

# Absorption Spectra and Dynamics of Some Excited and Ionic Dicarbazolyl Compounds with Specific Geometrical Structures

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**Abstract:** Absorption spectra of *N*-ethylcarbazole, 1,2-*trans*-di-*N*-carbazolylcyclobutane, 1,3-di-*N*-carbazolylpropane, *rac*-(*dd,ll*)-2,4-di-*N*-carbazolylpentane, and *meso*(*dl*)-2,4-di-*N*-carbazolylpentane in the excited singlet, triplet, cationic, and anionic states were measured with nanosecond and picosecond laser photolysis methods. The spectrum of the triplet state and anion radical is common to all these compounds, while the spectrum of the excited singlet state and cation radical is sensitive to their geometrical structure and shows the formation of different excimer and dimer cations. In the excited singlet state the sandwich structure gives an absorption spectrum that is different from the monomer  $S_n \leftarrow S_1$  spectrum, while the absorption spectral shape of the cation changes from that of the reference monomer and extent of the change increases in the order of sandwich structure < open form < partial overlap one. These results were compared with those for intramolecular naphthalene and phenanthrene systems. On the basis of the relative  $T_n \leftarrow T_1$  absorbance, the sandwich excimer formation was confirmed to increase the triplet yield. This was ascribed to the longer lifetime compared to that of the monomer fluorescent state and not to the increase of the rate constant of the corresponding intersystem crossing process. The intersystem crossing to the ground state is sensitive to the geometrical structure and enhanced in the partial overlap one. These dicarbazolyl compounds are noted to be good model systems for the study on carbazole aggregates.

Molecular interaction between aromatic hydrocarbons in solution is one of the interesting problems in chemistry and has been investigated extensively. In the excited and ionic states this interaction is enhanced compared to the ground state, leading to familiar phenomena of excimer and dimer ion formations. Most aromatic hydrocarbons show singlet excimer emission at high concentration, as revealed by measurement of fluorescence spectra, fluorescence lifetimes, and transient absorption spectra.<sup>1-8</sup> Although the history of excimer formation in the triplet state is also long, the possibility of impurity emission has always been raised.<sup>9</sup> Recently the absorption spectra of triplet excimers have been measured in intramolecular excimer systems with two aromatic groups combined with aliphatic hydrocarbon molecules.<sup>10-12</sup> Another problem related to the triplet systems is a relation between the intersystem crossing rate constant and the excimer interaction, but data concerning this aspect are scarce.<sup>13-16</sup>

On the other hand, interaction in the ionic states has been an important topic in radiation chemistry. Irradiation of rigid solutions containing aromatic hydrocarbons leads to the production of molecular ion radicals, and slight warming and successive rapid cooling result in the formation of cation radicals of dimer or high aggregates.<sup>17,18</sup> At room temperature, pulse radiolysis has been applied in order to elucidate the formation process of dimer cation radicals.<sup>19</sup> Dimer anion radical has been observed only in some olefinic compounds without an aromatic ring and acetonitrile as an intermediate of polymerization<sup>20</sup> and in the decomposition of dimer model compounds.<sup>21</sup>

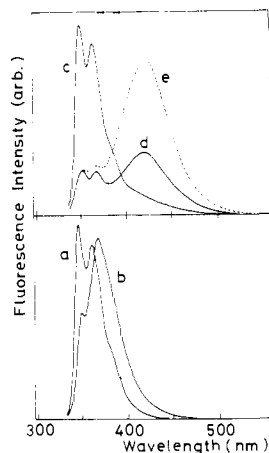
These interactions are closely related to primary photoprocesses of molecular aggregates and polymers. Although carbazole and phenanthrene are aromatic molecules that do not form excimers,<sup>22,23</sup> polymers having these chromophores show characteristic excimer emission.<sup>24-26</sup> In the case when these polymers in the excited state are quenched by an electron donor or acceptor in polar solvents, ion radicals bound in the polymer were detected.<sup>27-32</sup> It is expected that in polymer systems the above described dimeric interaction in the excited and ionic states is enhanced, or that a new electronic structure with delocalized excitation (or charge) is produced. There is also a possibility that the absorption spectrum of the excited (or ionic) polymers consists of a statistical

superposition of bands of different excimers (or dimer ions) with different geometrical configuration. It is thus very important to

- (1) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, London, 1970, Chapter 7.
- (2) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed., Academic Press, New York, 1971.
- (3) J. T. Richards and J. K. Thomas, *Chem. Phys. Lett.*, **5**, 527 (1970).
- (4) P. M. Post, J. Langelaar, and J. D. W. Van Voorst, *Chem. Phys. Lett.*, **10**, 468 (1971).
- (5) C. R. Goldschmidt and M. Ottolenghi, *J. Phys. Chem.*, **74**, 2041 (1970); **75**, 3894 (1971).
- (6) N. Nakashima, M. Sumitani, I. Ohmine, and K. Yoshihara, *J. Chem. Phys.*, **72**, 2226 (1980).
- (7) K. Hamanoue, T. Hidaka, T. Nakayama, and H. Teranishi, *Chem. Phys. Lett.*, **82**, 55 (1981).
- (8) H. Masuhara, H. Miyasaka, N. Ikeda, and N. Mataga, *Chem. Phys. Lett.*, **82**, 59 (1981).
- (9) J. Langelaar, R. P. H. Rettschnick, A. M. F. Lambooy, and G. J. Hoytink, *Chem. Phys. Lett.*, **1**, 609 (1968); M. Aikawa, T. Takemura, and H. Baba, *Bull. Chem. Soc. Jpn.*, **49**, 437 (1976).
- (10) P. C. Subudhi and E. C. Lim, *Chem. Phys. Lett.*, **56**, 59 (1978); *J. Chem. Phys.*, **63**, 5491 (1975); S. Okajima, P. C. Subudhi, and E. C. Lim, *ibid.*, **67**, 4611 (1977).
- (11) K. A. Zachariasse, R. Busse, U. Schrader, and W. Kühnle, *Chem. Phys. Lett.*, **89**, 303 (1982).
- (12) N. Tamai, H. Masuhara, N. Mataga, *J. Phys. Chem.*, in press.
- (13) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **62**, 1785 (1966).
- (14) W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969).
- (15) R. B. Cundall, L. C. Pereira, and D. A. Robinson, *Chem. Phys. Lett.*, **13**, 253 (1972).
- (16) R. R. Hentz and R. M. Thibault, *J. Phys. Chem.*, **77**, 1105 (1973).
- (17) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2576, 2582, 2588 (1969); **66**, 2939 (1970).
- (18) A. Kira, M. Imamura, and T. Shida, *J. Phys. Chem.*, **80**, 1445 (1976); A. Kira, T. Nakamura, and M. Imamura, *ibid.*, **81**, 511 (1977).
- (19) A. Kira, S. Arai, and M. Imamura, *J. Chem. Phys.*, **54**, 4890 (1971); *J. Phys. Chem.*, **76**, 1119 (1972).
- (20) S. Arai, A. Kira, and M. Imamura, *J. Phys. Chem.*, **81**, 110 (1977); Y. Hirata, N. Mataga, Y. Sakata, and S. Mijumi, *ibid.*, **87**, 1493 (1983).
- (21) T. Shida and S. Iwata, *J. Chem. Phys.*, **56**, 2858 (1972).
- (22) M. Yokoyama, T. Tamamura, T. Nakano, and H. Mikawa, *Chem. Lett.*, 499 (1972); M. Yokoyama, T. Tamamura, M. Atumi, M. Yoshimura, Y. Shirota, and H. Mikawa, *Macromolecules*, **8**, 101 (1975).
- (23) E. A. Chandross, J. W. Longworth, and R. E. Visco, *J. Am. Chem. Soc.*, **87**, 3259 (1965); E. A. Chandross and H. Thomas, *ibid.*, **94**, 2421 (1972).
- (24) G. E. Johnson, *J. Chem. Phys.*, **62**, 4097 (1975).
- (25) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976).
- (26) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **50**, 52 (1977).

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**Figure 1.** Fluorescence spectra of some dicarbazolyl compounds in THF (uncorrected): (a) DCzB, (b) r-DCzPe, (c) DCzP, (d) m-DCzPe, (e) m-DCzPe in  $\text{CH}_3\text{CN}$ . Excitation wavelength is 338 nm.

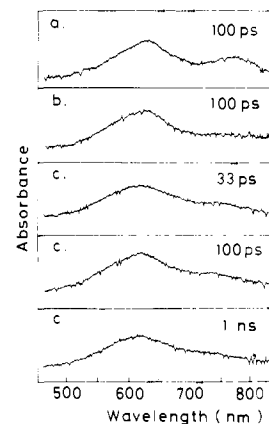
establish a relation between the electronic absorption spectra and the geometrical configuration of dimer compounds for elucidating the nature of molecular aggregates including polymers.

Generally speaking, geometrical configurations of excimer and dimer ions are still beyond our knowledge, and one fruitful method for obtaining the information on geometry is to estimate their stabilization energy by MO calculation.<sup>33,34</sup> Another approach was to investigate the behavior of dimer model compounds such as 1,3-diarylpropane,<sup>11,35-38</sup> which has been extended to the studies on bichromophoric compounds with specific configurational structures.<sup>39,40</sup> This approach has been strongly stimulated by the studies on polymer photophysics, and various kinds of model compounds have been synthesized. According to a recent study,<sup>40</sup> the carbazole chromophore is one of the best compounds for the relevant studies, since the electronic spectrum of this compound is very sensitive to the relative geometrical structure. From this viewpoint, some dicarbazolyl compounds with specific geometrical structures have been investigated by means of picosecond and nanosecond laser photolysis systems, and the absorption spectra as well as dynamics of the excited and ionic states are reported here.

### Experimental Section

1,3-Di-*N*-carbazolylpropane (DCzP) and 1,2-trans-di-*N*-carbazolylcyclobutane (DCzB) are the same samples as used before.<sup>41</sup> *rac*(*dd*,*ll*)-2,4-Di-*N*-carbazolylpentane (r-DCzPe) and *meso*(*dl*)-2,4-di-*N*-car-

- (27) H. Masuhara, S. Ohwada, N. Mataga, A. Itaya, K. Okamoto, and S. Kusabayashi, *Chem. Phys. Lett.*, **59**, 188 (1978).  
 (28) H. Masuhara, S. Ohwada, K. Yamamoto, N. Mataga, A. Itaya, K. Okamoto, and S. Kusabayashi, *Chem. Phys. Lett.*, **70**, 276 (1980).  
 (29) H. Masuhara, S. Ohwada, Y. Seki, N. Mataga, K. Sato, and S. Tazuke, *Photochem. Photobiol.*, **32**, 9 (1980).  
 (30) H. Masuhara, S. Ohwada, N. Mataga, A. Itaya, K. Okamoto, and S. Kusabayashi, *J. Phys. Chem.*, **84**, 2363 (1980).  
 (31) H. Masuhara and N. Mataga, *J. Lumin.*, **24/25**, 511 (1981).  
 (32) H. Masuhara, H. Shioyama, N. Mataga, T. Inoue, N. Kitamura, T. Tanabe, and S. Tazuke, *Macromolecules*, **14**, 1738 (1981).  
 (33) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3131 (1964); T. Azumi, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **41**, 3839 (1964); T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **42**, 1675 (1965).  
 (34) E. J. P. Malar and A. K. Chandra, *Theor. Chim. Acta*, **55**, 153 (1980).  
 (35) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).  
 (36) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 705 (1970).  
 (37) G. E. Johnson, *J. Chem. Phys.*, **61**, 3002 (1974); **63**, 4047 (1975).  
 (38) K. Zachariasse and W. Kühnle, *Z. Phys. Chem. (Wiesbaden)*, **101**, 267 (1976).  
 (39) (a) F. C. De Schryver, L. Moens, M. Van der Auweraer, N. Boens, L. Monnerie, and L. Bokobza, *Macromolecules*, **15**, 64 (1982). (b) F. C. De Schryver, K. De Mayer, M. Van der Auweraer, and E. Quanten, *Ann. N. Y. Acad. Sci.*, **93**, 366 (1981). S. Ito, M. Yamamoto, and Y. Nishijima, *Bull. Chem. Soc. Jpn.*, **54**, 35 (1981).  
 (40) F. C. De Schryver, J. Vandendriessche, S. Toppet, K. De Mayer, and N. Boens, *Macromolecules*, **15**, 406 (1982).  
 (41) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **52**, 3737 (1979); N. Kitamura, T. Inoue, and S. Tazuke, *Chem. Phys. Lett.*, **89**, 329 (1982).  
 (42) H. Masuhara, N. Ikeda, H. Miyasaka, and N. Mataga, *Bunko Kenkyu*, **31**, 19 (1982).  
 (43) S. Yasoshima, H. Masuhara, N. Mataga, H. Suzuki, T. Uchida, and S. Minami, *Bunko Kenkyu*, **30**, 93 (1981).



**Figure 2.** Time-resolved absorption spectra of some dicarbazolyl compounds in THF: (a) EtCz, (b) DCzB, (c) r-DCzPe. Delay times are indicated in the figure.

bazolylpentane (m-DCzPe) were synthesized and purified by the same method as reported previously.<sup>40</sup> *N*-Ethylcarbazole (EtCz) was used as a monomer model compound. 1,4-Diazabicyclo[2.2.2]octane (Dabco) (Tokyo Kasei) was purified by repeated recrystallization from the mixed solvent of acetone and *n*-hexane. Dimethyl terephthalate (DMTP) (Nakarai, GR) was 4 times recrystallized from ethanol. THF and *N,N*-dimethylformamide (DMF) (Dotite Spectrosol) were purified by distillation in a vacuum. These solvents dissolve poly(*N*-vinylcarbazole) and make it possible to compare its dynamics with that of the present model compounds in the same solvent. Acetonitrile (Dotite Spectrosol) was used without further purification. The absorbance at the excitation wavelength was adjusted to be  $\sim 0.5$ , which corresponds to  $\sim 10^{-3}$  and  $\sim 10^{-4}$  M solutions for the picosecond and submicrosecond laser photolyses, respectively. All the solutions were deaerated by flashing with  $\text{N}_2$  gas or by the freeze-pump-thaw method.

The time-resolved absorption spectra in the picosecond and a few nanosecond time range were measured with a microcomputer-controlled picosecond  $\text{Nd}^{3+}$ :YAG laser photolysis system the details of which were published elsewhere.<sup>42</sup> The carbazole chromophore was excited with the third harmonic (355 nm,  $\sim 22$  ps fwhm). The origin of the time axis corresponds to the time when both exciting and monitoring pulses take the maximum temporal overlap. The time-resolved absorption spectra in the submicro- to microsecond time range were obtained by using a microcomputer-controlled  $\text{N}_2$  gas laser photolysis system.<sup>43</sup> Fluorescence rise and decay curves were measured by a combination of the second harmonic of a picosecond ruby laser, a high speed microchannel plate photomultiplier (HTV R-1194UX), and Tektronix storage oscilloscope 7834 equipped with 7819 and 7B80. The monomer fluorescence and sandwich excimer emission were selected with an appropriate filter.

### Results

**Spectral and Temporal Aspects of the Fluorescence.** Fluorescence spectra of the present compounds were examined under the same experimental condition and are shown in Figure 1. The vibrational structure and fluorescence lifetime of DCzB are the same as those of EtCz, indicating no interchromophore interaction in the excited singlet state. The fluorescence spectrum of DCzP shows the monomer fluorescence and the sandwich excimer emission, as previously reported by Johnson.<sup>37</sup> The rise and decay time constants were measured to be 2.9 and 32 ns in acetonitrile, 5.2 and 31 ns in THF, and 6.8 and 28 ns in DMF, respectively. The relative contribution of the sandwich excimer is enhanced in the case of m-DCzPe and shows a solvent dependence as demonstrated in Figure 1. The sandwich excimer is formed within 1 ns, while the decay time constant equals 41 ns in acetonitrile and 38 ns in THF. In the case of r-DCzPe, a new broad structureless emission with a peak at 370 nm was observed in addition to the monomer fluorescence. This emission is different from that of the sandwich excimer and has been assigned to the second excimer where one phenyl moiety is on the top of that of the other carbazolyl group.<sup>40</sup>

(42) H. Masuhara, N. Ikeda, H. Miyasaka, and N. Mataga, *Bunko Kenkyu*, **31**, 19 (1982).

(43) S. Yasoshima, H. Masuhara, N. Mataga, H. Suzuki, T. Uchida, and S. Minami, *Bunko Kenkyu*, **30**, 93 (1981).

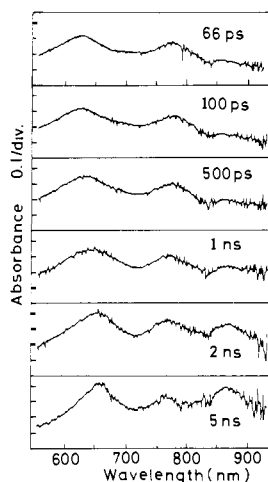


Figure 3. Time-resolved absorption spectra of DCzP in acetonitrile. Delay times are indicated in the figure.

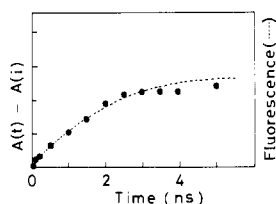


Figure 4. Rise curves of the difference transient absorbance ( $A(t) - A(i)$ ) (870 nm) (●) and the sandwich excimer fluorescence (---) of DCzP in acetonitrile. Here,  $A(t)$  and  $A(i)$  are the absorbances at the delay time  $t$  and immediately after excitation, respectively.

**Picosecond Laser Photolysis of Quencher-Free Systems.** The absorption spectrum of EtCz in THF, observed at 100 ps after excitation, shows two bands at 625 and 780 nm, as shown in Figure 2a. This spectrum is observed immediately after excitation, and the relative intensity of the 780-nm band decreases at later stages. In cyclohexane (less polar than THF) and in the case of low excitation intensity in THF, the relative contribution of the 780-nm band is suppressed. Taking into consideration these results and the spectral similarity to the reference bands of the excited singlet and cationic states of EtCz,<sup>27,30,44,45</sup> the bands at 625 and 780 nm are safely ascribed to the fluorescence and cation states of EtCz, respectively. The latter cation was considered to be produced biphotonically because the same process was observed with nanosecond pulse excitation whose photon density per unit time was smaller than that of the present ps pulse excitation.<sup>40a</sup> The absorption band shape of DCzB at 625 nm (Figure 2b) is identical with that of EtCz, which is consistent with the fluorescence studies described above. The broad band in the wavelength region longer than 700 nm may be ascribed to DCzB cation (see later).

The time-resolved absorption spectra of r-DCzPe are shown in Figure 2c. Its spectral shape is almost similar to that of EtCz except that the peak position is a little shifted to the blue side. Its peak absorbance is almost the same as that of EtCz and DCzB. The absorption above 700 nm is due to its cation radical.

The absorption spectrum of DCzP in acetonitrile shows an interesting spectral change, which is clearly demonstrated in Figure 3. The spectrum obtained at 66 ps is similar to that of EtCz, including the wavelength region beyond 800 nm. The absorption band maximum shifts from 625 to 660 nm at long delay times, which is accompanied by the increase of a new absorption band at 870 nm. The rise kinetics of the latter band is reported in Figure 4, and a good agreement with that of the sandwich excimer emission was obtained, indicating that the spectrum observed at

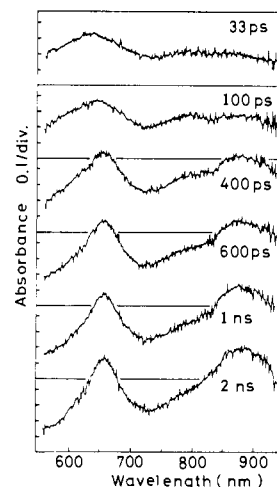


Figure 5. Time-resolved absorption spectra of m-DCzPe in THF. Delay times are indicated in the figure.

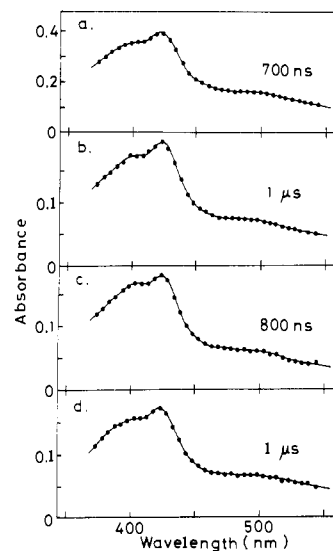


Figure 6. Transient absorption spectra of some dicarbazolyl compounds in THF: (a) m-DCzPe, (b) r-DCzPe, (c) DCzB, (d) EtCz. Delay times are indicated in the figure.

a few nanosecond delay time is mainly due to the sandwich excimer. The second excimer is excluded as a candidate giving the present transient absorption bands, because DCzP shows only the sandwich excimer besides the monomer fluorescence. A similar absorption spectral change was observed in THF, and its time scale is longer than that in acetonitrile.

Time-resolved absorption spectra of m-DCzPe in THF are shown in Figure 5. The differences in behavior in comparison with DCzP are the rapid rise of the sandwich excimer and the suppressed biphotonic ionization. Since the relative emission intensity of the sandwich excimer over the monomer fluorescence of m-DCzPe is larger than that of DCzP, the present spectrum at long delay time is more distinctly assigned to the sandwich excimer rather than to DCzP. The rise component of this sandwich excimer is plotted by applying tentatively the biexponential excimer kinetics  $A \exp(-\beta_1 t) - B \exp(-\beta_2 t)$ . By use of 38 ns for  $\beta_1^{-1}$ ,  $\beta_2^{-1}$  was determined to be 640 ps. Similarly the rise time in acetonitrile was obtained to be 250 ps.

**N<sub>2</sub> Laser Photolysis of Quencher-Free Systems.** By use of a microcomputer-controlled N<sub>2</sub> gas laser photolysis system, sub-microsecond transient absorption spectra of the present dicarbazolyl compounds were measured. As shown in Figure 6, the observed absorption spectrum, having a maximum peak at 420 nm and shoulders at 390 and 450 nm, is almost common to the compounds studied here. The same spectrum was observed also in cyclohexane, indicating no solvent effect. Since the present

(44) (a) Y. Taniguchi, Y. Nishina, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 1646 (1973). (b) U. Lachish, R. W. Anderson, and D. J. Williams, *Macromolecules*, **13**, 1143 (1980); U. Lachish, D. J. Williams, and R. W. Anderson, *Chem. Phys. Lett.*, **65**, 574 (1979).

(45) A. Kira, private communication (1976).

Table I. Relative Triplet Yields of Some Dicarbazolyl Compounds

samples	solvents	
	THF	acetonitrile
EtCz	1	1
DCzB	0.94 ± 0.02	0.96 ± 0.04
r-DCzPe	1.15 ± 0.02	
DCzP	1.33 ± 0.04	1.71 ± 0.05
m-DCzPe	1.84 ± 0.07	1.89 ± 0.06

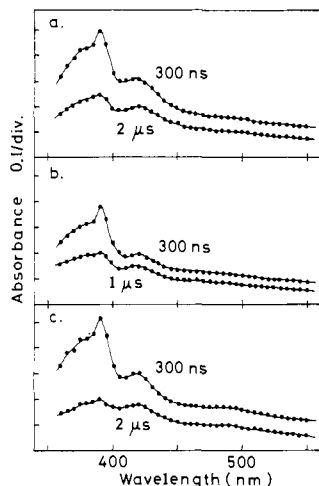


Figure 7. Time-resolved absorption spectra of some dicarbazolyl compounds quenched by Dabco in acetonitrile: (a) m-DCzPe, (b) r-DCzPe, (c) EtCz. Delay times are indicated in the figure.

spectrum of EtCz was assigned to the  $T_n \leftarrow T_1$  transition,<sup>32</sup> these spectra may not be ascribed to the triplet excimer but to the monomer triplet state. The decay time of this  $T_n \leftarrow T_1$  absorption band was roughly estimated by assuming a single exponential decay, although intermolecular interactions between the triplet states and between the triplet and the ground states are involved to some extent under the present experimental condition.<sup>43</sup> The decay time increases in the order of r-DCzPe ( $\sim 2.6 \mu\text{s}$ ) < DCzP ( $\sim 3.1 \mu\text{s}$ )  $\sim$  m-DCzPe ( $\sim 3.5 \mu\text{s}$ ) < EtCz ( $\sim 6 \mu\text{s}$ ) < DCzB ( $\sim 7.8 \mu\text{s}$ ). The excitation intensity dependence of the  $T_n \leftarrow T_1$  absorbance obtained by extrapolating the transient absorbance to zero delay time was examined. A linear relation was confirmed for all the systems, which makes it possible to estimate the relative yield of the triplet formation by comparing the extrapolated transient absorbance at a constant excitation intensity. The results are summarized in Table I.

**$N_2$  Laser Photolysis of Systems Containing Dabco as a Quencher.** The fluorescence quenching of the carbazole chromophore by Dabco in acetonitrile leads to formation of a carbazole anion and a Dabco cation. This ionic photodissociation is a very fruitful method for producing ion radicals in solution, and some fundamental aspects have been clarified in this laboratory.<sup>46</sup> The absorption band of the Dabco cation extends from 400 to 600 nm, but its molar extinction coefficient is small even at the maximum wavelength (about  $1000 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>47</sup> Therefore, the contribution of this band in the transient absorption spectra is considered to be negligible, and the observed spectrum can be ascribed to the carbazolyl chromophore. The time-resolved spectra observed for the present compounds show a similar change, depending on the delay time (Figure 7). The spectrum at early delay time has a maximum at 390 nm, a shoulder at 420 nm, and a tail descending to the long-wavelength region. The relative intensity of the 420-nm band is increased at later stages, indicating that at least two transient species are observed. According to the spectral similarity to the reference carbazole anion<sup>48</sup> and the triplet one, this behavior

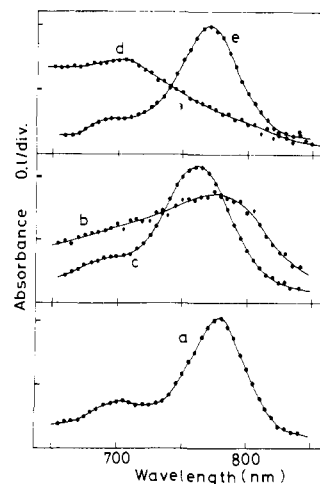


Figure 8. Time-resolved absorption spectra of some dicarbazolyl compounds quenched by DMTP in DMF, obtained at 500 ns after excitation: (a) EtCz, (b) DCzB, (c) DCzP, (d) r-DCzPe, (e) m-DCzPe.

is considered to be due to  $\text{Cz}^* + \text{Dabco} \rightarrow \text{Cz}^- + \text{Dabco}^+ \rightarrow {}^3\text{Cz} + \text{Dabco}$  and/or  $\text{Cz} + \text{Dabco}$ . This triplet formation through the recombination of photochemically produced radical ions is energetically possible in acetonitrile, since the free energy change associated with this recombination was calculated to be  $-0.605 \text{ eV}$ . The band at 390 nm is ascribed to the carbazole anion, and the shoulder at 420 nm is due to the triplet state.

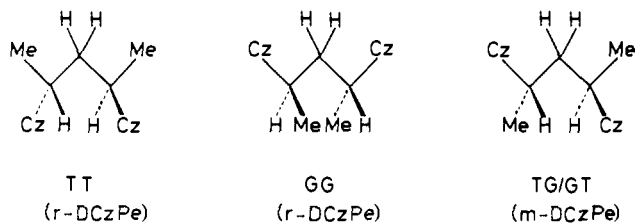
**$N_2$  Laser Photolysis of Systems Containing DMTP as a Quencher.** Ionic photodissociation of the carbazole-DMTP pair is a familiar photoprocess,<sup>27-32</sup> which provides information on the absorption spectra of carbazole cations. DMTP anion has a peak at 530 nm and no absorption above 600 nm,<sup>49</sup> while carbazole cation gives a characteristic band in the latter wavelength region. Namely, this donor-acceptor pair is the best system for elucidating a relation between the spectral shape and the geometrical configuration for the cations of carbazole model compounds. Their submicrosecond transient absorption spectra are shown in Figure 8. In the case of EtCz cation an absorption maximum and a shoulder are observed at 780 and 710 nm, respectively, which is in good agreement with the spectrum observed before.<sup>27,28,30,32,45</sup> The m-DCzPe and DCzP cations give a similar spectral shape to that of the EtCz cation, and only a little blue shift and broadening are observed. The wavelength of the peak band increases in the order of DCzP < m-DCzPe < EtCz by about 10 nm. In contrast to this observation, a different absorption spectral shape was found for r-DCzPe in which sandwich structure is impossible at room temperature. The absorption band of DCzB cation is very broad and structureless, while its peak position is identical with that of EtCz cation.

## Discussion

**Absorption Spectra and Geometrical Structure of Some Excited Dicarbazolyl Compounds.** The results on the excited singlet state are ascribed to an intramolecular interaction, since no ground-state association has been reported and the diffusion-controlled bimolecular interaction between the excited- and ground-state compounds is impossible during their fluorescence lifetime. The two carbazolyl groups of DCzB cannot take an overlap structure, which is confirmed also by using Büchi-Dreiding stereomodels. Concerning the geometrical structure of r-DCzPe and m-DCzPe, we summarize briefly the results given by De Schryver et al.<sup>40</sup> Analyzing the NMR data in deuterated methylene chloride, they proposed that the TG/GT conformation is the most stable ground-state conformation of m-DCzPe while the TT and GG conformations of r-DCzPe are present at room temperature. At 313 K the distribution is 82% TT and 18% GG. In r-DCzPe taking the TT conformation, the two carbazolyl groups are lying in such a spatial arrangement that one phenyl moiety is on top of the

(46) H. Masuhara and N. Mataga, *Acc. Chem. Res.*, **14**, 312 (1981).(47) T. Shida, Y. Nosaka, and T. Kato, *J. Phys. Chem.*, **82**, 695 (1978).(48) H. Masuhara, Y. Tohgo, and N. Mataga, *Chem. Lett.*, **59** (1975).

(49) M. Yamamoto, private communication (1976).



phenyl moiety of the other carbazole group. Therefore, it was concluded that this compound is an appropriate model for the second excimer.<sup>40</sup> A small conformational change is enough to induce the second excimer emission, and further rotation to total spatial overlap would be energetically very unfavorable. On the other hand, one rotation about the C–C bond of *m*-DCzPe is sufficient for the formation of the sandwich structure.

In the case of DCzB the  $S_n \leftarrow S_1$  absorption spectrum is identical with that of EtCz, which confirms no interaction between two carbazolyl groups in this configuration. The absorption spectrum of the excited *r*-DCzPe and its intensity is also similar to those of the monomer model compound, respectively, which is independent of the delay time. This indicates that the relative concentration of the monomer fluorescent state over the second excimer is large even at later stages or that the second excimer gives a similar absorption spectrum as that of the monomer excited state. Since the radiative transition from the excimer state to the ground one is forbidden as a first approximation in the MO treatment, the radiative rate constant of the second excimer is considered to be smaller than that of the monomer fluorescence. Therefore the facts that their fluorescence lifetimes are almost equal to each other and that the stronger emission intensity of the second excimer in comparison with that of the monomer fluorescence (Figure 1) mean a higher concentration of the second excimer than that of the monomer excited state at long delay times. It is concluded that the absorption spectrum of the second excimer is similar to the monomer  $S_n \leftarrow S_1$  spectrum. The interchromophore interaction in the partial overlap structure is concluded to be small in view of the absorption spectroscopy.

According to the same considerations, it is expected that the relative concentration of the sandwich excimer over the monomer fluorescent state is high in DCzP and *m*-DCzPe systems. Therefore, the absorption spectrum observed at long delay times (Figures 3 and 5) is concluded to be mainly due to the sandwich excimer. Particularly, the spectrum of *m*-DCzPe at a few nanoseconds is considered to have no appreciable contribution from the monomer  $S_n \leftarrow S_1$  bands. The absorption band at 660 nm of the sandwich excimer may be related to the 625-nm band of the EtCz system, and this shift may correspond to the conformational change from the loose form to the sandwich type of structure. One possible explanation for the present spectral change is to assume a gradual electronic and geometrical structural change in the course of the sandwich excimer formation. The absorption spectral shape observed before the complete relaxation to the sandwich structure is due to conformations with a small overlap between two carbazolyl groups. Another explanation is that the transient absorption spectrum consists of the bands of the monomer fluorescent and the sandwich excimer states, and their relative contribution determines the present shift from 620 to 660 nm. In view of the fact that the band at 870 nm, characteristic of the sandwich excimer, increases without any change of band shape, the latter explanation is considered to be correct. Actually the excited singlet-state absorption spectrum in the 100-ps and 2-ns time range is reproduced by the superposition of the spectra at 66 ps and 5 ns.

Now it is concluded from the viewpoint of the present  $S_n \leftarrow S_1$  absorption spectra that the interaction in the excited singlet state satisfies the relation of EtCz  $\sim$  DCzB  $\sim$  *r*-DCzPe  $<$  DCzP  $\sim$  *m*-DCzPe. The sandwich excimer induces a large stabilization energy compared to the partial overlap structure (*r*-DCzPe) and the open form (DCzB). In contrast to the present conclusion, the excimer stabilization in the triplet state of carbazole is negligible, since the observed spectra showed no dependence on geometrical

configuration. Concerning the transient absorption spectra of singlet and triplet excimers, intramolecular model compounds with naphthyl and phenanthryl groups have been reported besides our data. Studying the dynamic behavior of di- $\alpha$ -naphthyl-substituted methane, ethane, propane, and butane, Lim et al.<sup>10</sup> concluded that the sandwich structure is favored by the singlet excimer but not by the triplet one. On the other hand, the sandwich excimer was confirmed to be suitable for both excimers with phenanthryl groups.<sup>11,12</sup> The present results on carbazole systems are different from both cases, suggesting the complicated character of excimer formation energy. Malar and Chandra determined the contributions of the various forces to naphthalene excimer potentials of the singlet and the triplet states by using a perturbative approach.<sup>34</sup> They calculated the interaction energy by dividing it into (a) electrostatic, (b)  $\pi$ -overlap repulsion, (c) exciton-resonance, (d) nonbonded repulsion, (e) charge-transfer, (f)  $\pi$ - $\pi$  dispersion, and (g)  $\sigma$ - $\pi$  dispersion terms. (a) and (b) are repulsive, (d) and (e) are almost independent of the interchromophore distance, and (f) and (g) are attractive in both singlet and triplet states. Term c is sensitive to the spin state and is a determining factor for the geometrical structure of the excimers. For example, absence of the singlet excimer of phenanthrene systems was ascribed to the fact that the contribution of the higher excited state to the exciton-resonance stabilization energy is small.<sup>50</sup> A quantitative MO approach is considered to be necessary for the present dicarbazolyl compounds.

**Absorption Spectra and Geometrical Structure of Some Ionic Dicarbazolyl Compounds.** The present studies indicate that the absorption spectral shape of the dimer cation is very sensitive to the geometrical configuration. Although extended and folded conformations should be considered in the case of DCzP, *m*-DCzPe, and *r*-DCzPe, the contribution of the EtCz cation band at 780 nm was hardly detected in their cation absorption spectra. Most of these cations are considered as a first approximation to be a dimer ion radical. This explanation is supported by the observation of dimer cation formation of DCzP in acetonitrile. As shown in Figure 3, the monomer cation band shows a shift from 780 to 760 nm in the course of a few nanoseconds. This time scale is similar to that of sandwich excimer formation and corresponds to the conformational change to the dimer cation.

The absorption spectrum of the DCzB cation is broad and structureless compared to that of the EtCz cation. Since the dicarbazolyl groups of DCzB are in the open form with a very small interchromophore overlap, a rather long-range electrostatic interaction between both  $\pi$  electronic systems or the molecular distortion characteristic of the cationic state may be responsible for the present spectral change. A large spectral change from the monomer cation was observed in the case of *r*-DCzPe cation, which suggests rather strong interaction between two carbazolyl chromophores in the partial overlap structure. The absorption spectrum of the *m*-DCzPe and DCzP cations, in which only the sandwich structure is possible, is similar to that of the EtCz cation, suggesting that the sandwich structure is not so favored compared to the open and partial overlap structures. Actually, the shift of the absorption peak of the DCzP cation from the EtCz cation is larger than that of the *m*-DCzPe cation, which is due to the fact that the distortion from the sandwich type of structure in DCzP is easier compared to that in *m*-DCzPe.

This explanation is consistent with the radiation chemical formation of EtCz dimer cation.<sup>45</sup> The slight warming and successive rapid cooling of irradiated rigid 3-methylpentane-*sec*-butyl chloride solution containing EtCz result in the formation of a dimer cation whose absorption spectrum is identical with that of the *r*-DCzPe cation. Judging from the absorption spectral data, it is concluded that the interaction in the dimer cation increases in the order of *m*-DCzPe  $\lesssim$  DCzP  $<$  DCzB  $<$  *r*-DCzPe.

Absorption spectra of the present dicarbazolyl anions are the same as that of EtCz anion. This is also the case for *m*-DCzPe where two carbazolyl groups take the sandwich structure very easily.

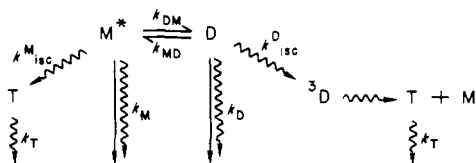
The present results on the dicarbazolyl compounds are in good agreement with a number of data for dimer ion radicals. The

Table II. Rate Constants of Some Dicarbazoyl Compounds in Scheme I

samples	solvents	$\eta$ , cP	$\beta_2$ , s <sup>-1</sup>	$\beta_1$ , s <sup>-1</sup>	$k_{DM}$ , <sup>c</sup> s <sup>-1</sup>	$k_{MD}$ , <sup>c</sup> s <sup>-1</sup>	$k_{DM}/k_{MD}$
DCzP	DMF	0.80	$1.5 \times 10^5$	$3.6 \times 10^7$	$5.7 \times 10^7$	$3.5 \times 10^7$	1.6
	THF	0.46	$1.9 \times 10^5$	$3.2 \times 10^7$	$9.9 \times 10^7$	$3.5 \times 10^7$	2.8
m-DCzPe	ACN <sup>a</sup>	0.33	$3.4 \times 10^8$	$3.1 \times 10^7$	$2.2 \times 10^8$	$5.7 \times 10^7$	3.8
	THF	0.46	$1.6 \times 10^9$ <sup>b</sup>	$2.6 \times 10^7$	$1.4 \times 10^9$	$1.1 \times 10^8$	12.6
	ACN <sup>a</sup>	0.33	$4.0 \times 10^9$ <sup>b</sup>	$2.4 \times 10^7$	$3.8 \times 10^9$	$1.2 \times 10^8$	31.8

<sup>a</sup> Acetonitrile. <sup>b</sup> Obtained by transient absorption spectral measurement (see Figure 6). <sup>c</sup> Calculated by assuming that the excimer decay time of DCzP at -60 °C ( $44 \pm 2$  ns) is the lifetime of the sandwich excimer.<sup>37</sup>

Scheme I



formation of dimer cation radical is quite a general phenomenon, while the examples concerning dimer anion are limited. A theoretical consideration for this different behavior has been given recently by Lim et al. for the benzene dimer with the sandwich structure.<sup>51</sup> By use of a perturbative method described above, (a) electrostatic, (b) exchange repulsion, (c) charge-resonance, (d) nonbonded repulsion, and (e)  $\sigma$ - $\pi$  and  $\pi$ - $\pi$  dispersion energies were calculated term by term for benzene dimer cation and anion. Terms b and d are of course repulsive while terms c and e increase the stabilization energy for both dimer ions. A factor determining its formation is (a) electrostatic energy, which predicted the stabilized dimer cation and unstable dimer anion for benzene systems with sandwich type of structure. This consideration can be applied also to the present carbazole systems. In the dimer cation formation an electrostatic interaction is important, while different stabilization energies of singlet and triplet excimers are ascribed to exciton-resonance interaction.<sup>34</sup> This theoretical result is consistent with the present results that the most favorable structure for carbazole dimer cation is different from that for singlet excimer and that no triplet excimer was detected. These are considered to be the most systematic experimental study of the geometrical structures of excimers and dimer ions.

**Intersystem Crossing and Geometrical Configuration of Some Dicarbazoyl Compounds.** Although there are rather few data on the triplet formation and decay processes of bichromophoric systems except the ultrafast intersystem crossing in some intramolecular heteroexcimer systems,<sup>52</sup> the present dicarbazoyl compounds give relevant information. We first consider the formation of the triplet state from the sandwich excimer. This process was suggested by the fact that the triplet formation yield is in parallel with the relative intensity of the sandwich excimer emission. By use of Scheme I, the rate parameters  $k_M$ ,  $k_D$ ,  $k_{isc}^M$ , and  $k_{isc}^D$  are defined in addition to  $k_{DM}$  and  $k_{MD}$ . Here the processes  $M^* \rightarrow T$  and  $D \rightarrow {}^3D$  represent the intersystem crossing of the monomer excited and excimer states, respectively. On the basis of our absorption spectral measurements, it is assumed that the dissociation from  ${}^3D$  to T is quite rapid and occurs with unit quantum yield. Equations 1-3 can be derived;  $I_0$  is the

$$\frac{d[T]}{dt} = k_{isc}^M[M^*] + k_{isc}^D[D] - k_T[T] \quad (1)$$

$$[M^*] = \frac{I_0}{\beta_2 - \beta_1} \{ (X - \beta_1)e^{-\beta_2 t} + (\beta_2 - X)e^{-\beta_1 t} \} \quad (2)$$

$$[D] = \frac{I_0 k_{DM}}{\beta_2 - \beta_1} \{ e^{-\beta_1 t} - e^{-\beta_2 t} \} \quad (3)$$

excitation intensity and  $\beta_1$ ,  $\beta_2$ ,  $X$ , and  $Y$  are derived in the usual manner (eq 4, 5).

$$\beta_{1,2} = \frac{1}{2}[(X + Y) \mp \{(X - Y)^2 + 4k_{DM}k_{MD}\}^{0.5}] \quad (4)$$

$$X = k_M + k_{isc}^M + k_{DM}, \quad Y = k_D + k_{isc}^D + k_{MD} \quad (5)$$

The following equation was derived by integrating eq 1,

$$[T] = I_0 \{ C_1(e^{-k_T t} - e^{-\beta_1 t}) + C_2(e^{-k_T t} - e^{-\beta_2 t}) \} \quad (6)$$

where

$$C_1 = \frac{1}{\beta_2 - \beta_1} \frac{k_{isc}^M(\beta_2 - X) + k_{isc}^D k_{DM}}{\beta_1 - k_T}$$

$$C_2 = \frac{1}{\beta_2 - \beta_1} \frac{k_{isc}^M(X - \beta_1) - k_{isc}^D k_{DM}}{\beta_2 - k_T}$$

Neglecting the contribution of  $k_T$  compared to that of  $\beta_1$  and  $\beta_2$  and extrapolating eq 6 to zero time give eq 7. A similar equation

$$[T]_{t=0} = \frac{I_0}{\beta_1 \beta_2} \{ (\beta_2 + \beta_1 - X)k_{isc}^M + k_{DM}k_{isc}^D \} \quad (7)$$

is given also for EtCz, which does not give the excimer.

$$[T]_{R,t=0} = \frac{I_0 k_{isc}^M}{k_M + k_{isc}^M} \quad (8)$$

Now, the relative triplet yield, which was measured in the present work, is given in the following form.

$$\frac{[T]_{t=0}}{[T]_{R,t=0}} = \frac{k_M + k_{isc}^M}{\beta_1 \beta_2} \left\{ (\beta_1 + \beta_2 - X) + k_{DM} \frac{k_{isc}^D}{k_{isc}^M} \right\} \quad (9)$$

The rise and decay times of the sandwich excimer ( $\beta_2$  and  $\beta_1$ ) have been measured in the present work. The  $\beta_2$  values of the m-DCzPe systems were obtained by the transient absorption spectral measurement, while others were given by fluorescence data. With these data and the reference fluorescence lifetimes, the association ( $k_{DM}$ ) and dissociation ( $k_{MD}$ ) rate constants and the equilibrium constant were calculated and are listed in Table II. By use of these values,  $k_{isc}^D/k_{isc}^M$  is obtained to be  $0.7 \pm 0.1$  for DCzP and m-DCzPe in THF and acetonitrile. Therefore, it is concluded that the enhanced yield of the triplet formation in DCzP and m-DCzPe systems is due to the longer excimer lifetime than that of the monomer excited state and not to the increase of the intersystem-crossing rate constant.

Here, the enhanced triplet yield from the sandwich excimer has been analyzed with Scheme I where the excimer is in equilibrium with the monomer excited state. However, the detailed experiments on intramolecular excimer<sup>39a,53,54</sup> and exciplex<sup>55</sup> systems have recently revealed that the conformation, which does not take the structure of excimer (or exciplex) during the monomer fluorescence lifetime, contributes to fluorescence decay curves to some extent. Concerning DCzP in benzene, Ng and Guillet

(53) M. Goldenberg, J. Emert, and H. Morawetz, *J. Am. Chem. Soc.*, **100**, 7171 (1978).

(54) A. M. Halpern, M. W. Legenza, and B. R. Ramachandran, *J. Am. Chem. Soc.*, **101**, 5736 (1979).

(55) F. Meeus, M. Van der Auweraer, and F. C. De Schryver, *Chem. Phys. Lett.*, **74**, 218 (1980); M. Van der Auweraer, A. Gilbert, and F. C. De Schryver, *Nouv. J. Chim.*, **4**, 153 (1980); M. Van der Auweraer, A. Gilbert, and F. C. De Schryver, *J. Am. Chem. Soc.*, **102**, 4007 (1980); R. Todesco, J. Gelan, H. Martens, J. Put, and F. C. De Schryver, *ibid.*, **103**, 7304 (1981).

(50) J. B. Birks in "The Exciplex", M. Gordon and W. R. Ware, Eds., Academic Press, New York, 1975, p 39.

(51) B. T. Lim, S. Okajima, A. K. Chandra, and E. C. Lim, *J. Chem. Phys.*, **77**, 3902 (1982).

(52) T. Okada, I. Karaki, E. Matsuzawa, N. Mataga, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, **85**, 3957 (1981).

proposed that its fluorescence rise and decay curve is interpreted by three-exponential fitting and not by a two-exponential one.<sup>56</sup> This might raise a question on the applicability of Scheme I to the present systems. However, it should be remembered that an advantage of the transient absorption spectral measurement is to identify the main transient species and its dynamic range is not as large as that of the single photon counting one. Actually, the monomer  $S_n \leftarrow S_1$  absorption band was not detected in the DCzP and m-DCzPe spectra at long delay times. This indicates that the monomer component that does not form the sandwich excimer is a minor contribution in transient spectral analysis. It is considered that the present analysis is correct as a first approximation.

In contrast to the above DCzP and m-DCzPe systems, the triplet formation yield of r-DCzPe in THF is slightly higher than that of EtCz. This result means that the triplet yield from the second excimer is not large, since the concentration of this excimer is higher than that of the monomer fluorescence state. This difference in behavior from the sandwich excimer is consistent with the fact that the  $S_n \leftarrow S_1$  spectrum and the lifetime of the second excimer are almost equal to those of EtCz, respectively.

Although the same triplet absorption spectrum was observed for the present dicarbazolyl compounds, their decay time depends on the geometrical configuration. Since the intermolecular interactions between the triplet states and between the triplet and ground states are involved to some extent, the fact that the lifetime of the DCzB triplet is larger than that of the EtCz triplet is acceptable in view of the more rapid diffusional motion of the latter. On the other hand, the decay of DCzP and m-DCzPe is faster than that of EtCz, suggesting an additional deactivation process. This tendency is more pronounced in the case of r-DCzPe. Therefore this intersystem crossing to the ground state is considered to be sensitive to the geometrical configuration. The intramolecular interaction between the triplet- and ground-state carbazolyl groups induces the deactivation to the ground state, which is more efficient in the partial overlap structure than in the sandwich structure.

(56) D. Ng and J. E. Gullet, *Macromolecules*, **14**, 405 (1981).

**Model Compounds for Polymer Photophysics.** We have studied the excited-state dynamics of poly(*N*-vinylcarbazole) and related polymers in solution and in film by using pico- and nanosecond laser photolysis methods.<sup>27-32,57</sup> The excitation and the positive charge in the polymer have been considered to be stabilized by taking dimer forms, which indicates the importance of the detailed investigations on carbazole excimers and dimer ions. From this viewpoint the diastereoisomeric model compounds with different geometrical configurations are considered to be appropriate models,<sup>40</sup> since isotactic and syndiotactic sequences result in the formation of two types of excimers. The present work has offered such information on the excited and ionic states of dicarbazolyl compounds with specific geometrical structures. The electronic structure and dynamics of the excited states and ion radicals of poly(*N*-vinylcarbazole) can be elucidated by comparing their absorption spectral data with the present ones. A distribution of these excimers and dimer ions might determine the properties of polymers, or a new state not identified as a dimer might be produced in the polymer. In the latter case a new electronic process and reactivity, not present in the monomer and oligomer system, will be expected. Along this line we are performing absorption spectral studies on polymers in the excited and ionic states, which will be published shortly.

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(57) H. Masuhara, N. Tamai, K. Inoue, and N. Mataga, *Chem. Phys. Lett.*, **91**, 109 (1982); H. Masuhara, N. Tamai, N. Ikeda, N. Mataga, A. Itaya, K. Okamoto, and S. Kusabayashi, *ibid.*, **91**, 113 (1982); H. Masuhara, N. Tamai, and N. Mataga, *ibid.*, **91**, 209 (1982).

## Proton Nuclear Magnetic Relaxation of <sup>15</sup>N-Labeled Nucleic Acids via Dipolar Coupling and Chemical Shift Anisotropy

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**Abstract:** We have observed a differential in the relaxation rates of the imino proton NMR doublet of 3-<sup>15</sup>N-substituted 2',3',5'-tri-*O*-benzoyluridine. The differential is ascribed to interference between dipole-dipole and chemical shift anisotropy mechanisms of relaxation. A value of 5.7 ppm is derived for the proton chemical shift anisotropy, using a theory described in the Appendix, and due to M. Goldman (manuscript in preparation). Differential broadening of <sup>15</sup>N-substituted transfer ribonucleic acid by the same mechanism is shown to be quantitatively compatible with published observations. We conclude that these observations do not provide strong evidence of base-pair tautomerism.

Changing the conditions of magnetic resonance experiments may modify the relative importance of various relaxation mechanisms. Thus the use of large magnetic fields enhances the effects

of chemical shift anisotropy, and the exploration of large molecules with long tumbling times reveals broadening mechanisms whose contribution in small molecules might go unnoticed.

Consider for instance a proton bound to <sup>15</sup>N. The spectrum is a doublet with a splitting of ca. 90 Hz due to scalar coupling. The amplitude of the dipolar field of <sup>15</sup>N at the proton site is *d*

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