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Time-Resolved Fluorescence Study of Triple Exciplex Formation in 1,3-Dinaphthylpropane and 1,4-Dicyanobenzene

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Contribution from the Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan. Received June 2, 1975

Abstract: The triple exciplex formation between two naphthyl moieties in 1,3-dinaphthylpropane ($\beta\beta$ - and $\beta\alpha$ -DNP) and 1,4-dicyanobenzene (DCB) was studied by a nanosecond time-resolved fluorescence spectroscopy. The fluorescence spectrum of a dioxane solution of $\beta\beta$ -DNP and DCB in the 380–600-nm region consists of three fluorescence spectra of the intramolecular excimer ($\lambda_{\max} \sim 400$ nm, $\tau = 52$ ns), the exciplex (DA)* (~ 420 nm, 9 ns), and the triple exciplex (DDA)* (~ 490 nm, 110 ns). The fluorescence lifetimes of these three excited species exhibit no concentration dependence of DCB. From no dependence of the excimer fluorescence lifetime on the DCB concentration, it was concluded that the triple exciplex was not formed from the excimer but formed from the exciplex (DA)*. The structure of the triple exciplex and the mechanism of formation are discussed from the results of the triple exciplex formation in $\beta\beta$ - and $\beta\alpha$ -DNP. Furthermore, the association and dissociation rate constants in these excited species are discussed in terms of the inter- and intramolecular interactions.

It has been well established that the exciplex is an intermediate of the bimolecular electron donor-acceptor (EDA) interaction in the excited state, and that the exciplex is an intermediate of the photochemical and photobiological transformations. It is also believed that the exciplex consists of the bimolecular or two electronic systems (1:1). The triple exciplex (2:1) formation between two naphthalene molecules and 1,4-dicyanobenzene (abbreviated to DCB) was reported first by Beens and Weller on a steady-state fluorescence spectroscopy.¹ Little is known, however, regarding the mechanism of formation and the structure of the triple exciplex.

On the other hand, the intramolecular excimer and exciplex were reported in several EDA systems in which the electron donor and acceptor moieties were linked by a trimethylene chain. These intramolecular exciplex formations have several advantages in their efficiency and in the decision of their geometrical conformation. Chandross et al.²

suggested that the strong geometrical preference is unessential in the exciplex formation in the (naphthalene)-(CH₂)₃-(dimethylamine) system. Okada et al.³ also concluded in the intramolecular system of (anthracene)-(CH₂)₃-(*N,N*-dimethylaniline) that a parallel sandwich structure might be favorable but not necessary for the exciplex formation. Itoh et al.,⁴⁻⁶ nevertheless, reported that the exciplex (above ~ 150 K) and the fluorescent EDA complex (below ~ 120 K) were formed both in the intra- and intermolecular systems of 9,10-dicyanoanthracene and alkyl-naphthalenes in the nonpolar solvent, and their experimental and theoretical studies revealed that the exciplex needs geometrically a strong favorable structure.⁷ Furthermore, Chandross and Dempster⁸ reported strong intramolecular excimer formation in the two symmetrical 1,3-dinaphthylpropanes (abbreviated to $\beta\beta$ - and $\alpha\alpha$ -DNP), which implies that the stable excimer conformation is the symmetrical sandwich arrangement. On the other hand, Avouris et al.⁹

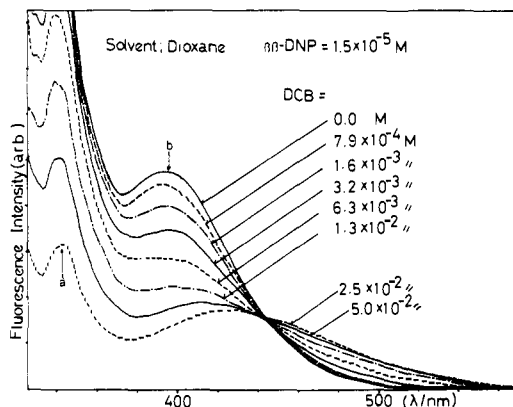


Figure 1. Concentration dependence of the fluorescence spectra of a dioxane solution of $\beta\beta$ -DNP and DCB at room temperature; a and b show the fluorescence from the naphthyl moiety in $\beta\beta$ -DNP and from the intramolecular excimer, respectively. The fluorescence spectra in dioxane are somewhat different with those in methylcyclohexane reported by Chandross and Dempster.⁸ It is ascribed to the solvent viscosity (dioxane, 1.4 cP; methylcyclohexane, 0.7 cP)

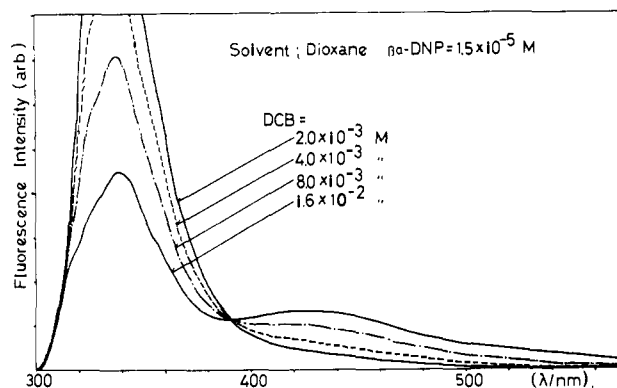


Figure 2. Concentration dependence of the fluorescence spectra of a dioxane solution of $\beta\alpha$ -DNP and DCB at room temperature.

demonstrated that the association rate constant of this intramolecular excimer ($\alpha\alpha$ -DNP) was $\sim 10^4$ times greater than the dissociation rate constant.

In these circumstances, this paper describes the formation and mechanism of the triple exciplex between two naphthyl moieties of DNP and DCB studied by a nanosecond time-resolved fluorescence technique in comparison with the results in the intermolecular system of 2-methylnaphthalene (2-MN) and DCB. The fluorescence of a dioxane solution (or chloroform) of DNP and DCB in the 380–600-nm region consists of three fluorescence spectra of the intramolecular excimer, the exciplex (DA)*, and the triple exciplex (DDA)*. Although the complication of four excited species, including naphthalene, prevents us from analyzing their photochemical process, the intramolecular system provides us with a simplified photophysical study of the exciplex (DA)* and the triple exciplex (DDA)*. It is because the fluorescence lifetimes of the excimer, the exciplex, and the triple exciplex show no concentration dependence of DCB, and the association equilibrium in the triple exciplex, as well as the excimer, is much greater in the intramolecular interaction than in the intermolecular interaction in general. Therefore, the structure of the triple exciplex and the mechanism of formation are discussed from the results of $\beta\beta$ - and $\beta\alpha$ -DNP and also in comparison with the results of the 2-MN and DCB system.

Experimental Section

The samples ($\beta\beta$ - and $\beta\alpha$ -DNP) were synthesized by an analogous method and identified with those reported by Chandross and

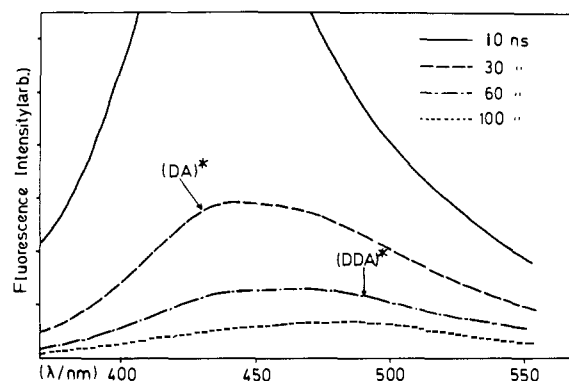


Figure 3. Time-resolved fluorescence spectra of the $\beta\beta$ -DNP and DCB (saturated) system in dioxane. The time indicated is after a laser-pulse excitation.

Dempster.⁸ The fluorescence spectra were recorded with a Hitachi MPF-2A spectrophotometer with an exciting light of 313 nm. Good commercial solvents (Dortite Spectrosols) were used, and chloroform was used after purification through an alumina column (Woelm, Activity I) for removal of methanol as a stabilizer. The solutions of the samples were contained in a rectangular quartz cell (1 cm) equipped with graded seals and degassed by freeze-thaw cycles at $\sim 10^{-4}$ – 10^{-5} Torr. The concentration of DNP was always 10^{-4} – 10^{-5} M in each measurement, where the intermolecular interaction of DNP can be neglected. The time-resolved fluorescence spectra and the fluorescence lifetimes were determined by analyzing exponential decay curves measured by an oscilloscope (Tektronix 465) and a photomultiplier (HTV-R342 or R666) and by an excitation with a coaxial N₂ gas laser which has a maximum ~ 20 -kW photon peak intensity at 3371 Å¹⁰ and ~ 3.5 -nsec duration.

Results and Discussion

A dioxane or chloroform solution of $\beta\beta$ -DNP exhibits the intramolecular excimer fluorescence at room temperature, while a solution of $\beta\alpha$ -DNP exhibits very weak excimer fluorescence, as reported by Chandross and Dempster in the methylcyclohexane solution. The fluorescence spectra of the dioxane solutions of $\beta\beta$ - and $\beta\alpha$ -DNP with various concentrations of DCB are shown in Figures 1 and 2, respectively. In the $\beta\beta$ -DNP and DCB system, the fluorescence due to the naphthyl moiety and the intramolecular excimer (390–400 nm) were markedly quenched with increasing of the DCB concentration, while a broad fluorescence spectrum in the 400–500-nm region appeared, as shown in Figure 1. In the $\beta\alpha$ -DNP and DCB system, a similar fluorescence behavior to that in the $\beta\beta$ -DNP and DCB system was observed, though the fluorescence quenching of the excimer was not seen with increasing DCB concentration. Nanosecond time-resolved fluorescence spectra were determined in the dioxane solutions of both systems of $\beta\beta$ - and $\beta\alpha$ -DNP with DCB. These transient fluorescence spectra are shown in Figures 3 and 4. From these time-resolved spectra and the fluorescence lifetimes, it was demonstrated that the broad fluorescence consists of two fluorescence spectra which are the exciplex (DA)* in the ~ 420 -nm region ($\tau = 9$ ns) and the triple exciplex in the ~ 500 -nm region ($\tau = 110$ ns for $\beta\beta$ -DNP and 117 ns for $\beta\alpha$ -DNP). Figure 5 displays the examples of fluorescence decay curves in the $\beta\beta$ -DNP-DCB system.

The intermolecular triple exciplex fluorescence (~ 480 nm), as well as the exciplex (~ 420 nm), was observed in a dioxane solution of DCB and 2-MN in very high concentration. These intermolecular exciplex and triple exciplex formations are so complicated in the transformation between several excited species that the photophysical or kinetical treatment is rather difficult.

The photochemical scheme of the excimer, the exciplex,

Table I. Fluorescence Maxima and Lifetimes of the Excimer, the Exciplex, and the Triple Exciplex, and Their Association Rate Constants

	Fluorescence lifetimes, ns (λ_{\max} , nm)			Rate constant		
	(DD)*	(DA)*	(DDA)*	$\times 10^7$ s ⁻¹ k_4	$\times 10^9$ s ⁻¹ M ⁻¹ k_3	$\times 10^7$ s ⁻¹ k_9
Dioxane						
$\beta\beta$ -DNP	52 (400)	9 (420)	110 (490)	2.9	4.9 (4.7) ^a	4.4
$\beta\alpha$ -DNP	65	9 (420)	117 (490)	4.6	2.8 (4.4)	4.4
Chloroform						
$\beta\beta$ -DNP	43 (400)	8 (430)	76 (510)	11.0	4.5 (5.0)	5.5
$\beta\alpha$ -DNP	57	8 (430)	68 (510)	8.9	4.2 (7.3)	5.5

^a The rate constant in parentheses is obtained from the fluorescence lifetime of D* as mentioned in the text.

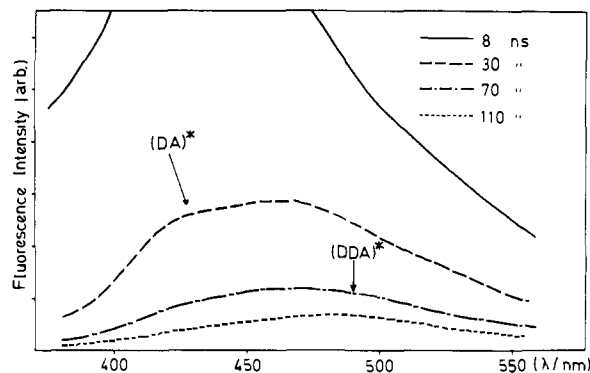


Figure 4. Time-resolved fluorescence spectra of the $\beta\alpha$ -DNP and DCB (saturated) system in dioxane.

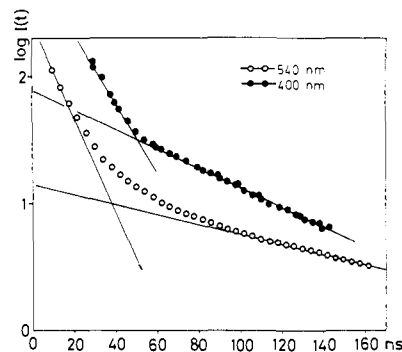
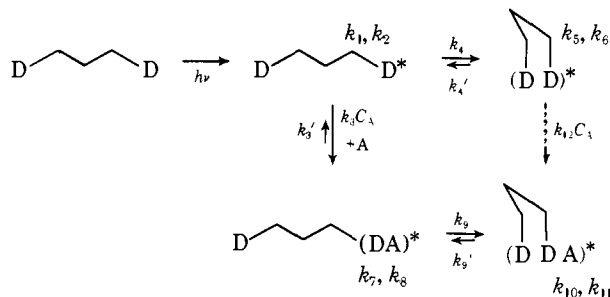


Figure 5. Plots of fluorescence decay curves of a dioxane solution of $\beta\beta$ -DNP and DCB (2×10^{-2} M).

Scheme I



and the triple exciplex is shown in Scheme I, where D is the naphthyl moiety in DNP, or 2-MN in the intermolecular system; A is the DCB molecule, the concentration of which is expressed by C_A . The rate constants k_1 , k_5 , k_7 , and k_{10} are the radiative rate constants of each excited species, and k_2 , k_6 , k_8 and k_{11} are nonradiative rate constants, respectively. The rate constants of k_3 , k_4 , k_9 , and their primed counterparts are the association and dissociation rate constants of the excimer, the exciplex, and the triple exciplex, respectively. It is noteworthy that the association and dissociation rate processes in the intramolecular interaction cannot depend on the concentration of DCB.

The fluorescence intensity and lifetime monitored at 350 or 360 nm of the naphthyl moiety of DNP were determined in the various concentrations of DCB. The association rate constant of the exciplex (k_3) was obtained from the Stern-Volmer plots which exhibited a linear relation against the DCB concentration. The fluorescence lifetime of D* in DNP is represented as $(k_1 + k_2 + k_3 C_A + k_4)^{-1}$. Then, the rate constant k_3 was also obtained from the fluorescence lifetimes of D* in the solutions with several concentrations of DCB. The rate constants obtained by the two methods mentioned above are in good agreement, as summarized in Table I. This means that k_3' can be neglected compared with k_3 .

The fluorescence lifetime of the exciplex (DA)* may be

expressed as the following equation in the intramolecular system of DNP and DCB:

$$\tau = (k_3' + k_7 + k_8 + k_9)^{-1}$$

Since the association from (DA)* to (DDA)* in the intermolecular system may be neglected in a very dilute solution of 2-MN compared with DCB, the fluorescence lifetime of (DA)* in this intermolecular system is expressed by $(k_7 + k_8 + k_3')^{-1}$. Therefore, the radiative and nonradiative rate constants of the exciplex (DA)* in the DNP and DCB system were assumed to be the same as the corresponding rate constants obtained in the 2-MN and DCB system, respectively. From these assumptions, the association rate constant of the triple exciplex (k_9) was obtained from the fluorescence lifetimes of the exciplex (DA)* in the inter- and intramolecular systems.

The association rate constant of the intramolecular excimer ($\alpha\alpha$ -DNP) was reported to be 10^4 times greater than the dissociation rate constant from the fluorescence rise and decay curves of the excimer in ethanol-glycerol, as mentioned in the introductory section.⁹ Furthermore, Chuang et al.^{11,12} reported very rapid intramolecular exciplex formation (picosecond) in the (anthracene)-(CH₂)₃-(N,N-dimethylaniline) system. In dioxane or chloroform solution, fluorescence rise was detected neither in the intramolecular excimer nor in the triple exciplex of DNP and DCB. Therefore, it was reasonably assumed that $k_4 \gg k_4'$, and also $k_9 \gg k_9'$, as will be mentioned later.

If the association process (rate constant, k_{12}) between the excimer and DCB was taken into account, the fluorescence lifetime of the excimer was represented as follows:¹³

$$\tau = (k_4' + k_5 + k_6 + k_{12} C_A)^{-1}$$

Here, it was observed that the fluorescence lifetimes of the excimer in dioxane and chloroform solutions of DNP did not depend on the DCB concentration, as shown in Figure 6. No concentration dependence of the excimer fluorescence lifetimes demonstrates that the triple exciplex was not formed through the excimer, but formed from the exciplex

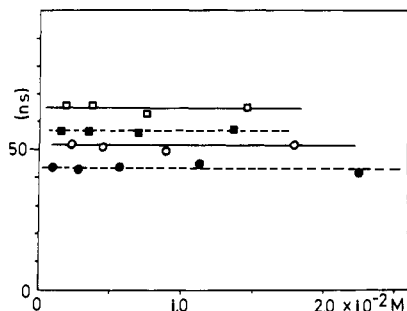


Figure 6. Fluorescence lifetimes (an ordinate) of the intramolecular excimers of $\beta\beta$ - and $\beta\alpha$ -DNP in both solvents of dioxane (O and \square) and chloroform (\bullet and \blacksquare) monitored at 400 nm with various concentrations (an abscissa) of DCB, respectively.

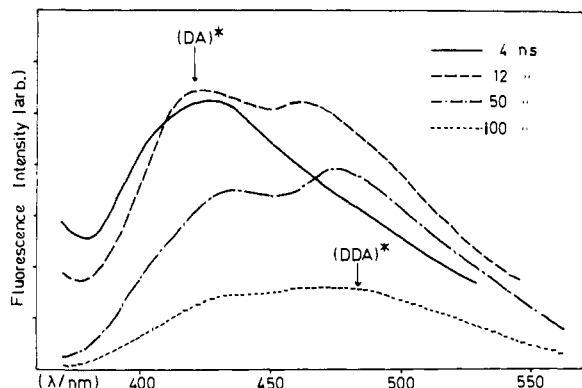


Figure 7. Time-resolved fluorescence spectra of the intermolecular system of 2-MN (2×10^{-1} M) and DCB (2×10^{-2} M) in dioxane.

(DA)*. This is a somewhat mysterious phenomenon. It may be due to the fact that the absolute energy level of (DD)* is lower than that of (DDA)*. The triple exciplex fluorescence was also observed to be independent of the DCB concentration. This is consistent with the postulation of $k_9 \gg k_9'$, as mentioned above. From these arguments, the association and dissociation rate processes in the intramolecular system are worth comparing with the subsequent results in the intermolecular system of 2-MN and DCB. In a dioxane or chloroform solution of 2-MN and DCB, the excimer formation was neglected under our condition. Figure 7 shows the time-resolved fluorescence spectra of the dioxane solution. Time development of the triple exciplex fluorescence exhibits its rise and decay processes, as shown in Figure 8, though no rise time was observed in the exciplex (DA)* fluorescence. Slow formation of the intermolecular triple exciplex is consistent with the observation of the double exponential decay curve of the exciplex (DA)*, which implies a significant dissociation process from the triple exciplex to (DA)*.¹⁴ The photochemical or photophysical study of the intermolecular exciplex and triple exciplex are reported elsewhere.¹⁵

The fluorescence lifetimes and the association rate constants of the excimer, the exciplex, and the triple exciplex obtained here are summarized in Table I. The association rate process in the exciplex between a naphthyl moiety of DNP and DCB seems to be a usual diffusion-controlled reaction in the solution. In the intramolecular interactions, an entropy factor and also a rotational barrier of the trimethylene chain might affect considerably their association and dissociation in the less viscous solvent. However, the intramolecular association in the triple exciplex as well as the excimer cannot be compared with the intermolecular association, because the former obeys different kinetics from those of the latter. On the other hand, the dissociation rate con-

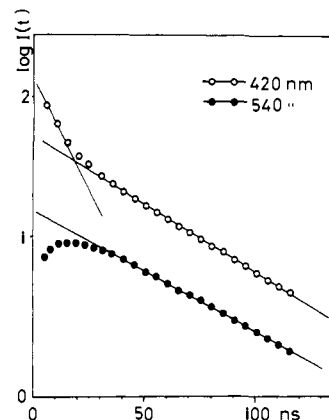


Figure 8. Typical two-component fluorescence decay curves of a dioxane solution of 2-MN and DCB. The plot monitored at 540 nm is determined in the solution of 2-MN (2×10^{-1} M) and DCB (2×10^{-2} M), and the plot monitored at 420 nm is determined in the solution of 2-MN (1.8×10^{-3} M) and DCB (2×10^{-2} M).

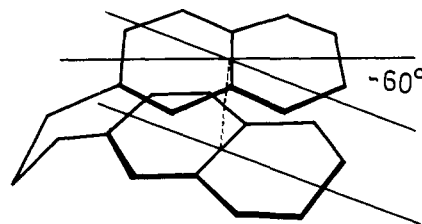


Figure 9. A tentatively proposed model of the DNP portion of the triple exciplex (shown in the case of $\beta\beta$ -DNP).

stants seem to be negligibly lower in the intramolecular interaction than in the intermolecular interaction. This is attributable to the effect of the trimethylene chain that locks the molecule in the favorable conformation of the triple exciplex or excimer. The association rate constants and the fluorescence lifetimes of the triple exciplex in $\beta\beta$ - and $\beta\alpha$ -DNP are almost identical with each other, while the fluorescence behavior of the intramolecular excimer of these compounds exhibits considerable difference. As mentioned above, the favorable intramolecular excimer of DNP was regarded as a parallel sandwich structure of the long axis in the naphthyl moiety, and the excimer of $\beta\alpha$ -DNP which cannot take the parallel conformation may have a different structure from that of $\beta\beta$ -DNP. However, both $\beta\beta$ - and $\beta\alpha$ -DNP can have a common sandwich geometry, where two naphthyl moieties are twisted in the molecular plane by a small angle (approximately 60°) around an axis perpendicular to the plane, as shown in Figure 9. From these arguments, it is likely that two naphthyl moieties in the triple exciplex of both $\beta\beta$ - and $\beta\alpha$ -DNP have a similar geometry to this twisted model.

Acknowledgment. The authors are indebted to Dr. Keitaro Yoshihara of the Institute of Physical and Chemical Research for suggesting to us the construction of a nitrogen-gas laser.

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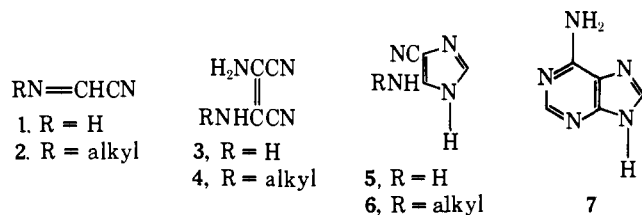
N-Alkylformimidoyl Cyanides and Isocyanides¹

Joseph H. Boyer* and Johannes Kooi

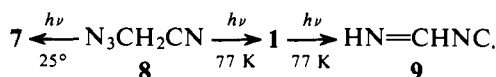
Contribution from the Chemistry Department, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680. Received June 18, 1975

Abstract: An *N*-chloro derivative (**11**), from an *N*-alkylaminoacetonitrile (**10**) and calcium hypochlorite, was dehydrochlorinated by calcium hydroxide into (*E*)- and (*Z*)-*N*-alkylformimidoyl cyanides (**2**) and the isomeric isocyanide **12**; similar dehydrochlorination gave an *N*-alkylchloroformimidoyl cyanide (**13**) from the α ,*N*-dichloro-*N*-alkylaminoacetonitrile. Both diethyl azodicarboxylate and *o*-chloranil dehydrogenated the amine **10d** ($R = (CH_3)_3C$) into the imidoyl cyanide **2d** ($R = (CH_3)_3C$), but gave intractable mixtures with **10b** ($R = C_2H_5$) and **10c** ($R = (CH_3)_2CH$); aminoacetonitrile and diethyl azodicarboxylate gave *N,N'*-dicyanomethylazodicarboxamide. Stannic chloride, and other Lewis acids, catalyzed the dimerization of **2** into an *N,N'*-dialkylaminomaleonitrile (**19**), but did not dimerize an *N*-alkylacetimidoyl cyanide (**14**).

Identification of a dimer of hydrogen cyanide as formimidoyl cyanide (**1**) was justified by the kinetic requirement for the combination of a cyanide anion and hydrogen cyanide to be rate determining in tetramerizing the latter at pH 9.2 into diaminomaleonitrile (**3**).²⁻⁴ Formation of a mono-*N*-alkyl derivative **4** of the tetramer **3** from an *N*-alkylformimidoyl cyanide (**2**) and 2 mol of hydrogen cyanide, and the photoisomerization of both **3** and **4** into the corresponding 4-amino-5-cyanoimidazole **5** and **6** confirmed this structural assignment for $(HCN)_2$.⁵⁻⁷ Addition of hydrogen cyanide transformed **5** into adenine⁶ (**7**), but a similar transformation was unavailable to **6**.



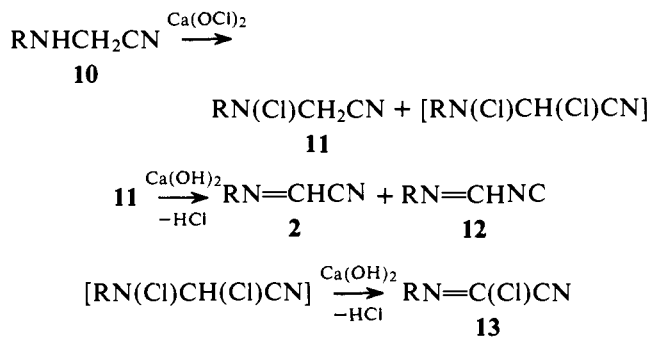
Formimidoyl cyanide (**1**) was first obtained from azidoacetonitrile (**8**) by the photoelimination of nitrogen at 77 K. A slow change has been attributed to photoisomerization at 77 K into formimidoyl isocyanide (**9**).⁸⁻¹¹ At room temperature, photolysis of the azide **8** gave hydrogen cyanide (27%), adenine (**7**) in low yield, and **1** as a transient detected by infrared spectroscopy.⁸



Heretofore, *N*-alkyl derivatives **12** of formimidoyl isocyanide (**9**) were unknown. Photoisomerization of cyanide **2** into isocyanide **12** was reported in error.⁸

Results and Discussion

An *N*-alkylaminoacetonitrile (**10**) and calcium hypochlorite below 25° gave an *N*-chloro-*N*-alkylaminoacetonitrile **11**. Near 40° the *N*-chloro compound (**11**) reacted slowly with calcium hypochlorite to give an α ,*N*-dichloro-*N*-alk-



a, R = CH₃; b, R = C₂H₅; c, R = *i*-C₃H₇; d, R = *t*-C₄H₉

ylaminoacetonitrile. Dehydrochlorination by calcium, lithium, sodium, or barium hydroxide transformed **11** into an *N*-alkylformimidoyl cyanide (**2**) sometimes contaminated with traces of the corresponding *N*-alkylformamide and *N*-alkylchloroformimidoyl cyanide (**13**). Optimum yields of **2** [$R = CH_3$ (25%), CH_3CH_2 (50%), $(CH_3)_2CH$ (72%), and $(CH_3)_3C$ (76%)] were obtained when the last step occurred under temperatures of 25, 32, 38, and 78°, respectively.

Aminoacetonitrile underwent a similar transformation into the short-lived formimidoyl cyanide (**1**) detected by its absorption⁸ at 3270 (NH), 2960 (CH), 2205 (C≡N), 1605 (>C=N—), 1405, and 1320 cm⁻¹; it rapidly darkened as polymerization occurred.

The *N*-alkylformimidoyl isocyanide **12** was also produced when dehydrochlorination occurred in methylene chloride at 35°, $R = CH_3$; at 41°, $R = C_2H_5$ and $(CH_3)_3CH$; and in carbon tetrachloride at 78°, $R = (CH_3)_3C$. Dehydrochlorination of **11** with triethylamine gave cyanide **2** but did not give isocyanide **12**.

When *N*-ethyl- (**11b**) or *N*-isopropyl-*N*-chloroaminoacetonitrile (**11c**) was treated with an excess of calcium hypochlorite in refluxing methylene chloride for 2 weeks, the corresponding *N*-alkylchloroformimidoyl cyanide **13b** or **13c** was the predominant product along with traces of the appropriate cyanide **2b** or **2c**. The similar transformation of **11d** → **13d** was not detected.