

FLUORESCENCE LIFETIMES AND TIME-RESOLVED SPECTROSCOPY OF 9-CYANOANTHRACENE CRYSTALS IN THE TEMPERATURE RANGE 77 - 300 K

ANITA C. JONES, KATARZYNA JANECKA-STYRCZ[†] and JOHN O. WILLIAMS
Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth (Gt. Britain)

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Summary

Time-resolved spectra have been recorded for a variety of different 9-cyanoanthracene (9CNA) crystals over the range 400 - 600 nm and 77 - 300 K. The fluorescence decay profiles consist of up to three exponential functions. With excitation at about 300 nm all crystals exhibit monomeric fluorescence in time-resolved spectra gated at short times, *i.e.* 0 - 3 ns, and the decay profiles at short wavelengths are fitted to two exponentials yielding lifetimes $\tau_1 = 2.3 \pm 0.7$ ns and $\tau_2 = 9 \pm 2$ ns at 77 K. These are identified with two monomeric species in the dimer-containing crystals. The nature of these species is discussed. Emission from two excimeric species is observed at longer wavelengths: between 540 and 600 nm a species with a lifetime of 167 ± 7 ns at 77 K is identified with the mirror-symmetric (*cis*) excimer and at about 470 - 490 nm a species with a lifetime of 40 ± 10 ns at 77 K is identified as a centrosymmetric excimer which is the main precursor of the photodimer. Our results are consistent with earlier interpretations of the mechanism for the excimer emission and photodimerization of 9CNA and with the recent work of Berkovic and Ludmer.

1. Introduction

A number of studies over the past decade have been concerned with the photodimerization [1] of crystalline 9-cyanoanthracene (9CNA) and with the spectroscopic properties [2 - 6] of this material in a variety of forms ranging from molecules in solution, in glasses and in the crystalline state. Single-crystal material is difficult to purify and spectroscopic investigations have to be approached and interpreted with caution since the irradiation employed to excite fluorescence may also induce photodimerization at all

[†] Present address: Department of Chemistry, University of Kielce, Kielce, Poland.

but extremely low temperatures (below 77 K). Despite these difficulties a consensus has been reached concerning the mechanism of excimeric emission and photodimerization in crystalline 9CNA. The achiral molecules crystallize in a chiral space group ($P2_12_12_1$) and are stacked in a mirror-symmetric arrangement (Fig. 1(a)), which is not conducive to the formation of the resulting centrosymmetric photodimer. Accordingly, it has been suggested [1] that photodimerization initially occurs in defective regions where the molecules are arranged locally in a centrosymmetric arrangement (Figs. 1(b) and 1(c)). The autocatalytic nature of the photodimerization reaction where the quantum yield increases with the degree of conversion from monomer to dimer and the observation of more than one excimeric species supports this kind of mechanism [4, 5, 8]. The predominant steady state emission from pure 9CNA crystals at longer wavelengths is generally attributed to the mirror-symmetric excimer and a broad emission at a higher energy has been attributed to a centrosymmetric excimer ("incipient" dimer) which yields the photodimer. A shorter lifetime is therefore expected of this last excimer at temperatures where photodimerization is favoured.

Preliminary lifetime measurements, in which decay curves have been fitted to single exponentials, have been reported for 9CNA [5 - 7]. In this communication we report our more recent studies where decay curves, found to consist of up to three exponential components, and time-resolved spectra have been recorded over the wavelength range 400 - 600 nm and for temperatures from 77 to 300 K for a variety of 9CNA crystals prepared in different ways. Our results allow us to comment on and to extend the interpretation of the spectroscopy and photodimerization of this material.

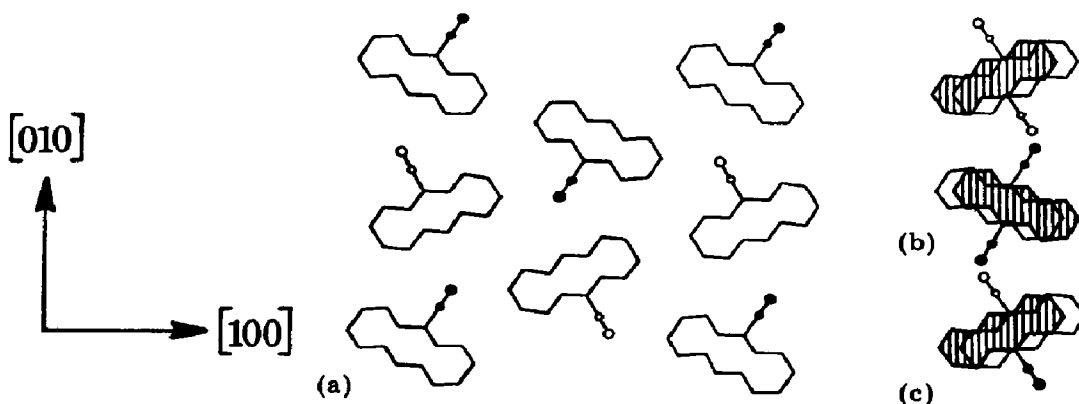


Fig. 1. Schematic representation of the 9CNA crystal structure viewed down the c axis: (a) perfect structure in which the molecules are related by screw axes and mirror-symmetric excimers result (○, cyano groups projecting out of the (001) plane; ●, cyano groups projecting into the (001) plane); (b) "incipient" dimer pairs with cyano groups projecting into and out of the (001) plane (the shaded molecules are shifted along the c axis by $\pm c$); (c) "incipient" dimer pair formed as a result of the substitution of enantiomorphous stacks into the perfect structure (see ref. 7). The orientations of molecules depicted in (b) and (c) are drawn without accounting for lattice relaxation and are only an approximate representation of possible centrosymmetric excimers.

2. Experimental details

Several types of single crystal were investigated: vapour-grown 9CNA, 9CNA grown by dissociative sublimation of the photodimer, vapour-grown 9CNA partially photodimerized by UV irradiation at room temperature and partially thermally cleaved 9CNA photodimer (9CNAD). The purification of the starting materials and the methods of crystal growth have been described elsewhere [4, 5].

Fluorescence lifetimes and time-resolved spectra were monitored over the temperature range 77 - 300 K. The sample was excited by the frequency-doubled cavity-dumped output of a Spectra Physics rhodamine 6G dye laser, synchronously pumped by a mode-locked Spectra Physics 171 argon ion laser. The excitation wavelength was about 290 nm with a pulse duration of less than 80 ps, and a repetition of either 4 or 0.8 MHz was employed. Fluorescence response functions and time-resolved spectra were measured using an Ortec time-correlated single-photon counting system [9]. The time-resolved spectra were recorded by gating the output of the time-to-amplitude converter with upper and lower level voltage discriminators, so that only photons arriving within a certain "time window" were recorded.

3. Data analysis

The observed fluorescence response functions are due to the decay of one or more excited state species and thus can be described by functions of the form

$$I(t) = \sum_{i=1}^n A_i \exp\left(-\frac{t}{\tau_i}\right)$$

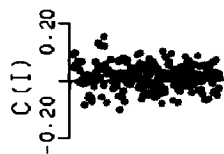
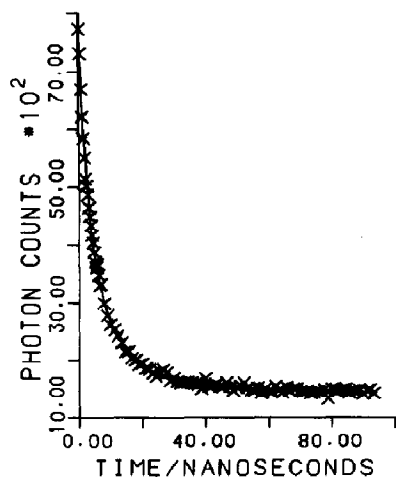
where n is the number of different excited species, τ_i is the fluorescence lifetime for the decay of the i th species and A_i is the relative intensity of the i th component. In the present investigation it was found that, depending on the wavelength of the emission, the decay curves consisted of one, two or three exponential components.

In fitting fluorescence decay curves with functions of this type it is important to have some criterion with which to judge the goodness of fit of the least-squares solution to the experimental data. Two such criteria were in fact used, namely the reduced χ^2 statistic and the autocorrelation function of weighted residuals. The number of parameters in the theoretical function used to describe the experimental data must be no more than is dictated by the statistical error in the data. The reduced χ^2 statistic χ_ν^2 represents the ratio of the weighted mean variance of the fit to the weighted mean variance of the data and is given by

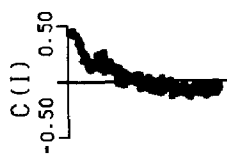
$$\chi_\nu^2 = \frac{1}{\nu} \sum_{i=1}^m \frac{\{I_o(i) - Y(i)\}^2}{I_o(i)}$$

where $I_o(i)$ is the observed number of counts in channel i , $Y(i)$ is the theoretically predicted number of counts in channel i and $\nu = m - j - 1$ is the number of degrees of freedom remaining after fitting m data points with j parameters. If the theoretical function $Y(i)$ is a good fit to the experimental data then χ_ν^2 should on average be unity. However, although $\chi_\nu^2 = 1.0$ indicates a perfect fit, the range of acceptable values of χ_ν^2 is difficult to define. For this reason a second criterion, the autocorrelation function of weighted residuals, was employed.

If the theoretical function provides an adequate description of the experimental decay curve then the temporal distribution of weighted residuals across the fluorescence response function should be random about zero: there should be no correlation between residuals. The weighted residual $R(i)$ for a particular channel corresponds to the observed deviation between the experimental and theoretical functions at that point, weighted according to the standard deviation of that data point:



(b)



(a)

Fig. 2. Fluorescence response function at 77 K and 470 nm for vapour-grown 9CNA, and the fit to (a) the bi-exponential function and (b) the tri-exponential function in terms of the autocorrelation $C(i)$ of the weighted residuals.

$$R(i) = \frac{1}{I_0(i)^{1/2}} \{I_0(i) - Y(i)\}$$

The randomness of the temporal distribution of weighted residuals can be quantified by the autocorrelation function $C(i)$, given by

$$C(i) = \frac{1}{l} \sum_{k=1}^l R(k)R(k+i) \bigg/ \frac{1}{m} \sum_{k=1}^m R(k)^2$$

where $l = m/2$ and $i = 1, \dots, l$.

For a set of random residuals, indicating an acceptably good fit, a plot of the autocorrelation function $C(i)$ versus i ($i = 1, \dots, l$) thus consists of a set of points with values close to and random about zero.

It must be emphasized that in the present investigation a bi-exponential function was only fitted to the data if a mono-exponential function did not provide a satisfactory fit according to these criteria, and a tri-exponential function was only postulated following the failure of a bi-exponential function to provide an adequate fit to the experimental data. The latter case is illustrated in Fig. 2 where the autocorrelation function corresponding to a bi-exponential theoretical function (Fig. 2(a)) is markedly non-random whereas that corresponding to the accepted tri-exponential function (Fig. 2(b)) is entirely random.

4. Results

4.1. Monomer emission

Although too low in intensity relative to the excimer emission to be apparent in the steady state spectra, monomer emission was observed in time-resolved spectra gated at short times for all samples. As shown in Fig. 3, two monomer peaks are present at 77 K (at about 413 nm and about 440 nm) and a third monomer peak is concealed beneath the broad excimer emission band. The relative intensity of monomer emission was greater in the partially cleaved photodimer crystal than in the 9CNA and partially photodimerized 9CNA crystals, as can be seen in Figs. 3 and 4. The monomer fluorescence intensity was generally lowest in unphotodimerized vapour-grown crystals.

The monomer fluorescence response functions in the wavelength range 420 - 460 nm were satisfactorily fitted by bi-exponential decays for all samples. The lifetime values for a vapour-grown crystal are shown in Table 1: the monomer lifetimes obtained varied from sample to sample but overall were in the range $\tau_1 = 2.3 \pm 0.7$ ns and $\tau_2 = 9 \pm 2$ ns at 77 K with $A_1 \approx A_2$. The two monomeric components persist over the temperature range 77 - 298 K and show no significant change in lifetime or pre-exponential factor with temperature.

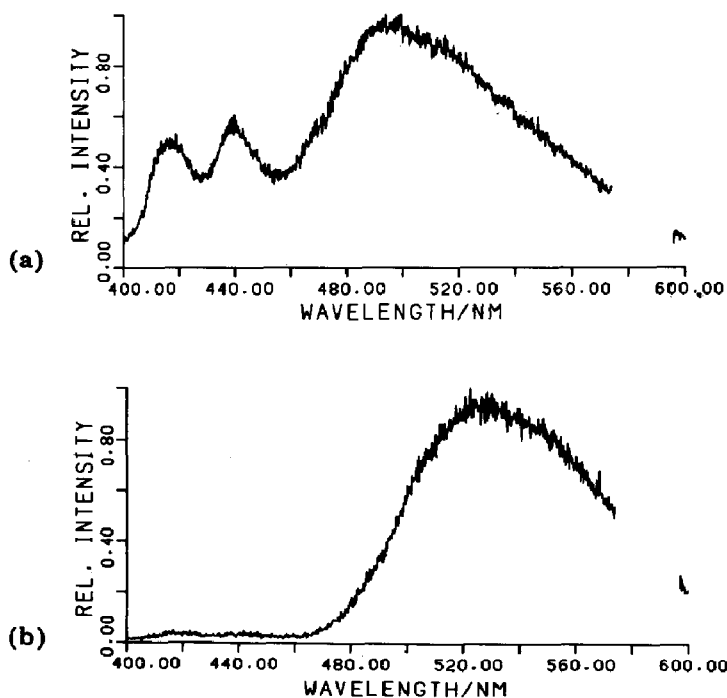


Fig. 3. Time-resolved spectra at 77 K (time window, 0 - 3 ns) of (a) thermally cleaved 9CNAD and (b) 9CNA grown by dissociative sublimation of the photodimer.

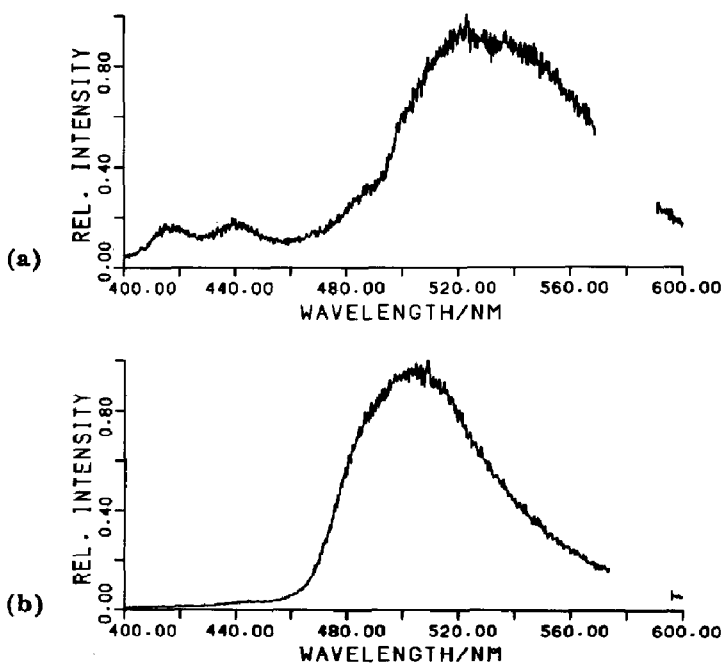


Fig. 4. Time-resolved spectra at (a) 77 K and (b) 298 K (time window, 0 - 10 ns) of a partially photodimerized vapour-grown crystal.

TABLE 1

Vapour-grown 9CNA at 77 K

λ (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	χ^2_ν
420	0.6	2.0 ± 0.4	0.4	7.9 ± 1.0	—	—	0.95
440	0.5			7.9 ± 1.0	—	—	0.94
460	0.6	2.0 ± 0.4	0.4	7.9 ± 1.0	—	—	1.08
470	0.45	2.0 ± 0.4	0.45	7.9 ± 1.0	0.1	40 ± 10	1.12
480	0.3	2.0 ± 0.4	0.4	7.9 ± 1.0	0.3	40 ± 10	1.07
490	0.25	7.9 ± 1.0	0.25	40 ± 10	0.5	167 ± 7	1.00
540 - 600	1.0	167 ± 7	—	—	—	—	<1.10

4.2. Excimer emission

As can be seen in Table 1, the fluorescence response functions (540 - 600 nm) for a vapour-grown 9CNA crystal at 77 K were described by single-exponential functions with a lifetime of 167 ± 7 ns.

The experimental fluorescence response function recorded at 600 nm and the fitted theoretical function are shown in Fig. 5. Fluorescence response functions in the range 470 - 490 nm could only be fitted satisfactorily by the tri-exponential function, as illustrated in Fig. 2, since a second excimer component with lifetime 40 ± 10 ns is present in this region. The large estimated uncertainty in the value of this lifetime is due to the fact

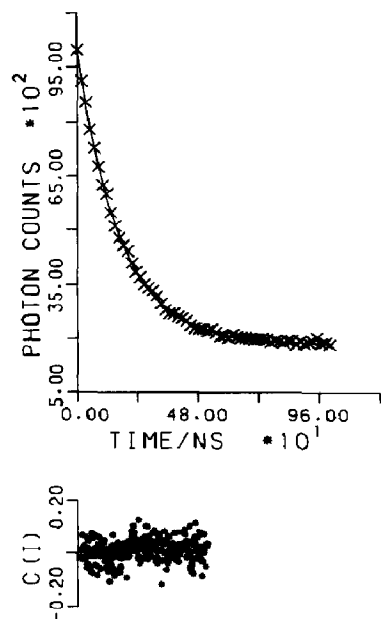


Fig. 5. Fluorescence response function at 77 K and 600 nm for a vapour-grown 9CNA crystal and the fit to a single-exponential decay.

that it can be derived only from tri-exponential functions or from a minor contribution to bi-exponential fluorescence functions between 500 and 540 nm where the longer-lived excimer dominates. The two species were observed in all samples at 77 K and their lifetimes are in agreement with those given for the vapour-grown crystal within the range of error quoted.

The excimer emission spectrum at 77 K for the crystal grown by dissociative sublimation of 9CNAD (Fig. 3) is representative of excimer fluorescence from all samples except the thermally cleaved photodimer crystal. As indicated in Fig. 3, the partially cleaved 9CNAD crystal exhibits a markedly greater proportion of the shorter wavelength excimer emission.

The time-resolved spectra in Fig. 4 illustrate the shift to higher energy and symmetry of the excimer emission at higher temperature. For all crystals except the unphotodimerized vapour-grown 9CNA, only one excimer lifetime was observed over the entire excimer emission envelope at temperatures of 250 K or above. The value of this lifetime at 300 K is given in Table 2 for the three different crystal types. For the vapour-grown 9CNA, two excimer lifetimes were observed over the entire temperature range 77 - 300 K. At 300 K the longer-lived excimer remains the dominant species in this crystal over the range 450 - 570 nm, with lifetime 93 ± 5 ns; the shorter-lived excimer, detected at shorter wavelength, has a lifetime of about 40 ns.

TABLE 2

Trans excimer lifetimes of 9CNA at 298 K

<i>Partially cleaved photodimer</i>	<i>Partially photodimerized sample</i>	<i>Grown by dissociative sublimation of the photodimer</i>
31 ± 2 ns	27 ± 2 ns	21 ± 1 ns

5. Discussion

In a perfect (defect-free) 9CNA crystal the formation of *cis* excimers is expected to occur with unit quantum efficiency and there should thus be no emission from monomer molecules. However, in the crystals studied we observed monomeric emission exhibiting lifetimes of several nanoseconds, the intensity of which was greater the more photodimer was present. This emission is attributed to monomer molecules that are prevented from forming excimers as a result of segregation within a matrix of the photodimer. This is in agreement with the interpretation of MacFarlane and Philpott [2] who observed similar emission following photodimerization. Since monomer emission was observed to some extent from all crystals investigated, it follows that all of our crystals contained at least a small amount of 9CNAD. The longer of the monomer lifetimes is assigned to single isolated 9CNA molecules, and the shorter lifetime to disordered regions of

monomer molecules (aggregates) cut off from the bulk of the crystal during the photodimerization process and oriented so as to prevent excimer and presumably dimer formation.

The observation of two excimer species at 77 K is consistent with the findings of Ebeid *et al.* [5], Berkovic and Ludmer [7] and MacFarlane and Philpott [2]. The longer-lived lower energy emission is due to the *cis* excimer which forms as a result of the stack structure of the 9CNA crystal and is characteristic of the bulk of the crystal. The shorter-lived excimer emission at 77 K and the only excimer emission observed from all except the vapour-grown sample at 298 K are attributed to the same species, namely a *trans* excimer which is a fluorescent precursor of the photodimer. Ferguson and Miller [10] have shown that the immediate "sandwich pair" precursor of the 9CNA photodimer, when produced in the photodimer crystal, has no detectable fluorescence spectrum and rephotodimerizes with unit quantum yield. The *trans* excimer that we observed is presumably the fluorescent precursor of the sandwich pair with the two molecules displaced from the perfect topochemical configuration. Excimeric emission at about 490 nm has previously been assigned to a centrosymmetric excimer by Ebeid *et al.* [5], who proposed that photodimerization originates at structural defects where the formation of an "incipient *trans* dimer" is allowed, and by Morsi *et al.* [6]. Berkovic and Ludmer [7] have recently provided the more general explanation that centrosymmetric pairs occur in interfacial regions between domains of opposite enantiomeric form arising from the chirality of the 9CNA crystal structure (see Fig. 1(c)).

Trans excimer fluorescence was observed from all crystals at 77 K, consistent with the fact that all 9CNA crystals are capable of photodimerization and with the presence of photodimer in all the samples, as indicated by the observation of monomer emission. The *trans* excimer is present to a much greater extent in the thermally cleaved 9CNAD crystal than in the other types because of its production in the thermolytic process.

In monitoring fluorescence lifetimes between 77 and 298 K a small area of the sample was subjected to UV irradiation for a considerable period of time, enabling photodimerization to occur. The observation of only one excimeric emission at temperatures above 250 K can therefore be explained as follows. The region of the crystal from which emission was observed had undergone a high degree of photodimerization and the only excimeric fluorescence seen was that from the *trans* excimer present in this region as a precursor to the dimer. In the vapour-grown crystal, which contained little photodimer, the photodimerization process, which is known to be autocatalytic in nature [1], proceeded slowly and thus two excimeric species were observed at 298 K with the *cis* excimer remaining dominant.

Acknowledgments

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