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Solution and supersonic jet studies of the intramolecular exciplex of dinaphthyl propanes

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Abstract

The *newly* synthesized dinaphthyl propanes: 1,3-di-(2-naphthyl)-propane and 1-(1-naphthyl), 3-(2-naphthyl)-propane were studied spectroscopically under supersonic jet conditions and in solution. Under supersonic jet conditions, both molecules exhibit a broad, *structureless fluorescence excitation spectrum* and relatively short non-exponential decay of the highly red shifted fluorescence, consistent with strong interchromophore coupling in the excited state, resulting in, at least, partial excitation directly into an exciplex-like state. These observations are in contrast to the observed spectra and fluorescence decay of *all* other dinaphthalene bichromophoric molecules. Solution studies support these findings. The optimal flexible sandwich type geometry of both molecules is probably responsible for the observed exciplex state stabilization.

Keywords: Fluorescence; Excitonic interaction

1. Introduction

The dynamics of electronically excited bichromophoric aromatic systems [1] and, in particular, binaphthalenic systems [2–14], has attracted a considerable interest. In many systems it can analyzed in terms of competition between processes involving locally excited states and those involving exciplex states which are stabilized by excitonic interaction, while states of other nature can be disregarded. In solution exciplex states are relatively stabilized by solvent molecules, by contrast to the isolated molecules conditions prevailing in supersonic jet.

In supersonic jet evidence for exciplex states was found in highly asymmetric donor–acceptor systems [15–32], and for systems that consisted of two energetically similar or identical aromatic chromophores [2–7,33–51]. Sandwich-like structures that permit maximum overlap and minimum separation between π-systems of the chromophores were found to be optimal for facilitating exciplex formation [9]. In many bichromophoric systems an energy barrier can be defined, along an interchromophore vibrational coordinate, for transition from the initially excited state to an exciplex state [46]. Different measured values for this barrier have been reported for different systems [20,34,46].

An exciplex state is stabilized by excitonic interaction due to strong interchromophore coupling, compared to that found in locally excited state or in the electronic ground state. This leads to a large interchromophore geometry change accompanying the transition to an exciplex state, resulting in negligible Franck–Condon factors for direct excitation of this state. Thus, observations of such direct excitation to an exciplex state are rare. One such example might be the dibenzofuran dimer [45,46]. In this system the barrier for exciplex formation is so low that the excitation spectrum features are broadened by coupling to the exciplex state by $\sim 80\,\mathrm{cm}^{-1}$, implying a single-cycle transition [46]. In this system the interchromophore bond is relatively strong even in the ground electronic state, due to the dipole–dipole interaction, which improves the coupling to the exciplex state.

In an earlier publication we presented studies of interchromophore interactions under supersonic jet conditions in a large number of *novel* dinaphthyl bichromophoric molecules by measuring their laser induced fluorescence (LIF) excitation spectra [52]. The molecules were 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 i,j'-N*n*N, were N denotes naphthalene moiety, *n* the number of methylene units in the bridge, (i,j') are the α or β positions of the bridge at each of the chromophores. In *all* these molecules the LIF spectra are characterized by

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an intense 0–0 region, together with a series of, well resolved, 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) and/or by excitation of different populated conformers. The lifetimes of the exponential fluorescence decay associated with these spectra ranged between 150 and 300 ns, typical of other naphthalene derivatives, for *all* these molecules. No evidence for exciplex formation for any of these molecules was observed.

In this paper we report on extending these studies to examine two *novel* bichromophoric molecules of the binaphthalene $n = 3$ series [2,52], 1-(1-naphthyl), 3-(2-naphthyl)-propane 1,2′-N3N and 1,3-di-(2-naphthyl)-propane 2,2′-N3N. Since it is well-known that in the methylene bridge series, the three methylenes-chain bridge is optimal for sandwich-type conformer formation [48], we expected to see different type of excited state interactions in these compounds. A comparison is made between solution and solvent free, jet-cooled, conditions to account for the role of the solvent in stabilizing the exciplex state.

2. Experimental

The experimental setup for LIF supersonic jet experiments was described earlier [53]. Briefly, bichromophoric substance vapor was expanded with Ramot pulsed valve nozzle operating at 10 Hz from a chamber heated to above 200°C and containing helium at pressures over 3 atm to a diffusion pumped 10^{-6} Torr vacuum chamber via an 0.5 mm orifice. The resulting supersonic jet was crossed 20–40 mm downstream by a pulsed tunable UV laser beam obtained by frequency doubling Continuum ND6000 dye laser output, which was pumped by Continuum Powerlite 7000 10 Hz Nd:YAG second harmonic. The resulting fluorescence was collected to a Hamamatzu R928 fast PMT via 2″ quartz lens and an appropriate red cut-off filter. The signal was processed via Tektronix TDS 220 digital oscilloscope.

The fluorescence excitation and emission spectra in solution were measured with Perkin-Elmer LS50 fluorimeter via 5 nm slits for deoxygenated 1×10^{-4} M hexane solutions of the substances at room temperature. 5×10^{-4} M solutions were used in each case for comparison to ascertain absence of concentration-dependent effects (dimers, etc.).

The *novel* dinaphthylpropanes compounds were prepared by a Diels-Alder reaction between 7,8-dibromocyclobutabenzene and the corresponding dienophile [54,55]: 4-(1-naphthyl)butene for 1,2′-N3N (19% yield) and 4-(1-naphthyl)butene for 2,2′-N3N (41% yield). ^{1}H NMR, δ (ppm): 1,2′-N3N: 2.2 (m, 2H), 2.93 (t, 2H), 3.19 (t, 2H), 7.35–7.49 (m, 7H), 7.77–7.80 (m, 6H), 8.1 (m, 1H). 2,2′-N3N: 2.13 (m, 2H), 2.84 (t, 4H), 7.31–7.45 (m, 6H), 7.62 (s, 2H), 7.75–7.79 (m, 6H).

The dienophiles were prepared by (DPPP)NiCl$_2$ catalyzed coupling of 4-megnesiumbromidebutene and the respective bromonaphthalene; 4-(1-naphthyl)butene in 87% yield and 4-(2-naphthyl)butene in 82% yield [56]. ^{1}H NMR, δ (ppm): 4-(1-naphthyl)butene: 2.60 (q, 2H), 3.20 (t, 2H), 5.20 (m, 2H), 6.00 (m, ^{1}H), 7.36–7.60 (m, 7H). 4-(2-naphthyl)butene: 2.57 (q, 2H), 2.90 (t, 2H), 5.13 (m, 2H), 5.96 (m, 1H), 7.40–7.92 (m, 7H).

3. Results and discussion

The main observations for the *novel* dinaphthyl propanes, in supersonic jets and in solution, are as follows.

3.1. LIF of 1,2′-N3N in supersonic jet

Upon excitation at 31875 cm^{-1} of 1,2′-N3N an intense fluorescence signal was observed. The signal intensity was

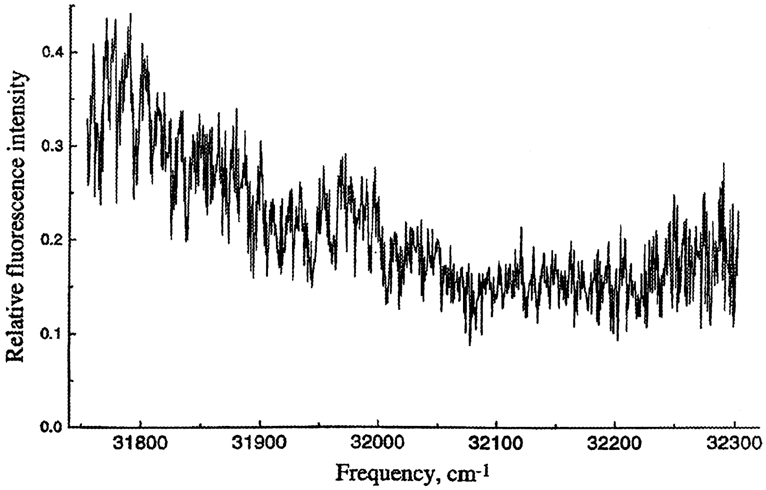

Fig. 1. LIF excitation spectrum of jet expanded 1,2′-N3N typical of strongly coupled electronically excited naphthalene bichromophoric molecules such as, A3N and A6N [53] and naphthalene dimers [3–7].

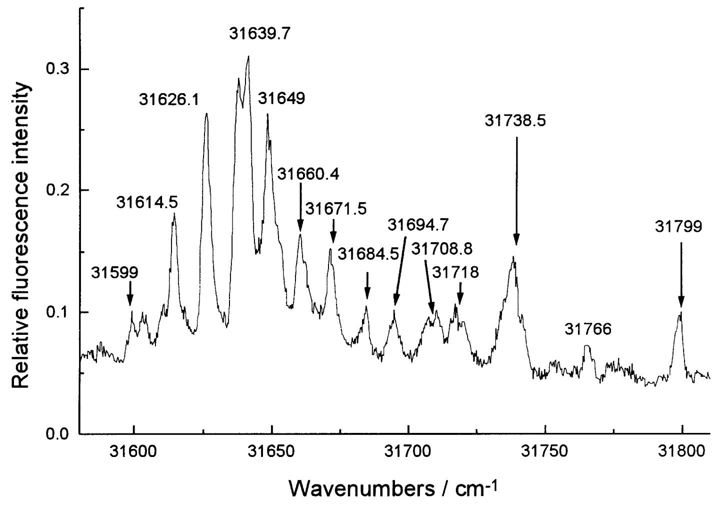

Fig. 2. LIF excitation jet spectrum of the 0–0 region of 2,2′N2N.

essentially independent of the excitation wavelength in the studied excitation region of 307–322 nm (i.e. all fluorescence bands are broadened by at least 1500 cm^{-1}), resulting in a broad, structureless excitation spectrum. Such structureless excitation jet spectra, as shown in Fig. 1, were observed for strongly coupled electronically-excited naphthalene bichromophoric molecules, such as naphthalene dimer [3–7], A3N and A6N [53] and 2,2′ binaphthyl [56]. For comparison we show in Fig. 2 the well resolved spectrum of 2,2′-N2N [56], typical of the LIF excitation spectra of all i, j'-NnN molecules, but for $n = 3$ [52].

Due to lack of proper instrumentation no reasonable disperse fluorescence spectra could be recorded. However, it was observed that most of the fluorescence signal was *highly red-shifted* compared to all other dinaphthalenes [52], as revealed by monitoring the fluorescence decay after passing it through a series of cut-off filters (Fig. 3). The decay was non-exponential, with apparent decay times of 34 ns for the whole signal and 22 ns for the red part of the signal. This again is in contrast to the general observation of relatively long exponential fluorescence decay of all other

Table 1
Transition lifetimes in N2N(2,2′)

Line position (cm^{-1})	Lifetimes ±5 (ns)
31614	218
31626	240
31639.7	252
31649	232
31660.4	220
31671	219
31738	174

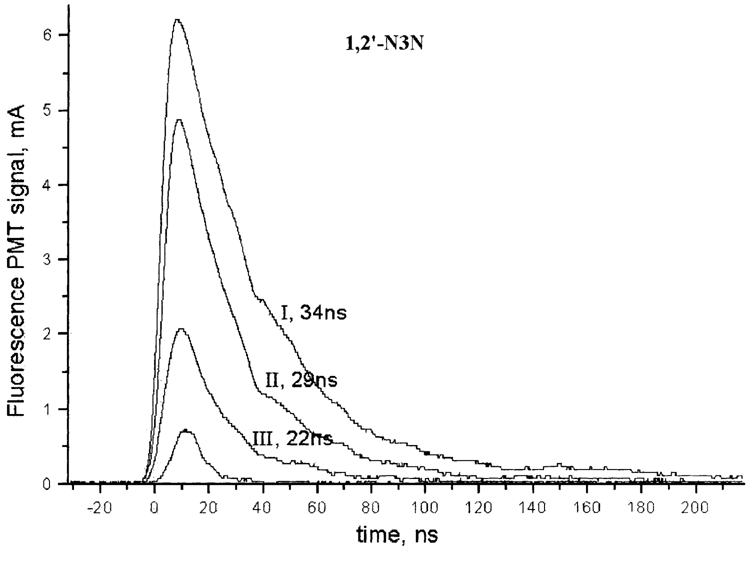

Fig. 3. Fluorescence decay signal for 1,2′-N3N in supersonic jet, following excitation at 31875 cm^{-1}: (I) signal monitored after 322 nm cut-off filter, (II) signal monitored after 375 nm cut-off filter, (III) signal monitored after 450 nm cut-off filter, a trace of the scattered laser signal is also shown.

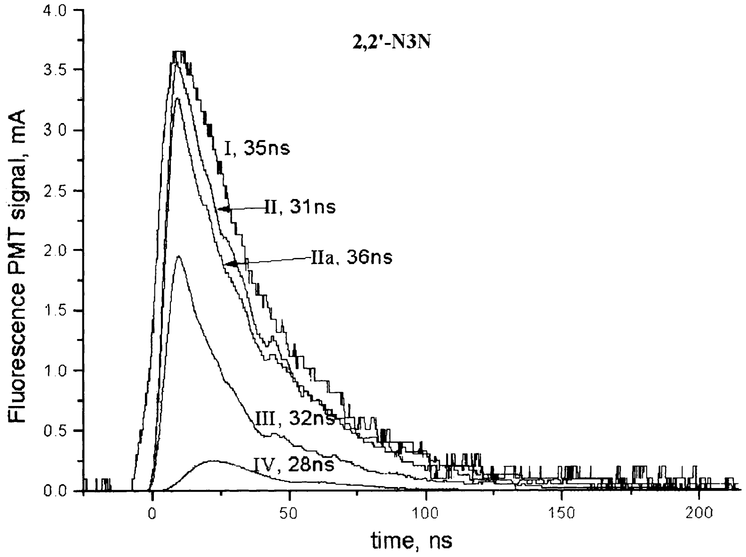

Fig. 4. Fluorescence decay signal of 2,2′-N3N in supersonic jet: (I) signal with no cut-off filter present, (II and IIa) signals monitored after 322 nm cut-off filter, (III) signal monitored after 375 nm cut-off filter, (IV) signal monitored after 450 nm cut-off filter. “Jet off” signals recorded at identical conditions are subtracted from corresponding traces. (I, II, III, IV) excitation at 31875 cm^{-1}, (IIa) excitation at 31496 cm^{-1}.

dinaphthalenes. For example we present, in Table 1, the lifetime data for 2,2′- N2N [56].

3.2. LIF of 2,2′-N3N in supersonic jet

The general features observed for this molecule are similar to that observed for 1,2′-N3N. 2,2′-N3N also produced a strong fluorescence signal, which was essentially independent of the excitation wavelength at 307–322 nm spectral region, characterized by a very similar broad, structureless excitation spectrum. The fluorescence decay signal recorded via different cut-off filters is presented in Fig. 4. The scattered excitation laser signal was relatively significant; hence each trace in Fig. 4 represents a fluorescence signal trace from which a corresponding scattering trace is subtracted. The scattering signal was the strongest when no filter was used, accounting for the low signal to noise ratio of the resulting signal. Most measurements were performed at $\nu_{\mathrm{exc}} = 31875\,\mathrm{cm}^{-1}$ (at which the naphthalene chromophore signal is the strongest in most substances [52]). A signal at a different excitation wavelength ($\nu_{\mathrm{exc}} = 31496\,\mathrm{cm}^{-1}$) is added for comparison, its amplitude and decay time being very close to those of the corresponding signal at $\nu_{\mathrm{exc}} = 31875\,\mathrm{cm}^{-1}$. The decay was non-exponential, with apparent decay times of 35 ns for the whole signal and 28 ns for the red part of the signal.

3.3. Fluorescence spectroscopy of 1,2′-N3N and of 2,2′-N3N in solution

Fluorescence excitation and emission spectra of 1,2′-N3N in solution are presented in Figs. 5 and 6, respectively.

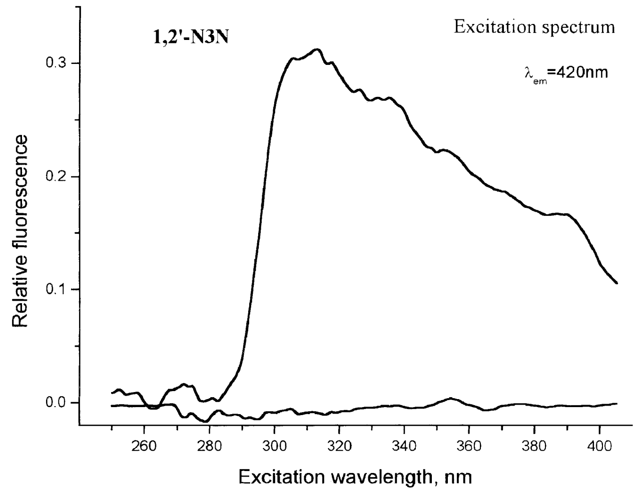

Fig. 5. 1,2′-N3N excitation spectrum in 1×10^{-4} M hexane solution monitored at 420 nm. Traces of pure solvent are shown for reference. Each trace represents average over three measurements.

Each trace represents averaging over three measurements. Pure solvent spectra taken under identical conditions are presented as a reference. The emission spectrum clearly consists of two bands, the regular naphthalenic emission and the red-shifted exciplex emission. This is in accord with previous studies of dinaphthylpropanes in solution [57]. The excitation spectrum is extended far to the red (substituted naphthalenes usually do not absorb in solution above 340 nm, e.g. [58]). Thus, the red-shifted activity is necessarily due to a low-lying intramolecular electronic state involving both chromophores.

The corresponding spectra for 2,2′-N3N are shown in Figs. 7 and 8. They are similar to those of 1,2′-N3N,

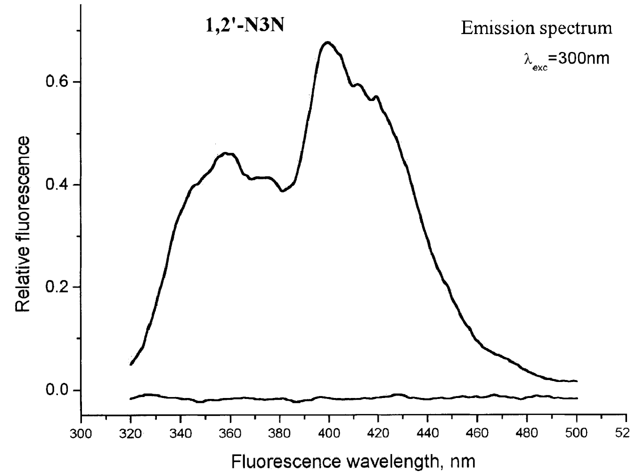

Fig. 6. 1,2′-N3N fluorescence spectrum in 1×10^{-4} M hexane solution upon excitation at 300 nm. Traces of pure solvent are shown for reference. Each trace represents average over three measurements.

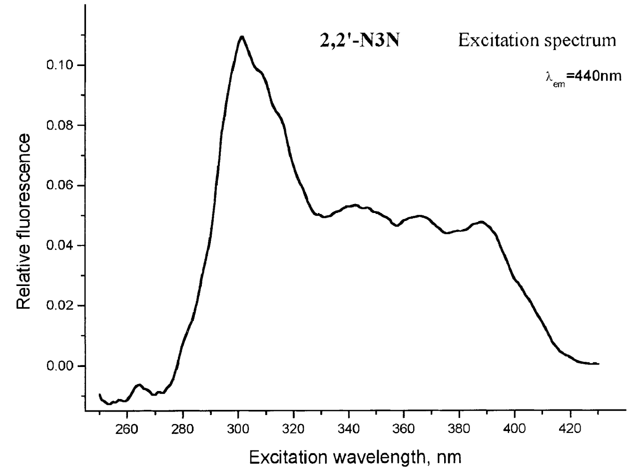

Fig. 7. 2,2′-N3N — excitation spectrum in 1×10^{-4} M hexane solution monitored at 440 nm. Each trace represents average over three measurements.

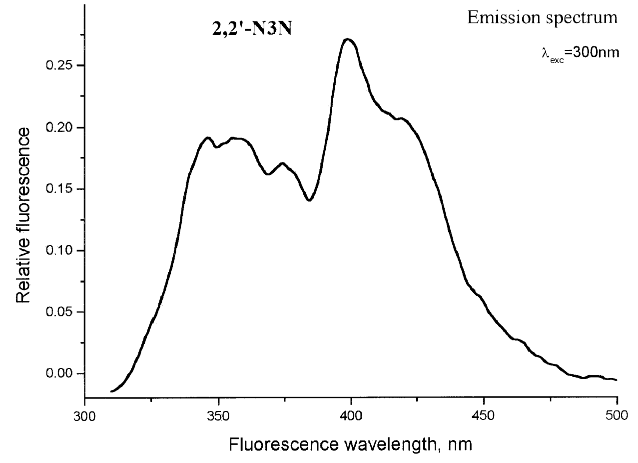

Fig. 8. 2,2′-N3N fluorescence spectrum in 1×10^{-4} M hexane solution upon excitation at 300 nm. Each trace represents average over three measurements.

although the red-shifted part appears to be relatively weaker.

3.4. Discussion

The results of the supersonic jet studies of the *two novel* N3N molecules are unique in comparison to *all* other members of the binaphthalene i, j'-NnN series [2,52]. All other i, j'-NnN molecules exhibit rather reach and discrete LIF excitation spectra, as observed for 2,2′-N2N (Fig. 2), showing vibronic progressions that could be assigned to interchromophore bridge modes have been observed. In addition, exponential fluorescence decay with rather long fluorescence life times (170–270 ns) typical of methylnaphthalene, were recorded for all i, j'-NnN molecules (Table 1), but for $n = 3$. The observed broad featureless excitation spectra for both N3N molecules (Fig. 1) and the much shorter non-exponential decay (Figs. 3 and 4) are very similar to that observed for other strongly coupled naphthalene bichromophoric molecules [53,56], such as the naphthalene dimer [3–7] which exhibits excited state dynamics governed by the change in the relative orientation of the naphthalenic moieties in the sandwich structure through rotation around the interchromophore axis, due to the change in the van der Waals interaction between the chromophores, induced by the change in the electronic π-systems structure. This is the probable cause of the enhanced probability for creating the exciplex state over that of the locally excited S_1 state both in the dimer and in N3N. In N3N such rotation is blocked

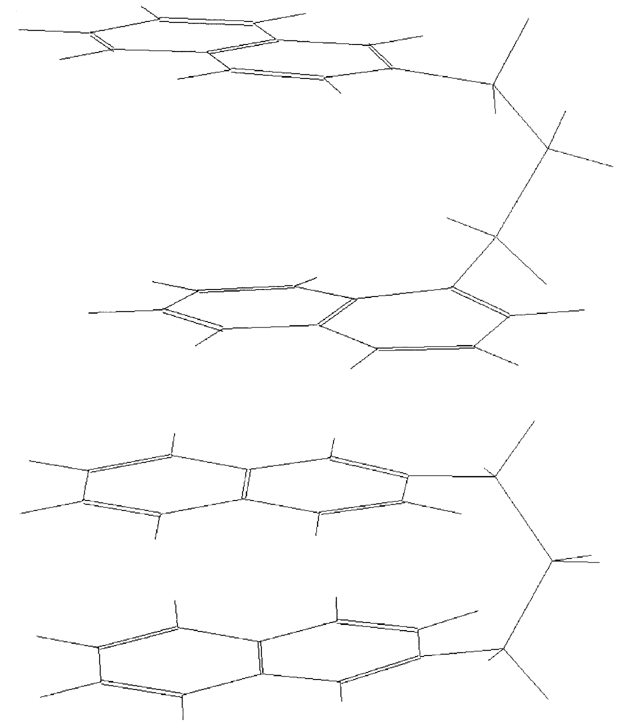

Fig. 9. Calculated conformations of the N3N bichromophoric molecules.

by the bridge, making the effect even stronger compared to the dimer case.

The solution data support this picture. The two emission bands indicate the existence of folded conformers that are directly excited into an intramolecular exciplex state, along with open conformers that are directly excited into a conventional locally excited naphthalenic state. Fig. 9 shows the results of conformational calculations using AMBER force field methods [59], showing the sandwich type conformation typical of $n = 3$ methylene bridge, for which intramolecular exciplex formation is optimized. This observation is in agreement with the kinetic and spectroscopic results obtained for 1,1′ N3N by Smith et al. [12].

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