J. Phys. Chem. A **1999,** *103,* 2857−2860 **2857**

Quantum Chemical Calculations of the Electronic States and Fluorescence Properties of Carbazolyl- and Carbazolylmethylene-Substituted Diacetylenes

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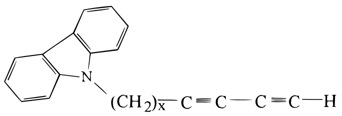
Received: November 5, 1998

The carbazolyldiacetylenes show very different fluorescence behaviors depending on how the carbazolyl (Cz) moiety is connected to the diacetylenic backbone. In fact, when Cz is attached to the backbone through one or more CH_2 spacer(s) fluorescence properties are observed which are closely related to those of the fluorescent Cz group. On the contrary, almost no fluorescence is observed when Cz is directly attached to the backbone. In this paper, these phenomena are studied quantum chemically and an explanation for the observed facts is provided. The relevant excited states are studied in detail, showing that in the lowest singlet excited state a considerable intramolecular charge transfer occurs from Cz to the backbone when they are directly bonded.

Introduction

Polydiacetylenes ($(=C-C\equiv C-C)_n$) (PDAs) are conjugated systems produced by the solid state topochemical polymerization of the diacetylenic monomers. They are particularly attractive because of their large optical nonlinearities and fast recovery times.[1]

To obtain PDAs with improved nonlinear optical properties, we have prepared a series of novel diacetylenic monomers having a carbazolyl group directly or indirectly (through a spacer) attached to the skeleton. In fact, as already pointed out in a previous paper,[2] the carbazolyl group is quite promising as far as nonlinear optical properties of the polycarbazolyldiacetylenes (PCzDAs) are concerned. The processability of the polymers has been also considered so that some of the monomers have been synthesized with long aliphatic chains on the 3,6 positions of the Cz group. The availability of a very large number of novel carbazolyldiacetylenes (CzDAs) having peculiar spectroscopic properties has focused our interest in their detailed structure−property study. The results obtained on the vibrational assignment of the triple bonds stretching vibrations of CzDAs have been reported in a previous publication.[3] Fluorescence spectra have been measured on the same systems, and a very interesting difference has been found among the directly and indirectly substituted monomers. Indeed, in all the diacetylenes in which the carbazolyl group is attached to the backbone through a spacer, fluorescence properties are observed which are clearly related to those of the fluorescent carbazolyl group. On the contrary, when the carbazole is directly bonded to the diacetylene moiety, the monomers are practically not fluorescent. All the results obtained will be fully presented and discussed elsewhere. Here, we will only report the experimental data concerning the absorption and emission behavior of the two simplest representatives of the different monomeric species, i.e., and discuss them in relation to the results of quantum chemical calculations. This comparison provides significant insight into the fluorescent behavior of these compounds in relation to the interaction between the Cz group and the diacetylenic moiety.



x = 1 , C1

x = 0 , C2

Experimental and Theoretical Procedures

The synthetic procedure for the preparation of the monomers studied in the present paper is reported in ref 3. The room-temperature electronic absorption spectra were recorded in methanol solutions using a Perkin-Elmer model Lambda 9 spectrophotometer. Fluorescence spectra were measured at 20 °C in the same solvent with a Perkin-Elmer MPF44A spectrofluorimeter. The wavelength $\lambda = 334$ nm was used for excitation. The fluorescence yields were evaluated from plots of the intensity (I_F) of the lower energy peak of the fluorescence spectra against the value of the solution absorbance (below 0.1) at 334 nm. *N*-methylcarbazole (MC) was taken as the reference compound.

Quantum chemical calculations have been carried out on the lowest singlet excited states of carbazole (Cz), the diacetylene $H-C\equiv C-C\equiv C-H$ (M) and the carbazolyl substituted monomers C1 and C2. The geometries of the ground states of all these compounds have been optimized at the AM1 level using the MOPAC program[4] without any symmetry restriction. The optimizations of the geometries of the excited states have been performed by using GAUSSIAN 94[5] in the ab initio CIS (configuration interaction-singles) approximation. The optimized geometries have been then used as input for the ZINDO program[6] which does the excited state calculations. All the singly excited configurations involving the 15 highest occupied and

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10.1021/jp984307k CCC: $18.00

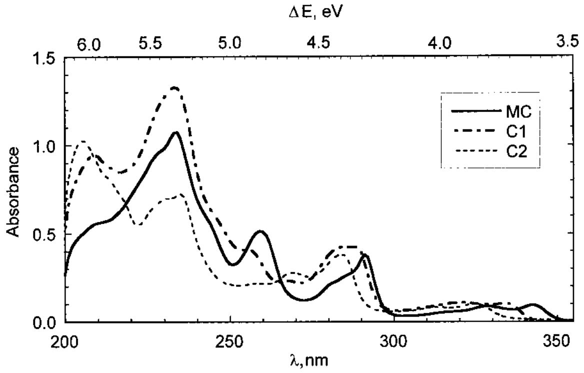


Figure 1. Absorption spectra of C1 (-•-), C2 (- - -), and MC (—) in methanol solutions.

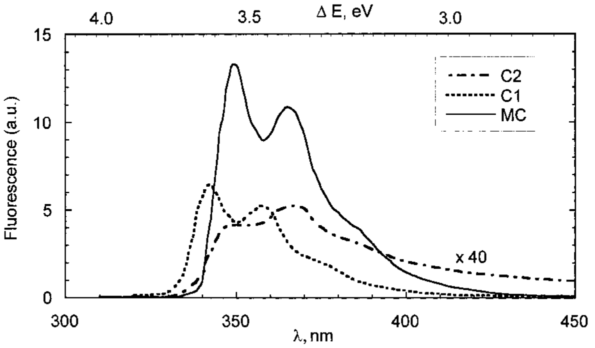


Figure 2. Uncorrected fluorescence spectra of C1 (-•-), C2 (- - -), and MC (—) in methanol solutions at 20 °C; $\lambda_{ex} = 334$ nm.

the 15 lowest empty molecular orbitals have been included in the CI using the Mataga—Nishimoto parameters.[6] Increasing the number of occupied and virtual MO's did not affect appreciably the results.

Results

The electronic absorption spectra of C1 and C2 in methanol are reported in Figure 1 and the corresponding fluorescence spectra in Figure 2. The absorption peaks in the near UV region are typical of the carbazole group. As expected, an overall similarity in the wavelengths of the bands in the two spectra is observed. However, some differences are present, in particular in the region above 300 nm, where for C1 the peaks fall at 321, 334 nm while for C2 at 313, 327 nm. A substantial difference in the relative intensity is evident in the peaks below 250 nm.

The corresponding normalized fluorescence spectra exhibit a red shift of the C2 bands (350, 368 nm) relative to those of the C1 emission (342, 358 nm), accompanied by a strong intensity decrease. The apparent inversion of the ratio between the intensities of the two peaks could be somewhat affected by stray light contribution due to the very low level of the intensity emission of C2. From absorption and emission spectra, the Stokes shifts (Δ) can be determined and result to be about 700 and 2000 cm^{-1} for C1 and C2, respectively. For comparison, we report in Figures 1 and 2 also the spectra of *N*-methylcarbazole (MC). It is evident that in the far UV C1 and MC are quite similar, but the near UV bands of MC are somewhat red-shifted from those of C1. Also, similar though of different intensities are the emission spectra of the two compounds. Table 1 collects all the data relevant to the discussion of the results.

In the last column of this table, the values *R* of the slope of the fluorescence intensities versus the absorbance evaluated as described above and normalized to that of MC are reported.

TABLE 1: Near UV Absorption (λ_{a1}, λ_{a2}) and Fluorescence (λ_{e1}, λ_{e2}) Wavelengths (nm); Stokes Shift (Δ, cm^{-1}) and Relative Normalized Fluorescence Intensity (*R*) for MC, C1, and C2 in Methanol Solution

system	λ_{a1}	λ_{a2}	λ_{e1}	λ_{e2}	Δ	*R*
MC	329	343	349	365	500	1
C1	321	334	342	358	700	0.48
C2	313	327	350	368	2000	0.01

The diacetylenic substituent in C1 reduces to half the fluorescence emission relative to that of MC, but the lack of the $-CH_2-$ spacer reduces it by about 2 orders of magnitude. At the same time, the Stokes shift increases noticeably, thus showing a change in the excited state geometry more pronounced in C2 then in C1.

As far as the theoretical results are concerned, the geometry optimizations give a C_{2v} molecular symmetry for Cz and C2, a $D_{\infty h}$ symmetry for M, and a C_s symmetry for C1. The computed vertical excitation energies for the lowest singlet excited states of the four molecules are reported in Table 2.

For carbazole, the lowest experimental transition energies occur at 3.76 (polarized along the short molecular axis), 4.25 (long axis), 4.85 (long axis), 5.04 (tentatively assigned to the polarization along the short axis[7]), and 5.34 eV (no polarization data available).[7,8] On the basis of the polarization properties and the band intensities, we can assign these experimental peaks to our computed transitions at 3.89 (A_1), 4.25 (B_1), 4.61 (B_1), 5.25 (A_1), and 5.06 eV (B_1), respectively. The agreement with our results is nice for the excitation energies, oscillator strengths, and polarizations of the two lowest transitions, while in the last three cases, the differences between theoretical and experimental excitation energies are systematically greater than 0.2 eV. On the whole, we believe that the overall picture of the carbazole lowest singlet excited states can be considered as very satisfactory.

Referring now to the C1 and C2 monomers, we think it useful to correlate their computed excited states with those of carbazole and of the diacetylene. This is shown in Table 3. A strict correlation is found for the C1 monomer, in which there is a one-to-one correspondence between its excited states and those of carbazole and of the diacetylene, with the differences in the excitation energies amounting to few hundredths of an electronvolt. This clearly means that when the carbazolyl group and the diacetylenic moiety are separated by one CH_2 spacer as in C1 they act as almost separate subsystems. Due to the loss of symmetry, however, now *all* the excited states are in principle symmetry-allowed, which explains why the molecule is fluorescent. Our calculations also suggest a possible explanation for the reduction of the fluorescence quantum yield of C1 with respect to that of carbazole. If we compute the lowest triplets of carbazole and C1 with the same procedure used for singlets, we obtain a triplet state at 3.91 eV (first singlet at 3.89 eV) in the case of carbazole and three triplet states at 3.52, 3.53, and 3.54 eV (first singlet at 3.53 eV) in the C1 case. As a consequence, in both systems a nonradiative decay of the first singlet via intersystem crossing is favored, the energies of the states involved being very close to each other. In the C1 case, however, three distinct channels for this competing phenomenon are predicted, which should appreciably reduce the fluorescence decay of C1 with respect to that of carbazole.

More interaction between the carbazolyl and diacetylenic moieties can be expected in the C2 monomer, and in fact, only the eight symmetry-allowed excited states can be directly correlated with those of carbazole and of the M diacetylene, with deviations in the excitation energies which are slightly

TABLE 2: Computed ZINDO Excitation Energies (eV) and Oscillator Strengths (in Parentheses)[a] for the Lowest Singlet Excited States

carbazole (Cz), C_{2v}	HC≡C−C≡CH diacetylene (M), $D_{\infty h}$	Cz−CH$_2$−C≡C−C≡CH C1 monomer, C_s	Cz−C≡C−C≡CH C2 monomer, C_{2v}
A_1 3.89 (0.02), 5.25 (0.34), 5.46 (0.35)	Σ_g^+ 5.75 (∗)	A′ 3.84 (0.03), 3.91 (0.00), 5.19 (0.18), 5.34 (0.50)	A_1 3.63 (0.09), 3.88 (0.02), 4.98 (0.51), 5.07 (0.18)
A_2 6.06 (∗)	Π_g 7.93 (∗), 7.93 (∗)	A″ 3.53 (0.00), 3.91 (0.00), 4.27 (0.15), 4.55 (0.01), 5.01 (1.57), 5.27 (0.00)	A_2 3.26 (∗), 3.76 (∗), 5.11 (∗)
B_1 4.25 (0.21), 4.61 (0.00), 5.06 (1.54)	Δ_g 5.27 (∗), 5.75 (∗)		B_1 4.29 (0.13), 4.49 (0.00), 4.91 (1.32)
B_2 5.98 (0.00)	Σ_u^+ 3.99 (0.00), 8.54 (2.18) Π_u 3.99 (∗), 6.28 (∗), 6.28 (∗) Δ_u 3.57 (∗)		B_2 5.23 (0.00), 5.99 (0.00)

[a] (∗) means a symmetry-forbidden transition.

TABLE 3: Correlation between the Lowest Excited States (eV) of Carbazole and Diacetylene with Those of C1 and C2 (Oscillator Strengths in Parentheses)[a]

carbazole (Cz), monomer (M)	C1	C2
		3.26 (∗)
3.57 (∗), M	3.53 (0.00)	3.63 (0.09)
		3.76 (∗)
3.89 (0.02), Cz	3.84 (0.03)	3.88 (0.02)
3.99 (∗), M	3.91 (0.00)	
3.99 (0.00), M	3.91 (0.00)	
4.25 (0.21), Cz	4.27 (0.15)	4.29 (0.13)
4.61 (0.00), Cz	4.55 (0.01)	4.49 (0.00)
5.06 (1.54), Cz	5.01 (1.57)	4.91 (1.32)
		4.98 (0.51)
5.25 (0.34), Cz	5.19 (0.18)	5.07 (0.18)
		5.11 (∗)
5.27 (∗), M	5.27 (0.00)	5.23 (0.00)
5.46 (0.35), Cz	5.34 (0.50)	

[a] (∗) means a symmetry-forbidden transition.

higher than those in C1. This corresponds to the already noted overall similarity of the absorption spectra of C1 and C2. Allowing the MO's of carbazole to interact with those of the diacetylene through perturbation theory[9] to give the MO's of C2 reveals that very small or no interaction takes place between the majority of the near-to-frontier MO's. This general behavior, however, has two important exceptions, as we shall see below. For the moment, we note that in the low-energy range the two degenerate excited states of M at 3.99 eV cannot be directly correlated with any excited state of C2, and on the other hand, two new symmetry-forbidden states appear at 3.26 and 3.76 eV, respectively. Of outstanding importance is the fact that the first of these turns out to be the lowest singlet excited state of C2, which explains why this molecule is nonfluorescent. Incidentally, a triplet state at 3.27 eV is found in this case, very close to the lowest excited singlet, which could imply a completely nonradiative decay of the latter. The above ordering of the lowest two singlet excited states in C2 is confirmed by ab initio CIS calculations (6-31G* basis set), which give vertical excitation energies of 4.73 and 5.47 eV for the 1^1A_2 and 2^1A_1 states, respectively, and the same arrangement for the excitation energies computed at the optimized excited state geometries. The ab initio excitation energies appear however overestimated, as is to be expected at the CIS level. To further confirm these results, at least ZINDO multireference (MR-CI)[10] calculations on C2 would be needed, but this is presently beyond our capabilities. Nonetheless, an indirect check can be obtained by noting that the substitution of carbazole with pyrrole in C2 gives a much more easily tractable system, whose excitation properties should on the other hand not be appreciably different. In fact, the lowest singlet excited states of the new compound, computed at the single-excitation level, result to be strictly similar to those of C2. In this case, however, a MR-CI calculation can be performed with an active space made of all the π/π^* molecular orbitals plus all the σ-type orbitals which are of the in-plane "π"/"π^*" type and are involved in the triple bonds. All the single and double excitations resulting from five reference configurations (SCF, H → L, H → L+1, H − 1 → L, and HH → LL) are included using the Ohno−Klopman parameters,[6] and the results still predict the 1^1A_2 state to be the lowest singlet excited state in this compound.

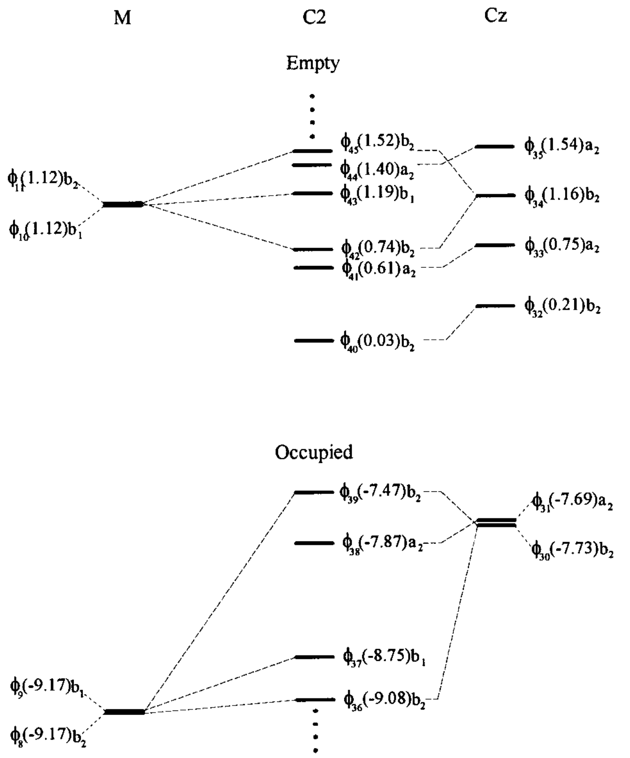


Figure 3. Correlation between the near-to-frontier (see text) ZINDO molecular orbitals of carbazole and of the diacetylenes M and C2. Orbital energies in parentheses (eV).

We want now to clarify the nature of the new symmetry-forbidden A_2 states in C2, with particular emphasis on the lowest one. It is useful in this respect to consider the correlations between the ZINDO near-to-frontier MO's of carbazole, M, and C2, which are mainly dictated by the C_{2v} symmetry of the composite system and are depicted in Figure 3. For the sake of brevity, we report in the figure only the correlations leading to the C2 MO's which are implied in the lowest four excited states (see Table 2).

As anticipated before, out of 10 carbazole (Cz) and diacetylene (M) starting MO's, six remain unchanged. Of the remaining four MO's, ϕ_8 of M interacts with ϕ_{30} of Cz to give ϕ_{36} and ϕ_{39} of C2, mainly because ϕ_{30} of Cz is 26% concentrated on N, while ϕ_8 of M is 33% concentrated on each of the terminal carbons, which implies a strong off-diagonal matrix element between the two interacting MO's. ϕ_{11} of M interacts with the nearly degenerate ϕ_{34} of Cz to give ϕ_{42} and ϕ_{45} of C2, while ϕ_9 and ϕ_{10} of M remain unchanged, giving rise to ϕ_{37} and ϕ_{43} of C2. Just the above six C2 MO's are seen to dominate the 1^1A_2 and 2^1A_2 wave functions

$$\psi(1^1A_2)(\Delta E = 3.26\text{ eV}) \approx -0.52(\phi_{36} \rightarrow \phi_{43}) - 0.74(\phi_{39} \rightarrow \phi_{43})$$

$$\psi(2^1A_2)(\Delta E = 3.76\text{ eV}) \approx 0.54(\phi_{37} \rightarrow \phi_{42}) + 0.69(\phi_{37} \rightarrow \phi_{45})$$

[where (a → b) means a configuration in which an electron is promoted from MO a to MO b], while ϕ_8, ϕ_9, ϕ_{10}, and ϕ_{11} of M dominated its two states at 3.99 eV. This explains the disappearing of the latter, which are somewhat replaced by the two symmetry-forbidden A_2 states in C2 due to the interaction of the fragment MO's. Let's now examine more deeply the character of the lowest excited state 1^1A_2. It is mainly described by the promotion of one electron from ϕ_{36} and ϕ_{39} of C2 (that is, ϕ_8 of M plus ϕ_{30} of Cz) to ϕ_{43} (that is, ϕ_{10} of M), and by consequence we can expect a strong intramolecular transfer of charge to take place in this state from carbazole to the diacetylene moiety. In fact, an excitation-induced piling up of charge in ϕ_{43} of 0.80e can be computed, 0.47e of which comes from ϕ_{30} of Cz (i.e., from the carbazole ring).

The symmetry-allowed states of C2 show small although significant deviations in optical transition energies with respect to Cz and C1. Let us look in particular to the two lowest ones, whose wave functions are

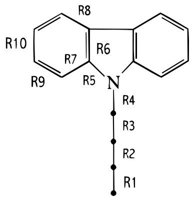
$$\psi(1^1A_1)(\Delta E = 3.63\text{ eV}) \approx 0.54(\phi_{37} \rightarrow \phi_{43}) + 0.46(\phi_{39} \rightarrow \phi_{40}) + 0.40(\phi_{39} \rightarrow \phi_{42}) + 0.35(\phi_{39} \rightarrow \phi_{45})$$

$$\psi(2^1A_1)(\Delta E = 3.88\text{ eV}) \approx 0.48(\phi_{38} \rightarrow \phi_{41}) + 0.64(\phi_{39} \rightarrow \phi_{40})$$

The 1^1A_1 state is connected to the state at 3.57 eV of M (see Table 3), which was dominated by ϕ_8, ϕ_9, ϕ_{10}, and ϕ_{11} of M. Out of these, however, only ϕ_9 and ϕ_{10} have been left unchanged giving ϕ_{37} and ϕ_{43} of C2, respectively, while ϕ_8 and ϕ_{11} have mixed with Cz MO's giving rise to ϕ_{36}, ϕ_{39}, ϕ_{42}, and ϕ_{45} of C2. These are precisely the MO's which appear in $\psi(1^1A_1)$ (together with ϕ_{40}, an unchanged Cz MO), which explains why this state is connected to the state at 3.57 eV of M but somewhat different from it. On the contrary, the 2^1A_1 state is strictly similar to the Cz state at 3.89 eV, being ϕ_{38}, ϕ_{40}, and ϕ_{41} unchanged Cz MO's.

Turning finally to the lowest 1^1A_2 state, we have optimized at the ab initio CIS level its geometry, and the results are reported in Table 4. With reference to the ground state geometry (also reported in the table) it is seen that the excitation-induced distortions occur essentially in the diacetylenic moiety. This clearly implies that the excitation is localized in this fragment, which on the other hand corresponds to the shortest conjugated path.

TABLE 4: Ab Initio 6-31G* Optimized Geometries (Å) of the Ground State (RHF) and of the Lowest 1^1A_2 Excited State (CIS) of C2



	ground state	1^1A_2 state
R1	1.189	1.246
R2	1.385	1.302
R3	1.190	1.273
R4	1.336	1.293
R5	1.401	1.424
R6	1.394	1.390
R7	1.384	1.379
R8	1.389	1.387
R9	1.383	1.385
R10	1.395	1.393

In conclusion, the different behavior of the C1 and C2 monomers is due to the different degree of interaction between the carbazole and diacetylene moieties in the two cases. In C1, the presence of the CH_2 spacer makes this interaction small and the excited states of the two moieties scarcely affected. Due to the C_s symmetry of the molecule, however, all excited states are allowed. In the second case, the strong interaction substantially lowers the excitation energy of the forbidden state of M discussed above, giving rise to the lowest (forbidden) state of C2 through a considerable intramolecular charge transfer from the carbazole to the diacetylenic moiety.

Acknowledgment. The support from the Italian MURST and CNR is gratefully acknowledged.

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