structures of the dication salts have been reported recently,[28] and theoretical studies of the I_4^{2+} cation have been reported.[29] The X-ray structure reveals that the dication is a cyclic 4-membered ring in the crystal. Since little is known about other dications, such as F_4^{2+} and Cl_2^{2+}, we carried out ab initio calculations for these two species. Optimization of I_4^{2+} exceeds our computational resources even with the minimal STO-3G basis set.

The optimization of F_4^{2+} with the 6-31G* basis set showed that it has an open Z-like geometry. All the fluorine atoms are in the same plane with the FFF angles equal to 110°. The central FF bond is 1.368 Å, which is shorter than the terminal FF bonds (1.572–1.575 Å). This dication was calculated to be 202 kcal/mol less stable than two isolated radical cation $F_2^{\bullet+}$ species.

The optimized geometry of Cl_4^{2+} is nonplanar and has C_2 symmetry, with a ClClClCl torsional angle of 95°. The central ClCl bond length is 2.013 Å and the terminal ones are 2.063 Å. The ClClCl bond angles are 108°. This dication is 135 kcal/mol less stable than two $Cl_2^{\bullet+}$ radical cations. The structures of both F_4^{2+} and Cl_4^{2+} resemble those of the corresponding $[HFFH]^{2+}$ and $[HClClH]^{2+}$ dications.[30]

Conclusion

The monatomic halogen cations have triplet ground states, while most of the triatomic cations and hydrohalonium ions have singlet ground states. These singlet complexes generally have bent geometries with halogen atom at the center. The triplet complexes adopt structures resembling the most stable radical cation of the diatomic species associated to a radical.

These data should be of use for the better understanding of halogenation reactions with halogen cations, since the consequences and complications on mechanisms of the existence of low-lying triplet states has not been considered previously.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research.

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Quenching of the Benzophenone Triplet State by Multifunctional Aromatic Quenchers

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Abstract: Enhanced quenching of the benzophenone triplet state is observed with a series of multifunctional aromatics in acetonitrile and carbon tetrachloride. After accounting for statistical differences, the multifunctional aromatic quenchers show reaction rates 3 to 13 times faster than a monofunctional model. The optimal quenching found with 1,3-diphenylpropane and 1,3,5-triphenylpentane is associated with DDA type exciplexes where the phenyl donor groups assume an excimer-like arrangement in a triple complex with the benzophenone triplet as the acceptor. The proposed mechanism involves initial formation of a DA exciplex, which undergoes conformational interchange to the DDA exciplex in competition with deactivation and dissociation. *p*-Methoxy-substituted analogues show relatively little accelerated quenching because conformation interchange is slow compared to quenching via the initially formed DA exciplex.

The quenching of the n,π^* triplet state of benzophenone (${}^3B^*$) and other phenyl ketones by benzene (Q) and its substituted analogues is well documented.[1-12] It is generally accepted that transient exciplexes (E) with some degree of charge transfer (CT) character are involved, with ${}^3B^*$ assuming either the acceptor or donor role ($E = {}^3B^*,Q \leftrightarrow B^-,Q^+$ or ${}^3B^*,Q \leftrightarrow B^+,Q^-$) depending on the redox capabilities of Q.[6,7,9,12] The kinetic scheme[8] for ${}^3B^*$ (Scheme I) adequately explains these observations.

Scheme I

All first-order radiative and nonradiative decays

$$ {}^3B^* \xrightarrow{k_1} B \tag{I.1} $$

Reversible exciplex formation

$$ {}^3B^* + Q \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} E \tag{I.2} $$

Exciplex deactivation

$$ E \xrightarrow{k_r} B + Q \tag{I.3} $$

This study explores the quenching capabilities of multifunctional aromatics, such as 1,3-diphenylpropane (**1b**) and 1,3,5-tri-

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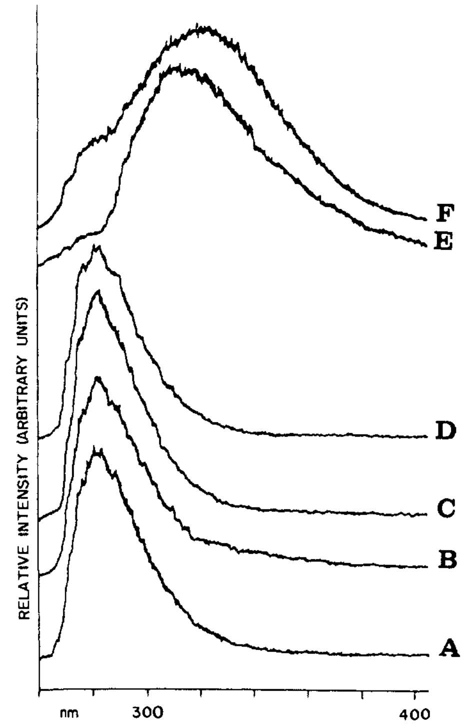
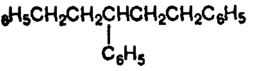


Figure 1. Emission spectra of (A) toluene (6.19×10^{-3} M), (B) 1,2-diphenylethane (5.10×10^{-3} M), (C) 1,4-diphenylbutane (2.96×10^{-3} M), (D) 1,5-diphenylpentane (3.10×10^{-3} M), (E) 1,3,5-triphenylpentane (1.42×10^{-3} M), and (F) 1,3-diphenylpropane (7.17×10^{-3} M) in cyclohexane at room temperature. Excitation at 253.7 nm.

phenylpentane (**4**), relative to appropriate monofunctional aromatic quenchers. The reactivity pattern of these and related compounds (**1**–**4**) follows from a few simple, but fundamental, factors that help elucidate the requirements for multifunctional quenching. These results should serve as a model for quenching of carbonyl triplets by macromolecules such as polystyrene in solution.[10]

$p\text{-}XC_6H_4(CH_2)_nC_6H_4Y\text{-}p$

1: X = Y = H; n = 2 (**a**), 3 (**b**), 4 (**c**), 5 (**d**)
2: X = H; Y = CH_3O–; n = 2 (**a**), 3 (**b**)
3: X = Y = CH_3O–; n = 2 (**a**), 3 (**b**)



$$C_6H_5CH_2CH_2\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCH_2CH_2C_6H_5$$

4

Experimental Section

Materials. Benzophenone (99%, Aldrich Chemicals) was recrystallized several times from diethyl ether/petroleum ether. **Toluene** (Analytical Reagent Grade from Baker-Analyzed) and ***p*-methylanisole** (99%, Aldrich Chemical) were refluxed over sodium metal for 24 h under a dry nitrogen atmosphere and distilled prior to use. **Carbon tetrachloride** (Spectrophotometric Grade from EM Science) was distilled prior to use. **Acetonitrile** (UV Grade from Burdick and Jackson Laboratories) was refluxed over phosphorus pentoxide for 24 h and distilled. The distillate was refluxed over calcium hydride for 24 h and redistilled under a nitrogen atmosphere prior to use. **Quencher Preparations.** All aromatic quenchers were prepared by conventional organic syntheses and rigorously purified by column chromatography prior to use. The physical and spectral properties of these compounds were in agreement with literature values.

Sample Preparation. Solutions containing 5.0×10^{-3} M benzophenone and variable concentrations of quenchers in carbon tetrachloride or acetonitrile were degassed to less than 1-μm pressure by several freeze–pump–thaw cycles and sealed in 1-cm² borosilicate cuvettes. The samples were protected from light prior to use.

Transient Measurements. The basic instrumentation used for transient measurements with a nitrogen laser (337-nm excitation) and boxcar integrator has been previously described.[13] The benzophenone phosphorescence decays were recorded at ambient temperature (approximately 20 °C).

Spectra. All ultraviolet–visible spectra were recorded on an Hewlett-Packard Model 8450A spectrometer attached to an HP 7225A plotter. All steady-state emission spectra were recorded at ambient temperature with an American Instrument Co. spectrofluorimeter. Emission spectra were not corrected for response of the Hamamatsu R446 photomultiplier tube.

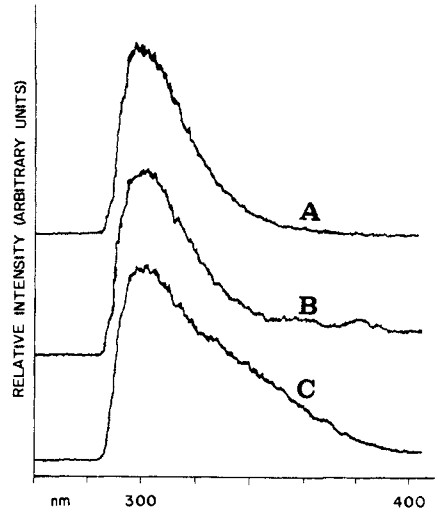


Figure 2. Emission spectra of (A) p-methylanisole (4.12×10^{-3} M), (B) 1,3-bis(4-methoxyphenyl)propane (1.64×10^{-3} M), and (C) 1-(4-methoxyphenyl)-3-phenylpropane (2.44×10^{-3} M) in cyclohexane at room temperature. Exctiation at 253.7 nm.

Table I. Quenching of Benzophenone Triplet by Multifunctional Aromatics

	$k_q \times 10^{-5}$,[a] $M^{-1}\ s^{-1}$		relative rates[b]	
quencher	CH_3CN	CCl_4	CH_3CN[c]	CCl_4[d]
toluene	5.6 ± 0.4	5.1 ± 0.3	(1.0)	(1.0)
1,2-diphenylethane	38 ± 6	34 ± 3	3.4	3.3
1,3-diphenylpropane	150 ± 10	120 ± 10	13	12
1,4-diphenylbutane	73 ± 8	70 ± 6	6.5	6.9
1,5-diphenylpentane	62 ± 5	51 ± 8	5.5	5.0
1,3,5-triphenylpentane	210 ± 20	160 ± 10	13	10

[a] An average of two or more determinations at 20 °C. [b] Relative rates = k_q(observed)/k_q(expected) where k_q(expected) is k_q(toluene) × statistical factor. [c] Values of k_q(expected) are 11.2×10^5 and 16.8×10^5 $M^{-1}\ s^{-1}$ for the diphenyl- and triphenylalkanes, respectively. [d] Values of k_q(expected) are 10.2×10^5 and 15.3×10^5 $M^{-1}\ s^{-1}$ for the diphenyl- and triphenylalkanes, respectively.

Results

Phosphorescence Quenching. The benzophenone phosphorescence decays in the presence and absence of added quenchers displayed exponential behavior through at least 3–4 half-lives. The k_q for each quencher was graphically determined from the relationship

$$\tau_{obs}^{-1} = \tau_L^{-1} + k_q[Q] \qquad (1)$$

where τ_{obs} and τ_L are the measured phosphorescence lifetimes in the presence and absence of [Q], respectively, and $\tau_L = k_l^{-1}$. These values of k_q in carbon tetrachloride and acetonitrile are summarized in Tables I and II.

Steady-State Emission Spectra of the Aromatic Quenchers. The fluorescence spectra of toluene, **1a**, **1b**, **1c**, **1d**, and **4** in cyclohexane are shown in Figure 1. The fluorescence spectra of the mono- and bis-methoxy compounds **2b** and **3b**, with p-methylanisole as a reference, are shown in Figure 2.

Discussion

According to earlier observations,[8] all of the aromatic quenchers used in this study should assume the donor role in the transient exciplexes (E). We expect a structure for E that facilitates electron transfer between the aromatic π-system and the electron-deficient n-orbitals of $^3B^*$.[8,12,14]

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Table II. Quenching of Benzophenone Triplet by Methoxy-Substituted Aromatics

quencher	$k_q \times 10^{-7}$,[a] $M^{-1}\ s^{-1}$		relative rates[b]	
	CH_3CN	CCl_4	CH_3CN	CCl_4
p-methylanisole	3.5 ± 0.2	2.6 ± 0.2	(1.0)	(1.0)
1-phenyl-2-*p*-methoxyphenylethane	4.1 ± 0.3	2.8 ± 0.2	1.2[c]	1.0[c]
1,2-bis(*p*-methoxyphenyl)ethane	8.8 ± 0.9	5.1 ± 0.3	1.2[d]	1.0[d]
1-phenyl-2-(*p*-methoxyphenyl)propane	5.0 ± 0.4	3.1 ± 0.2	1.4[c]	1.1[c]
1,2-bis(*p*-methoxyphenyl)propane	11 ± 1	7.1 ± 0.5	1.6[d]	1.3[d]

[a] An average of two or more determinations at 20 °C. [b] Relative rates = k_q(observed)/k_q(expected) where k_q(expected) is k_q(toluene) + k_q(*p*-methylanisole) or k_q(*p*-methylanisole) × statistical factor of 2. [c] Values of k_q(expected) are $3.6 \times 10^7\ M^{-1}\ s^{-1}$ in CH_3CN and $2.7 \times 17^7\ M^{-1}\ s^{-1}$ in CCl_4. [d] Values of k_q(expected) are $7.0 \times 10^7\ M^{-1}\ s^{-1}$ in CH_3CN and $5.2 \times 10^7\ M^{-1}\ s^{-1}$ in CCl_4.

Within the context of Scheme I, the experimentally determined quenching rate constant can be expressed as[8] $k_q = k_e k_r/(k_r + k_{-e})$. Since the observed k_q's are all less than the diffusion limit (ca. 10^9–$10^{10}\ M^{-1}\ s^{-1}$), $k_r < k_e$, k_{-e} so that $k_q \cong k_r(k_e/k_{-e})$. By this analysis, variations in the measured k_q mirror changes in the intrinsic rate of deactivation of E (k_r).

The Di- and Triphenylalkane Quenchers. All of the diphenylalkanes, as well as 1,3,5-triphenylpentane, show enhanced quenching capabilities relative to toluene, the monofunctional model, even after accounting for the statistical factor of 2 in the diaryl quenchers. The relative quenching profiles of these compounds in acetonitrile and carbon tetrachloride are similar. In both solvents, 1,3-diphenylpropane shows the largest enhancement in k_q among the diphenylalkanes over the expected value [$2k_q$(toluene)]. After accounting for the larger statistical factor, 1,3,5-triphenylpentane shows the same quenching rate enhancement as 1,3-diphenylpropane.

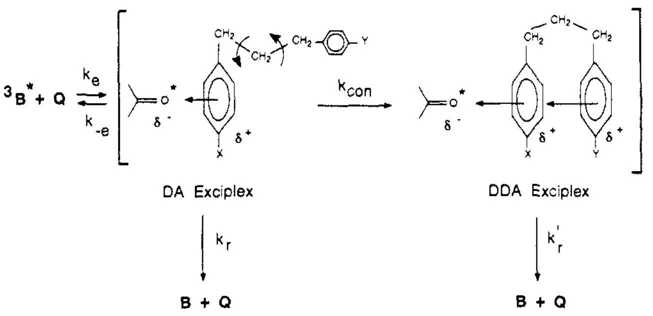
The reactivity profile of the diphenylalkanes parallels the ability of these compounds to form intramolecular excimers. As was pointed out some time ago by Hirayama,[15] intramolecular excimers are formed most easily in systems where the aryl rings are separated by three carbons ("1,3-Rule"). This structural arrangement allows the rings to approach one another in parallel planes approximately 3–4 Å apart without steric strain.

The fluorescence spectra in Figure 1 clearly show this pattern. The 1,2-, 1,4-, and 1,5-diphenylalkanes reveal only "monomer" (benzene ring localized) fluorescence identical with the model compound (toluene) near 285 nm while the spectra of 1,3-diphenylpropane and 1,3,5-triphenylpentane display excimer fluorescence near 320 nm.

This same 1,3-relationship of the aromatic rings seems to be the optimal arrangement for enhanced quenching of $^3B^*$. A plausible explanation of this observation is quenching of $^3B^*$ by way of an exciplex having a DDA structural assembly, with the donor groups assuming an excimer-like geometry. Triple complexes of the DDA type have been proposed previously for several singlet state exciplexes.[16]

The DDA structure is expected to be stabilized relative to a DA exciplex. Both experimental[17] and computational[18] studies indicate greater stability for a radical cation dimer ($D^{+}\cdot D$) relative to its dissociative state ($D^{+}\cdots D$) with benzene and its analogues because of the important contribution of charge resonance[18] in the former. For example, the gas-phase dissociation energy of the benzene radical cation dimer has been measured as 17.0 kcal/mol[17] while charge resonance results in a more favorable ionization potential for [3.3]paracyclophane (7.6 eV)[19] compared to toluene (8.2 eV).[20] Also, the symmetrical, parallel plane geometry proposed for the radical cation dimer structure[18,21] correlates with the accelerated quenching observed with the multifunctional aromatics capable of assuming an excimer-like geometry. In contrast to the DDA complexes, the very small attractive charge resonance term calculated for radical anion dimers[22] would seem to minimize the importance of triple complexes of the structure DAA.

Scheme II



The inherently more favorable features for cation stabilization in the dimer (DD) should lead to a greater CT contribution to the triple complex DDA with a resulting increase in spin–orbit coupling[23] and a related enhanced rate of deactivation. The somewhat greater solvent dependencies, $k_q(CH_3CN/k_q(CCl_4)$, of 1,3-diphenylpropane and 1,3,5-triphenylpentane (1.25 and 1.31, respectively) relative to toluene (1.10) support the picture of a greater CT contribution to the DDA exciplex in comparison with the DA structure.

Quenching within the DDA exciplex by triplet energy transfer between $^3B^*$ and the DD assembly cannot be conclusively ruled out but seems unlikely. Unfortunately, benzene and substituted-benzene excimer triplets are not well defined.[24] However, according to observations by Lim and co-workers,[25] the naphthalene excimer triplet does not have the symmetrical, sandwich-like geometry of the singlet excimer. The appearance of triplet excimer phosphorescence from 1,2-bis(α-naphthyl)ethane and bis(α-naphthyl)methane indicates a preferred skewed geometry. This structural requirement for a triplet state excimer is inconsistent with our results in Table I and would seem to rule out energy transfer as a likely quenching mechanism.

The DDA exciplex is also proposed for the 1,3,5-triphenylpentane system since it shows the same inherent reactivity as the 1,3-diphenylpropane system. There is no kinetic evidence at this time to support a DDDA exciplex.

Kinetic Scheme. Scheme II, a modification of the general exciplex quenching mechanism, is proposed as an explanation of the above observations. Diffusive encounter between $^3B^*$ and the multifunctional aromatics initially yields a DA exciplex that can dissociate (k_{-e}), deactivate (k_r), or, with conformational changes (k_{con}), yield a DDA exciplex that deactivates ($k_{r'}$).

Enhanced quenching by the multifunctional quenchers occurs when $k_{con} > k_r$. Recent studies on intramolecular excimer formation[26] suggest that $k_{con} > 10^8\ s^{-1}$ for 1,3-diphenylpropane and

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1,3,5-triphenylpentane under the experimental conditions. The *intrinsic* rate of quenching of the DA exciplex (k_r) may be estimated from k_q for toluene (5.6×10^5 M^{-1} s^{-1}) and the relationship $k_r \cong k_q(k_{-e}/k_e)$. Since $k_e \cong k_{\text{diffusion}}$, ($k_{-e}/k_e$) is expected to be close to or smaller than unity so that $k_r \leq k_q$ for toluene. Accordingly, $k_{con} > k_r$, which allows multifunctional quenching to be an operative mechanism in these systems.

It is not possible to determine from the current data whether the measured k_q's for the 1,3- and 1,3,5-systems reflect k_r' or k_{con}. For example, if $k_r' > k_{con}$, conformation interchange would be the rate-limiting step for multifunctional quenching.

The data in Table I indicate that the 1,2-, 1,4-, and 1,5-diphenylalkanes show lesser degrees of enhanced quenching reactivity than the 1,3-system. With 1,2-diphenylethane, conformational interchange should be much faster than in the 1,3 system, but the inability to achieve the preferred excimer-like geometry retards the *intrinsic* quenching step. Slower rates of conformational interchange in the 1,4- and 1,5-systems,[27] as well as steric strain considerations in the excimer-like structure, may inhibit multifunctional quenching.

The Methoxy-Substituted Diphenylalkane Quenchers. In contrast to the diphenylalkanes, the methoxy-substituted difunctional aromatic quenchers show little enhanced reactivity relative to *p*-methylanisole. However, to the extent that there is enhanced quenching, the 1,3-system again is a better quencher than the 1,2-system.

This modest quenching enhancement may simply result from the more competitive nature of k_r and k_{con} in the mono- and bis-methoxy systems. Note that the monofunctional model quencher, *p*-methylanisole, displays a k_q almost two orders of magnitude greater than toluene so $k_r \cong 10^7$–10^8 s^{-1}.

An upper estimate of k_{con} for the bis-methoxy system is available from fluorescence data on *p*-methylanisole. From the fluorescence lifetime of the locally excited monomer state (9 ns[28]) and the absence of excimer formation in **3b**, it appears that $k_{con} < 10^8$ s^{-1}. Accordingly, in the methoxy-substituted systems $k_r > k_{con}$ so most of the quenching occurs by way of the DA exciplex.

Conclusions. Quenching of the benzophenone triplet state by multifunctional aromatic quenchers involves both DA and DDA exciplexes. The initially formed DA exciplex dominates the quenching when its deactivation rate is much faster than conformational interchange, as is the case with the *p*-methoxy systems. When k_{con} is much faster than deactivation of the DA exciplex, the DDA exciplex intervenes. The enhanced quenching within the triple complex results from a greater CT contribution. The structural features of the DD component seem similar to those of intramolecular excimers with the aromatic rings being in parallel planes 3–4 Å apart.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the USC Faculty Research and Innovation Fund for their support of this work.

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Ground-State Dimers in Excimer-Forming Bichromophoric Molecules. 1. Bis(pyrenylcarboxy)alkanes[‡]

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Abstract: ^{1}H NMR spectra of the 1,*n*-bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC) and 1,*n*-bis(2-pyrenylcarboxy)alkanes (2PC(*n*)2PC) with *n* = 1–16, 22, and 32 were measured in chloroform-*d* at room temperature. From the changes in chemical shift of the aromatic protons in 2PC(*n*)2PC, as compared to the hexyl ester of 2-pyrenecarboxylic acid, it is concluded that an intramolecular ground-state dimer is present for *n* = 3–16, 22, and 32, a sandwich dimer for *n* > 8, and a shifted symmetric dimer for *n* = 3–8. With 1PC(*n*)1PC, dimer formation is found for *n* = 3–16: predominantly an asymmetric dimer, next to a symmetric one (especially for *n* = 3–7). The solvent dependence of the dimer formation (2PC(5)2PC) can be correlated with the Hildebrand solubility parameter. Variation of temperature has practically no influence (1PC(5)1PC). The conclusions based on the NMR data are confirmed by time-resolved (picosecond) excimer fluorescence measurements. In the case of 2PC(3)2PC, the presence of a ground-state dimer is seen from the dependence of its fluorescence spectrum on the excitation wavelength. In the series of 1PC(*n*)1PC and 2PC(*n*)2PC as well as with the dipyrenylalkanes 1Py(*n*)1Py and 2Py(*n*)2Py mutual through-bond interactions of the aromatic end groups are detected up to *n* = 8.

Excimers and exciplexes are generally defined as bimolecular species only existing in the electronically excited state,[1] setting them apart from dimers, EDA complexes, and other molecular aggregates in the ground state.[1b,2] This sharp distinction does not universally hold, however, as in a number of systems ground-state dimers have been detected next to the excimers.[3] Information on the absence or presence of excimer-like ground-

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[‡] Dedicated to Professor Anton Stier on the occasion of his 60th birthday.

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(1) Concerning the definitions of "excimer" or "exciplex" see: (a) *Molecular Luminescence*; Lim, E. C., Ed.; Benjamin: New York, 1969; p 907. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970. (c) An excimer or exciplex can be defined as a species, made up of at least two molecules, existing in the excited state. Whether or not a dimer is present in the ground state does not directly reflect on the excimer or exciplex.