

Laser-Induced Fluorescence Excitation Spectroscopy and Photophysics of Naphthalene Bichromophoric Molecules in Supersonic Jets

David Groswasser¹ and Shammai Speiser^{1,2}

Received September 28, 1999; accepted November 18, 1999

We present studies of interchromophore interactions under supersonic jet conditions in a large number of dinaphthyl bichromophoric molecules by measuring their laser-induced fluorescence (LIF) excitation spectra. The molecules are composed of two naphthalene chromophores connected by an n -methylene bridge. The length of the bridge was varied as a function of the number of methylene units ($n = 0, 1, 2, 4, 6$), of the general type $NnN(i,j')$, where N denotes naphthalene moiety, n the number of methylene units in the bridge, and (i,j') are the α or β positions of the bridge at each of the chromophores. We obtained high-quality LIF spectra of these bichromophoric molecules. In the molecules $N1N(2,2')$, $N1N(1,2')$, $N2N(2,2')$, and $N2N(1,2')$, the spectrum is characterized by an intense 0–0 region, with series of low-frequency progressions. These progressions are assigned as vibrational modes of the bridge. The appearance of several series of progressions is explained either by the excitation of different chromophores (in the mixed molecules) or by the excitation of different populated conformers. The spectrum of $N4N(1,1')$ is different in several aspects from these spectra. The origin is shifted farther to the red, to $31,402\text{ cm}^{-1}$. Low-frequency progressions or other transitions are not observed near the origin, but typical intrachromophore naphthalene vibrations are intense. The spectra of $N6N(1,1')$ and $N6N(2,2')$ are also characterized by intense intrachromophore vibrations, however, the spectrum of $N6N(2,2')$ is very complicated due to many populated conformations, while that of $N6N(1,1')$ is more simple.

KEY WORDS: Laser-induced fluorescence; supersonic jets; dinaphthalenes.

INTRODUCTION

The high vapor pressure (0.06 Torr at room temperature) and the high fluorescence quantum yield make naphthalene an ideal substance for gas-phase spectroscopy measurements and molecular beam (jet) experiments. In 1961 Craig *et al.* [1] measured the $S_1 \leftarrow S_0$ absorption

spectrum of naphthalene vapor; their analysis of the vibronic structure serves as a basis for the description of the naphthalene spectrum in later jet experiments and is used as an example of the Herzberg–Teller (HT) theory for vibronic coupling [2]. Stockburger *et al.* [3] published a series of papers about the photophysical processes and properties of naphthalene from the fluorescence measurements of different selectively excited vibronic levels and assigned all of the major vibrational transitions and described them in terms of b_{1g} and a_g modes. In their nomenclature, transitions of b_{1g} symmetry are distinguished from a_g symmetry by a bar over the mode number.

¹ Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel.

² To whom correspondence should be addressed. Fax: 972 4 8233735. e-mail: speiser@tx.technion.ac.il

This nomenclature was often used in later publications to describe naphthalene vibronic spectra and is utilized in the present paper.

The fluorescence excitation spectrum of naphthalene in a supersonic jet was later reported in 1980 by Beck *et al.* [5]. They have shown that the lifetimes of S_1 single vibronic levels are in the range of 120–350 ns.

The origin of the $S_0 \rightarrow S_1$ transition of naphthalene is polarized along the long (y) axis and has a weak oscillator strength ($f = 0.001$). This transition is symmetry allowed but is very weak due to “accidental cancellation” of the transition moments. The most prominent bands in the $S_0 \rightarrow S_1$ spectrum are induced by HT vibronic coupling, where the a_g -symmetry vibrations “borrow” intensity from the higher ${}^1B_{3u}$ state, and the b_{1g} -symmetry vibrations “borrow” intensity by vibronic coupling from the ${}^1B_{2u}$ state, whose origin lies near $35,900 \text{ cm}^{-1}$.

Spectroscopic studies of substituted naphthalenes under supersonic jet conditions were carried out to study the effect of the substitution on the different photophysical processes and mechanisms. It should be emphasized that the assignment of the transitions is “borrowed” from naphthalene, but this is just an approximation, since the substitution reduces the symmetry from D_{2h} to C_s and only implies that the vibrational modes in the substituted molecule are similar to naphthalene.

Warren *et al.* [6] investigated the relationship between the vibronic coupling and the mirror symmetry breakdown (MSB) associated with the $S_0 \leftrightarrow S_1$ absorption and fluorescence spectra. They measured the laser-induced fluorescence (LIF) spectra of 1(α)- and 2(β)-methylnaphthalene (1MN and 2MN, respectively). These spectra were also measured by us and the main features of the spectra are summarized in Table I. There are two important features in these spectra which are immediately noticed on comparison to the spectrum of naphthalene.

- (1) The spectrum of 1MN is more complex than that of naphthalene, but there is still a great resemblance between the two spectra; some of the naphthalene transitions can still be identi-

fied. In the case of 2MN the spectrum is much more complex, and it is even impossible to assign the intense $8(b_{1g})_0^1$ transition. This is due to the further reduction of symmetry, in the series naphthalene \rightarrow 1MN \rightarrow 2MN.

- (2) The second major difference among the three spectra is the enhancement in the intensity of the S_1 origin. Since this transition in naphthalene is very weak, it is expected that the band intensity will depend strongly on the substitution.

In contrast to the differences among the LIF spectra, the dispersed fluorescence spectra obtained from the excitation of the S_1 origins of 1MN and 2MN are very similar to that of naphthalene. The same was observed by Jacobson *et al.* [7] for 2-chloronaphthalene; this means that normal modes, which are independent in the ground state, are mixed in the excited state, and the amount of mixing is strongly affected by the substitution. Fluorescence lifetimes of 1MN and 2MN are similar to those of naphthalene, where the most dominant nonradiative decay channel is intersystem crossing (ISC).

In the present work we study processes of interchromophore interactions in a series of dinaphthyl bichromophoric molecules. These molecules are composed of two naphthalene chromophores connected by an n -methylene bridge. The length of the bridge was varied as a function of the number of methylene units ($n = 0, 1, 2, 4, 6$), of the general type $NnN(i,j')$, where N -denotes the naphthalene moiety, n is the number of methylene units in the bridge, and (i, j') are the α or β positions (1,1'), (2,2'), and (1,2') of the bridge connection at each of the chromophores. The number of methylene units and the position of the substitution determine the separation between the chromophores and their relative orientation. This affects the strength and nature of the interchromophore interactions. For example, the structure of $N2N(1,2')$ is shown in Fig. 1. The possible interactions to be considered in such systems are exciton splitting, intramolecular excimer formation, and processes of charge transfer, intramolecular

Table I. Naphthalene Transitions (0–0 Shifts; cm^{-1})

Transition	N	1MN	2MN
$\bar{8}^1$	435	419	384–484
7^1	910	815	—
8^1	700	661	720
9^1	501	484	—
7^1	984	970	967
0_0^0	32,020	31,773	31,705

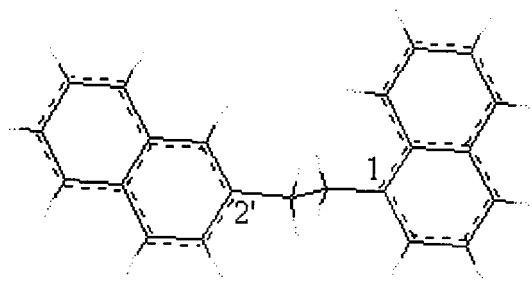


Fig. 1. The structure of $N2N(1,2')$.

electron transfer, and intramolecular electronic energy transfer (intra-EET) processes.

The purpose of this work was to address the questions (1) Can we distinguish between the two chromophores in the same molecule? (2) How do the spectra of these molecules compare to that of 1MN, 2MN, or a combination of the two? (3) Do the chromophores interact with each other? Will we observe exciton splitting or excimer formation in these molecule? and what role does the bridge play in such interactions? (4) Will we observe several ground-state or excited-state conformations? and (5) How does the molecular conformation affect any intramolecular interactions and photophysical processes?

EXPERIMENTAL

Synthesis of all bichromophoric compounds was performed in the laboratories of Professor Rubin and of Dr. Stanger of this department and is described elsewhere.

The molecules were seeded in helium in a supersonic jet using a pulsed nozzle apparatus. Briefly, 6-atm helium was passed over a heated cell containing liquid organic sample. The temperature was chosen so as to produce an organic vapor pressure of about 0.2 Torr. The gas containing the organic vapor was expanded through a 1.1-mm orifice into an evacuated chamber. The pressure in the vacuum chamber was typically 2×10^{-4} Torr. The jet was crossed with a laser beam (<1-mm spot size) 33 mm downstream. About 10% of the resulting fluorescence was collected by a lens to a photomultiplier.

The laser beam (~ 5 mW) was produced by frequency doubling or mixing a Nd:YAG (Continuum) second-harmonic pumped dye laser. The resulting laser bandwidth was about 0.2 cm^{-1} . The experimental uncertainties of absolute frequencies are $\pm 2 \text{ cm}^{-1}$ and those of relative frequencies are 0.2 cm^{-1} .

Conformation analysis of all molecules was carried out using AMBER force field methods [8].

RESULTS AND DISCUSSION

The LIF excitation spectra and single vibronic lifetimes are analyzed by comparison to 1MN and 2MN, which serve as reference compounds. This is done to estimate the “naphthalenic” character of the molecule by examining the shift in the position of the origin and of the vibronic $8b_{1g}$ transition and the relative intensities of these two transitions. The typical lifetimes of naphthalene, 1MN, and 2MN are about 300 ns, in the region of up to 100 cm^{-1} excess energy above the 0–0 transition. In naphthalene and naphthalene derivatives the main non-

radiative decay channel is intersystem crossing (ISC) [9], hence in the bichromophoric molecules we would expect interchromophoric interactions to be reflected by a decrease in the lifetime; in binaphthyl, for example, the typical lifetimes in this spectral region vary from 60 to 50 ns. Another suitable reference compound is 1-(2-naphthalenyl)-*N*-(9-acridinyl)-heptylamide, whose spectrum was measured by Schael *et al.* [10]. This bichromophoric molecule is composed of acridine and naphthalene moieties, connected by a flexible bridge. The bridge is attached to the naphthalene chromophore at position 2. It was shown that the spectrum of this molecule, in the spectral region of the naphthalene chromophore, resembles that of 2MN. The 0–0 transitions of the naphthalene–acridine bichromophoric molecule and the reference molecule (2MN) are shifted by only 2 cm^{-1} . In addition, the possibility of probing several stable conformers is considered. For example, Levy *et al.* [11] measured the spectrum of 2-naphthylcyclohexane (NPT-C6) and found two origins, at $31,964$ and $31,784 \text{ cm}^{-1}$, that belong to two different conformers (equatorial and axial). The possible interchromophoric interactions that might play a role, such as exciton interactions, are also of the same order of magnitude. In binaphthyl this interaction results in a splitting of $\sim 60 \text{ cm}^{-1}$ [12]; in 9,9'-bifluorenyl 29-cm^{-1} exciton splitting of the origin was reported by Smith *et al.* [13] and can be compared to data pertaining to naphthalene crystals [14,15] and to naphthalene clusters [16].

LIF Excitation Spectrum of 1N(2,2')

This compound is the best choice to start the analysis of the whole series. In this molecule both chromophores are substituted at the same position, thus making them identical, however, not necessarily equivalent for different relative orientations. This point can be clarified by employing molecular mechanics calculations for determining the most stable conformations of the molecule. The calculations predict two possible conformations; both have practically the same enthalpy of formation and therefore both are populated in the jet. In both conformers of the molecule the interchromophore separation is about 6.5 \AA and the tetrahedral angle between the planes of the two chromophores is 112° .

The spectrum of 1N(2,2,) is shown in Fig. 2. The most intense spectrum in this region is at $31,652.7 \text{ cm}^{-1}$ and is identified as the 0–0. Farther to the blue there is more activity around $32,090\text{--}32,240 \text{ cm}^{-1}$. This is $\sim 450\text{--}500 \text{ cm}^{-1}$ above the 0–0 transition and is most probably the $8b_{1g}^1$ mode of the chromophore (with analogy to naphthalene). In comparison to 2MN, we see that the

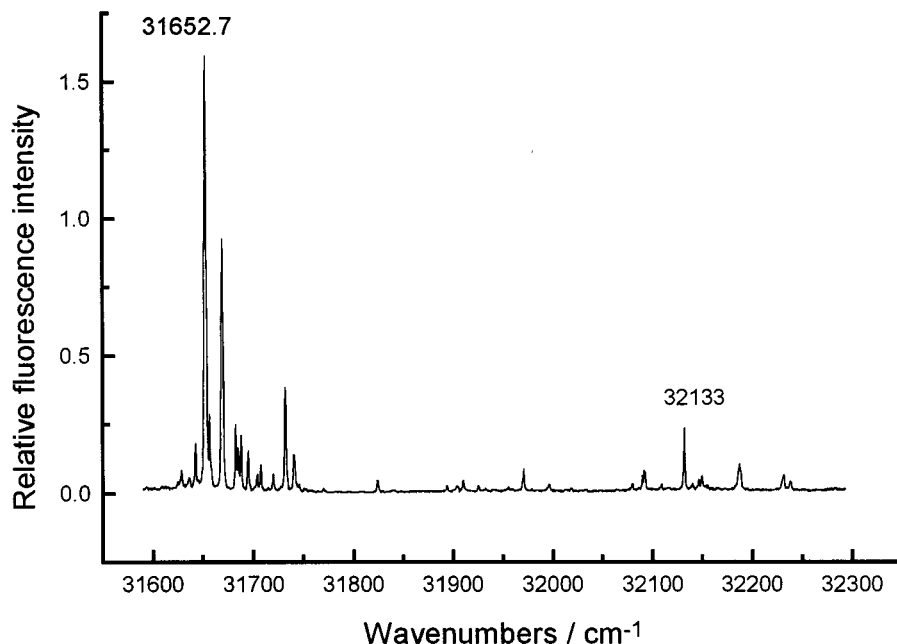


Fig. 2. LIF excitation spectrum of *N1N(2,2')*.

0–0 transition is shifted to the red by 52 cm^{-1} . The transitions, which are related to the $8b^{1g}$ mode, are shifted similarly. The relative intensities of the intense 0–0 band and the transition at $32,133\text{ cm}^{-1}$ are comparable to that in 2MN. These facts support the description of this molecule as a weakly coupled dimer.

The lifetimes of the transitions in this spectral region are summarized in Table II. With the exception of the 0–0 transition, which is only 168 ns, the typical lifetime near the origin is about 240 ns. Lifetime fluctuations in this spectral region are not exceptional in naphthalene spectroscopy and are attributed to accidental matching with triplet states. For comparison, in 2MN the typical lifetime is above 300 ns. The decrease in lifetimes in the

bichromophoric molecule can be attributed to several factors, like the reduction of symmetry, or to the increase in the density of states and, thus, the increased rate of ISC, which is the main nonradiative decay channel, [9]. On the other hand, the decrease in lifetime may be due to some interchromophoric interaction; in (1,1')binaphthyl, for comparison, such an interaction gives a typical lifetime of 50–60 ns [12].

An examination of the spectrum near the origin (Fig. 3) reveals a symmetric progression of $\sim 13\text{ cm}^{-1}$ (marked with asterisks), which starts at $31,628\text{ cm}^{-1}$. Only 5 of the 14 lines in this spectral region do not fall into this series, such a low vibrational frequency progression is due to a vibration mode of the bridge. In this case the transition at $31,628\text{ cm}^{-1}$ is the lowest 0–0 transition. A similar progression with such a symmetric structure and low frequency was observed and calculated for 9,9'-bianthryl [17–19]. It was shown in similar systems such as 1,1'-binaphthyl [12] and in 9-phenylanthracene [2] that such a pattern is characteristic of a double-well structure of the excited-state potential energy surface. It is also possible in this case that the 0–0 transition is not observed and is shifted farther to the red. The lines that do not fall into this series are probably due to excitation of another populated conformation. The intense transition at $31,652.7\text{ cm}^{-1}$ is one of the lines that do not fit into this series. We can consider this band to be the 0–0 transition of the second conformer. Another progression of $\sim 16.5\text{ cm}^{-1}$, which includes the lines at $31,652$ (0–0),

Table II. Transition Lifetimes of *N1N(2,2')*

Line position (cm^{-1})	Lifetime ± 5 (ns)
31,652.7	248
31,669.2	240
31,682.8	168
31,732	235
31,741	195
31,971	190
31,097	—
32,092	172
32,188	165
32,232	170
32,238	—

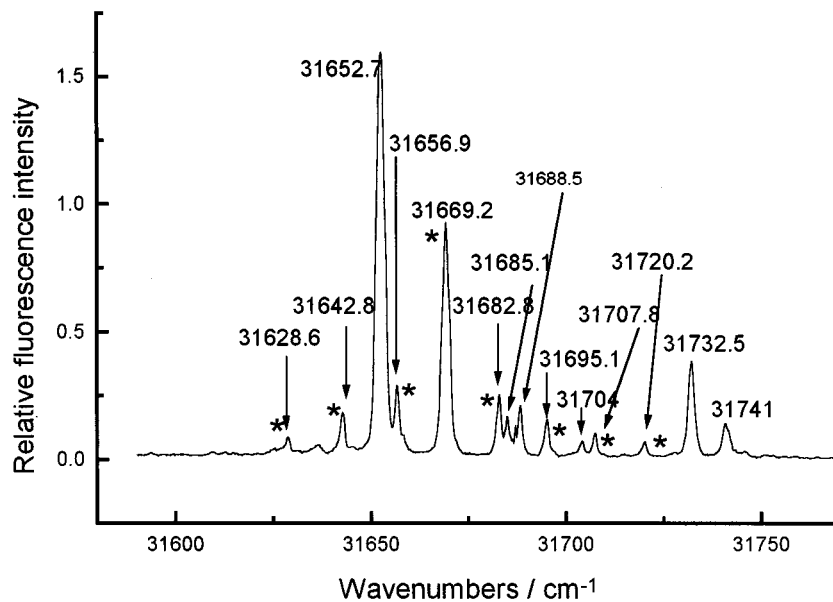


Fig. 3. A blowup of the origin spectral region of $N1N(2,2')$.

31,669.2, 31,685.1, 31,704, and 31,720.2 cm^{-1} , is also observed. This means that the lines at 31,669.2 and 31,720 cm^{-1} accidentally coincide in both series and may explain the enhanced intensity of the 31,669.2 cm^{-1} transition.

LIF Excitation Spectrum of $N1N(1,2')$

The LIF excitation spectrum of $N1N(1,2')$ is shown in Fig. 4. The strongest activity in this spectral ring is

around 31,640 cm^{-1} ; in this region we expect to identify the 0–0 transitions. Some more activity is observed around 32,200 cm^{-1} ; this frequency is too high to be identified as the $8b_{1g}$ transition. A blowup of the 0–0 region is shown in Fig. 5.

Surprisingly, the spectrum in this spectral range looks less complicated than the 0–0 region of $N1N(2,2')$. The strong activity in the spectrum starts at 31,607 cm^{-1} ; red to it, only weak “hot” bands are observed. Thus we

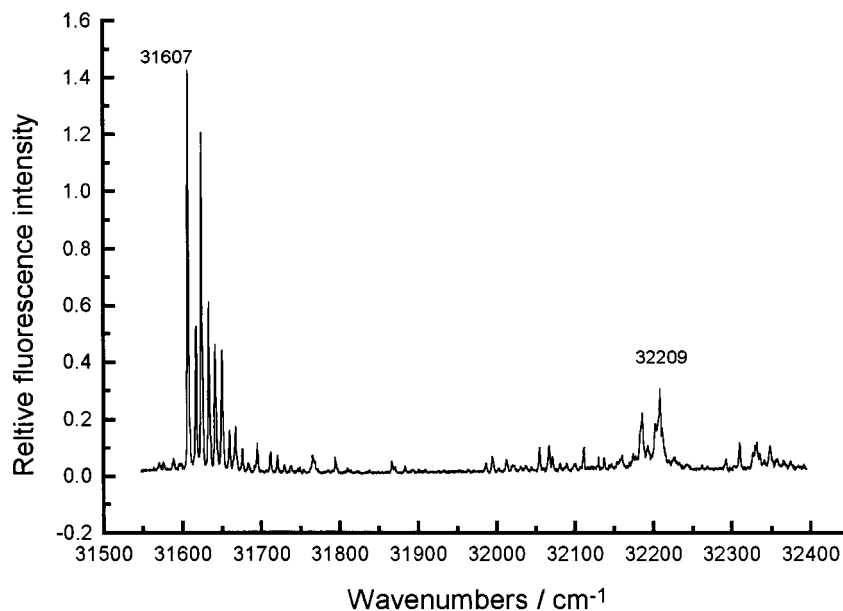


Fig. 4. LIF excitation spectrum of $N1N(1,2')$.

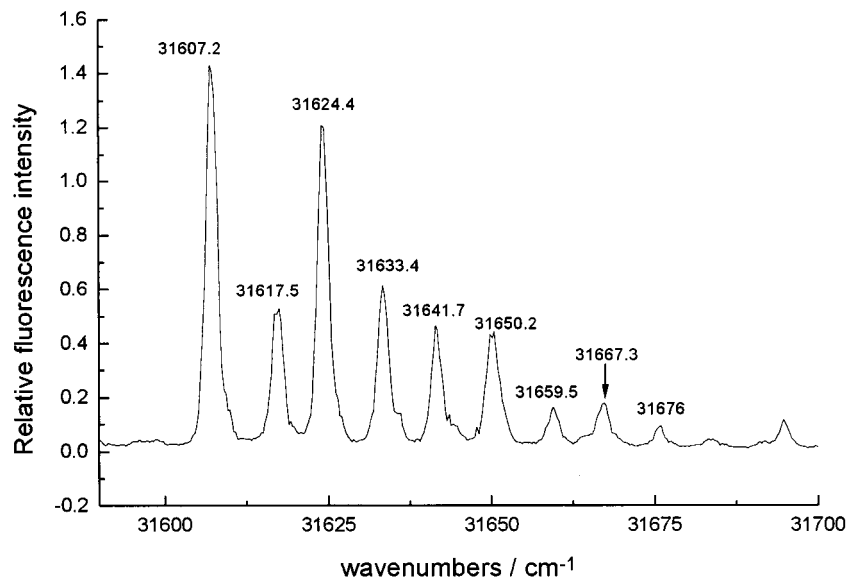


Fig. 5. The 0–0 spectral region of $1N(1,2')$.

conclude that this is a 0–0 transition. This is a shift of 98 cm^{-1} to the red from the origin of 2MN [and 45.7 cm^{-1} , compared with $31,652.7\text{ cm}^{-1}$ for $1N(2,2')$]. If we consider the chromophores to be distinguishable, and in the framework of the weak coupling limit, then this transition is most likely excitation of the β -substituted chromophore. The question, then, is Where is the 0–0 transition of the α -substituted chromophore? and Why is this transition shifted compared to the 0–0 of $1N(2,2')$?

The structure of the 0–0 region is made of distinct progression of bands with a separation of $\sim 7.8\text{--}10.3\text{ cm}^{-1}$, and lifetimes that vary from 266 to 142 ns. An examination of the line spacing shows that the first and second transitions are separated by 10.3 cm^{-1} ; the second and third, by 6.9 cm^{-1} . All of the other lines are separated by $8.5 \pm 0.8\text{ cm}^{-1}$. In addition, the first and third transitions are also the most intense in the spectrum. This is an indication that the line at $31,624.4\text{ cm}^{-1}$ is a second 0–0 transition. These vibronic progressions are summarized in Table III. If the transition at $31,607.2\text{ cm}^{-1}$ is the 0–0 of the β -substituted chromophore, then this is the 0–0 transition of the α -substituted chromophore. Another possibility is that these progressions belong to two different conformers; this point can be clarified only by performing hole burning experiments combined with dispersed fluorescence. Another possibility for assignment will rely on the difference in intensities of the 0–0 transitions between 1MN and 2MN. Based on this, the $31,624\text{-cm}^{-1}$ band could not be the 0–0 of the 1 chromophore since its intensity is similar to that of the band at

$31,607.2\text{ cm}^{-1}$; however, this is not very likely in view of the small shift between these two bands.

The drop in lifetimes in this spectral region is significant, a $>50\text{-ns}$ decrease in less than 70 cm^{-1} of excess excitation energy. This is a general tendency, and not a accidental fluctuation. Such a behavior can be indication that excitation of these modes promotes nonradiative decay channels, mainly ISC [9]. As in $1N(2,2')$, such low-frequency modes are very likely the interchromophore bending or libration motions. Intra-EET is one of the processes that we have to consider in such a molecule. Since the energy gap between the 0–0 transitions of the chromophores is so small (about 68 cm^{-1} by evaluating the chromophores as being 1MN and 2MN), this molecule is considered to be a limit case between a donor–acceptor and a donor–donor description. Due to the fact that the

Table III. Vibronic Progressions in the Excitation Spectrum of $1N(1,2')$

Position (cm^{-1})	Assignment	Shift from origin (cm^{-1})	Lifetime (ns)
31,607.0	A_0^0	0	266
31,617.3	A_0^1	10.3	142
31,624.4	B_0^0	0	246
31,633.4	B_0^1	8.8	248
31,641.7	B_0^2	$17.3 = 2 \times 8.7$	212
31,650.2	B_0^3	$25.8 = 3 \times 8.6$	210
31,659.5	B_0^4	$35.1 = 4 \times 8.8$	210
31,667.3	B_0^5	$42.9 = 5 \times 8.6$	205

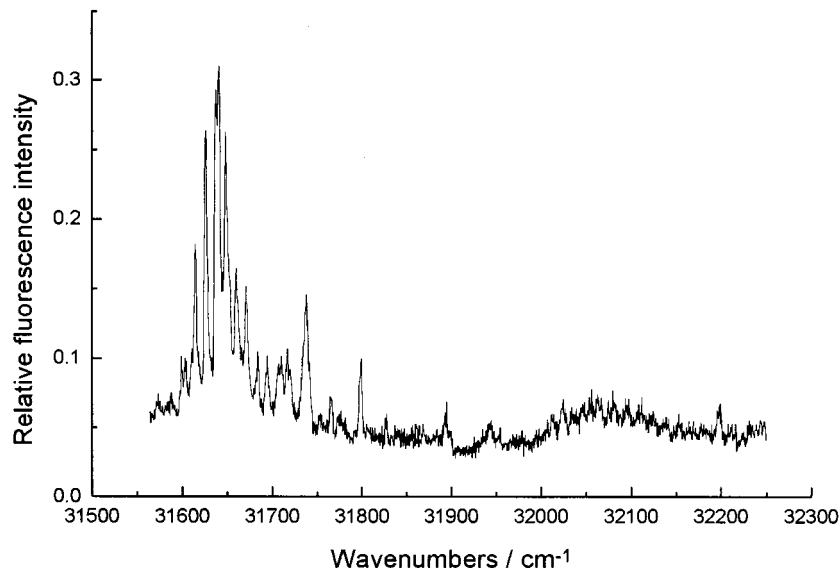


Fig. 6. LIF excitation spectrum of $N2N(2,2')$.

energy difference between the two 0–0 transitions is so small and since the chromophores are so similar, it is practically impossible to tell which of the chromophores is the donor and which the acceptor.

Our calculations predict at least two stable ground-state conformations with similar heats of formation (*ca.* 80 kcal/mol), thus a significant population of both conformers in the jet is expected. Hence, we cannot exclude neither the possibility that the two origins are of two different conformers nor the possibility of two different chromophores in the same molecular conformation. However, the shift of the origins and the small difference between them are an indication that the chromophores are indistinguishable.

LIF Excitation Spectrum of $N2N(2,2')$

As in the case of $N1N(1,2')$ and $N1N(2,2')$, most of the activity in the spectrum (Fig. 6) is in the region of

the origin, and besides a wide “hump” between 32,000 and 32,200 cm^{-1} , no special features are observed. The typical lifetimes of the transitions close to the origin are about 220 ns and are summarized in Table IV, but some lifetimes deviate significantly and drop to 174 ns (31,738 cm^{-1}). Such lifetimes are not particularly different from those measured for $N1N(1,2')$ and $N1N(2,2')$.

The most stable ground-state conformers that were predicted by molecular mechanics calculations are *gauche* and *anti*. These conformations have similar heats of formation (*ca.* 71 kcal/mol). Another, “sandwich” conformer has a higher heat of formation (*ca.* 74 kcal/mol). The separation between the centers of the chromophores is about 8.5 Å in the *gauche* and *anti* conformations and 5.5 Å for the sandwich conformer.

The spectrum of $N2N(2,2')$ is similar to that of $N1N(2,2')$ and $N1N(1,2')$ in the sense that we observe activity only near the origin. Beside the complex structure of the origin spectral region, we also note that it “sits” over a broad baseline signal. Another similar baseline hump is observed between 32,000 and 32,200 cm^{-1} .

The identification of the 0–0 transition is not an obvious task. The strong transition at 31,639.7 cm^{-1} is one candidate; its frequency is close to the origin of $N1N(2,2')$. However, if the minimum of the excited-state potential energy surface is shifted from that of the ground state, transitions with $\Delta\nu \neq 0$ will appear more intense. In such a case the 0–0 is shifted farther to the red and could be the band at 31,599 cm^{-1} ; this frequency is very close to that of the origin of $N1N(1,2')$ (31,607 cm^{-1}).

Table IV. Vibronic Progressions in the Excitation Spectrum of $N2N(1,2')$

Shift (cm^{-1})	Tentative assignment
0.0 (31,658.7) <i>A</i>	0_0^0 (<i>A</i>)
0.0 (31,678.2) <i>B</i>	0_0^0 (<i>B</i>)
<i>A</i> + 17.7	A_0^1
<i>B</i> + 8.5	B_0^1
<i>B</i> + 17.2 ($\sim B + 2 \times 8.5$)	B_0^2
<i>A</i> + 35.3 ($\sim A + 2 \times 17.7$)	A_0^2

The bands in this spectral range are very broad. Most of them have a FWHM of more than 4.5 cm^{-1} ; some of them ($31,639.7$ and $31,738.5\text{ cm}^{-1}$) have a FWHM of more than 8 cm^{-1} ! This may indicate that the ground-state potential energy surface has a very shallow minimum or that the transitions are broadened due to either unresolved exciton splitting or overlapping transitions of different chromophores and/or conformers.

The separation between the chromophores in this molecule is rather large, and the dipole–dipole interactions, which vary $\propto 1/R^3$, are expected to be smaller at such distances than in binaphthyl. Hence we can estimate that such interactions will result in a splitting of no more than several centimeters $^{-1}$ (the splitting observed in binaphthyl is 60 cm^{-1} [10]). Such a (crude) evaluation can explain the broadening or even splitting of transitions.

LIF Excitation Spectrum of $N2N(1,2')$

The LIF excitation spectrum of $N2N(1,2')$ is shown in Fig. 7. Figure 8 shows the fluorescence temporal behavior as a function of the fluorescence wavelength. It is seen that if we excite the molecule at the origin ($31,658.7\text{ cm}^{-1}$) and place a 470-nm cutoff filter in front of the photomultiplier, then most of the signal is gone. When we replace this filter with a 415-nm cutoff filter we see that the short-lived component of the fluorescence is enhanced, meaning that this short-lived component fluoresces between 415 and 470 nm; this is not typical of

naphthalene fluorescence, which is typically between 340 and 400 nm. Next, we replace this filter with a Schott UG11 filter, which has a transmission window between 300 and 400 nm. Now we can see the typical long-lived component of the naphthalene fluorescence, but we also see a reduced short-lived background which does not depend on the excitation wavelength.

The spectrum of $N2N(1,2')$ (Fig. 7) is similar to those of $N2N(2,2')$ (Fig. 6), $N1N(1,2')$ (Fig. 4), and $N1N(2,2')$ (Fig. 2), in the sense that the most active region of the spectrum is at $\sim 31,600\text{--}31,650\text{ cm}^{-1}$. The most intense band in the spectrum is at $31,658.7\text{ cm}^{-1}$ (Fig. 9); 450 cm^{-1} to the blue of this transition, at $32,109\text{ cm}^{-1}$, we can observe another band, which is probably the $8b_{1g}$ transition of this 0–0. These facts suggest that we are looking at a chromophore which is very little perturbed by the other one or by the aliphatic bridge. Farther to the red of this origin, we observe some activity around $31,500\text{ cm}^{-1}$. These spectral features might be “hot” bands, cluster bands, or another 0–0 region. Hot bands are not very likely since we do not observe similar activity blue to the 0–0 ($31,658.7\text{ cm}^{-1}$). These bands seem to be too intense to be cluster lines. Hence, we conclude that this is another 0–0 region. This is supported by the appearance of a small band at $31,426\text{ cm}^{-1}$. This band is shifted by 424 cm^{-1} to the blue from the second origin at $31,502\text{ cm}^{-1}$ and is possibly the $8b_{1g}$ transition of this 0–0. The 156-cm^{-1} separation between the origins is much greater than the difference between the origin

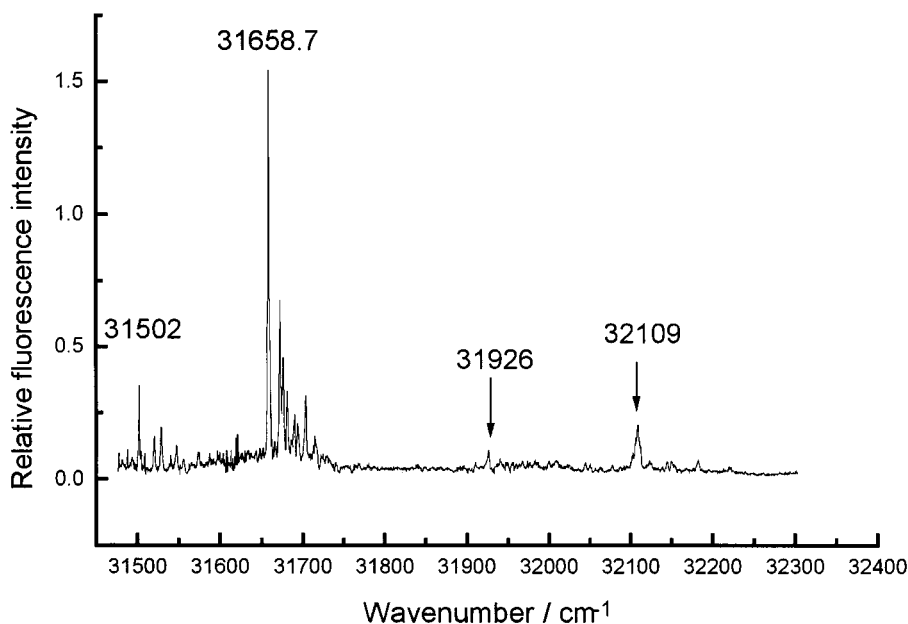


Fig. 7. LIF excitation spectrum of $N2N(1,2')$.

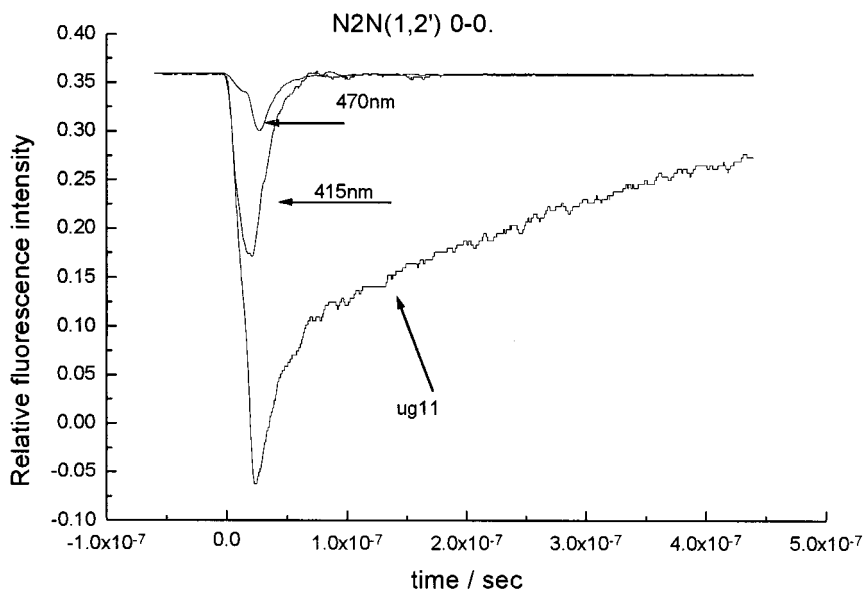


Fig. 8. The origin fluorescence temporal behavior of $N2N(1,2')$, as a function of the fluorescence wavelength.

of 1MN and that of 2MN. Additional factors must be considered to explain this large shift. In addition, besides the origin at $31,658.7 \text{ cm}^{-1}$, for which the lifetime is 240 ns, all of the other transitions have much shorter lifetimes, about 120 ns. Again, as in the case of $N1N(1,2')$, the relative intensities may suggest assigning the 1 origin near $31,500 \text{ cm}^{-1}$. The large red shift could then be attributed to intramolecular dispersion energy [21].

AM1 calculations predict the existence of several stable conformations of $N2N(1,2')$. The most stable ones

are the *gauch* and *anti* conformers, with similar heats of formation (*ca.* 73 kcal/mol). In both conformations $\sim 7.3 \text{ \AA}$ separates the chromophores. Dipole-dipole interaction at such distances is too weak to cause a split of 150 cm^{-1} . There are two other, less stable conformations.

An examination of the spectral region near the origin at $31,658 \text{ cm}^{-1}$ (Fig. 9) shows that this structure is composed of two series of transitions separated by 17.6 and 8.5 cm^{-1} as summarized in Table IV. The separation between the origins is only 14.1 cm^{-1} , which is too small

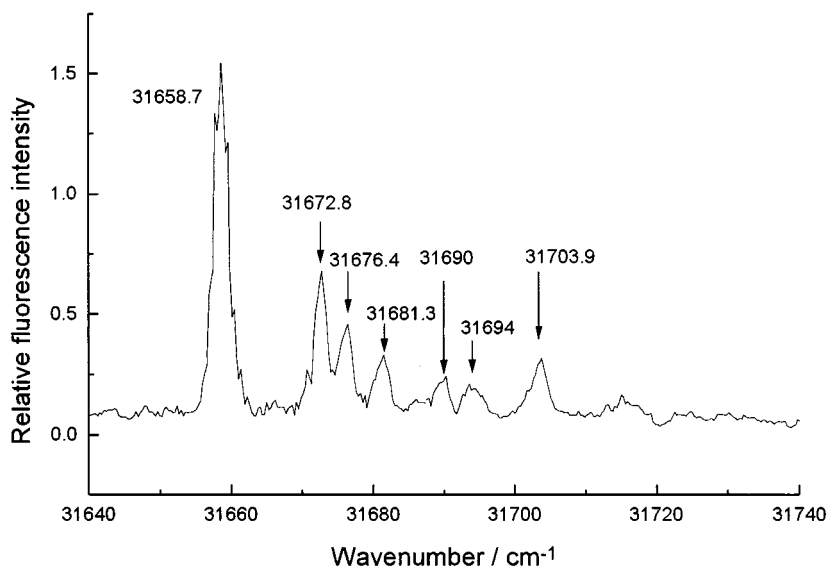


Fig. 9. A blowup of the region of the most intense band in the spectrum in Fig. 8.

to distinguish between the chromophores. The structure near $31,500\text{ cm}^{-1}$ is also complex, but due to the bad signal-to-noise ratio, the assignment of the transitions is unreliable. Still, it is most plausible that this spectral region contains more than one 0–0 transition. Hence we conclude that the spectrum is the result of the excitation of two different chromophores in two different conformers (possibly the *gauche* and the *anti*).

LIF Excitation Spectrum of $N2N(1,1')$

$N2N(1,1')$ was first studied by Rosenblum and Speiser [22] and was remeasured by us on a better-purified sample. This spectrum is presented in Fig. 10. The origin is at $31,776\text{ cm}^{-1}$. This frequency is almost-identical to the origin of 1MN. No signs for exciton splitting were observed. The simple spectrum of $N2N(1,1')$ is explained by excitation of the most stable anti conformer. In this geometry the chromophores are identical and do not interact with each other due to the large separation of 6.9 \AA . The other transitions are progressions of 16 cm^{-1} which are related to vibrational modes of the interchromophore bridge.

LIF Excitation Spectrum of $N4N(1,1')$

The spectrum of $N4N(1,1')$ (Fig. 11) is the most extraordinary of all the spectra that we have obtained. The major features are as follows: (1) The spectrum is rich in activity over a very wide spectral range. (2) The 0–0 transition is shifted deep to the red (by almost 400 cm^{-1}). (3) No low-frequency interchromophore activity

is observed close to the origin. We measured large variations in the lifetimes of the transitions, from less than 100 ns to almost 200 ns . There are strong fluctuations in the transition lifetimes. Near the origin the lifetimes vary from about 140 to 85 ns , but vibrations with long lifetimes are also observed: 195 ns was measured for the vibration at $32,464\text{ cm}^{-1}$. This is more than 1000 cm^{-1} above the origin! In general, the drop in lifetime is due to enhancement of the intrachromophore nonradiative decay process such as ISC moderated due to accidental mismatch with triplet states [9].

It seems that we observe transitions of only one conformer in the spectrum. This is surprising because, with such a long flexible bridge, the possibility for large number of stable ground-state conformations is high. We calculated the geometry and heat of formation of several conformers and found again that “open” conformations are more stable than “sandwich” conformations. Our experimental results suggest that one of the open conformers should have a much smaller heat of formation, but we were not able to find it in our calculations.

It is interesting to note the resemblance of this spectrum to that of 1MN; such a comparison is summarized in Table V. From Table V we learn that there is a similarity between the shifts of the intrachromophore vibrations of 1MN and $N4N(1,1')$; there are, however, major differences between the relative intensities of these transitions, which could be explained by the further drop in symmetry of each chromophore with respect to 1MN.

If we consider an open structure of the molecule, for which the two chromophores are highly separated, one can understand that the spectrum of this molecule

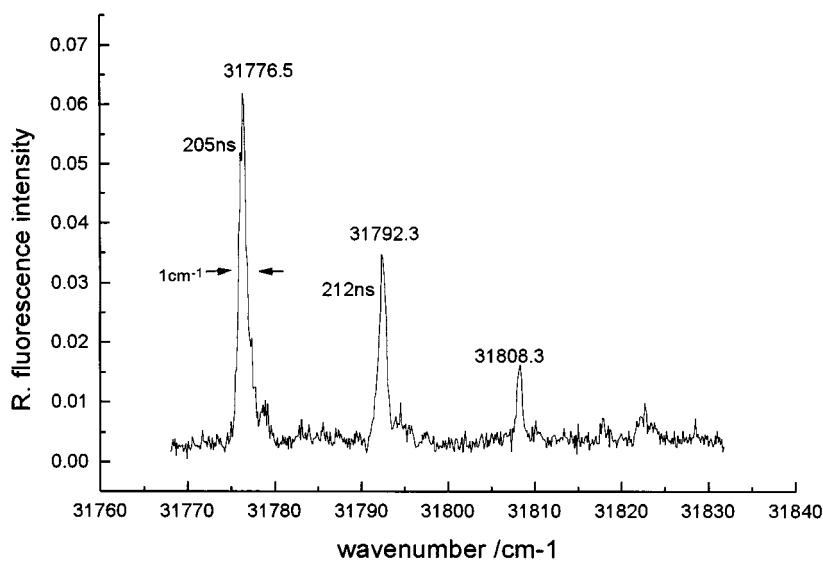


Fig. 10. LIF excitation spectrum of $N2N(1,1')$; transition lifetimes appear next to each band.

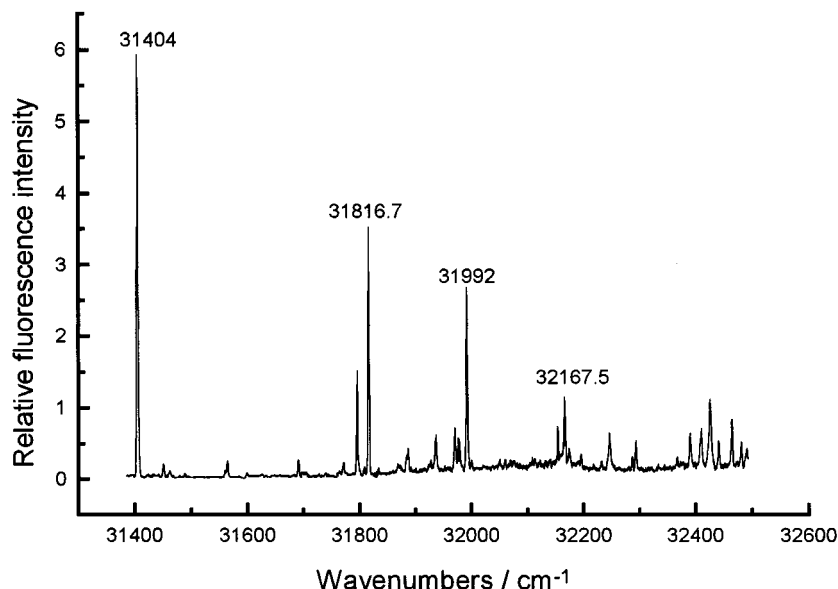


Fig. 11. The LIF excitation spectrum of $N4N(1,1')$.

will resemble that of 1MN. Yet we have difficulty to understand why the origin of the spectrum is shifted so much to the red. Why do we not observe low-frequency modes near the origin as in other spectra that we studied? and Why do we observe in this spectrum intrachromophoric vibrations that are not observed in other related compounds?

The shift of the 0–0 transition to the red compared to $N1N(1,2')$ or $N2N(1,2')$ indicates that the excited state in this molecule is more stabilized (or less perturbed). Such a red shift can occur in a folded conformation where interchromophore interactions are promoted. However, a folded conformation would also promote exciton splitting or excimer formation, which were not observed. Thus we conclude that the shift is due to interaction of the aromatic π system with the methylene bridge in a “stretched” conformation. This structure must also be

symmetric and rigid so that interchromophore vibrations are less coupled to the electronic transitions. We also note that the spectrum of $N4N(1,1')$ has a great resemblance to that of 1,8-dimethylnaphthalene and acenaphthene [23].

LIF Excitation Spectrum of $N6N(2,2')$

This spectrum (Fig. 12) is extremely rich and exhibits a very complex structure over almost all of the spectral region covered. The strongest transitions in this spectral range are between 31,600 and 31,700 cm^{-1} . In this region we observed the origin of $N1N(2,2')$ and $N2N(2,2')$, 31,652.7 and 32,639.7 cm^{-1} , respectively. Hence we identify the strong band at 31,654.5 cm^{-1} as the 0–0 transition of the most populated ground-state conformer. Very roughly, one can say that the spectrum has a naphthalenic character: an origin around 31,700 cm^{-1} , a featureless region of 400- cm^{-1} excess energy, and some vibronic activity at higher excitation energies. The transition lifetimes are also similar to those of methyl-substituted naphthalene and vary from 300 to 160 ns in this spectral range.

We ran molecular mechanics calculations to find the most stable ground-state conformation of the molecule, however, it is clear that such a complicated flexible molecule will have many conformations, some of them with similar energy contents. It is almost-inevitable that during the expansion more than one kind of conformation will remain populated, and we have seen some evidence for this in the spectrum.

Table V. Comparison Between the Spectral Feature of 1MN and $N4N(1,1')$

Tentative assignment	Line position (cm^{-1}), 1MN/ $N4N$	Shift from 0–0 (cm^{-1}), 1MN/ $N4N$	Normalized relative intensity ^a
0_0^0	31,773.6/31,404.4	0/0	1/1
$8(b_{1g})_0^1$	32,192.8/31,816.8	419.2/412.4	5.35/0.59
$2(b_{2g})_0^1$	32,257.6/31,887.2	484.0/482.8	0.99/0.069
$9(A_g)_0^1$	32,316.6/31,937.0	543.1/532.6	0.245/0.11
$8(A_g)_0^1$	32,435.2/32,061.4	661.6/657	0.92/0.046

^a Relative to the laser intensity, and normalized to the 0–0 intensity. 1MN data from Ref. 21.

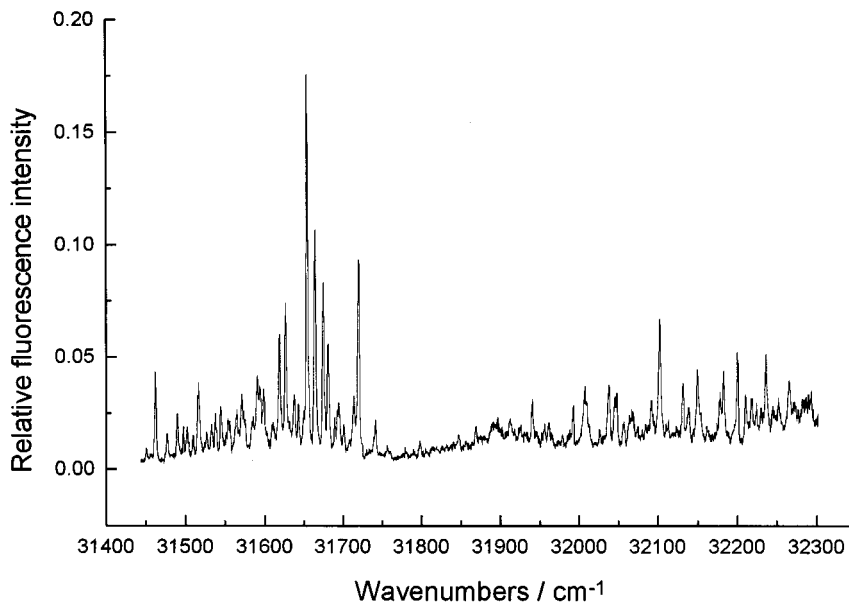


Fig. 12. LIF excitation spectrum of $N6N(2,2')$.

LIF Excitation Spectrum of $N6N(1,1')$

The spectrum of $N6N(1,1')$ (Fig. 13) looks different from all the spectra that we have previously seen. The spectrum is divided into three regions: the origin spectral region, from 31,680 to 31,780 cm^{-1} ; the “quiet” part of the spectrum, $\sim 31,780$ to 31,950 cm^{-1} ; and the intrachromophore vibronic spectral range, $\sim 32,000$ –32,200 cm^{-1} .

We have identified seven transitions in the origin spectral region. The simplicity of this spectral range is

surprising compared to the complexity of the origin spectral range of $N6N(2,2')$. The first transition is at 31,685 cm^{-1} ; this is a weak transition. To the blue from this band we observe three pairs of transitions; $7 \pm 2 \text{ cm}^{-1}$ splits each pair. The separation between the center of the first and that of the second pair is $27 \pm \text{cm}^{-1}$, and that between the second and the third is $26 \pm 1 \text{ cm}^{-1}$. Two possibilities are considered. The first is that we observe a progression of 27 cm^{-1} of two different chromophores

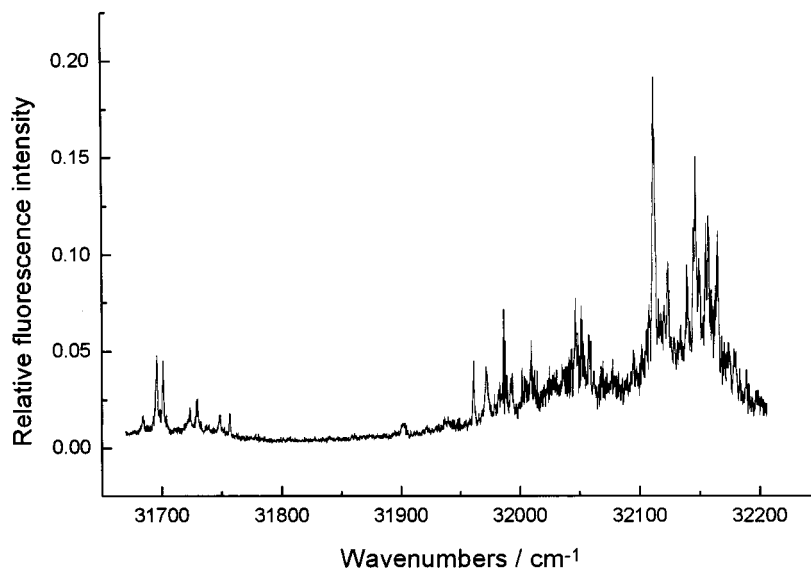


Fig. 13. LIF excitation spectrum of $N6N(1,1')$.

in the same molecular conformation. We note that even if the chromophores are substituted at the same position, they are not necessarily identical, due to their relative orientations and their orientation with respect to the aliphatic bridge. The second possibility is that this is a progression of 27 cm^{-1} , in which each band is split due to exciton interaction, as was concluded for binaphthyl (1,1') [10]. The lifetimes of the transitions in this spectral range are about 130 ns, with the exception of the strong transition at $31,696\text{ cm}^{-1}$, which is 239 ns. We tentatively assign the band at $31,696\text{ cm}^{-1}$ as the most intense 0–0 transition [compared to $31,674\text{ cm}^{-1}$ for $N2N(1,1')$].

The blue part of the spectrum is very active. The density of states in this spectral region is greater than the excitation step (0.24 cm^{-1}), even though we can still identify the intense bands in this spectral region. The strongest of them is at $32,112.2\text{ cm}^{-1}$. This transition is identified as the $8b_{1g}$ mode of the chromophores. This is a shift of 416.2 cm^{-1} from the origin that we have just identified. This is very similar to the 419-cm^{-1} shift in 1MN. The typical fluorescence lifetime in this spectral region is about 120 ns. The very complex structure near the $8b_{1g}$ transition compared to the “organized” structure near the origin can lead us to think that we observe excitonic interaction, with such a molecular geometry that the short and long axes of the chromophores are parallel. This spectrum looks very different from that of $N6N(2,2')$; it is less intense and complicated near the origin and more complex and intense in the intrachromophoric vibronic region.

SUMMARY

We have obtained high-quality LIF spectra of dinaphthyl bichromophoric molecules. In the molecules $N1N(2,2')$, $N1N(1,2')$, $N2N(2,2')$, and $N2N(1,2')$, the spectra are generally characterized by an intense 0–0 region, with series of low-frequency progressions. These progressions are explained as vibrational modes of the bridge. The appearance of several series of progressions is due to the excitation of different chromophores (in the mixed molecules) and/or the excitation of different populated conformers. Exciton splittings were not observed; this is supported by the relatively small shifts from the origins of 1MN ($31,773\text{ cm}^{-1}$) and of 2MN ($31,705\text{ cm}^{-1}$). In $N2N(1,2')$ a red-shifted fluorescence and a short lifetime (compared to naphthalene fluorescence) were observed. This fluorescence was independent of the excitation wavelength and may indicate intramolecular excimer formation.

The spectrum of $N4N(1,1')$ is different in several aspects from these spectra. The origin is shifted to $31,402\text{ cm}^{-1}$, and low-frequency progressions or other transitions are not observed near the origin, but typical intrachromophore naphthalene vibrations are intense. There is no evidence for interchromophore interactions. Thus we conclude that the molecule is symmetrical, with a large separation between the chromophores. The red shift of the origin is not due to interactions between the chromophores but, rather, due to interactions of the bridge with the aromatic π systems of the chromophores. This implies that the orientation of the bridge affects the shift more than the position of the substitution. Hence, even if the chromophores are substituted at different positions, they are practically indistinguishable.

The spectra of $N6N(1,1')$ and $N6N(2,2')$ are also characterized by intense intrachromophore vibrations. The spectrum of $N6N(2,2')$ is very complicated due to many populated conformations, while that of $N6N(1,1')$ is more simple.

ACKNOWLEDGMENTS

This research was supported by Grant 96-171-1 from the U.S.–Israel Binational Science Foundation and by the Fund for Promotion of Research at the Technion.

REFERENCES

1. D. P. Craig, J. M. Hollas, M. F. Redies, and S. C. Walt (1961) *Philos. Trans. Roy. Soc. London Ser. A* **253**, 543–568.
2. G. Herzberg (1966) *Electronic Structure of Polyatomic Molecules*, D. Van Nostrand, New York, p. 141.
3. M. Stockburger, H. Gattermann, and W. Klusmann (1975) *J. Chem. Phys.* **63**, 4519–4528; M. Stockburger, H. Gattermann, and W. Klusmann (1975) *J. Chem. Phys.* **63**, 4529–4540; M. Stockburger and H. Gattermann (1975) *J. Chem. Phys.* **63**, 4541–4545.
4. G. Orlandi and W. Siebrand (1973) *J. Chem. Phys.* **58**, 4513–4523.
5. S. M. Beck, D. E. Powers, J. B. Hopkins, and R. E. Smalley (1980) *J. Chem. Phys.* **73**, 2019–2028.
6. J. A. Warren, J. M. Hayes, and G. J. Small (1984) *J. Chem. Phys.* **80**, 1786–1790.
7. B. A. Jacobson, J. A. Guest, F. A. Novak, and S. A. Rice (1987) *J. Chem. Phys.* **87**, 269–282.
8. Program Hyperchem 3 (1993) Hypercupe.
9. S. Susuki, M. Sato, N. Mikami, and M. Ito (1986) *Chem. Phys. Lett.* **127**, 292–300.
10. H. T. Jonkman and D. A. Wiersma (1988) *Chem. Phys. Lett.* **269**, 592–598.
11. M. Chatteraj, B. Paulson, Y. Shi, G. L. Closs, and D. H. Levy (1993) *J. Phys. Chem.* **97**, 13046–13051.
12. H. T. Jonkman and D. A. Wiersma (1984) *J. Chem. Phys.* **81**, 1573–1582.
13. P. G. Smith, S. Gnanakaran, A. J. Kaziska, A. L. Motyka, S. M. Hong, R. M. Hochstrasser, and M. R. Topp (1994) *J. Chem. Phys.* **100**, 3384–3393.

14. S. D. Colson, D. M. Hanson, R. Kopelman, and G. W. Robinson (1967) *J. Chem. Phys.* **48**, 2215–2231.
15. D. M. Hanson (1970) *J. Chem. Phys.* **52**, 3409–3418.
16. J. A. Syage and J. E. Wessel (1988) *J. Chem. Phys.* **89**, 5962–5963; J. E. Wessel and J. A. Syage (1990) *J. Chem. Phys.* **94**, 737–747.
17. L. R. Khundkar and A. H. Zewail (1986) *J. Chem. Phys.* **84**, 1302–1311.
18. A. Subaric-Leitis, Ch. Monte, A. Roggen, W. Rettig, P. Zimmermann, and J. Heinze (1990) *J. Chem. Phys.* **93**, 4543–4555.
19. T. Fujiwara, Y. Fujiwara, and O. Kajimoto (1996) *Chem. Phys. Lett.* **261**, 201–207; K. Yamasaki, K. Arita, O. Kajimoto, and K. Hara (1986) *Chem. Phys. Lett.* **123**, 277–281.
20. D. W. West, W. R. Gentry, and P. F. Barbara (1985) *J. Chem. Phys.* **89**, 729–732.
21. N. A. van Dantzig, D. H. Levy, C. Vigo, and P. Piotrowiak (1995) *J. Chem. Phys.* **103**, 4894–4899.
22. G. Rosenblum and S. Speiser (1999) in S. H. Lin, A. A. Villaeys, and Y. Fujomura (Eds.), *Advances in Multi-Photon Processes and Spectroscopy, Vol 12*, World Scientific, Singapore, pp. 1–181.
23. T. Chakraborty and M. Chowdhury (1992) *Chem. Phys.* **159**, 439–448.