(Q^0) by transformation 31, where m designates the mth atom.

$$Q'_{im} = \sum_{\mu} Q_{\mu m}{}^{0}(\lambda_{im}{}^{2}/N_{i}{}^{2}) \tag{31}$$

Alternatively, as is done in the present work, one can take the charges Q' from quantum mechanical calculations of the relevant isolated fragments.

The EVB Hamiltonian for the gas-phase reaction is now given by eq 32, where E_i are the energies of the mixed states. The Hamiltonian for the solution reaction is given by eq 33. In the

$$\bar{\mathrm{H}}^{\mathrm{g}} = \begin{pmatrix} E_1{}^{\mathrm{g}} & \bar{H}_{12}{}^{\mathrm{g}} & 0 \\ \bar{H}_{12}{}^{\mathrm{g}} & E_2{}^{\mathrm{g}} & \bar{H}_{23}{}^{\mathrm{g}} \\ 0 & \bar{H}_{23}{}^{\mathrm{g}} & E_3{}^{\mathrm{g}} \end{pmatrix} \tag{32}$$

$$\bar{\mathrm{H}}^{\mathrm{w}} = \begin{pmatrix} E_1{}^{\mathrm{g}} + G_{\mathrm{sol}}^{(1)} & \bar{H}_{12}{}^{\mathrm{g}} & 0 \\ \bar{H}_{12}{}^{\mathrm{g}} & E_2{}^{\mathrm{g}} + G_{\mathrm{sol}}^{(2)} & \bar{H}_{23}{}^{\mathrm{g}} \\ 0 & \bar{H}_{23}{}^{\mathrm{g}} & E_3{}^{\mathrm{g}} + G_{\mathrm{sol}}^{(3)} \end{pmatrix} \tag{33}$$

present approximation we do not introduce the solvent effects in the off-diagonal elements. In this way the ground-state energies obtained by solving the Hamiltonian of the pure states and the restricted Hamiltonian of eq 33 are slightly different. However, since we parametrize the restricted Hamiltonian by choosing the α_i from solution reactions (eq 9), we can use it as a reliable tool for comparing reactions in solutions and in enzymes.

Registry No. L-His, 71-00-1; L-Asp, 56-84-8; L-Ser, 56-45-1; trypsin, 9002-07-7; serine proteinase, 37259-58-8.

Synthesis, Crystal Structure, and Absorption Spectroscopy of a Carbazole–Dinitrofluorene Bichromophore. Identity of Ground-State Molecular Interactions in the Single Crystal and Aggregates in Solution

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Abstract: The synthesis, crystal structure, conformational analysis, and absorption spectroscopy of the bichromophore 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) are reported. The torsion angles within the propyl part of the molecule correspond to a gauche–trans–gauche–gauche conformation while the dinitrofluorene and the carbazole groups of atoms are nearly planar and are at 25.6° from each other. The observed conformational behavior has been analyzed with the aid of a conformational analysis program based on empirical methods, and a good agreement between calculated and crystallographic minima has been found. It is shown by the comparison of spectra in polar and nonpolar solvents that no ground-state intramolecular interaction takes place in the bichromophore. All observed spectroscopic changes are due to solute–solute intermolecular interactions or to solute–solvent intermolecular interactions. It is clearly shown that the 2,7-dinitrofluorene chromophore is responsible for all of these interactions. A new band appearing at 370 nm in a solution of the bichromophore **1** in 3-methylpentane at high concentrations or at low temperatures is assigned to aggregates by comparison with the spectrum of a single crystal. Furthermore, single-crystal data allow evaluation of the energetics of the ground and first excited electronic states of the crystal. The exciton splitting is calculated as being 887 cm^{-1}, but this is the sum of the dipole–dipole interactions along with the charge-resonance interactions in the first excited singlet state which is mainly responsible for the 2380-cm^{-1} bathochromic shift observed in comparing the spectrum of the free molecule with that of the crystal.

The chemistry, spectroscopy, and structural analysis of bichromophoric compounds[1] continue to stimulate much interest in view of the fundamental objectives being pursued. Some recent examples range from elucidating the mechanism of photochemical reactions,[2-5] of electronic energy transfer,[6-9] or of electron transfer[10-13] to eventually establishing the structure and spatial arrangement of interacting chromophores in the ground and excited states.[14,15]

It is clear that the acquisition of basic knowledge concerning these systems can accelerate the solution of important fundamental problems such as the mechanism of the respiratory chain and the photosynthetic process[11] as well as favor the development of photoconducting polymers[16] and molecular electronics.[12,17]

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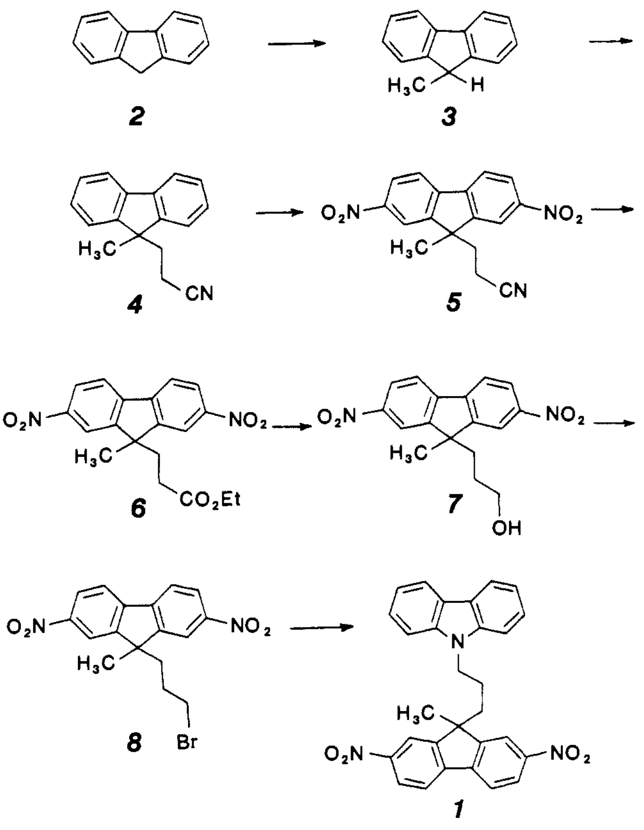
Scheme I



Our interest in the field of bichromophores is aimed at the generation of donor–acceptor (D–A) bichromophoric monomer models designed for the eventual development of photoconducting polymers. In the present paper we wish to report on the synthesis, the absorption spectroscopy, the conformational analysis, and the X-ray crystal structure of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**). This first new D–A bichromophore to be generated in the series is based on the well-known carbazole chromophore as donor which has yielded some of the best photoconducting polymers[18] in the form of acceptor-doped poly(vinylcarbazoles) (PVK). As acceptor, we chose the polynitrofluorene system with the 9-position (on both chromophores) as the point of attachment of a trimethylene chain widely recognized as a favorable link group between two chromophores.[1,3,7,14,15,19] Finally, because of the well-known reactivity of benzylic type hydrogens in photochemical and radical type reactions, the remaining 9-position of the fluorenyl moiety was protected by a methyl group.

Results and Discussion

Synthesis of the D–A Bichromophore 1. As represented in Scheme I, synthesis of the title compound **1** was achieved in a straightforward manner starting from fluorene (**2**). In a first step, the anion of fluorene (**2**) was treated with methyl iodide to yield 72% of 9-methylfluorene (**3**). Introduction of the three-carbon link was then achieved via cyanoethylation of **3** to give 72% of the cyanoethyl derivative **4** which was nitrated at this stage of the sequence, because of the stability of the cyano group to the nitrating conditions, to yield 85% of the corresponding dinitro derivative **5**. The rest of the sequence then involved manipulation of the nitrile group to a bromomethyl group for displacement by the carbazole anion. Thus, ethanolysis of the dinitro cyanoethyl compound **5** gave the dinitro ethyl ester **6** in a 65% yield which was reduced to the dinitro alcohol **7** in a 62% yield by the calcium chloride–sodium borohydride couple. Finally, substitution of the primary hydroxyl of **7** for bromine was carried out very efficiently by the triphenylphosphine–carbon tetrabromide couple to yield 95% of the desired bromopropyl derivative **8**. The latter was then condensed with the sodium anion of carbazole to give 96% of the desired bichromophoric compound **1**.

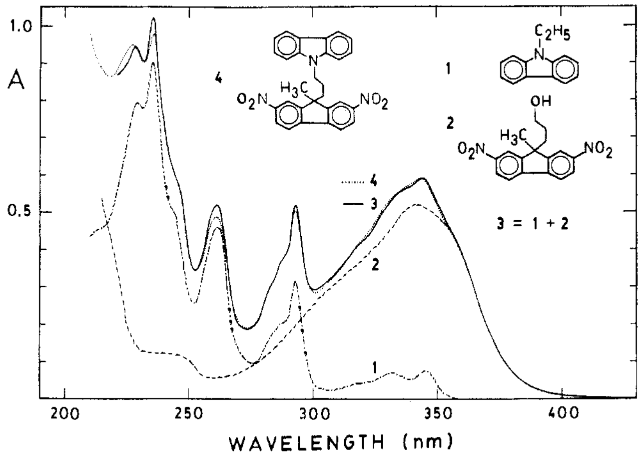


Figure 1. Electronic absorption spectra of *N*-ethylcarbazole = 1, $c = 2 \times 10^{-5}$ M, $l = 1$ cm; 9-(γ-hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) = 2, $c = 1 \times 10^{-5}$ M, $l = 1$ cm; $A \times 2$; sum of the absorption spectra 1 and 2 (=3) and electronic absorption spectrum of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) = 4, $c = 2 \times 10^{-5}$ M, $l = 1$ cm in acetonitrile.

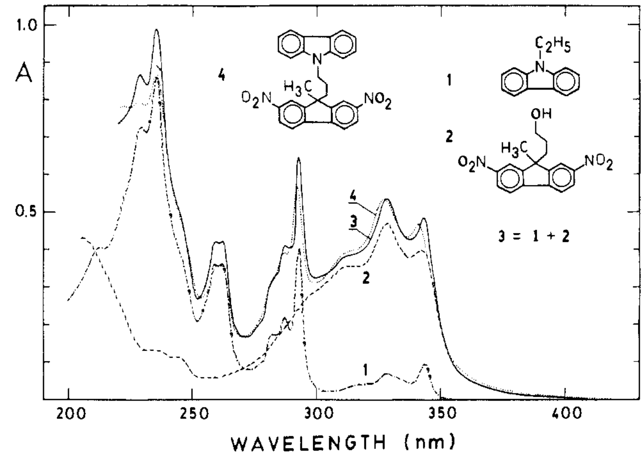


Figure 2. Electronic absorption spectra of *N*-ethylcarbazole = 1, $c = 2 \times 10^{-5}$ M, $l = 1$ cm; 9-(γ-hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) = 2, $c = 2 \times 10^{-6}$ M, $l = 10$ cm; sum of the absorption spectra 1 and 2 (=3) and electronic absorption spectrum of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) = 4, $c = 1 \times 10^{-6}$ M, $l = 10$ cm, $A \times 2$ in 3-methylpentane.

Spectroscopic Investigation. One of the primary conditions to be met by photoconducting materials is that they be good insulators in the dark but good conductors upon illumination with light of the appropriate wavelength, i.e., that they not electronically interact in the ground state but that they give electron transfer upon excitation. It was therefore encouraging to observe that, in spite of the excellent electron-donating properties of carbazole and its substituted derivatives,[20] the expected good acceptor properties

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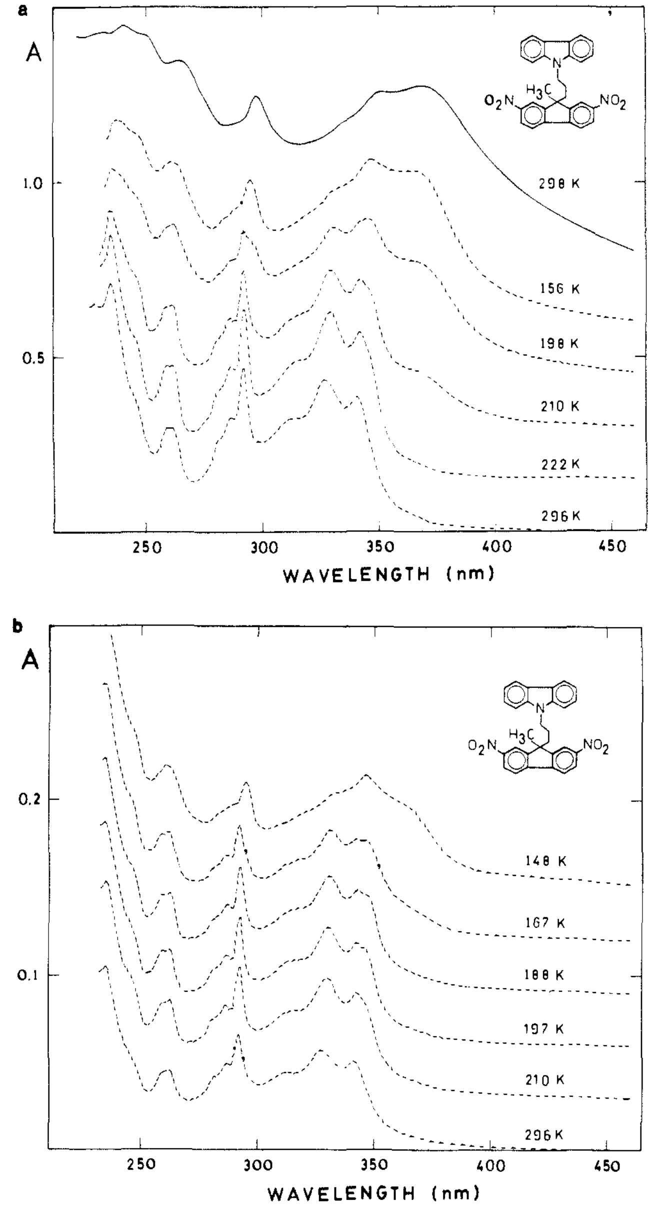


Figure 3. (a, top) Changes in the electronic absorption spectrum of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) (1.2×10^{-5} M) in 3-methylpentane when temperature decreases. The solid line shows the absorption spectrum of the compound in the solid state. (b, bottom) Changes in the electronic absorption spectrum of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) (1.6×10^{-6} M) in 3-methylpentane when temperature decreases. (l = 1.4 cm.)

of dinitrofluorene,[21] and the favorable length of the link chain,[1,3,7,14,15,19] no ground-state interaction takes place between the chromophores.

This has been shown by comparison of the sum of the absorption spectra of 9-(γ-hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) and *N*-ethylcarbazole with the absorption spectrum of the bichromophore **1** in polar and nonpolar solvents at room temperature (see Figures 1 and 2).

The electronic absorption spectrum of the bichromophoric compound **1** in acetonitrile is the exact superposition of the absorption spectra of the two chromophores, carbazolyl and 2,7-dinitrofluorenyl. In 3-methylpentane however, one can observe a small difference in the solvent effect on the absorption spectra of the two chromophores in the bichromophoric compound **1** and the chromophores in the separated molecules. The shape of the

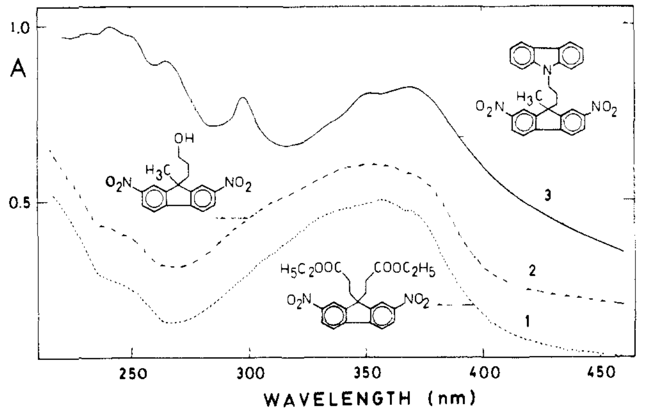
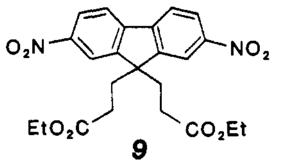


Figure 4. Electronic absorption spectra of 9,9-bis(β-carbethoxyethyl)-2,7-dinitrofluorene (**9**) (1), 9-(γ-hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) (2), and 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) (3) in the solid state.

absorption spectrum of the bichromophoric compound **1** in 3-methylpentane at 1.2×10^{-5} M remains the same when the concentration of the solution is decreased at room temperature. On the other hand, marked changes in the absorption spectrum of this compound are observed when the temperature of the solution is decreased (see Figure 3a,b). A new absorption band at 365 nm appears and increases in intensity, shifting to 370 nm as the temperature of the solution decreases. These changes in the absorption spectrum depend also on the concentration of the solution studied. As a matter of fact, at a concentration of 1.6×10^{-6} M the same behavior in terms of temperature effect is observed except that the new band appears at lower temperatures, which is typical for a solute–solute interaction phenomenon. This fact is even more emphasized in the solid-state spectrum where the band at 370 nm is at its maximum.

On the other hand, *N*-ethylcarbazole in the solid state does not exhibit any characteristic absorption in the range of 360–380 nm while the dinitro alcohol **7** in the solid state possesses a broad absorption band with the characteristic shoulder at 375 nm. In order to verify that this behavior was due to the dinitrofluorenyl moiety and not to the nature of the side chain functionality, the solid-state spectrum of the dinitro diester **9**[22] was recorded. Figure 4 shows that it also possesses a broad absorption band with a shoulder at 375 nm. These results therefore show that the new absorption of the bichromophoric compound **1** in 3-methylpentane at low temperature and the absorption of the bichromophoric compound **1** in solid state are due to the intermolecular interaction taking place between 2,7-dinitrofluorene chromophores. It is further apparent that in 3-methylpentane (3MP) solution, the decrease in temperature is likely to cause a gradual aggregation of the molecules of the bichromophoric compound **1** due to the low solubility of this compound in a nonpolar solvent like 3MP. Furthermore, since the new absorption band (365–375 nm) appeared both in the solid and in solution at lower temperatures, it became interesting to attempt to probe the structure of these aggregates via the crystal structure of the bichromophore **1** in order to look for the suspected dinitrofluorene chromophore interactions. This was done, and the results of the X-ray crystal structure of bichromophore **1** are reported and discussed below.



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Before proceeding to the X-ray investigation the results of the variable-temperature absorption spectroscopy of the above series of compounds in acetonitrile will be presented.

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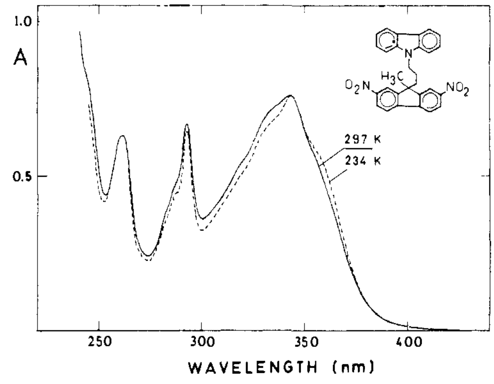

Figure 5. Electronic absorption spectra of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) (2 × 10^{-5} M) in acetonitrile at 297 (—) and at 234 K (---). (l = 1.4 cm.)

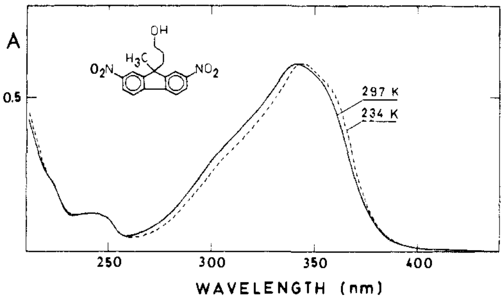

Figure 6. Electronic absorption spectra of 9-(γ-hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) (2 × 10^{-5} M) in acetonitrile at 297 (—) and at 234 K, normalized (---). (l = 1.4 cm.)

Figure 5 shows the absorption spectra of the bichromophoric compound **1** (2 × 10^{-5} M) in acetonitrile at room temperature (297 K) and at 234 K, close to the freezing point of the solvent. The temperature decrease of the solution causes a small but apparent modification in the shape of the absorption band of this compound. The same behavior is also observed for a 1.5 × 10^{-6} M solution. In order to provide an explanation for this behavior, we also measured the absorption spectra of *N*-ethylcarbazole (2 × 10^{-5} M) and the dinitro alcohol **7** (2 × 10^{-5} M) in acetonitrile at the same temperatures. It turned out that while the absorption spectrum of *N*-ethylcarbazole does not change with the temperature decrease of the solution, the absorption band of the dinitro alcohol **7** undergoes a red shift of about 130 cm^{-1} when the temperature decreases (see Figure 6). Moreover, the absorption spectrum of the latter in acetonitrile does not change when the concentration of the solution is varied between 2 × 10^{-4} and 2 × 10^{-6} M. The above results therefore lead us to conclude that the observed changes in the absorption band of the bichromophoric compound **1** in acetonitrile are closely related to the increase in the solute–solvent interaction when the temperature is lowered (i.e., increase in the dipole–dipole interaction between the dinitrofluorenyl moiety of the bichromophoric compound **1** and the solvent). In conclusion, the absorption spectroscopy has clearly shown that (1) no intramolecular interaction exists between the carbazolyl and the 2,7-dinitrofluorenyl groups in the electronic ground state of the bichromophoric compound **1** and (2) solute–solute (in nonpolar solvent and in the crystal) and solute–solvent (in polar solvent) interactions allow us to explain the complete behavior of the electronic absorption spectra. In both cases, the 2,7-dinitrofluorenyl moiety in the bichromoric compound **1** is responsible for the interactions which take place.

X-ray Crystallographic Investigation. As indicated above, it became interesting to attempt to probe the structure of the aggregates via the crystal structure of bichromophore **1** in order to look for the suspected dinitrofluorene chromophore interactions.

The atomic positional coordinates of compound **1** and their standard deviations are listed in Table I while the atomic numbering adopted is shown on a schematic diagram of the molecule in Figure 7. There are no unusual features among the bond distances and angles of this structure. The standard deviations of the interatomic bond distances and angles for the non-hydrogen atoms are 0.006 Å and 0.4°, respectively, and 0.03 Å for the bond distances involving the hydrogen atoms.

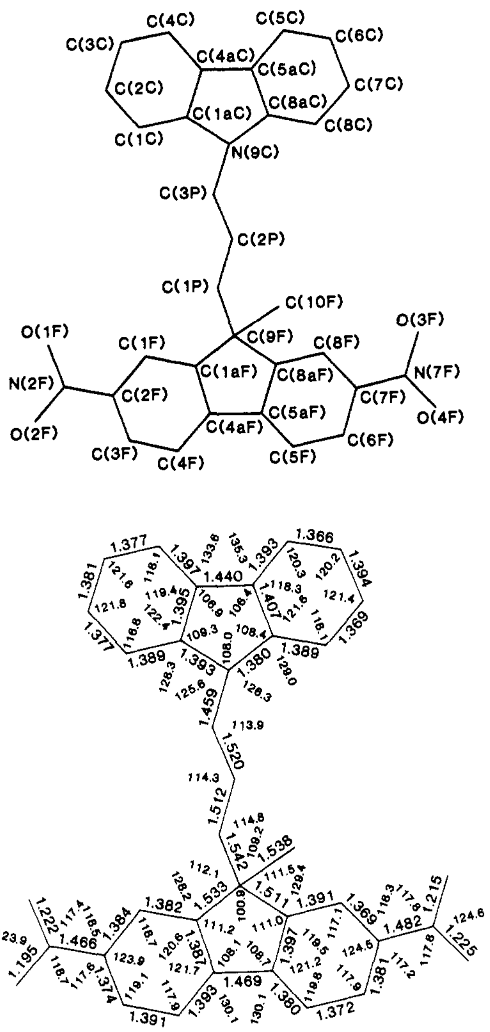

Figure 7. Schematic diagram of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) showing the atomic numbering and the bond distances and angles.

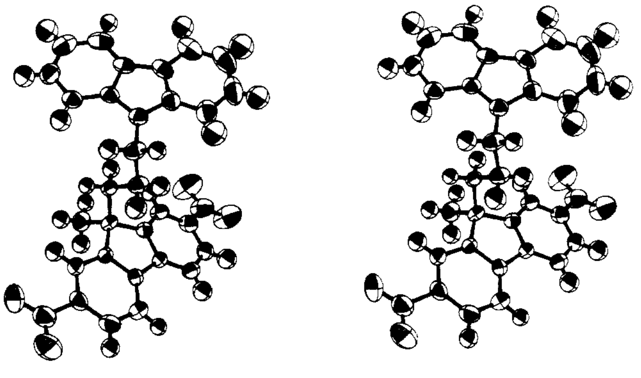

Figure 8. Stereopair showing the molecular conformation of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**).

Description of the Structure. A stereoscopic pair showing the molecular structure of bichromophore **1** and its thermal ellipsoids is shown in Figure 8. By design, the molecule is constituted of two nearly planar groups, the fluorene (plane F) and the carbazole planes (plane C) linked by a trimethylene chain. A least-squares plane calculation showed that the atoms C(1aF), C(4aF), C(5aF), C(8aF), C(4F), C(5F), C(6F), C(8F), and C(9F) which constitute plane F do not deviate from the best plane by more than 4σ. There is a similar deviation of the atoms of the carbazole group [C(1aC),

Table I. Fractional Atomic Coordinates and Their esd's ($\times 10^4$) and U_{eq} (Å^2, $\times 10^3$)

atom	*x*	*y*	*z*	U_{eq}
O(1F)	9860 (3)	-1289 (3)	6109 (2)	1272
O(2F)	9756 (4)	-2493 (3)	5131 (2)	1328
O(3F)	3742 (3)	608 (3)	332 (2)	929
O(4F)	3455 (3)	2116 (3)	914 (2)	1063
N(2F)	9508 (3)	-1647 (4)	5382 (2)	844
N(7F)	3929 (3)	1266 (3)	912 (2)	721
C(1aF)	7619 (3)	-733 (3)	3417 (2)	386
C(4aF)	7220 (3)	182 (3)	3742 (2)	370
C(5aF)	6351 (3)	602 (3)	3068 (2)	368
C(8aF)	6248 (3)	-51 (3)	2330 (2)	356
C(1F)	8395 (3)	-1341 (3)	3939 (3)	488
C(2F)	8745 (3)	-986 (4)	4786 (3)	547
C(3F)	8397 (3)	-61 (4)	5114 (3)	562
C(4F)	7609 (3)	543 (4)	4588 (3)	524
C(5F)	5681 (3)	1466 (3)	3092 (3)	497
C(6F)	4900 (3)	1697 (4)	2379 (3)	549
C(7F)	4814 (3)	1039 (4)	1658 (3)	502
C(8F)	5458 (3)	173 (3)	1604 (3)	454
C(9F)	7067 (3)	-942 (3)	2469 (2)	388
C(10F)	6512 (4)	-2035 (4)	2380 (3)	593
C(1P)	7870 (3)	-876 (3)	1827 (2)	396
C(2P)	8485 (3)	159 (3)	1853 (3)	524
C(3P)	9128 (4)	292 (3)	1118 (3)	524
N(9C)	9987 (3)	-491 (3)	1132 (2)	466
C(1aC)	11014 (3)	-438 (4)	1648 (3)	531
C(4aC)	11632 (3)	-1294 (4)	1449 (3)	553
C(5aC)	10960 (3)	-1895 (3)	772 (3)	488
C(8aC)	9955 (3)	-1371 (3)	598 (3)	441
C(1C)	11424 (4)	327 (4)	2263 (3)	754
C(2C)	12480 (5)	201 (5)	2680 (3)	970
C(3C)	13105 (4)	-642 (5)	2495 (3)	971
C(4C)	12701 (4)	-1400 (4)	1884 (3)	781
C(5C)	11091 (4)	-2811 (4)	299 (3)	701
C(6C)	10259 (4)	-3183 (4)	-316 (3)	740
C(7C)	9281 (4)	-2633 (4)	-492 (3)	637
C(8C)	9112 (3)	-1738 (4)	-35 (3)	511

Table II. Torsion Angles Describing the Conformation between the Fluorenyl and the Carbazolyl Groups of Atoms

δ_1	C(1aF)–C(9F)–C(1P)–C(2P)	-55.9 (4)°
Φ	C(9F)–C(1P)–C(2P)–C(3P)	-170.1 (3)°
Ψ	C(1P)–C(2P)–C(3P)–N(9C)	-63.1 (5)°
δ_2	C(2P)–C(3P)–N(9C)–C(1aC)	-82.2 (5)°

C(4aC), C(5aC), C(8aC), and C(1C) through C(8C)] from their least-squares plane (plane C). The dihedral angle between plane F and plane C has a value of 25.6°. The NO_2 groups are planar but tilted with respect to the fluorene plane by 10.5° and 10.7°, respectively.

The torsion angles which characterize the conformation of the propyl part of the molecule are given in Table II. They indicate a gauche–trans–gauche–gauche conformation from the dinitrofluorenyl part of the molecule to the carbazolyl fragment.

Conformational Analysis. The conformational behavior of bichromophore **1** is described by the Φ,Ψ map of Figure 9. The main feature revealed by the Φ,Ψ map is the drastic restriction imposed on the conformational angle Φ. Its value remains close to 180° (trans conformation). This is due to the severe steric interactions between the rigid fluorenyl and carbazolyl fragments. The pair of δ_1 and δ_2 torsion angles have been kept constant, to values of -60° and -80°, respectively, in order to prevent important steric clashes between the nitro and methyl groups of the dinitrofluorenyl and the carbazolyl fragments. The Ψ angle has the largest conformational freedom, as shown by the three distinct regions of low energy centered around the values of -60°, 180°, and 60°. The absolute energy minimum has been found at $\Phi = -172.0°$ and $\Psi = 59°$. The next lowest minimum calculated at ($\Phi = -170°$ and $\Psi = -60°$) is quite close to the crystallographic conformation ($\Phi = -170.1°$ and $\Psi = -63.1°$). These minima have energies which are respectively 0.40 and 0.48 kcal mol^{-1} higher than the energy of the absolute minimum. Finally, the third minimum is calculated at ($\Phi = -170.0°$ and $\Psi = 180°$) and is in a higher domain of accessibility, 1.1 kcal mol^{-1} above the absolute minimum.

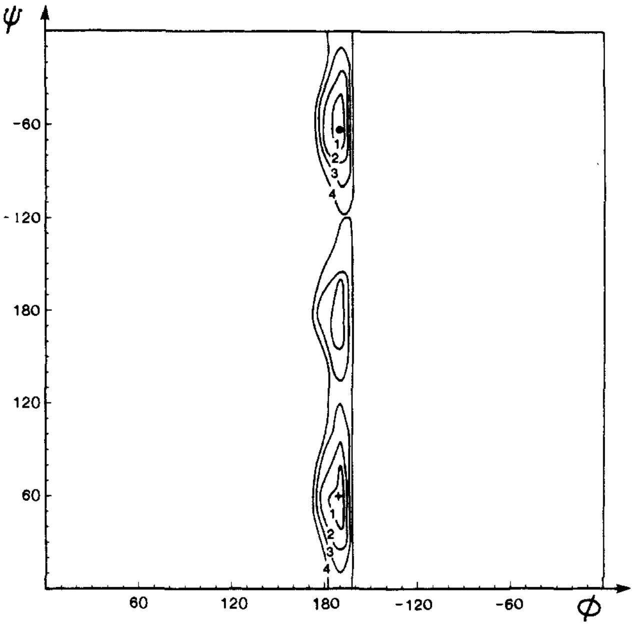

Figure 9. Energy diagram computed for 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**). The black dot indicates the observed crystallographic conformation, whereas the cross refers to the calculated absolute minimum.

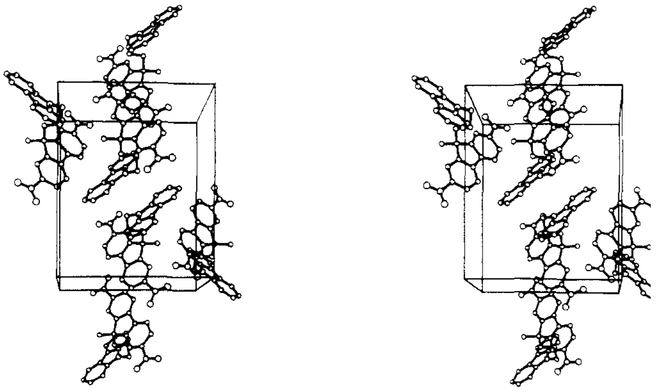

Figure 10. Packing of the molecules. The *b* axis is horizontal; the *c* axis is vertical.

It is, therefore, gratifying to observe that the minimum-energy conformations obtained by a calculation based solely on van der Waals interactions are almost identical with those found in the crystal, which means that there are no important attractive interactions between the donor part and the acceptor part of the bichromophore. This result then confirms nicely one of the conclusions reached in the spectroscopic study to the effect that "no intramolecular interaction exists between the carbazolyl and the 2,7-dinitrofluorenyl groups in the electronic ground state of the bichromophoric compound **1**".

Molecular Packing. The packing of the molecules in the unit cell is shown in Figure 10. The molecules display an antiparallel arrangement. The cohesion of the system is only maintained through van der Waals forces. The carbazole planes of two centrosymmetrically related molecules are parallel to each other and separated by 3.8 Å, a value too high for stacking effects between the groups concerned. On the other hand, the distance separating the least-squares planes of two centrosymmetrically related fluorene moieties is only 3.30 Å. As is revealed in Figure 11, the overlap observed involves only small fractions of the fluorene moieties, but nevertheless it is sufficient to cause a major perturbation in the electronic absorption spectrum of the solid.

Origin of the Bathochromic Shift in the Electronic Absorption Spectrum of the Crystal and the Aggregates in Solution. Once

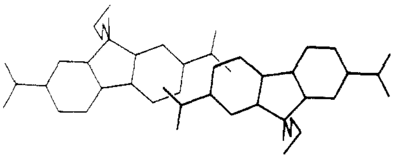

Figure 11. Projection of two centrosymmetrically related dinitrofluorenyl moieties showing the weak overlap of these rings.

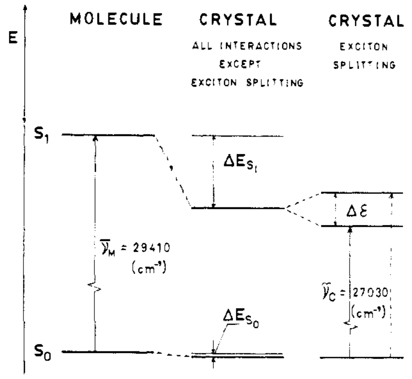

Figure 12. Term diagram of the monomer and the crystal of 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**). The arrows indicate observed transitions. The broken line indicates the forbidden transition in the displaced molecular system.

the positioning of the molecules in the crystal has been established, the molecular exciton model[23] can be applied in order to evaluate the ground- and excited-state molecular interactions. Figure 12 shows an energy-level diagram where three contributions remain unknown once the frequency of the lower energy branch of the crystal has been obtained experimentally. It is well-known that for a coplanar inclined transition dipole (see Figure 11), the higher energy branch of the crystal is forbidden for an angle θ evaluated to be less than 54.7°.[24] On the other hand, the exciton band splitting in this case is given by

$$\Delta\epsilon = (2|M|^2/R^3)(1 - 3\cos^2\theta)$$

where M is the magnitude of the transition dipole moment, R is the distance between the centers of the moments, and θ is the angle between the direction of the moments and the line connecting the centers of the moments. The first electronic transition in the dinitrofluorenes studied here corresponds mainly to the $^1L_a \leftarrow {}^1A$ transition polarized along the long axis of the molecules with a small possible contribution of the $^1L_b \leftarrow {}^1A$ transition mixed in the absorption band at 340 nm in solution. The solution spectrum has been used to evaluate the magnitude of the transition dipole moment of the individual molecules, and a value of 5.99 D has been obtained from the spectrum; R and θ have been evaluated from the crystallographic data. By use of the assumption that the transition dipoles extend throughout the entire length of the molecules, R and θ have been calculated from molecular center to center and equal 8.6 Å and 22.5°, respectively. With these parameters in the equation for $\Delta\epsilon$, an exciton splitting ($\Delta\epsilon$) of 887 cm^{-1} is obtained. The magnitude of this exciton splitting is much too low to explain the bathochromic shift (2380 cm^{-1}) observed from the isolated molecule to the crystal.

Some other kind of interactions are taking place in the crystals. Dipole–dipole interactions in the ground and excited states and charge resonance in the excited state are expected to contribute to the red shift. The dipolar interaction is maximum when the interacting molecules in the aggregate or crystal are antiparallel to each other with some lone-pair electron clouds approximately on top of each other. On the other hand, the charge resonance is probably negligible in the case of $\pi\pi^*$ excitation because of the very small overlap between the π system of the molecules in the crystal. By use of the point dipole–point dipole approximation,[25] the stabilization energy of the ground state is approximately defined as

$$\Delta E_{S_0} = \mu^2/R_3$$

where R is the distance between the molecular dipoles in the crystal and μ is the permanent dipole moment, which is not known experimentally for this dinitrofluorene chromophore but can be evaluated on the basis of the sum of vectors by using the bond lengths in Figure 7 and the permanent dipole moment of nitrobenzene, which is 4.22 D.[26] A value of μ = 1.70 D has been calculated, and these dipoles are aligned along the short axis of the molecules and separated by R = 8.6 Å. The stabilization energy of the ground state of the crystal using the point dipole–point dipole approximation is only 23 cm^{-1}. When the crystal is excited, it is well-known that the dipole–dipole interaction term in general changes. To this term we must also add the contribution of the charge-resonance term. The sum of these interactions can also be evaluated from Figure 12 to be

$$\Delta E_{S_1} = \bar{\nu}_M - \bar{\nu}_C + \Delta E_{S_0} - \tfrac{1}{2}\Delta\epsilon$$

$$\Delta E_{S_1} = 1960 \text{ cm}^{-1}$$

In view of the above considerations it is then concluded that the electronic absorption red shift observed from the free molecule to the crystal is mainly explained by the stabilization of the first excited singlet state through dipole–dipole interactions and also by a 25% contribution of the exciton splitting. It also follows that this conclusion equally applies to the solution spectra in 3-methylpentane at high concentrations or at low temperatures where dimers or aggregates are in equilibrium with the monomer species. This also means that the arrangement of the molecules in these small agglomerates is the same as that in the single crystal.

Further work is in progress on a variety of other bichromophores and will be reported in due course.

Experimental Section

Synthetic Investigation. Melting points were determined on a Büchi apparatus and are uncorrected. Infrared spectra were taken in KBr pellets (unless otherwise specified) on a Perkin-Elmer Model 710-B apparatus using the 1601-cm^{-1} band of polystyrene as reference. High-resolution mass spectra (CI) were recorded on an AEI MS-902 apparatus. The ^{1}H NMR spectra were determined in deuteriochloroform ($CDCl_3$) (unless otherwise indicated) on a Bruker WH-90 (90-MHz) spectrometer; the chemical shifts are expressed in parts per million (ppm), downfield from tetramethylsilane (Me_4Si) used as internal standard. The symbols s, d, t, q, and m are respectively used for singlet, doublet, triplet, quartet, and multiplet. Thin-layer chromatography (TLC) analyses were done on Merck, 0.2-mm, silica gel 60 F_{254} aluminum sheets and were visualized with UV light. Column chromatography was carried out on Baker, 60–200 mesh, silica gel (for precolumns) and on Merck 60, 230–400 mesh, silica gel (for flash chromatography). Microanalytical data were obtained from Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Spectroscopic Investigation. Materials. *N*-Ethylcarbazole (99%) was obtained from Aldrich Chemical Co. and was further recrystallized 3 times in pure ethanol. 9-(γ-Hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) and 9-(γ-(*N*-carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**) were synthesized, purified, and characterized as below. See ref 22 for the synthesis, purification, and characterization of 9,9-bis(β-carbethoxyethyl)-2,7-dinitrofluorene (**9**).

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Table III. Crystal Data of Interest for 9(γ-(*N*-Carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (**1**)

formula	$C_{29}H_{23}N_3O_4$
M_r	477.1689
mp, °C	260–262
unit cell	monoclinic
space group	$P2_1/n$
a, Å	12.557 (5)
b, Å	12.594 (5)
c, Å	15.254 (3)
β, deg	100.30 (2)
V, Å^3	2415.45
d_o, g cm^{-3}	1.32 (1)
d_c, g cm^{-3}	1.314
Z	4
λ(Mo K$\bar{\alpha}$), Å	0.71069
μ(Mo Kα), cm^{-1}	0.829
F(000)	1000

3-Methylpentane (3MP), pure grade (99%) from Phillips Petroleum Co., was further purified by refluxing with concentrated sulfuric acid (4 mL of H_2SO_4/1000 mL of 3MP) for 24 h. The acid was removed by washing with distilled water, and the solvent was then refluxed over sodium for 4 h and then distilled twice before use. Acetonitrile, 99%, spectrophotometric grade, was obtained from Aldrich Chemical Co. and was distilled before use.

Apparatus. Absorption spectra were recorded on a Cary 17 spectrophotometer using 0.1-, 1.0-, and 10-cm quartz cells. Quartz plates were used to obtain the absorption spectra of solids. The low-temperature Dewar was designed and built in our laboratory. The mixture of propionitrile–*n*-butyronitrile (1:1 v/v) cooled by liquid nitrogen was used to stabilize the temperature in the range 297–148 K of the solutions studied. The temperature of the solutions and the solvent were measured in the cell with a calibrated copper–constantan thermocouple with an accuracy of 0.5 K.

X-ray Investigation. Crystals of the bichromophore **1** were obtained from dioxane–water. They are in the shape of very thin yellow–orange platelets. The experimental density was measured by flotation in a $ZnCl_2$ aqueous solution. The unit-cell dimensions, given in Table III with other crystallographic data of interest, were obtained by a least-squares fit to the settings of 25 well-centered reflections in the range $12° < 2\theta < 23°$. Intensity data were collected from a crystal of dimensions 0.02 × 0.20 × 0.40 mm on a Nonius CAD4 diffractometer using the Mo K$\bar{\alpha}$ graphite-monochromatized radiation. The $\omega/2\theta$ scan mode was used with a scan width defined by $\Delta\omega = (1.00 + 0.14 \tan \theta)°$. The intensities were measured for all reflections within the two octants *hkl* and $hk\bar{l}$ limited by $2\theta_{max} = 45°$ and $0 < h < 13$, $0 < k < 13$, and $-16 < l < 16$. The intensities of four standard reflections, monitored every hour, decreased by less than 1% of their initial values over the duration of the data collection. The orientation of the crystal was verified every 100 measurements, and readjustment was made when needed. The data reduction including scaling and Lorentz and polarization corrections was performed in the usual way.[37] The absorption correction was judged unnecessary since the absorption coefficient has a small value for the Mo radiation.

Of the 3148 independent reflections collected, 1686 (54%) were declared observed since they have a net intensity greater than $1.90\sigma(I)$. The structure was solved by application of MULTAN using all *E*'s ≥ 1.55. The *E* map, computed for the set of phases corresponding to the highest combined figure of merit, revealed all the non-hydrogen atoms. The atomic coordinates and individual isotropic temperature factors were refined with unit weights by full-matrix least squares. After transformation to anisotropic temperature factors the refinement was continued by the block-diagonal approximation. All the H atoms were located on a Fourier-difference synthesis and were included in the weighted least-squares refinement with individual isotropic temperature factors.

Each reflection was assigned a weight $w = 1/\sigma^2(F_o)$. The final agreement indices were $R^{38} = 0.052$, $R_w = 0.045$, and $S = 1.202$. The average and largest parameter shifts of the atomic coordinates were 0.07σ and 0.25σ, respectively. A final difference Fourier synthesis showed no significant residual electron density, the extreme fluctuations being in the range −0.18 to 0.17 e Å^{-3}. The X-ray scattering factors were taken from ref 31 for O, N, and C atoms and from ref 32 for H atoms.

Conformational Analysis Investigation. The potential energy was calculated by including the partitioned contributions arising from the van der Waals interactions within the molecule and the torsional contributions of the two main torsion angles of the propyl chain: Φ = C(9F)–C(1P)–C(2P)–C(3P) and Ψ = C(1P)–C(2P)–C(3P)–N(9C). (See Figure 7 for the atomic numbering adopted for this molecule.) All other contributions to the energy have been omitted from this calculation. The van der Waals interactions were evaluated by using the 6–12 Lennard-Jones potential functions, with the parameters of ref 33. A three-fold intrinsic torsional potential was used for the rotations around C(1P)–C(2P) and C(2P)–C(3P) bonds with barrier heights of 1.25 kcal mol^{-1} according to ref 34. The crystal structure coordinates were taken as the basis for the molecular description. The energy maps were computed, by using a modified version of the PHIPSI program,[35] as a function of Φ and Ψ at 10° intervals. Isoenergy contours were drawn by 1 kcal mol^{-1} increments from the lowest energy minimum which was arbitrarily set at 0. The 4 kcal mol^{-1} contour was selected as the outer limit.

Synthesis of 9-(γ-(*N*-Carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (1). 9-Methylfluorene (3). A solution of fluorene (**2**) (10.0 g, 0.060 mol) in dry THF (200 mL) is treated, under argon and at −78 °C, with a 1.5 M solution of *n*-butyllithium in THF (40 mL, 0.060 mol) over a 45-min period. After the addition, the temperature is allowed to rise to room temperature and stirring pursued for 1 h. The mixture is then cooled to −78 °C and treated over a 45-min period with a solution of methyl iodide [8.50 g (3.72 mL), 0.060 mol] in THF (10 mL). The temperature is then allowed to rise to room temperature and the mixture stirred for 12 h. The red solution obtained is neutralized with 10% HCl and the THF evaporated in vacuo.

Extraction of the aqueous phase with $CHCl_3$ (3 × 10 mL) yields after the usual treatment a brown oil which crystallizes. Distillation in vacuo yields a slightly yellowish solid (7.58 g, 72%), homogeneous on TLC (30% ethyl acetate–70% hexane): bp 92 °C/0.75 mmHg [lit.[36] bp 142 °C/8 mmHg]; mp 44–45 °C [lit.[36] mp 43–45 °C]; IR 1480, 1600, 2880, 2930, 2990, 3040, and 3060 cm^{-1}; NMR δ 1.51 (d, 3 H), 3.90 (q, 1 H), and 7.20–7.80 (m, 8 H); mass spectrum, exact mass calcd for $C_{14}H_{12}$ 180.0939, found 180.0895.

9-(β-Cyanoethyl)-9-methylfluorene (4). A solution of 9-methylfluorene (**3**) (5.5 g, 0.030 mol) in dioxane (25.6 mL) is treated under argon with a 40% aqueous solution of Triton B (0.18 g, 0.44 mol). The resulting solution is then treated over a 30-min period with a solution of acrylonitrile (distilled over P_2O_5; (2.07 g, 0.039 mol) in dioxane (5 mL); the temperature of the reaction mixture is maintained between 30 and 40 °C throughout the addition period. The orange solution thus obtained is then stirred at room temperature for 12 h.

The yellow solution is neutralized with 10% HCl and the yellow product precipitated by the addition of distilled water (35 mL). Recrystallization from 95% ethanol yields white crystals (5.1 g, 72%), homogeneous on TLC (15% ethyl acetate–85% hexane): mp 102–103 °C; IR 1480, 1600, 2250, 2860, 2940, 2960, 3050, and 3060 cm^{-1}; NMR δ 1.36–1.53 (m, 5 H), 2.42 (t, broadened, 2 H), and 7.35–7.75 (m, 8 H); mass spectrum, exact mass calcd for $C_{17}H_{15}N$ 233.1206, found 233.1218.

9-(β-Cyanoethyl)-9-methyl-2,7-dinitrofluorene (5). A solution of 9-(β-cyanoethyl)-9-methylfluorene (**4**) (3.0 g, 0.013 mol) in acetic anhydride (8.7 mL) is cooled to −40 °C and treated dropwise with fuming nitric acid (11.5 mL) over a 30-min period, with care being taken to ensure that the temperature of the solution does not exceed −10 °C. Throughout the addition, a yellow precipitate is formed which persists during the 2 h that the reaction mixture is allowed to stir and warm up to room temperature.

The yellow solid is filtered and washed with distilled water, which causes more yellow solid to precipitate in the filtrate; however, TLC analysis (30% ethyl acetate–70% hexane) of both solids reveals that the solid in the filtrate, which melts at 190–192 °C, is a mixture of four products while that which was originally isolated on the filter melts at 228–229 °C and is almost pure. Flash chromatography of the latter (15% ethyl acetate–85% hexane) yields a pure-yellow solid (3.5 g, 85%), homogeneous on TLC (30% ethyl acetate–70% hexane): mp 228–229 °C; IR 1360, 1540, 1480, 1630, 2250, 2900, 2950, 3000, 3050, and 3110

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(38) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w\Delta F^2/\sum wF_o^2]^{1/2}$, $S = [\sum w\Delta F^2/(m - n)]^{1/2}$.

cm^{-1}; NMR δ 1.69–1.74 (m, 5 H), 2.95 (t, broadened, 2 H), and 7.94–8.45 (m, 6 H); mass spectrum, exact mass calcd for $C_{17}H_{13}N_3O_4$ 323.1736, found 323.0903.

9-(β-Carbethoxyethyl)-9-methyl-2,7-dinitrofluorene (6). A solution of 9-(β-cyanoethyl)-9-methyl-2,7-dinitrofluorene (**5**) (4.0 g, 0.012 mol) in absolute ethanol (220 mL) is treated with concentrated sulfuric acid (66 mL) and the resulting reaction mixture heated to reflux for 24 h on an oil bath at 150 °C. The yellow solution is then allowed to cool to room temperature, and the yellow solid which precipitates is filtered out and recrystallized from 95% ethanol to yield yellow crystals (2.9 g, 65%), homogeneous on TLC (25% ethyl acetate–75% hexane): mp 158–159 °C; IR 1360, 1540, 1470, 1490, 1600, 1740, 2880, 2950, and 3010 cm^{-1}; NMR δ 1.12 (t, 3 H), 1.50–1.68 (m, 5 H), 2.54 (t, broadened, 2 H), 3.93 (q, 2 H), and 7.90–8.42 (m, 6 H); mass spectrum exact mass calcd for $C_{19}H_{18}N_2O_6$ 370.1165, found 370.1147.

9-(γ-Hydroxypropyl)-9-methyl-2,7-dinitrofluorene (7). A solution of 9-(β-carbethoxyethyl)-9-methyl-2,7-dinitrofluorene (**6**) (0.2 g, 0.17 mmol) in THF (2.0 mL) is treated, at 0 °C and under argon, with calcium chloride (0.06 g, 0.54 mmol) and sodium borohydride (0.08 g, 2.16 mmol). The mixture is then allowed to warm to room temperature and kept stirring for 20 h. The green reaction mixture is cooled to 0 °C and the reaction quenched with 1.2 mL of distilled water and 0.2 mL of concentrated HCl. The orange THF solution is evaporated and the aqueous phase extracted with chloroform. Treatment of the organic phase in the usual manner yields an orange solid which is flash chromatographed (15% ethyl acetate–85% hexane) and then recrystallized from methanol to yield yellow crystals (0.12 g, 62%), homogeneous on TLC (40% ethyl acetate–60% hexane): mp 204–205 °C; IR 1360, 1540, 2875, 2950, 3000, and 3200–3500 cm^{-1}; NMR (Me_2SO-d_6–$CDCl_3$, 35:65%) δ 0.71–0.96 (m, 2 H), 1.50 (s, 1 H), 1.63 (s, 3 H), 2.15–2.33 (m, 2 H), 3.16–3.34 (t, broadened, 2 H), and 7.95–8.37 (m, 6 H); mass spectrum, exact mass calcd for $C_{17}H_{16}N_2O_5$ 328.1059, found 328.1076.

9-(γ-Bromopropyl)-9-methyl-2,7-dinitrofluorene (8). A solution of 9-(γ-hydroxypropyl)-9-methyl-2,7-dinitrofluorene (**7**) (0.2 g, 0.61 mmol) in anhydrous THF (2 mL) is treated with triphenylphosphine (0.31 g, 1.18 mmol) and carbon tetrabromide (0.39 g, 1.18 mmol). The solution is stirred for 30 min and then directly flash chromatographed (20% ethyl acetate–80% hexane) to yield a yellow solid which is recrystallized from benzene again to yield yellow crystals (0.226 g, 95%), homogeneous on TLC (25% ethyl acetate–75% hexane): mp 184–185°C; IR 1330, 1510, 1480, 1580, 2850, 2900, 2950, and 3050 cm^{-1}; NMR δ 1.05–1.25 (m, 2 H), 1.63 (s, 3 H), 2.23–2.39 (m, 2 H), 3.16 (t, 2 H), and 7.90–8.42 (m, 6 H); mass spectrum, exact mass calcd for $C_{17}H_{15}N_2O_4Br$ 392.0196, found 392.0188.

9-(γ-(*N*-Carbazolyl)propyl)-9-methyl-2,7-dinitrofluorene (1). Under an argon atmosphere, a suspension composed of 60% sodium hydride (0.015 g, 0.38 mmol) and carbazole (0.020 g, 0.12 mmol) in anhydrous THF (2 mL) is stirred at room temperature for 15 min, heated to reflux for 30 min, and then cooled to room temperature.

The resulting carbazole anion solution is treated over a 5-min period with 9-(γ-bromopropyl)-9-methyl-2,7-dinitrofluorene (**8**) (0.051 g, 0.13 mmol) in anhydrous THF (1 mL). The green reaction mixture is heated to reflux for 18 h, during which it turns brown. The cooled mixture is quenched with distilled water (2 mL) and the THF evaporated in vacuo. The residue is taken up with distilled water (6 mL) and chloroform (10 mL) and the resulting aqueous phase extracted with chloroform (2 × 10 mL). The chloroform extract is treated in the usual manner to yield a crude solid which is recrystallized from dioxane–water to give yellow crystals (0.055 g, 96%), homogeneous on TLC (25% ethyl acetate–75% hexane): mp 260–262 °C; IR 1340, 1510, 1480, 1590, 2850, 2925, and 3050 cm^{-1}; NMR δ 1.06–1.25 (m, 2 H), 1.46 (s, 3 H), 2.04–2.20 (m, 2 H), 4.08 (t, 2 H), and 6.98–7.41 and 7.79–8.30 (2 m, 14 H); mass spectrum, exact mass calcd for $C_{29}H_{23}N_3O_4$ 477.1689, found 477.1703. Anal. Calcd for $C_{29}H_{23}N_3O_4$: C, 72.94; H, 4.85; N, 8.80. Found: C, 72.76; H, 4.51; N, 8.53.

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Registry No. 1, 103851-64-5; **2**, 86-73-7; **3**, 2523-37-7; **4**, 103851-65-6; **5**, 103851-66-7; **6**, 103851-67-8; **7**, 103851-68-9; **8**, 103851-69-0; **9**, 103851-70-3; CH_2=CHCN, 107-13-1; carbazole, 86-74-8; 9-ethylcarbazole, 86-28-2.

Supplementary Material Available: Bond distances and angles, tables of H atom atomic positions, and anisotropic thermal parameters of all non-H atoms (4 pages); tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.