Intramolecular charge-transfer fluorescence as a mobility probe in poly(methylmethacrylate)

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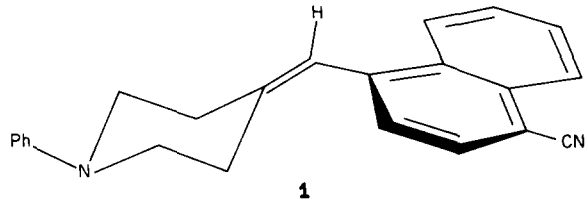
The (time-resolved) fluorescence spectra of 1-phenyl-4-(4-cyano-1-naphthylmethylene)piperidine (1) have been measured during the polymerization of methylmethacrylate (MMA). It was found that the fluorescence maximum of 1 shows a large hypsochromic shift as polymerization of the MMA medium progresses. While the emission maximum is located at 565 nm in the monomer, it is found at 450±5 nm in the polymer (PMMA). The polarization of the fluorescence increases strongly during the polymerization, indicating that the rotational motion of 1 ceases on the timescale of the fluorescence lifetime (about 10 ns). Fluorescence measurements performed with a detection time delay with respect to the exciting laser pulse showed that within the time range 0–100 ns the molecule 1 undergoes reorientation and/or internal relaxation even in a PMMA matrix; a red shift of the emission with time occurs, together with a decrease of the degree of fluorescence polarization.

(Keywords: fluorescence; time-resolved; charge-transfer; polarization; mobility probe; polymerization probe)

INTRODUCTION

In a recent publication[1] it was reported that 1-phenyl-4-(4-cyano-1-naphthylmethylene)piperidine (1) displays strong intramolecular charge-transfer fluorescence.



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Ultra-violet excitation ($\lambda < 365$ nm) of 1 produces a highly polar excited state for which a dipole moment of 25 (±2)D was estimated[1]. Evidently, complete photoinduced, intramolecular electron transfer from the anilino moiety towards the 1-vinyl-4-cyano-naphthalene chromophore takes place across the interconnecting saturated framework that separates the electron-donating and -accepting moieties. While such rapid electron transfer across saturated spacers has now been established in many cases[2,3], the behaviour of 1 is rather special because the depopulation of the dipolar, excited charge-transfer (CT) state occurs largely via radiative decay to the ground state. The maximum of the corresponding intense CT fluorescence was found[1] to be shifted strongly towards longer wavelengths with increasing solvent polarity, thus making 1 a solvent polarity probe of unprecedented sensitivity.

The above-mentioned red shift exhibited by 1 in polar solvents is largely due to the interaction energy connected with the reorientation[4,5] of the surrounding solvent molecules with respect to the CT excited state of 1. Therefore, it might be expected that the maximum of the CT fluorescence of 1 depends not only upon the polarity but also upon the mobility of the medium. If this mobility is sufficiently low to prevent dipole–dipole relaxation on the timescale of the CT state's lifetime, the red shift will be less pronounced; the solvatochromic effect of 1 is thus expected to be dependent on the viscosity of the (solvent) matrix too.

To investigate the dependence of the red shift of 1 as a function of the mobility (viscosity), compound 1 was dissolved in methylmethacrylate (MMA) and its emission spectrum was recorded as a function of the polymerization time. Simultaneously the polarization of the emitted radiation was measured to gain insight into the rotational and/or conformational mobility of 1 in the (P)MMA matrix. Further, in (solid) PMMA the fluorescence wavelength was determined as a function of temperature.

In addition, time-resolved fluorescence and fluorescence polarization measurements were performed to investigate the dynamics of the processes following excitation of 1 in a (P)MMA matrix.

EXPERIMENTAL

Compound 1 was available from our previous studies[1]; the other chemicals were obtained commercially.

Basically, two types of measurements have been carried

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out for recording the emission features:

(i) Continuous (monochromatic) excitation and scanning wavelength detection (further referred to as continuous spectra).

(ii) Pulsed monochromatic excitation followed by time-resolved multiwavelength emission and polarization measurements (further referred to as time-gated spectra).

For the continuous measurements a SPEX Fluorolog 2 spectrofluorimeter was used in a configuration which applies a double monochromator to select the excitation wavelength (310 nm, bandwidth 10 nm) from a 150 W xenon lamp light source. The resulting fluorescence was detected at right angles or in front-face geometry, depending on the dimensions of the sample, by scanning of the single detection monochromator and counting the output pulses of a Hamamatsu R928 photomultiplier attached to the exit slit. Spectra were corrected for the wavelength-dependent sensitivity of the detection system to represent relative intensities in quanta/wavelength interval.

For the pulsed experiments the frequency-tripled output of a Q-switched Nd:YAG laser (354.5 nm) was used. The emission detection was performed using a gated optical multichannel analyser (E.G. & G.Par OMA III) whose detection time-gate (width 5 ns) has been synchronized to the exciting laser pulse. The selectable wavelength range that can be detected simultaneously by the multichannel system spans about 450 nm. A variable delay between the linearly polarized laser pulse and the detection gate (0–250 ns) permitted time-dependent fluorescence measurements; by placing a polarization analyser in front of the spectrometer, the polarization ratio of the emitted radiation was determined.

The temperature-dependent spectra were taken with the sample placed in an electrically heated miniature furnace equipped with a light entrance and exit facility or in a liquid-nitrogen-cooled cryostat.

Samples to be polymerized thermally were prepared by dissolving **1** (about 10^{-4} M) in MMA in a fused silica cuvette or ampoule without the addition of initiators and were deoxygenated by purging with argon before sealing. In addition thin-film samples of **1** in prepolymerized PMMA (Aldrich) were prepared by codissolving these in dichloromethane and allowing the solvent to evaporate after spreading a few drops of this solution on a glass substrate. The emission spectrum of these samples (obtained under front-face excitation) was identical to that of the bulk polymerized samples.

RESULTS AND DISCUSSION

Variation of the probe fluorescence during bulk polymerization of the matrix

The continuous fluorescence spectrum of **1** in freshly distilled MMA is displayed in *Figure 1* (curve A) while relevant photophysical data for **1** in this and several other solvent media are compiled in *Table 1*. The emission maximum in MMA (565 nm) compares well with that observed previously[1] in a solvent of comparable polarity such as ethylacetate (573 nm).

The MMA solution was then cured at 85°C which took about 15 h. During this time the sample was removed from the oven at regular intervals to measure its emission spectrum at room temperature. A very large hypsochromic shift (> 100 nm) was found to occur (see *Figure 1*), accompanied by an increase of the fluorescence quantum yield.

The procedure was repeated (see *Figure 2*) using the time-gated multichannel system. A similar hypsochromic shift and increase of fluorescence quantum yield was observed accompanied by an increase of the fluorescence lifetime (see *Table 1*). In this case also the degree of fluorescence polarization was measured, which serves as a measure[6,7] for the rotational mobility of the probe molecules in the surrounding matrix on the relevant timescale. Both the emission maxima and the fluorescence polarization in *Figure 2* refer to detection with 'zero' time delay, which means that the 5 ns wide detection window coincides with the maximum of the 10 ns long exciting laser pulse. The MMA sample used in this experiment had

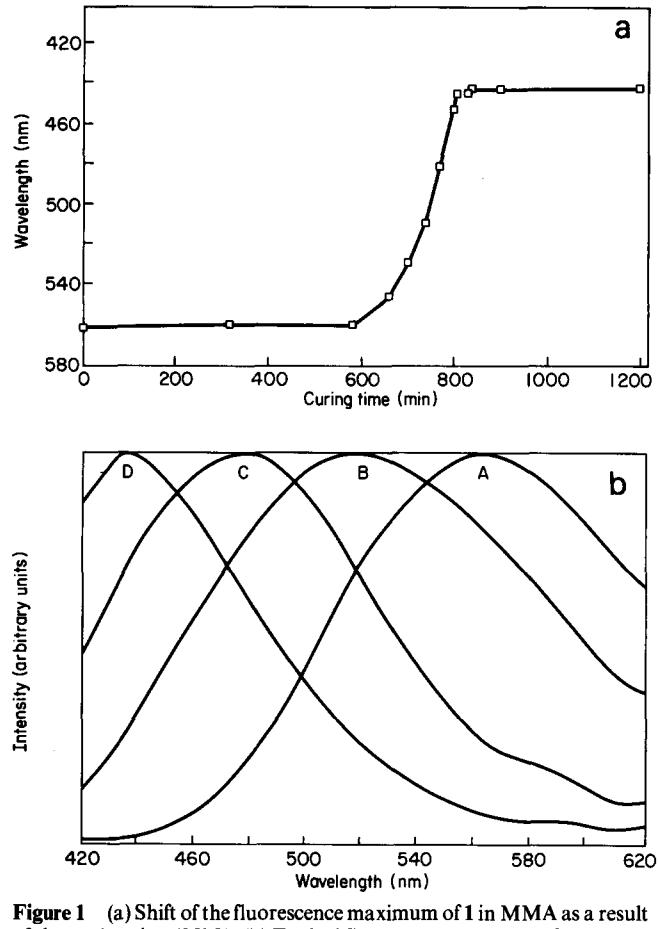

Figure 1 (a) Shift of the fluorescence maximum of **1** in MMA as a result of thermal curing (85°C). (b) Typical fluorescence spectra at four stages of polymerization: curve A, freshly distilled MMA; B, after 720 min; C, after 770 min; and D, after 1200 min. All spectra were recorded in continuous mode at 20°C

Table 1 Fluorescence data for **1** in various media

Medium	Temp. (K)	λ_{max} (nm)	τ (ns)[a]	ϕ[c]	Ref.
Ethyl acetate	293	573	6	0.11	1
Di-n-butyl ether	293	468	12	0.60	1
Methylmethacrylate	293	565	7.8	0.19	this work
PMMA	293	450[d]	10.8	0.66	this work
PMMA	433	480[d]	–[b]	–[b]	this work
PMMA	110	430[d]	–[b]	–[b]	this work

[a] Fluorescence lifetime
[b] Not determined
[c] Fluorescence quantum yield
[d] Average values (±5 nm) for several PMMA samples

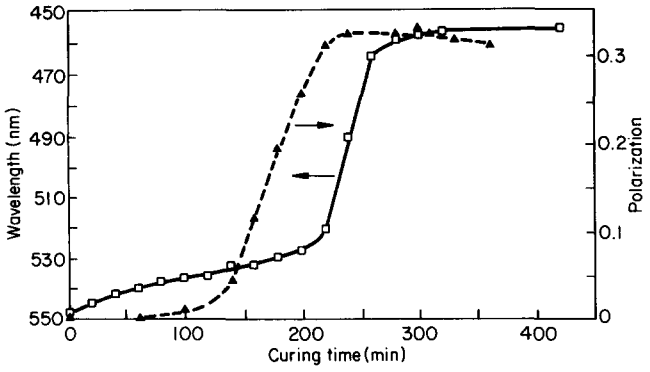

Figure 2 Fluorescence maximum (□) (in nm) of **1** in (P)MMA and fluorescence polarization (▲) ($p=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$) as a function of the thermal curing time. Curing was performed at 85°C; spectroscopic measurements at room temperature in time-gated mode with zero delay

been stored for several weeks after distillation. Prepolymerization of this sample is evident from the shorter fluorescence wavelength at zero curing time and the shorter time needed for complete thermal curing (compare *Figures 1* and *2*).

The data presented in *Figure 2* clearly demonstrate that the fluorescence shift occurs over a wider range of polymerization than the increase of the fluorescence polarization. Moreover, the steep rise of the fluorescence shift occurs only after the polarization has started to level off, i.e. after the rotational mobility has largely been lost on the 5 ns timescale. The maximum value observed for the polarization ($p=0.35$) approaches that ($p=0.5$) characteristic[6] for randomly oriented molecules exhibiting parallel absorption and emission transition dipole moments.

The observations presented above indicate that the optical emission of **1** is a sensitive probe for the conversion of MMA to PMMA, even if the polymerization has progressed to a stage where rotational mobility has been lost on the photophysical timescale. This behaviour stands in marked contrast to that of optical probes based upon the kinetics of inter- or intramolecular (hetero)excimer formation[8-13] or upon the measurement of fluorescence polarization[7] only. These systems lose their probe function if the viscosity of the medium rises above a level which still lies far below that typical for total curing of many polymers, including PMMA.

Temperature-dependent emission of 1 in PMMA

It was observed that even in completely cured PMMA the maximum emission wavelength of **1** seems to be sensitive to changes in the rigidity of the matrix as brought about by temperaure variations over a large temperature range. As shown in *Table 1*, cooling the sample below room temperature causes a blue shift, while heating leads to a red shift.

In *Figure 3* this temperature-dependent behaviour is shown by plotting the ratio of the fluorescence intensity at two different wavelengths (430 and 480 nm) *versus* the temperature. This procedure was adopted to avoid the arbitrariness in determining the position of the maximum of the broad (see *Figure 1*) emission band in the continuous experiment. A reversible behaviour was observed in the temperature range from −170 to +150°C over several cycles of heating and cooling, the only apparent change being a decline of the emission intensity with increasing number of cycles owing to the decomposition of **1** at high temperature (>140°C). The change of the emission maximum proceeds rather gradually; even in the region of the glass transition temperature ($T_g \approx 120$°C) no sudden change was observed.

Temperature-dependent measurements have also been performed over a more limited temperature range with the gated multichannel system in which the spectra were digitized, thus enabling more precisely the determination of the emission maximum. The results obtained are also displayed in *Figure 3* where the relevant wavelength has been plotted *versus* the temperature for 'zero' time delay between excitation and emission. Once again a red shift with increasing temperature is evident. Furthermore a slight jump in the amount of red shift is now observable around T_g. This may be caused by the change in the time dependence of the emission profile that occurs as the viscosity sharply decreases around T_g (see below).

The shape of the curves in *Figure 3* suggests that, upon increasing the temperature, relaxation pathways become energetically available, leading to a stabilization of the excited state of **1** on the photophysical timescale. This stabilization (as well as the accompanying destabilization of the Franck–Condon ground state) causes a bathochromic shift of the emission.

Time-resolved emission studies of 1 in PMMA

To obtain more insight into the molecular dynamics of **1** after excitation, time-resolved emission spectra have been recorded both in liquid and solid (P)MMA. The time-resolved spectra have been measured by scanning the 5 ns wide detection gate of the optical multichannel system with respect to the exciting laser pulse. The detection delay ranged from 0 to 250 ns. However, for reasons of fluorescence intensity, most measurements were carried out up to a time delay of 100 ns, representing about 10 times the fluorescence lifetime of the excited state; the intensity has dropped then to about 10^{-5} of that corresponding to zero time delay.

In liquid solutions of **1** (MMA, benzene, etc.) no shift of the fluorescence maximum as a function of the time delay was observed. This suggests that the reorientation of the surrounding molecules with respect to molecule **1** is a very fast process compared to the detection timescale[13]. In solid PMMA the situation is very much different; a pronounced red shift (about 20 nm) occurs within about

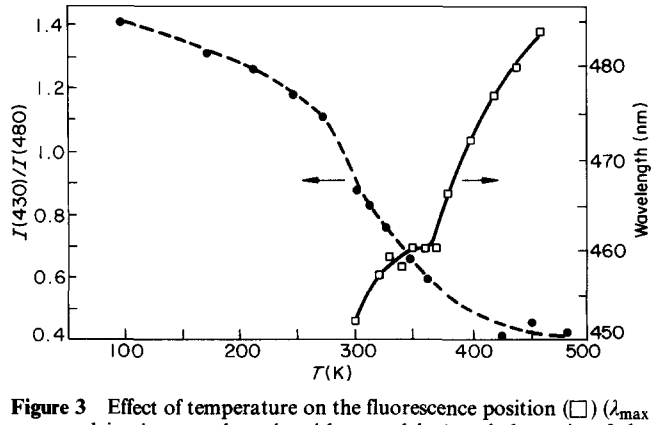

Figure 3 Effect of temperature on the fluorescence position (□) (λ_{max} measured in time-gated mode with zero delay) and the ratio of the fluorescence intensities at two wavelengths (●) (measured in continuous mode) for **1** in PMMA

100 ns after excitation of the molecule **1** (see *Figure 4a*). By plotting the shift *versus* the time delay (10 ns increments) it appears that the emission maximum reaches a plateau after an initial fast increase. This behaviour is shown in *Figure 4b*. For increasing temperature both the initial and final emission maxima exhibit a bathochromic shift. The initial shift may be due to a relaxation on subnanosecond timescales, escaping the time resolution of the applied detection system.

The present data already reveal the dynamics of **1** in the solid matrix as a function of the temperature. Although no full description of the relaxation phenomena after excitation of **1** can be given, it is clear that in sufficiently mobile media containing dipolar functionalities (low-molecular-weight solvents above the freezing point or polymers above the T_g) the environmental reorganization relative to the highly polar excited CT molecule **1** constitutes an important relaxation mechanism on a subnanosecond timescale[1,13]. Moreover, the present measurements have revealed that even below the T_g molecular reorientations take place, but now on a timescale of several tens of nanoseconds. Mechanic dynamical[14] and dielectrical measurements[15] show that, below the T_g of solid polymers, molecular relaxation phenomena occur on a timescale much longer than that of the fluorescence lifetime of **1** and can therefore not be connected with the fluorescence red shift that occurs in solid PMMA over the first 100 ns following excitation.

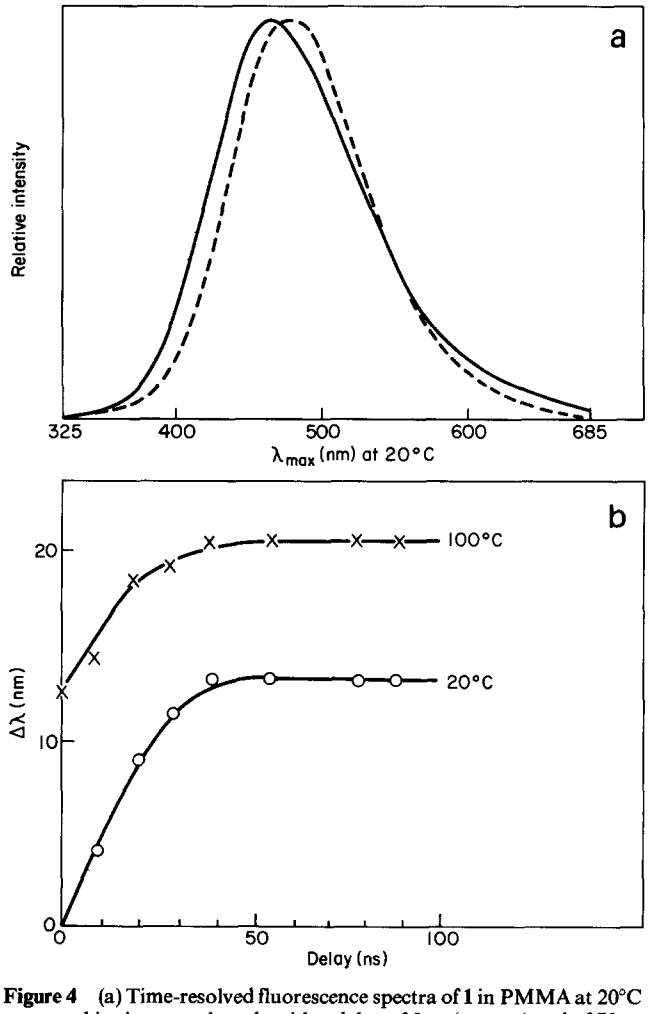

Figure 4 (a) Time-resolved fluorescence spectra of **1** in PMMA at 20°C measured in time-gated mode with a delay of 0 ns (———) and of 70 ns (– – –). (b) The shift of the maximum ($\Delta\lambda$) as a function of the time delay at two temperatures

Since relaxation of the medium is thus no major stabilizing factor for the dipolar excited CT state of **1** in PMMA at temperatures below the T_g, it is concluded that the additional relaxation mechanism observed in this temperature range is the intramolecular relaxation of **1** from its Franck–Condon excited state as explained hereafter.

Figure 5 displays the ground-state conformation of **1** as determined[16] by single-crystal X-ray diffraction. As expected, the central piperidine ring adopts a chair-type conformation. The anilino nitrogen is definitely pyramidal with the phenyl group occupying an equatorial position. The conjugation between the exocyclic double bond and the cyanonaphthalene moiety is partly disrupted by a twist of 50° around the interconnecting bond. Upon excitation, essentially complete one-electron transfer is known[1] to occur from the anilino chromophore to the 1-vinyl-4-cyanonaphthalene chromophore. This drastic charge redistribution will provide a driving force for substantial conformational reorientation processes in both chromophores. Increased coplanarity of the 1-vinyl-4-cyanonaphthalene system will aid in delocalizing the extra electron gained by this moiety, while rehybridization of the amino nitrogen into a planar trigonal situation is expected to occur upon electron loss from the anilino moiety. The energy gain for the latter process has been estimated to amount to 0.77 eV (17.7 kcal mol^{-1}) for a simple trialkylamine[17]. In liquid solutions such conformational rearrangements are expected to occur on the timescale of a molecular vibration. However, it may be expected that incorporation of **1** in a rigid polymer matrix diminishes the rate of such conformational changes and the extent to which they can be realized. The present time-dependent fluorescence measurements suggest that in the temperature range where matrix reorientation is negligible, a stabilization of the CT state still occurs owing to such molecular rearrangement of **1** rather than that of the surroundings. Additional evidence for the conformational and/or rotational rearrangement of **1** is the decrease of the degree of polarization of the fluorescence with increasing time delay after the excitation. In the timespan 0–50 ns the polarization decreases from the maximum value of 0.35 to 0.24.

CONCLUDING REMARKS

The data presented above show that the isothermal position of the charge-transfer fluorescence of **1** can be employed as a probe for the mobility of a polymerizing MMA/PMMA medium. This probe function extends over a wide range of polymerization, including full curing. Furthermore, the emission position of **1** in a fully cured PMMA matrix is sensitive to the temperature over a range extending from about the T_g down to the cryogenic regime. The results of time-resolved emission spectroscopy suggest that the latter phenomenon is due to the restriction of the conformational relaxation of the excited state in a PMMA matrix at lower temperatures.

Preliminary experiments indicated that the probe function of **1** can be extended to other polymeric matrices (e.g. polystyrene, etc.). Investigations are in progress to determine the scope of these phenomena as well as to reveal in more detail the nature of the underlying molecular mechanisms.

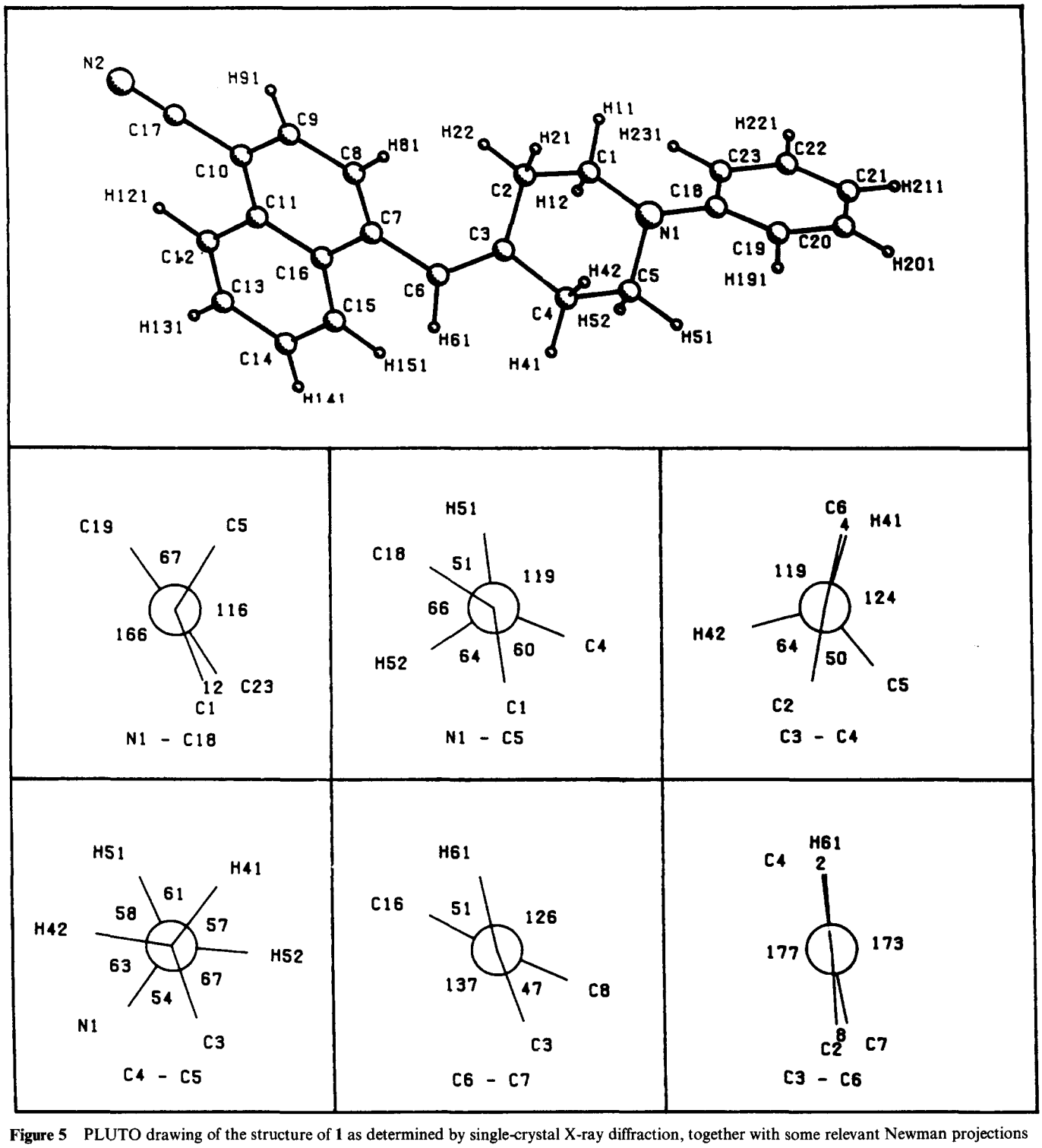

Figure 5 PLUTO drawing of the structure of **1** as determined by single-crystal X-ray diffraction, together with some relevant Newman projections

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REFERENCES

1 Mes, G. F., de Jong, B., van Ramesdonk, H. J., Verhoeven, J. W., Warman, J. M., de Haas, M. P. and Horsman van den Dool, L. E. W. *J. Am. Chem. Soc.* 1984, **106**, 6524
2 Hush, N. S., Paddon-Row, M. N., Cotsaris, E., Oevering, H., Verhoeven, J. W. and Heppener, M. *Chem. Phys. Lett.* 1985, **117**, 8
3 Jordan, A. D., Leland, B. A., Geller, G. G., Hopfield, J. J. and Dervan, P. B. *J. Am. Chem. Soc.* 1984, **106**, 6090
4 Lippert, E. *Z. Elektrochem.* 1957, **61**, 962
5 Pasman, P., Mes, G. F., Koper, N. W. and Verhoeven, J. W. *J. Am. Chem. Soc.* 1985, **107**, 5839
6 Badley, R. A. in 'Modern Fluorescence Spectroscopy', (Ed. E. L. Wehry), Heyden, London, 1976, Vol. 2, Chap. 3, p. 101
7 Scarlata, S. F. and Ors, J. A. *Polym. Commun.* 1986, **27**, 41
8 Pajot-Augy, E., Bokobza, L., Monnerie, L., Castellan, A., Bouas-Laurent, H. and Millet, C. *Polymer* 1983, **24**, 117
9 Bokobza, L., Pajot-Augy, E., Monnerie, L., Castellan, A. and Bouas-Laurent, H. *Polym. Potochem.* 1984, **5**, 191

10 Zachariasse, K. A., Vaz, W. L. C., Sotomayor, C. and Kühnle, W. *Biochim. Biophys. Acta* 1982, **21**, 323
11 Almeida, L. M., Vaz, W. L. C., Zachariasse, K. A. and Madeira, V. M. C. *Biochemistry* 1982, **21**, 5972
12 Wang, F. W., Lowry, R. E. and Grant, W. H. *Polymer* 1984, **25**, 690
13 Kenney-Wallace, G. A. and Jonah, C. D. *J. Phys. Chem.* 1982, **86**, 2572 and references therein
14 Heijboer, J. in 'Molecular Basis of Transitions and Relaxations', (Ed. D. J. Meier), Midland Macromol. Monographs, Gordon and Breach, 1978, Vol. 4, pp. 75 and 297
15 Smyth, C. P. in 'Physics and Chemistry of the Organic Solid State', (Eds. D. Fox, M. M. Labes and A. Weissberger), Interscience, New York, 1963, Vol. 1, p. 697
16 Krijnen, L. B. and Stam, C. H. to be published
17 Meot-Ner, M., Nelsen, S. F., Willi, M. R. and Frigo, T. B. *J. Am. Chem. Soc.* 1984, **106**, 7384