PERKIN 2

Vibrational properties of novel diacetylenic monomers

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Received (in Cambridge) 28th May 1998, Accepted 5th August 1998

The frequency and intensity of the infrared and Raman C≡C modes have been investigated for a large number of molecules. A series of symmetrical and asymmetrical substituted diacetylenic monomers having the carbazole group attached directly or indirectly to the diacetylenic backbone have been studied in their microcrystalline or liquid state. A qualitative assignment has been proposed and particular attention has been given to those systems for which a peculiar behaviour of the infrared and Raman intensities has been observed. This behaviour is found when the diacetylenic skeleton is directly attached to either the 9*H*-carbazolyl or triethylsilyl group.

Introduction

The development of functional conjugated materials with desirable physical properties for practical applications has become one of the fast-growing research areas.[1] The design of molecular systems is particularly favourable in the case of polydiacetylenes $(=RC-C\equiv C-CR')_n=$, (PDAs), because polymer single crystals are obtained by topochemical polymerization from monomer single crystals thus offering the possibility of achieving quasi monodimensional wires which exhibit large third-order optical non-linearities coupled to ultrafast response times.

In our work aimed at obtaining a novel processable polydiacetylene with outstanding optical and electronic properties, we have designed and synthesized a variety of diacetylenic monomers having as a substituent at least one carbazole group. Our choice has been dictated by the fact that this fluorescent chromophore gives photoconductive materials and that a particularly high value of the non-linear optical response has been measured for poly[1,6-di(9*H*-carbazol-9-yl)hexa-2,4-diyne] (polyDCHD).[1]

From the spectroscopic point of view, diacetylenic monomers have received so far little attention. Only a few often controversial and incomplete assignments of their vibrational spectra have been proposed[2–5] due to the fact that the vibrational dynamics of the diacetylenic moiety are strongly affected by the substituents and that these monomers are usually highly reactive in the solid state thus favouring the formation of polymers or byproducts.

The availability of a series of symmetrical and asymmetrical substituted diacetylenic monomers having the carbazole group attached directly or indirectly to the diacetylenic backbone led us to study their vibrational properties with the purpose of contributing to this field and providing new data to be used as a starting point for the explanation of the chemical and physical properties of the polymers derived through their topochemical polymerization.

Since the electronic properties of PDAs are mainly related to the delocalization of the π electrons of the backbone which is strongly influenced by the nature of the substituents, the vibrational spectra of the monomers will be analyzed in the region of the C≡C stretchings which is known to give a reliable indication of the extent of the conjugation achieved.

This work is organized as follows. First we deal with the infrared and Raman data of the monomers with the carbazolyl group attached to the diacetylenic system through one or more $-CH_2-$ spacers (groups **A** and **B** for the symmetrical and asymmetrical monomers, respectively). The corresponding data for the diacetylenes having the carbazole directly attached to the backbone (group **C**) are then reported. Finally a comparison of these results will be made and discussed.

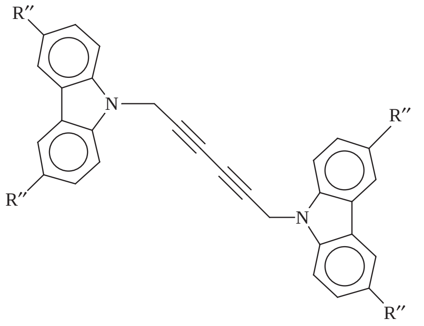
Results and discussion

The molecular structures of the monomers studied in the present work are reported in Figs. 1–3. Infrared and Raman spectra have been measured for all the samples in the whole spectral range, but, as indicated in the introduction, only the stretching frequencies of the triple bond will be here reported.

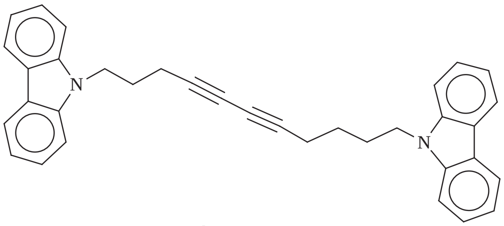
Table 1 collects all the data relative to the monomers belonging to group **A** (columns 2 and 3). Since during measurement some polymerization may occur (due to exposure to light or to heating of the sample), in column 4 the polymer Raman frequency is also reported for the sake of completeness.

The structure of these molecules which possess an inversion center of symmetry predicts the activation in the Raman spectrum of only the symmetric stretching of the triple bond. Accordingly, as shown in the third column of Table 1, only one very strong Raman peak at around 2260 cm^{-1}, whose intensity is in agreement with the large polarizability change associated with this vibration, is observed for all the monomers. The very strong Raman peaks of the polymer appear at noticeably lower frequencies relative to the monomer signals. The antisymmetric stretching mode which is predicted to be IR active is instead not observed probably due to the very small dipole moment change accompanying this vibration.

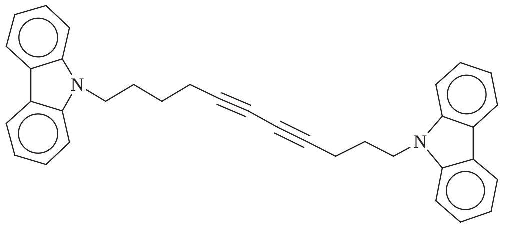
The removal of the inversion center of symmetry does not completely change these observations for those systems having the $R' = -CH_2X$ substituent. Indeed as shown in Table 2 for the **B1** and **B2** monomers, a strong Raman peak at 2253 cm^{-1} originated by the -C≡C- in-phase stretching is observed. In this case however, due to the asymmetry of the environment a breakdown of the selection rules occurs which leads to the observation in the IR of a very weak band originated by the same mode. For those systems characterized by the presence of a $-SiEt_3$ group directly bonded to the diacetylenic moiety, such as **B3** and **B4**, the symmetry is destroyed and both the in-phase and out-of-phase vibrational modes of the triple bonds become infrared and Raman active as shown in the same table. Notice first of all that none of these frequencies coincides with those previously observed. Moreover the intensity of the high frequency mode is strong in the Raman effect and weak in the infrared as expected for the in-phase vibration. In contrast, the intensity of the low frequency C≡C mode is medium in the infrared and medium or weak in the Raman effect. The high intensity of the IR band does not correspond to that expected



A1–A6



A7



A8

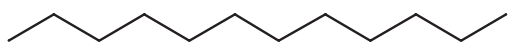
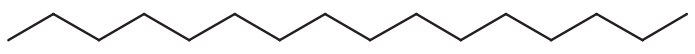
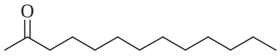
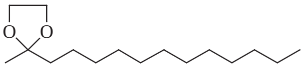
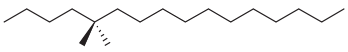
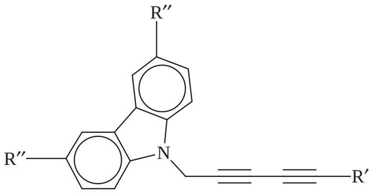
Sample	R″
A1	H
A2	
A3	
A4	
A5	
A6	

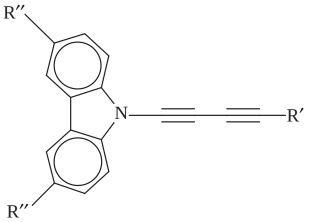
Fig. 1 Molecular structures of symmetrically substituted carbazolyl-diacetylenes having a carbazolyl group attached to the skeleton through one (**A1**–**A6**), three (**A7**) or four (**A8**) -CH_2- spacers.

for the out-of-phase vibration of the triple bond stretching. Usually this vibration is associated with a very small dipole moment change as shown by some literature data[2] and found by us in the monomer $CH_3(CH_2)_{11}C\equiv C–C\equiv C-(CH_2)_8COOH$,[6] whose C≡C vibrations give rise to a strong Raman peak at 2256 cm^{-1} and a weak IR band at 2178 cm^{-1}. The enhancement of the IR band can be ascribed to the influence of the -$SiEt_3$ group which strongly modifies the electronic properties of the diacetylenic system. The observed data seem to be consistent with a charge flux from the electron-donor -$SiEt_3$ group to the skeleton which is responsible for the creation of a strong oscillating dipole during the C≡C out-of-phase motion. We can discard any assignment of the weak lower energy peak to the polymer as all our attempts to polymerize these monomers failed.



Sample	R″	R′
B1	H	$(CH_2)_8COOH$
B2		$(CH_2)_8COOH$
B3	H	$SiEt_3$
B4		$SiEt_3$
B5	H	H
B6		H

Fig. 2 Molecular structures of different asymmetrical diacetylenes having the carbazolyl group attached to the skeleton through one -CH_2- spacer.



Sample	R″	R′
C1	H	CH_2OH
C2	H	CH_2OCOCH_3
C3	H	$CH_2OCOC_2H_5$
C4	H	$(CH_2)_8COOH$
C5	H	$CH_2OCONHCH_2COOC_2H_5$
C6	H	$(CH_2)_2OCONHCH_2COO(CH_2)_3CH_3$
C7	H	$CH_2OCONHCH_2CH_2COO(CH_2)_3CH_3$
C8	H	$CH_2OCONH(CH_2)_7COOC_2H_5$
C9	H	$CH_2OCONH(CH_2)_{17}COOC_2H_5$
C10		CH_2OH
C11	H	$SiEt_3$
C12		$SiEt_3$
C13	H	H
C14		H

Fig. 3 Molecular structures of different asymmetrical diacetylenes having the carbazolyl group directly attached to the skeleton.

In Table 2 are also reported the monomers **B5** and **B6** for which R′ = H. These monomers easily polymerize in the solid state. The vibrational frequencies of **B5** in the solid state could not be obtained because the monomer polymerizes during measurement as shown by the very strong Raman peak at 2115 cm^{-1}. A very weak peak could instead be observed for the **B6** monomer as well as the very strong polymer peak in the Raman spectrum at 2123 cm^{-1}. The frequency of this monomer is very close to the strongest Raman peaks of **B4**. We report this value in order to stress the importance of a correct assignment of reactive systems which easily polymerize or form byproducts.

Among the diacetylenes having the carbazolyl group directly attached to the diacetylenic systems (Fig. 3) the compounds from **C1** to **C10** present similar general features (Table 3). In all these monomers a very strong Raman band is observed in the 2235–2260 cm^{-1} range, which can be assigned to the in-phase C≡C stretching mode. The presence of a polymer phase is also evidenced by a strong Raman peak shifted to lower frequency. Notice that the intensity of the corresponding IR bands is here higher than expected for this type of vibration and observed for the monomers in Table 3. Moreover for all these systems

Table 1 Infrared and Raman frequencies of the monomers of group **A**. In the last column the polymer Raman frequencies are also reported

Sample	IR/cm^{-1}	Raman/cm^{-1}	Raman (polymer)/cm^{-1}
A1	—	2264vs	2084vs
A2	—	2265vs	2087vs
A3	—	2261vs	2091vs
A4	—	2263vs	2124vs
A5	—	2263vs	*a*
A6	—	2265vs	*a*
A7	—	2259vs	*a*
A8	—	2262vs	2080vs

[a] No polymerization occurs.

Table 2 Infrared and Raman frequencies of the monomers of group **B**. In the last column the polymer Raman frequencies are also reported

Sample	IR/cm^{-1}	Raman/cm^{-1}	Raman (polymer)/cm^{-1}
B1	2254vw	2253vs	*a*
B2	2254vw	2253vs	*a*
B3	2224vw; 2105m	2224vs; 2105w	*a*
B4	2224vw; 22107m	2217m; 2116m	*a*
B5	—	—	2115vs
B6	—	2217vvw	2123vs

[a] No polymerization occurs.

Table 3 Infrared and Raman frequencies of the monomers of group **C**. In the last column the polymer Raman frequencies are also reported

Sample	IR/cm^{-1}	Raman/cm^{-1}	Raman (polymer)/cm^{-1}
C1	2257m; 2169w	2258vs	2120vs
C2	2253m; 2179w	2252vs	2135vs
C3	2244m; 2176w	2249vs	2135vs
C4	2258w; 2169m	2259vs	*a*
C5	2234m; 2165w	2235vs	2127vs
C6	2254m; 2174m	2255vs	2114vs
C7	2247m; 2175w	2248vs	*a*
C8	2248m; 2178w	2247vs	2116vs
C9	2248m; 2177w	2245vs	2116vs
C10	2248m; 2172w	2245vs	2128vs
C11	2226ms; 2109mw; 2064w	2223s; 2110mw	*a*
C12	2224ms; 2100vvw; 2065w	2222vs; 2112mw	*a*
C13	2230ms; 2070vw	2229vs; 2061w	*a*
C14	2235ms; 2067vw	2236m; 2069w	2147vs

[a] No polymerization occurs.

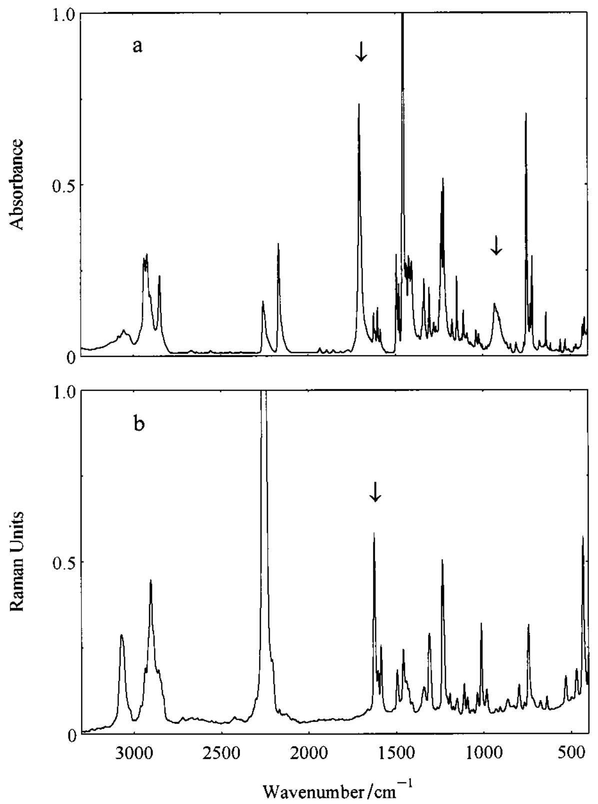


Fig. 4 Infrared (a) and Raman (b) spectra of **C4**. The arrows indicate: (a) infrared C=O stretching at 1705 cm^{-1} and OH out-of-plane vibration at 933 cm^{-1}; (b) Raman C=O stretching at 1624 cm^{-1}.

another medium or weak band around 2170 cm^{-1} is observed, most likely originated by the out-of-phase vibration of the triple bond. No corresponding band is observed in the Raman spectra.

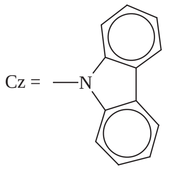
It can be stressed that a different behaviour is exhibited by the vibrations of the triple bonds when the carbazole ring is directly attached to the diacetylene moiety relative to that observed when at least one -CH$_2$- spacer separates the two groups. In the latter case (see **B1**, **B2** in Table 2) a very small dipole moment change and a very large polarizability variation are associated with the in-phase vibrational mode of the triple bond, in agreement with previous observations. In the former case the in-phase vibrations, which give rise to strong Raman peaks, show in the IR medium intensity bands. The peculiar enhancement of the IR band could be again ascribed to the formation of a charge on the diacetylene moiety due to its direct attachment to the carbazolyl ring. Quantum mechanical calculations on these different monomers could be of great help for a complete vibrational assignment of these molecules which is here presented at a qualitative level.

Another comment on Table 3 concerns the anomalous behaviour of the relative intensity of the infrared bands exhibited by sample **C4** with respect to the other cases. We believe this difference to be due to a different packing of this monomer which, unlike all the others, forms a centrosymmetric dimer of all the carboxylic groups. The dimer formation is established unambiguously on the basis of the following features observed in Fig. 4. The C=O asymmetric stretching of the carbonyl group is observed only in the IR spectrum at 1705 cm^{-1}, while the C=O symmetric stretching appears as a weak Raman band at 1624 cm^{-1}. Moreover the OH out-of-plane vibration gives rise at 933 cm^{-1} to an infrared band whose shape and position are characteristic of the dimer.[7,8] It seems clear that the dimer formation is responsible for a geometrical packing of the crystal different from those observed when the carbazolyl rings are assembled in stacked form. The crystal structure is known to affect to some extent the intensity of the vibrational bands.

From the above discussion the assignment of the frequencies of **C11** and **C12** is straightforward as the vibrational frequencies of these monomers behave as the homologous systems of Table 2. The observed coincidence in band positions of these different systems is quite surprising. Notice however that the intensities of both infrared and Raman bands are greatly influenced by the carbazolyl ring when it is directly attached to the diacetylenic backbone. Indeed the strong Raman peak around 2230 cm^{-1} observed for both **B3** and **C11** corresponds to a very weak (**B3**) and a strong (**C11**) IR band. Moreover the quite strong 2105 cm^{-1} IR band in **B3** becomes weak in **C11**. The same behaviour is found by comparing **B4** and **C12**. The third peak observed in **C11** and **C12** is probably due to a partial hydrolysis of the -SiEt$_3$ during the preparation of the sample for IR measurement. Indeed this band is coincident with the low frequency band of **C13** and **C14**. The presence of the high frequency band of the impurity cannot be detected because the high frequency peaks for all the last four monomers are

Table 4 Infrared and Raman frequencies of monoacetylenic compounds

Sample	IR/cm^{-1}	Raman/cm^{-1}
Cz–C≡C–H	2147ms	2147ms
Cz–CH$_2$C≡C–H	2119w	2119vs
SiEt$_3$–C≡C–H	2033ms	2033ms



coincident. This assignment is confirmed by the absence of these impurity peaks in the Raman effect as the sample preparation in this case is not affected by moisture. The vibrational assignment of **C13** and **C14** follows from that just discussed for **C11** and **C1**.

The vibrational assignment carried out in terms of the in-phase and out-of-phase modes can provide an overall picture of all the experimental data here presented. However, the assignment of the different bands to uncoupled C≡C stretchings as already proposed by us[9] seems to be uncorrect. Indeed as shown in Table 4 for a few compounds synthesized in our laboratory, the vibrational frequencies of single C≡C stretching bands are different from those of the diacetylenic monomers. However in the carbazolyl substituted acetylenes the relative intensity of the infrared to Raman bands follows the same trend observed in the corresponding diacetylenic monomers. The third system in Table 4 (SiEt$_3$–C≡C–H) shows lower frequencies with respect to Cz–C≡C–H but similar intensity behaviour.

In conclusion the vibrational properties of the triple bond in diacetylenic compounds are here reported for a large number of molecules. A qualitative assignment is proposed and the influence of the electronic properties of the substituents discussed. Since to our knowledge no complete assignment of the triple bond has been so far carried out even for very small molecules, the data here presented should stimulate interest in carrying out theoretical calculations which could provide a greater understanding of all the interesting properties of this class of compounds.

Experimental

In this paper we will report the synthesis of those diacetylenic monomers (**A5**, **A6**, **B3**, **B4**, **C11**, **C12**, **C13**) whose structure prevents their topochemical polymerization.[10] The synthesis of the other polymerizable monomers has been either published[9,11,12] or will be reported elsewhere along with their polymer properties.

Equipment

^{1}H NMR spectra were taken on a Varian Gemini 200 spectrometer, TMS was used as internal standard and chemical shifts are reported as δ values (ppm). J values are given in Hz.

Infrared spectra were obtained on a Bruker Fourier transform spectrometer (FTIR, IFS 66). Raman spectra were recorded with a Bruker FT spectrometer (FRS 100), working with a Nd : YAG laser ($\lambda_{\text{exc}} = 1064$ nm) and are reported without corrections for instrumental responses.

All the solid systems have been studied in their microcrystalline form as KBr pellets for IR and as powders for Raman measurements. Triethylsilyl compounds have been used in the liquid form for Raman and as thin films between KBr windows for IR measurements.

Materials

Petroleum ether refers to the fraction with the boiling range 40–60 °C. Column chromatographies were performed using Merck Kieselgel 60 silica gel. The solvents used as eluents were distilled before use. Tetrahydrofuran (THF) was distilled from sodium–benzophenone immediately prior to use. Pyridine was distilled prior to use from KOH pellets and then from CaH$_2$. Toluene-*p*-sulfonic acid monohydrate, tetrabutylammonium bromide, butyllithium 1.6 M solution in hexane, propargyl bromide (prop-2-yn-1-yl bromide), ethynyl(triethyl)silane were commercial products used as received. 3,6-Didodecanoyl-9*H*-carbazole,[11] the copper(I) salts of acetylenic derivatives[13] and bromoethynyl(triethyl)silane[14] were prepared according to literature methods.

Synthesis of intermediates and monomers

3,6-Bis[1,1-(ethylenedioxy)dodecyl]-9*H*-carbazole (I). A 100 ml two-necked flask was fitted with a magnetic stirring bar and a 10 ml water separator (fitted with molecular sieves and benzene) to which was attached a condenser topped with a silica gel tube. The flask was charged with 2 g (3.77 mmol) of 3,6-didodecanoyl-9*H*-carbazole, 50 ml of dry benzene, 4.67 g (4.20 ml, 75.3 mmol) of ethylene glycol and 0.04 g (0.21 mmol) of toluene-*p*-sulfonic acid monohydrate. Under vigorous stirring the solution was refluxed for 21 h. The mixture was cooled to room temperature, poured in a separating funnel and the ethylene glycol was separated. Successively the benzene solution was added with vigorous stirring to 80 ml of 10% aqueous sodium carbonate and extracted with ether. The organic phase was washed with 10% aqueous sodium carbonate, then with brine and finally dried over sodium sulfate. Removal of the solvent on a rotary evaporator provided about 2 g (92%) of a light cream-colored solid, mp 103–105 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (6 H, t), 1.21 (36 H, m), 2.0 (4 H, t), 3.75–4.15 (8 H, m), 7.38 (2 H, d), 7.51 (2 H, dd), 8.07 (2 H, s br), 8.18 (1 H, s br, NH). (Found: C, 77.41; H, 9.88; N, 2.23. $C_{40}H_{61}NO_4$ requires C, 77.50; H, 9.92; N, 2.26%).

***N*-propargyl-3,6-bis[1,1-(ethylenedioxy)dodecyl]-9*H*-carbazole (II).** A solution of **I** (1 g, 1.74 mmol), tetrabutylammonium bromide (0.032 g, 0.1 mmol) and 3-bromopropyne (0.4 ml of 80 wt% solution in toluene, 2.6 mmol) in toluene (35 ml) was treated with 50% NaOH (1.5 ml) and stirred vigorously at room temperature in an ultrasonic bath for 4 h. After addition of ether, the organic layer was separated, washed with water and dried over Na$_2$SO$_4$. Evaporation of the solvent gave a practically pure product which after crystallization from ethanol afforded 0.82 g (77%) of a white solid, mp 87.5–89.5 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (6 H, t), 1.21 (36 H, m), 2.0 (4 H, t), 2.27 (1 H, t, J 2.4), 3.75–4.15 (8 H, m), 5.04 (2 H, d, J 2.4), 7.44 (2 H, d), 7.59 (2 H, dd), 8.20 (2 H, s br). (Found: C, 78.55; H, 9.61; N, 2.22. $C_{43}H_{63}NO_4$ requires C, 78.49; H, 9.65; N, 2.19%).

1,6-Bis{3,6-bis[1,1-(ethylenedioxy)dodecyl]-9*H*-carbazolyl}-hexa-2,4-diyne (A5). To a solution of **II** (0.5 g, 0.81 mmol) in a 1 : 1 (v/v) mixture of methanol (20 ml) and dry pyridine (20 ml), anhydrous (MeCO$_2$)$_2$Cu (1.48 g, 8.1 mmol) was added and the mixture was heated under reflux for 2 h. The cooled mixture was poured into an excess of 4% HCl and extracted with ether. The combined extracts were washed with 4% HCl, water and dried (Na$_2$SO$_4$). After removal of the solvent, the residue was dissolved into cold dioxane and precipitated with ethanol to give 0.35 g (70%) of a white solid, mp 117–118 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (12 H, t), 1.25 (72 H, m), 1.97 (8 H, m), 3.75–4.1 (16 H, m), 5.04 (4 H, s), 7.33 (4 H, d), 7.54 (4 H, dd), 8.17 (4 H, br s). (Found: C, 78.68; H, 9.55; N, 2.11. $C_{86}H_{124}N_2O_8$ requires C, 78.61; H, 9.51; N, 2.13%).

3,6-Bis[(1-hydroxy-1-butyl)dodecyl]-9*H*-carbazole (III). To a solution of 2 g (3.76 mmol) of 3,6-didodecanoyl-9*H*-carbazole in dry THF (50 ml), 13.5 ml (16.95 mmol) of a 1.3 M solution of BuLi in hexane was added dropwise, under argon, at −10 °C and the mixture was stirred for 1 h at −10 °C. The reaction mixture was then poured into 200 ml of water and extracted with ether. Evaporation of the solvent gave 2.4 g (98%) of **III** as a brown oil. ^{1}H NMR (CDCl$_3$): δ 0.86 (12 H, m), 1.21 (44 H, m), 1.87 (8 H, m), 7.38 (4 H, m), 7.98 (1 H, br s, NH), 8.14 (2 H, br s). (Found: C, 81.64; H, 11.30; N, 2.10. $C_{44}H_{73}NO_2$ requires C, 81.55; H, 11.35; N, 2.16%).

3,6-Bis(1-butyldodecyl)-9*H*-carbazole (IV). A solution of 2.4 g (3.7 mmol) of **III** and 0.065 g (0.37 mmol) of toluene-*p*-sulfonic acid monohydrate in toluene (15 ml) was heated at 50 °C for 7 h. The toluene solution was then washed with water, dried and evaporated. The residue was purified by filtration on a short silica gel column using a mixture of petroleum ether: dichloromethane (1:3) as eluent, yielding 1.92 g (84%) of a yellow oil. The oil obtained (1.92 g, 3.14 mmol) dissolved in dichloromethane was reduced by shaking for 7 h with hydrogen in the presence of palladium 10% on carbon. After filtration, the solution was evaporated to give 1.81 g (93%) of an oil. The product obtained was purified by chromatography on a silica gel column using a mixture of petroleum ether: dichloromethane (4:1) as eluent. Obtained 1.57 g (81%) of pure product. ^{1}H NMR (CDCl$_3$): δ 0.84 (12 H, m), 1.21 (44 H, m), 1.66 (8 H, m), 2.61 (2 H, m), 7.17 (2 H, dd), 7.32 (2 H, d), 7.80 (2 H, br s), 7.85 (1 H, br s, NH). (Found: C, 85.70; H, 11.89; N, 2.23. $C_{44}H_{73}N$ requires C, 85.78; H, 11.94; N, 2.27%).

***N*-Propargyl-3,6-bis(1-butyldodecyl)-9*H*-carbazole (V).** A procedure similar to that described for **II** was used to prepare **V** starting from **IV** and 3-bromopropyne. The crude oil obtained (yield 96%) was purified by chromatography on a silica gel column with a mixture of petroleum ether: dichloromethane (4:1) as eluent. ^{1}H NMR (CDCl$_3$): δ 0.84 (12 H, m), 1.21 (44 H, m), 1.66 (8 H, m), 2.25 (1 H, t, *J* 2.4), 2.62 (2 H, m), 5.0 (2 H, d, *J* 2.4), 7.24 (2 H, dd), 7.37 (2 H, d), 7.83 (2 H, br s). (Found: C, 86.22; H, 11.51; N, 2.08. $C_{47}H_{75}N$ requires C, 86.30; H, 11.56; N, 2.14%).

1,6-Bis[3,6-bis(1-butyldodecyl)-9*H*-carbazol-9-yl]hexa-2,4-diyne (A6). A procedure similar to that described for **A5** was used to prepare **A6** starting from **V**. The crude product obtained (yield 94%) was purified by chromatography on a silica gel column with a mixture of petroleum ether: dichloromethane (6:1) as eluent. ^{1}H NMR (CDCl$_3$): δ 0.84 (24 H, m), 1.22 (88 H, m), 1.65 (16 H, m), 2.61 (4 H, m), 5.0 (4 H, s), 7.19–7.30 (8 H, m), 7.80 (4 H, br s). (Found: C, 86.36; H, 11.39; N, 2.11. $C_{94}H_{148}N_2$ requires C, 86.43; H, 11.42; N, 2.14%).

***N*-[5-(Triethylsilyl)penta-2,4-diynyl]-9*H*-carbazole (B3).** The copper(I) salt of *N*-propargyl-9*H*-carbazole (1.3 g, 0.048 mol), suspended in pyridine (20 ml), was thoroughly purged with argon, and then a solution of bromoethynyl(triethyl)silane (1 g, 0.048 mol) in pyridine (5 ml) was added dropwise, maintaining the temperature at 55 °C. The solution obtained was then poured into iced HCl 12 M and extracted with ether. The ether layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a dark oil. The pure product was isolated by chromatography on a silica gel column using a mixture of petroleum ether: dichloromethane (4:1) as eluent. Obtained 0.98 g (59%) of a yellow solid melting at 88–89 °C. ^{1}H NMR (CDCl$_3$): δ 0.57 (6 H, q), 0.94 (9 H, t), 5.1 (2 H, s), 7.27 (2 H, m), 7.49 (4 H, m), 8.1 (2 H, d). (Found: C, 80.38; H, 7.36; N, 4.10. $C_{23}H_{25}NSi$ requires C, 80.41; H, 7.34; N, 4.08%).

***N*-[5-(Triethylsilyl)penta-2,4-diynyl]-3,6-didodecyl-9*H*-carbazole (B4).** A procedure similar to that described for **B3** was employed to prepare **B4**, starting from the copper(I) salt of 3,6-didodecyl-*N*-propargyl-9*H*-carbazole (1.65 mmol) and bromoethynyl(triethyl)silane (1.65 mmol). Obtained 1.04 mmol (63%) of **B4** as a yellow oil. ^{1}H NMR (CDCl$_3$): δ 0.56 (6 H, q, *J* 3.3), 0.82–0.98 (15 H, m), 1.25 (36 H, m), 1.70 (4 H, m), 2.77 (4 H, t, *J* 7.7), 5.1 (2 H, s), 7.26 (2 H, br s), 7.30 (2 H, br s), 7.86 (2 H, br s). (Found: C, 83.04; H, 10.80; N, 2.01. $C_{47}H_{73}NSi$ requires C, 82.99; H, 10.82; N, 2.06%).

***N*-[4-(Triethylsilyl)buta-1,3-diynyl]-9*H*-carbazole (C11).** This compound was prepared with a procedure similar to that described for **B3**, starting from the copper(I) salt of *N*-ethynyl carbazole (2.65 g, 10.4 mmol) and bromoethynyl(triethyl)silane (2.28 g, 10.4 mmol). After chromatography on a silica gel column using a mixture of petroleum ether: dichloromethane (4:1) as eluent, 2.42 g (70%) of a yellow oil was obtained. ^{1}H NMR (CDCl$_3$): δ 0.68 (6 H, q), 1.03 (9 H, t), 7.35 (2 H, t), 7.51 (2 H, t), 7.70 (2 H, d), 8.0 (2 H, d). (Found: C, 80.13; H, 6.98; N, 4.28. $C_{22}H_{23}NSi$ requires C, 80.19; H, 7.04; N, 4.25%).

***N*-[4-(Triethylsilyl)buta-1,3-diynyl]-3,6-didodecyl-9*H*-carbazole (C12).** This compound was prepared with a procedure similar to that described for **B3**, starting from the copper(I) salt of 3,6-didodecyl-*N*-ethynyl-9*H*-carbazole (4.4 mmol) and bromoethynyl(triethyl)silane (4.4 mmol). After chromatography on a silica gel column using a mixture of petroleum ether: dichloromethane (2:1) as eluent, 3.46 mmol (79%) of a yellow oil was obtained. ^{1}H NMR (CDCl$_3$): δ 0.68 (6 H, q), 0.84–1.06 (15 H, m), 1.25 (36 H, m), 1.70 (4 H, m), 2.75 (4 H, t, *J* 7.7), 7.28 (2 H, dd, *J* 0.7 and 4.1), 7.56 (2 H, d, *J* 4.47), 7.76 (2 H, br s). (Found: C, 82.88; H, 10.69; N, 2.08. $C_{46}H_{71}NSi$ requires C, 82.94; H, 10.74; N, 2.10%).

***N*-(Buta-1,3-diynyl)-9*H*-carbazole (C13).** A solution of **C11** (1.8 g, 5.45 mmol) in a mixture of MeOH (15 ml) and dioxane (10 ml) was thermostatted at 25 °C and aqueous 5 M NaOH (3.5 ml) was added. After 5 min the mixture was acidified with 2 M HCl and the solid precipitated was filtered off. Obtained 1 g (78%) of a solid which, on heating, decomposes at about 100 °C. After crystallization from benzene 100–130 °C 0.82 g of a white solid was obtained. ^{1}H NMR (CDCl$_3$): δ 2.70 (1 H, s), 7.37 (2 H, t), 7.52 (2 H, t), 7.69 (2 H, d), 8.0 (2 H, d). (Found: C, 89.32; H, 4.24; N, 6.46. $C_{16}H_9N$ requires C, 89.28; H, 4.21; N, 6.51%).

Acknowledgements

This work was supported by the Italian Ministry of University and Scientific and Technological Research (MURST) and by the National Research Council (CNR).

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Paper 8/04011G