agreement with the present work. By combining the line-shape data at 60° with the equilibrium data at −10° and using the relationship $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ with $\Delta H^\ddagger$ and $\Delta S^\ddagger$ as temperature-independent quantities, we obtain $\Delta H^\ddagger_1 = 20.6 \pm 0.2$, $\Delta H^\ddagger_{-1} = 22.1 \pm 0.2$ kcal/mol, $\Delta S^\ddagger_1 = 4.4 \pm 0.7$, $\Delta S^\ddagger_{-1} = 4.5 \pm 0.7$ eu. These values are much more accurate than those obtained from the NMR line-shape data alone because of the limited temperature range over which rate constants can be determined by line-shape studies.[4]

The efficiency of the equilibrium trapping cannot be calculated from the present data since the assumption of temperature-independent $\Delta H°$ and $\Delta S°$ terms is probably not valid over a large temperature range, and in any event, $\Delta G°$'s in the gas phase and in solution may well be different. It is clear, however, that substantially perturbed populations over the equilibrium values can be obtained.

Methylcyclohexane was deposited at −175° from a temperature of 500° and the $^1$H NMR spectrum was observed at −160° in a 1:1 mixture of $CHClF_2$ and $CCl_2F_2$ (Figure 1). A doublet (δ 1.00), ascribed to the axial methyl group, is visible downfield from the resonance of the equatorial methyl group.[5] The population of the axial form is at least 10% and could be as high as 25%. Overlap of the equatorial methyl group doublet with ring proton bands prevents a more accurate measurement of the axial–equatorial ratio. From the known thermodynamic data on methylcyclohexane,[6] the population of the axial form at 500° should be about 30%. The apparent trapping efficiency in this case may be low owing to adventitious reequilibrium at various stages prior to NMR measurements. Further experiments involving $^{13}$C NMR and $^1$H NMR of undeuterated and partially deuterated methylcyclohexane are in progress.

It appears that high-vacuum cryogenic deposition will become a valuable tool in conformational analysis.[7] The method should be applicable to systems with barriers as low as 4–5 kcal/mol by deposition near liquid helium temperatures and observation by infrared or other suitable spectroscopic techniques, and such experiments are underway.

**Acknowledgment.** This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

### References and Notes

(1) E. Hedaya and D. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967).

(2) The trapping efficiency should be very good provided that the barrier which prevents reversion of the minor to the major form is much greater than *RT* (*T* = temperature of the hot gas). There are scattered reports (e.g., R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectrosc.*, **30**, 290 (1969); G. A. Crowder and H. K. Mao, *J. Mol. Struct.*, **18**, 33 (1973); G. A. Crowder and P. Priettlangkura, *ibid.*, **18**, 177 (1973)) that compounds deposited as films at cryogenic temperatures from the vapor state at *room temperature* consist of nonequilibrium mixtures of rotamers. This phenomenon has generally been considered as a nuisance which can be overcome by suitable annealing of the deposited film. A recent review dealing with matrix isolation (H. E. Hallam in "Vibrational Spectroscopy of Trapped Species", H. E. Hallam, Ed., Wiley, New York, N.Y., 1973, pp 115 and 116) mentions that the rotameric populations obtained by cryogenic deposition from *room temperature* possibly reflect the equilibrium at the latter temperature, but that proof of this is lacking.

(3) L. A. La Planche and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

(4) T. Drakenberg and S. Forsén, *Chem. Commun.*, 1404 (1971). The errors in $\Delta G$, $\Delta H$, and $\Delta S$ given by these authors are ±0.3 kcal/mol, ±1.8 kcal/mol, and ±5 eu, respectively; however, it can be calculated from the errors given for the rate constant and temperature in the above reference that the error in $\Delta G$ must be no greater than 0.03 kcal/mol. Errors in $\Delta H$ and $\Delta S$ are correlated and can be quite large if $\Delta G$ is obtained over a small temperature range, even if $\Delta G$ is quite accurate (K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1964, p 378).

(5) The equatorial methyl group has a chemical shift of 0.86 ppm. *cis*-1,4-Dimethylcyclohexane under the same conditions exhibits methyl resonances at 0.96 (a-Me) and 0.86 ppm (e-Me).

(6) F. A. L. Anet and V. J. Basus, to be submitted for publication; see also F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, *J. Am. Chem. Soc.*, **93**, 258 (1971).

(7) Nonequilibrium populations of conformations have been obtained by dissolving conformationally homogeneous crystals in solvents at low temperatures and by related techniques (F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, **91**, 3223 (1969)). These methods are difficult or impossible to apply to conformations whose populations are very small.

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## Spectroscopic Detection of the Twist-Boat Conformation of Cyclohexane. A Direct Measurement of the Free Energy Difference between the Chair and the Twist-Boat

*Sir:*

Theoretical calculations on cyclohexane[1] and experimental data on some highly constrained cyclohexane derivatives[1a,2] indicate that the twist-boat conformation of cyclohexane lies about 5–6 kcal/mol above the chair conformation. The equilibrium proportion of cyclohexane twist-boat form at room temperature should be of the order of 0.1% or less,[3] and thus it is not surprising that no direct observation of this form has been reported. However, thermodynamic considerations based on the expected values of $\Delta H°$ and $\Delta S°$ between the chair and twist-boat forms indicate that the concentration of the twist-boat becomes quite substantial at high temperatures, e.g., 30% at 800°.[4] Detection of boat forms at high temperatures by infrared or Raman spectroscopy presents difficulties because of the possible presence of "hot" bands arising from the chair form. We have therefore chosen to trap the high-temperature equilibrium by a high-vacuum deposition technique[5] before carrying out a spectroscopic investigation. The infrared spectrum of the mixture of chair and twist-boat conformations can then be observed at very low temperatures and can be compared with that of the chair form in the pure state. The rate at which the twist-boat returns to the chair can also be obtained by raising the temperature to a suitable value. Since the energy barrier for the isomerization of the twist-boat to the chair is expected to be about 5 kcal/mol,[1] the twist-boat should have a virtually infinite life at 20°K, but should be fairly rapidly transformed to the chair at liquid nitrogen temperature (77°K).

The considerations described above led us to carry out the following experiments. Cyclohexane gas at about 0.2 Torr pressure was heated to ca. 800° (contact times ≃ 10 msec) and allowed to deposit, either in the neat state or in the presence of a large excess of argon (also at 800°) onto a CsI plate cooled to 20°K. The same type of experiment was also carried out with the cyclohexane (and the argon, if used) initially at room temperature instead of at 800°. A well-resolved infrared spectrum (measured at 10°K) of the pure chair conformation is obtained by deposition at 20°K of room-temperature cyclohexane vapor in the presence of argon (mole ratio 1:500). The matrix-isolated chair cyclohexane shows bands (between 600 and 2000 cm$^{-1}$) at the following frequencies (relative intensities are given in parentheses): 861 (0.38), 865 (0.39), 906 (0.42), 1021 (0.10), 1034 (0.07), 1047 (0.10), 1262 (0.20), 1454 (0.60), and 1457 (1.0). This spectrum is similar to that reported for crystalline (phase II) cyclohexane at liquid nitrogen temperature[6] but is missing some bands[7] because of the absence of intermolecular crystal effects in the argon matrix.[8]

The infrared spectrum at 10°K of cyclohexane deposited from 800° in the presence of argon shows all the bands de-

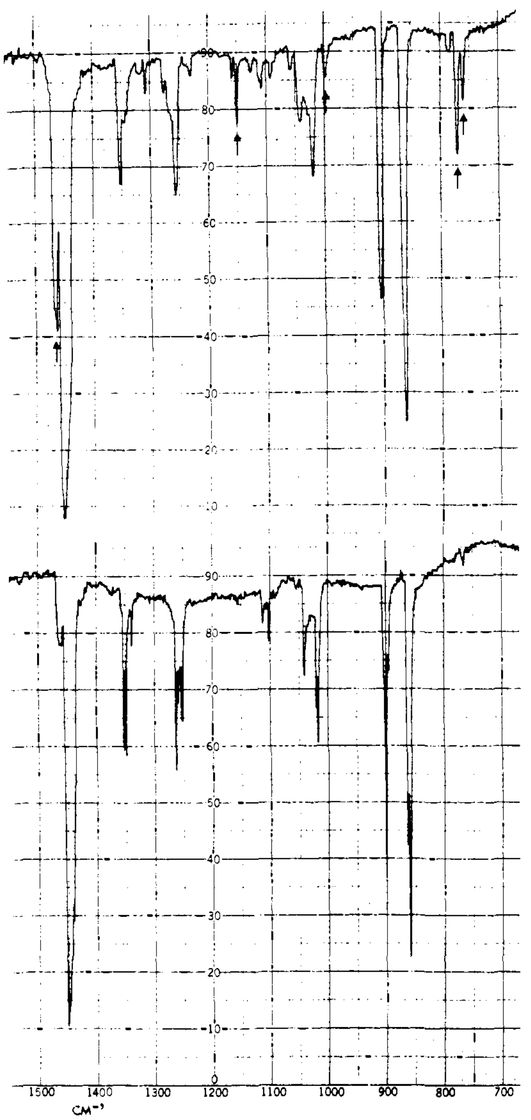

**Figure 1.** Top: infrared spectrum between 700 and 1500 $cm^{-1}$ at 10°K of neat cyclohexane deposited from the vapor at 800°C. The arrows show bands assigned to the twist-boat. Bottom: same sample as above, but after warming to 74°K for several hours before measuring the spectrum at 10°K.

scribed above for the chair, plus the following bands, which are assigned to the twist-boat: 760 (0.15), 770 (0.33), 772 (0.30), 869 (0.38), 1000 (0.11), 1153 (0.26), 1469 (1.0), 1471 (0.98). It is significant that the two bands at 1469 and 1471 $cm^{-1}$, which can be ascribed to $CH_2$ scissoring vibrations in the twist-boat, occur at higher frequencies than the corresponding bands (1454 and 1457 $cm^{-1}$) of the chair,[9] in agreement with data on cyclohexane derivatives that are constrained to exist in twist-boat forms by substituents.[2] On the assumption that the scissoring vibrations in the chair and the twist-boat conformations of cyclohexane have similar absorptivities, it appears that the twist-boat is present to about 25% in the cyclohexane deposited from 800°. The percentage of the twist-boat in the gas phase at 800° is therefore at least 25% and possibly more, depending on the efficiency of trapping of the twist-boat.[10]

Because the twist-boat is too long-lived at temperatures where argon (or even xenon) can be used as a matrix, we have studied the change of the twist-boat to chair in a cryogenically deposited film of neat cyclohexane. Under these conditions the infrared spectrum of pure chair cyclohexane (obtained from room temperature cyclohexane) shows bands that are broader than those of the matrix-isolated chair form or of the chair form in the phase II crystals. The infrared spectrum of neat cyclohexane deposited from 800° onto a CsI plate cooled to 40°K (Figure 1) shows all the peaks observed in the chair as well as bands corresponding to those previously assigned to the twist-boat in the matrix isolation experiments. On warming above 70°K the bands of the twist-boat gradually decrease in intensity, and the remaining spectrum corresponds to the chair form[11] (Figure 1). Rates of decay were obtained at 72.5, 73.0, and 74.0°K in separate experiments by measuring the absorbance at 770 $cm^{-1}$ giving the rate constants $2.1 \times 10^{-4}$, $2.8 \times 10^{-4}$, and $3.3 \times 10^{-4}$ $sec^{-1}$, respectively. The free energy of activation ($\Delta G^{\ddagger}$) for each experiment was calculated using the absolute rate equation from transition state theory.[12] The results from the three experiments agree very well and give $\Delta G^{\ddagger} = 5.27 \pm 0.05$ kcal/mol for the twist-boat to chair isomerization.

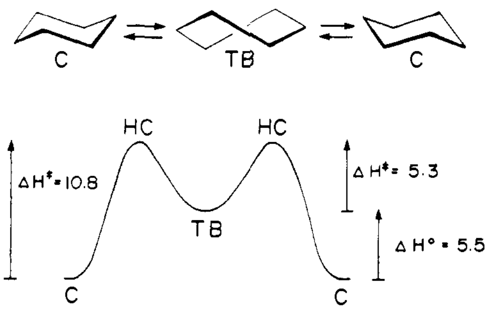

**Figure 2.** Energy diagram (units are kilocalories per mole) for ring inversion in the cyclohexane chair (C), showing the twist-boat (TB) and the half-chair (HC) (i.e., the transition state for the C to TB interconversion). Pseudorotation[1] in the TB and HC is not shown.

The isomerization of the twist-boat to the chair described above takes place in the solid state and may not be comparable to an isomerization occurring in the gas phase or in solution. However, both conformations have zero dipole moments and have similar shapes, and thus it is likely that effects of the (distorted) lattice on the rate of isomerization are small.[13] If this is correct, the following deductions can be made. The value of 5.3 kcal/mol for $\Delta G^{\ddagger}$ (twist-boat to chair) can be equated to $\Delta H^{\ddagger}$ since the entropy difference between the twist-boat and the transition state is likely to be small[1b] and the temperature is low ($T\Delta S^{\ddagger}$ is thus small). For the chair to twist-boat process, $\Delta H^{\ddagger}$ is 10.8 kcal/mol.[14] Thus $\Delta H°$ (chair to twist-boat) is 5.5 kcal/mol (Figure 2) and from the estimated 25% population of the twist-boat at high temperatures, a $\Delta G°_{800}$ of 1.3 kcal/mol and hence as $\Delta S°$ of 4 eu can be calculated. All of these parameters are in excellent agreement with expectations.[1] The agreement suggests that trapping of the twist-boat cyclohexane at 20°K is quite efficient.

Attempts to observe the NMR spectra of the twist-boat conformation of cyclohexane are in progress.

**Acknowledgments.** Financial support by the National Science Foundation, Grant No. GP-43960, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged.

## References and Notes

(1) Virtually all calculations indicate that the twist-boat is lower in energy than the boat and that the latter form is a transition state for a more or less free pseudorotation in the twist-boat: (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley-Interscience, New York, N.Y., 1965; (b) K. B. Wiberg and R. H. Boyd, *J. Am. Chem. Soc.*, **94**, 8426 (1972); (c) H. M. Pickett and H. L. Strauss, *ibid.*, **92**, 7281 (1970); (d) J. R. Hoyland, *J. Chem. Phys.*, **50**, 2775 (1969); (e) H. G. Schmid, A. Jaeschke, H. Friebolin, S. Kabuss, and R. Mecke, *Org. Magn. Reson.*, **1**, 163 (1969); (f) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968); (g) R. Bucourt and D. Hainaut, *Bull. Soc. Chim. Fr.*, 4563 (1967);

(h) J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7036 (1967).

(2) H. van Bekkum, M. A. Hoefnagel, L. de Lavieter, A. van Veen, P. E. Verkade, A. Wemmers, B. M. Wepster, J. H. Palm, L. Schäfer, H. Dekker, C. Mosselman, and G. Somsen, *Recl. Trav. Chim. Pays-Bas*, **86**, 1363 (1967).

(3) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 207.

(4) The value given is based on $\Delta H^\circ = 5.7$ kcal/mol and $\Delta S^\circ = 4$ eu.[1b]

(5) F. A. L. Anet and M. Squillacote, preceding paper.

(6) R. J. Abremski, C. W. Brown, and E. R. Lippincott, *J. Chem. Phys.*, **49**, 185 (1968).

(7) The band system near 1350 $\text{cm}^{-1}$ is moderately strong in the crystal[6] but is virtually absent in the matrix.

(8) H. E. Hallam in "Vibrational Spectroscopy of Trapped Species", H. E. Hallam, Ed., Wiley, New York, N.Y., 1973, p 67.

(9) For assignments of the vibrational spectra of cyclohexane (and $C_6D_{12}$), see ref 6 and references therein, and K. B. Wiberg and A. Shrake, *Spectrochim. Acta, Part A*, **27**, 1139 (1971); H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **53**, 376 (1970); M. A. Moskaleva and G. N. Zhizhin, *Opt. Spectrosc.* (*USSR*), **36**, 535 (1974).

(10) Nonequilibrium rotamer populations have been reported in films deposited from vapors at room temperature onto cold surfaces, but quantitative aspects of this phenomenon do not appear to have been investigated: R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectrosc.*, **30**, 290 (1969); G. A. Crowder and H. K. Mao, *J. Mol. Struct.*, **18**, 33 (1973); G. A. Crowder and P. Pruettiangkura, *ibid.*, **18**, 177 (1973); A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, **66**, 1932 (1970); see also ref 8, pp 115 and 116.

(11) On further warming to 170°K and cooling back to 10°K, a very sharp infrared spectrum identical with that described[6] for (annealed) crystalline phase II cyclohexane is obtained showing that no chemical decomposition of the cyclohexane took place during the brief heating at 800°.

(12) S. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1960, p 250.

(13) Interconversions between rotamers have been observed in an inert gas matrix at 35°K, O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 244 (1973); photochemical interconversions have been reported at 20°K, A. Krantz, T. D. Goldfarb, and C. Y. Lin, *ibid.*, **94**, 4022 (1972).

(14) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).

(15) National Science Foundation Predoctoral Fellow.

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## Exciplex Quenching. Geometric and Electronic Requirements

*Sir:*

Much indirect evidence has accumulated for the intermediacy of excited state complexes (exciplexes) in photochemical reactions.[1] We have recently established the role of singlet exciplexes in some photocycloaddition reactions of phenanthrenes and olefins using an exciplex fluorescence quenching method.[2,3] We now report on the generality of exciplex quenching and an apparent geometrical requirement for this "termolecular" process.

The fluorescent exciplex ($\lambda_{\text{emission}}$ 444 nm) formed[2] between the excited singlet state of 9-cyanophenanthrene (9-CNP) and *p*-(isobutenyl)anisole (*p*-BA) was quenched by the addition of fumaronitrile (Figure 1). A value of $k_Q\tau_{ex}{}^{air} = 90$ was obtained by the usual Stern–Volmer analysis.[4] Other electron acceptors also quench the exciplex fluorescence; $k_Q\tau_{ex}{}^{air}$ values from linear Stern–Volmer plots are given in Table I. The effect of air saturation on the exciplex fluorescence[2,5] intensity allows us to estimate a lifetime ($\tau_{ex}{}^{air}$) of 16 nsec. Thus fumaronitrile, dimethyl fumarate, and dimethyl acetylene dicarboxylate quench the exciplex at essentially diffusion-controlled rates (Table I). Exciplex quenching experiments run at varying olefin concentrations but at constant 9-CNP concentration led, within experimental error, to identical $k_Q\tau_{ex}$ values indicating that ground-state complexation between *p*-BA and the quenchers is not important to the quenching process.

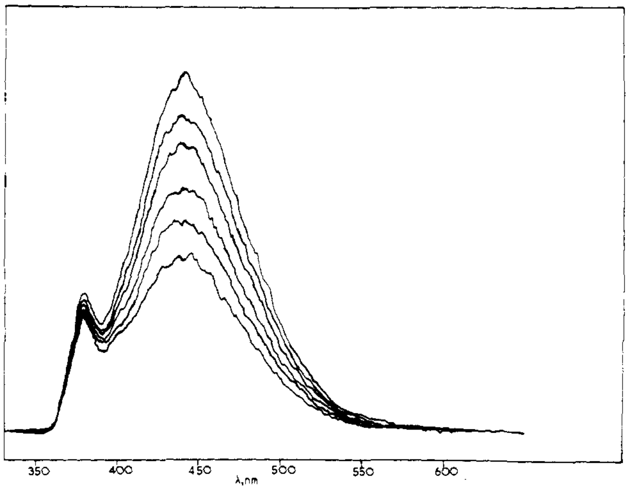
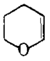
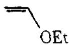
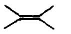
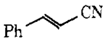
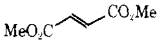
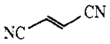


**Figure 1.** Quenching of 9CNP-*p*-BA exciplex by fumaronitrile: $k_Q\tau_{ex}{}^{air} = 90\ M^{-1}$.

**Table I.** Rate Constants for Exciplex Fluorescence Quenching[a]

| Quenchers | 9CNP–*trans* Anethole 11.3 (8.0)[b] | 9CNP–*p*-BA 39 (16)[b] | Anth–DEA[c] 120 (22)[b] | P–FN 23.5 (12.5)[b] |
|---|---|---|---|---|
| $Ph_3N$ | $1.9 \times 10^8$ | $1.5 \times 10^8$ | — | — |
| $Et_3N$ | $1.5 \times 10^8$ | $2.0 \times 10^8$ | $1.4 \times 10^7$ | $7.0 \times 10^9$ |
|  | $<6 \times 10^6$ | $<2 \times 10^6$ | $<2 \times 10^5$ | $2.2 \times 10^9$ |
|  | $<6 \times 10^6$ | $<2 \times 10^6$ | — | $1.6 \times 10^8$ |
|  | $<6 \times 10^6$ | $<2 \times 10^6$ | $<2 \times 10^5$ | $1.6 \times 10^9$ |
|  | $1.0 \times 10^8$ | $8.2 \times 10^7$ | $1.6 \times 10^8$ | |
|  | $8.1 \times 10^9$ | $7.6 \times 10^9$ | $3.3 \times 10^9$ | $1.4 \times 10^8$ |
|  | $7.2 \times 10^9$ | $6.9 \times 10^9$ | $3.4 \times 10^9$ | $1.3 \times 10^8$ |
| $MeO_2CC{\equiv}CCO_2Me$ | $7.7 \times 10^9$ | $7.6 \times 10^9$ | | $<4 \times 10^7$ |

[a] Air-saturated benzene at room temperature. Rate constants ($= k_Q\tau_{ex}{}^{air}/\tau_{ex}{}^{air}$). [b] Exciplex lifetimes given as $\tau_{ex}{}^{deoxygenated}$ ($\tau_{ex}{}^{air}$), in nanoseconds, estimated from the effect of aeration on exciplex emission intensity. [c] Anthracene–diethylaniline.

The results of quenching of several other exciplexes are given in Table I. Results for the phenanthrene–fumaronitrile (P–FN) exciplex[6] parallel those we have previously reported for the phenanthrene–dimethyl fumarate exciplex.[3] Where necessary, corrections were made for the simultaneous quenching[7] of monomer and exciplex and for the absorption of incident light by ground state charge-transfer (CT) complexes. The possibility that the latter leads to exciplex quenching can be ignored since the fraction of complexed quencher molecules is in all cases very small[8] (<1%). Exciplex lifetimes were obtained by the air saturation technique and were consistent (±10%) with those obtained[10] by nanosecond flash spectroscopy.

Inspection of Table I leads to several generalizations. (1) Each exciplex can be quenched to some extent by both powerful ground-state CT donors and CT acceptors. Since a CT term dominates exciplex binding, e.g., a ≫ b, c, or d for the (D,A)* exciplex in the equation below,[11] it is not surprising that further CT interaction dominates exciplex quenching.

$$\psi_{(D,A)*} = a\psi_{D^+A^-} + b\psi_{D^-A^+} + c\psi_{D*A} + d\psi_{DA*}$$

(2) Neither weak donors (ethyl vinyl ether) nor weak acceptors (cinnamonitrile) are particularly effective exciplex quenchers.

(3) Each exciplex shows a marked preference for quench-