coupled to the ground state. It has to be noted that the representation in fig. 4.7. is a two-dimensional cross section taken from a multi-dimensional potential energy surface.

4.6.3 Conformational aspects

A conformational search performed on a model system of compound **C₆₀[3]DMA** (a similar adduct of pyracylene) revealed that two conformations can be found (see Fig. 4.8). The only relevant conformational freedom resides in the pyrrolidine ring and in nitrogen inversion. These conformations may explain the two short components of the fluorescence decay data presented above in the results section (see Fig. 4.5).