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Investigations of the Influence of Molecular Geometry on the Spectroscopic and Photochemical Properties of α-Oxo[1.*n*]paracyclophanes (Cyclophanobenzophenones)

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Abstract: The spectroscopic and photochemical properties of a family of α-oxo[1.*n*]paracyclophanes (**8–12**) for $n = 8$–12, respectively) have been investigated. Compared to a model structure possessing a nominal $T_1(n\pi^*)$ state (4,4′-dimethylbenzophenone, DM-BZ), photochemical and photophysical evidence is presented that the $n\pi^*$ character of T_1 decreases as the cyclophane ring size decreases. For example, the rate constants for hydrogen atom abstraction from 1,4-cyclohexadiene in acetonitrile are 1.6×10^8, 0.93×10^8, 0.30×10^8, 0.06×10^8, and 0.04×10^8 M^{-1} s^{-1} for triplet **12–8**, respectively, a result consistent with decreasing $n\pi^*$ character and decreasing reactivity toward hydrogen atom abstraction with decreasing value of *n*. The spectroscopic properties (vibrational structure of the phosphorescence spectrum, phosphorescence lifetime, phosphorescence excitation spectra, triplet–triplet absorption spectra) also vary in a manner consistent with decreasing $n\pi^*$ character as the cyclophane ring size decreases.

Since the early 1960s it has been known that aryl–alkyl ketones and diaryl ketones may possess nearly isoenergetic $^3n\pi^*$ and $^3\pi\pi^*$ states.[1-3] The relative energies of the two states, each with its own distinctive photophysical and photochemical behavior, can and have been manipulated by chemical substitution and solvent polarity. Substantial efforts have been devoted to understanding these effects. Some ketones, such as acetophenone, have their two triplets so close in energy that they may be inverted simply by adjusting the polarity of the solvent. When the states are very close, interesting consequences may arise due to the proximity effect, state mixing, or dynamic equilibrium between the states.[1-3]

In spite of extensive research on the role of conformation on photochemical and photophysical behavior,[4] there has been relatively little work reported on the influence of molecular geometry on the photochemical and photophysical properties of a family of structurally related compounds.

The lifetime of the triplet state of benzophenone (BZ) molecules in a random rigid environment is subject to significant variations about an average value of 5 ms.[5] A hypothesis put forward is that in a glass matrix random twisting of the phenyl rings is frozen, which results in a range of noninterconverting conformations that possess different spin–orbit coupling.[6a] At ordinary temperatures conformational averaging often occurs, although many examples are known for which conformational interconversions are rate limiting for the photo processes.[4]

The extent of spin–orbit coupling and the energy gap between triplets for ketones is expected to vary with molecular conformation, and thus the configuration of the lowest triplet of an aromatic ketone such as benzophenone is a function of ring conformation.[6] Out-of-plane vibronic motion or matrix-induced deformation of the phenyl and carbonyl groups mix the $n\pi$ and $\pi\pi^*$ wave functions via spin–orbit coupling when the two levels are sufficiently close. Moreover, semiempirical calculations suggest that the energies of the excited states are also sensitive functions of geometry.[6b,c] If different conformers could be "frozen" on the time scale of measured photophysical or photochemical properties, each conformer would behave as an independent species.

Semiempirical quantum mechanical calculations lead to the conclusion that the delocalization of n and π^* orbitals in the triplet state of BZ is a function of the dihedral angles, θ_1 and θ_2, that each of the phenyl rings makes with the C–CO–C plane (Chart I).[6b,c] MNDO calculations by Weitzel and Baessler show S_0–T_1 energy gap minima at approximately 30° and 90°. These authors concluded that the lowest triplet was $n\pi^*$ throughout the full rotation. Earlier extended Hückel calculations by Hoffmann and Swenson show a single ΔE (S_0–$^3n\pi^*$) minimum at about 30° and a maximum at 90°, but these authors did not track the behavior of the lowest $\pi\pi^*$ state. Both studies concluded that increased planarity of the system (lower values of θ) caused *delocalization* of the $^3n\pi^*$ state and that the 30° offset from planarity at the

Chart I

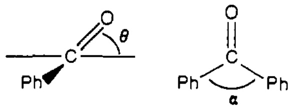
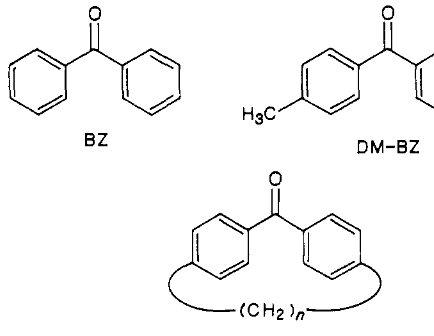


Chart II



BZ

DM-BZ

8, $n=8$
9, $n=9$
10, $n=10$
11, $n=11$
12, $n=12$

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Table I. Absorption Spectra Maxima at 300 K (nm)

	acetonitrile		hexane	
compd	$\pi\pi^*$	$n\pi^*$	$\pi\pi^*$	$n\pi^*$
BZ	250	337	250	335
12	256	325	254	340
11	253	326	250	330
10	254	324	250	330
9	248	324	240	330
8	229	314	<240	316

energy minimum was due to steric interactions of the α-hydrogens. It is also interesting to note that, of MM2,[7a] extended Hückel,[6c] CNDO/2,[6b,c], MNDO,[6b] MNDOC,[6b] and MINDO/3, only the extended Hückel method predicts the correct ground-state geometry of benzophenone with $\theta = 33°$.

Since the extent of delocalization is expected to modify the energy gap between the $^3n\pi^*$ and $^3\pi\pi^*$ states, it would be informative to investigate a series of benzophenones possessing nearly identical constitution, but with differing geometries of the phenyl and carbonyl chromophores, in order to experimentally establish the influence of ring conformation on the photochemical and photophysical properties of a prototype structure.

Such an investigation has been made feasible by the recent syntheses[8a] of the α-oxo[1.*n*]paracyclophanes **8–12** (for *n* = 8–12, respectively), whose structures are shown in Chart II. Benzophenone (BZ) is used as a bench mark for measurements in the series while 4,4′-dimethylbenzophenone (DM-BZ) is used as a benzophenone derivative, which possesses the basic constitution, whose geometry is to be varied, under the assumption that the methylene chains serve mainly to vary the molecular geometry of the system and do not introduce significant direct electronic effects. The cyclophanes **8–12** possess the same basic substitution pattern of DM-BZ but differ in configurational geometry. The stepwise change is clear from spectroscopic evidence and model building,[8b] the latter showing the gradual increase in θ from about 30° to virtually 90° with decreasing cyclophane size, a trend confirmed by the X-ray structure of **8**. Thus, as the cyclophane size decreases, the extent of delocalization of the $n\pi^*$ state should decrease and its energy should increase. In addition, the C–CO–C bond angle, α, decreases with decreasing ring size as evidenced by the positions of the respective IR carbonyl stretches and ^{13}C NMR chemical shifts.[8a] We have previously reported a study of the geometrical effects on the carbenes derived from ketones **8–12**.[8b] We report here an investigation of how the geometric factors induced by the cyclophane structure exert a significant influence on the measured photophysical and photochemical parameters and of whether the variations could be correlated to a specific mechanism of state mixing or inverting of states.

Results

Photophysical Properties. We have employed BZ and DM-BZ as model compounds possessing nominal $T_1(n\pi^*)$ for the cyclophane benzophenones.[9] The photophysical parameters measured were the absorption spectra, the emission spectra at room temperature and at 77 K, the phosphorescence excitation spectra at 77 K, and the triplet–triplet absorption spectra at room temperature. In most cases, a comparison was made between the results for a polar and a nonpolar solvent. The photochemical parameters measured were the rate constants for hydrogen abstraction and charge-transfer quenching.

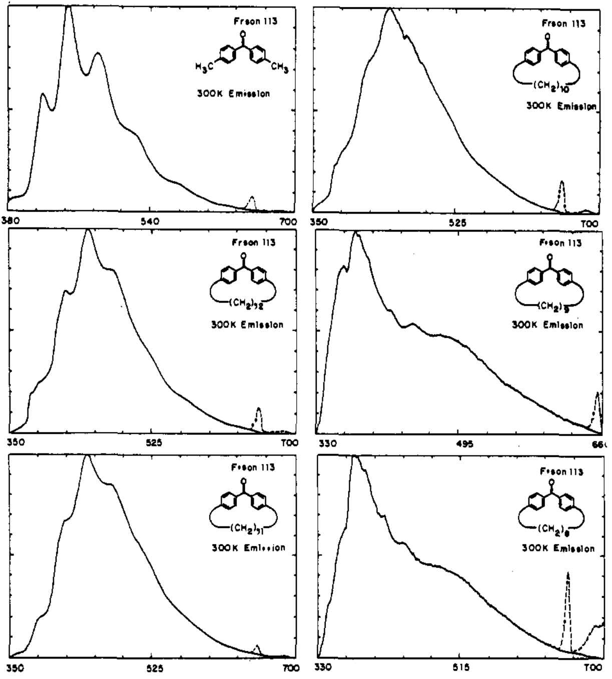

Figure 1. Phosphorescence emission spectra, in Freon solvent at 300 K, of DM-BZ and the family of cyclophanes investigated. The dotted line is the result of scattered light.

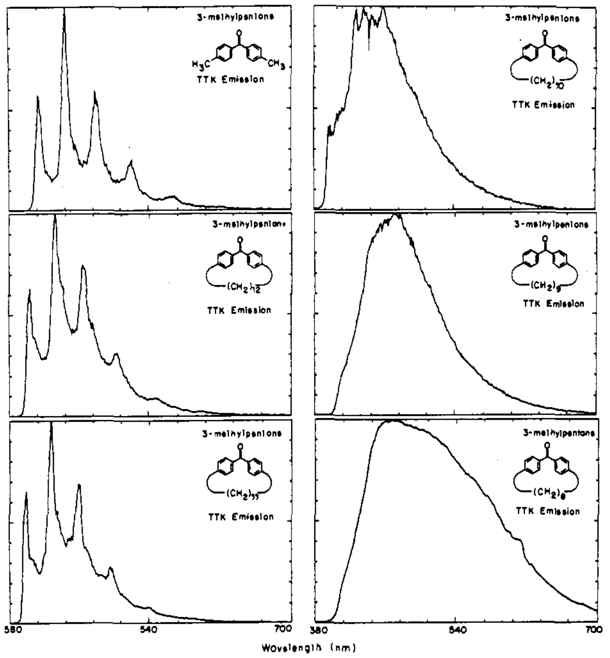

Figure 2. Phosphorescence emission spectra, in 3-methylpentane solvent, at 77 K, of DM-BZ and the family of cyclophanes investigated.

The absorption maxima for the family of ketones, which were measured at room temperature in hexane and acetonitrile, are summarized in Table I. The assignment of the bands is straightforward, with the longer wavelength band corresponding to a S_0–$S_1(n\pi^*)$ transition and the shorter wavelength band corresponding to a S_0–$S_2(\pi\pi^*)$ transition.

The phosphorescence excitation spectra in the S_0–S_n region for each ketone (at 77 K), except **8**, were very similar with maxima

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(7) (a) Preliminary calculations carried out as part of this study. (b) Judging by the difficulty of the previous authors in generating the correct geometry for benzophenone, semiempirical calculations were not attempted. Molecular mechanics are not well-parameterized for molecules such as these and give asymmetric results, even for benzophenone. The average value for θ found in very rough calculations were 42°, 42°, 58°, 70°, 81°, 78°, and 88° for BZ, DM-BZ, **12**, **11**, **10**, **9**, and **8**, respectively. We do not believe these to be quantitative data, but they are generally consistent with expectations from model building.

(8) (a) Alt, R.; Staab, H. A.; Reisenauer, H. P.; Maier, G. *Tetrahedron Lett.* **1984**, 633. Staab, H. A.; Alt, R. *Chem. Ber.* **1984**, *117*, 850. (b) Alt, R.; Gould, I. R.; Staab, H. A.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 6911.

(9) The energy gap between T_1 and T_2 for benzophenone is 7–8 kcal. See, for instance: Morris, J. F.; Williams, D. F. *Chem. Phys. Lett.* **1974**, *25*, 312. For a discussion of the criteria for distinguishing between state mixing and thermally equilibrating triplets, see: Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856. Encinas, M. V.; Lissi, E. A.; Lemp, E. A.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856. Berger, M.; McAlpine, E.; Steel, C. *J. Am. Chem. Soc.* **1978**, *100*, 5147. Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1970**, *92*, 5280 and ref 2.

Table II. Emission Maxima from 3-Methylpentane at 77 K

compd	maxima
BZ	416, 446, 482, 522, 571, 614
DM-BZ	414, 445, 479, 521, 567, 620
12[a]	(404, 412 s), (433, 442 s), (465, 476 s), (504, 516 s), 548
11	400, 427, 460, 499
10	399, 409, 427, 437
9	411, 442, 473, 510
8	470

[a] Each vibrational band showed a substantial shoulder whose size relative to the main band was a function of the exciting wavelength. See text for explanation.

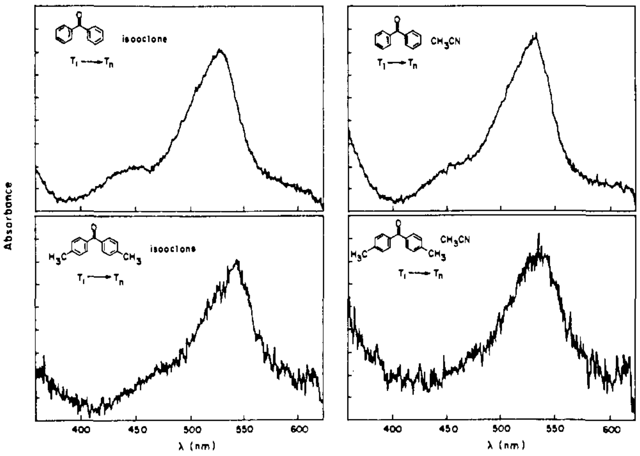

Figure 3. Triplet–triplet absorption spectra of BZ and DM-BZ in isooctane (left) and acetonitrile (right) at 300 K.

at ca. 291–293 and 335–340 nm. Maxima for **8** were blue-shifted relative to the other ketones. In further contrast, an external heavy-atom effect was observed for **8**, but not for **9–12**, in the region of 380–420 nm, corresponding to the S_0–T_1 transition.[10]

The phosphorescence emission spectra of the family of ketones were investigated at room temperature (Freon-113 solvent, Figure 1) and at 77 K, both steady state (3-methylpentane solvent, Figure 2) and time resolved at the lower temperature. The emission maxima of the spectra and the observed lifetimes are summarized in Tables II and III.

The triplet–triplet absorption spectra of the ketones were also measured at room temperature in acetonitrile and isooctane. Representative spectra of BZ and DM-BZ are shown in Figure 3, the spectra of the cyclophane ketones are shown in Figure 4, and the key parameters (lifetime and absorption maxima) are summarized in Table IV.

Photochemical Properties. The phosphorescence quenching rate constants for the family of ketones in Chart II were measured in Freon and acetonitrile solvent for 1,4-hexadiene as quencher and in acetonitrile for isopropyl alcohol and *tert*-butylamine as quenchers. All measurements were made at room temperature with ketone concentration ca. 5×10^{-5} M in solvents that were saturated with argon. The data are summarized in Table V.

Discussion

In one of the classic phases of organic photochemistry during the 1960s, various observables derived from emission spectscopy were related to the orbital characteristics of triplet states.[11] Hallmark criteria of the emission of a "pure" $T_1(n\pi^*)$ state of an aromatic ketone (e.g., benzophenone) include (1) a clearly defined vibrational structure with band separations of ca. 1700 cm^{-1} (the ground-state C=O stretching frequency), (2) a radiative phosphorescence lifetime of the order of 10 ms or less (due to the inherently strong internal spin–orbit coupling of triplet $n\pi^*$ states), and (3) an excitation spectrum that is insensitive to external heavy-atom effects (also due to the inherently strong internal spin–orbit coupling of triplet $n\pi^*$ states). In addition, the triplet–triplet absorption spectrum is expected to change, although only an empirical correlation of the change with the degree of $n\pi^*$ character has been reported.[12]

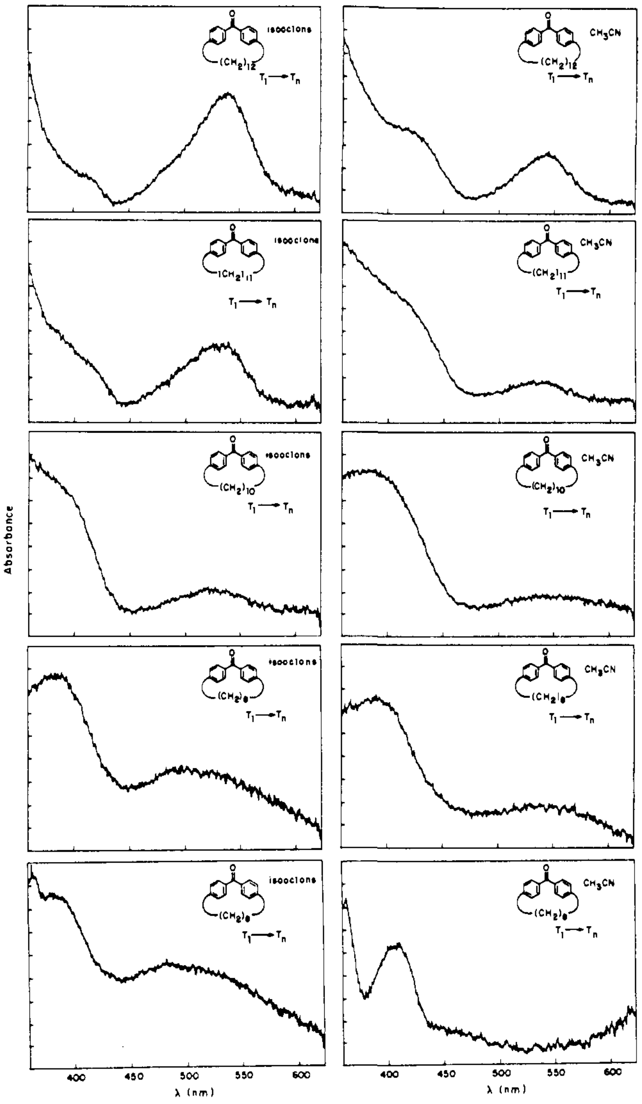

Figure 4. Triplet–triplet absorption spectra of the family of cyclophanes in isooctane (left) and acetonitrile (right) at 300 K.

In light of the results tabulated above we suggest that the lowest triplet for the largest of the cyclophane benzophenones is $n\pi^*$ but that a $\pi\pi^*$ type state has become the lowest triplet in the smallest cyclophane.[13] Depending on the conditions, the "crossing" occurs somewhere in the middle of the series. In some of these intermediate cases, apparently mixed behavior arises.

The situation in which the interaction energy betwen the $n\pi^*$ and $\pi\pi^*$ states is not small compared to the energy separating the states has been termed "strong coupling".[1,3] In such cases, the wave function cannot be accurately described as pure $n\pi^*$ or $\pi\pi^*$ but rather takes the form

$$\Psi = a(\Psi_{n\pi^*}) + b(\Psi_{\pi\pi^*})$$

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(13) A reviewer has pointed out that the lowest $\pi\pi^*$ triplet in acyclic ketones correlates with the ^1L_a transition near 250 nm. He noted that the energies of these states *increase* with decreasing ring size (Table I) and that charge-transfer quenching of "traditional" $\pi\pi^*$ states by amines is as effective as that of $n\pi^*$ states and thus concluded that the triplets we observe in the smaller ketones are of a completely new type of molecular orbital configuration. We agree that the $\pi\pi^*$ states of the smaller ketones must be severely perturbed by their overlap with the oxygen n-orbital, but we feel that such a novel conclusion is too speculative for the evidence we present.

Table III. Phosphorescent Lifetimes at 77 K (ms)

	3-methylpentane				ethanol			
compd	%	τ_1	%	τ_2	%	τ_1	%	τ_2
BZ	100	5.1			100	5.6		
DM-BZ	100	6.0			22	4.6	78	7.7
12	34	3.1	66	6.0	22	2.8	78	7.9
11	100	5.9			5	2.0	95	10.6
10[a]	37	4.1	35	14.2	17	3.1	83	22.0
9	36	6.6	64	24.8	21	6.1	79	16.7
8	5	6.1	95	44.5	22	5.7	78	46.5

[a] **10** shows a third component in 3-methylpentane: 27% 1.3 ms.

Table IV. Triplet-Triplet Absorption Maxima (nm) at 300 K

	maxima		lifetime, μs	
compd	isooctane	CH_3CN	Freon	CH_3CN
BZ	448, 526	451, 531	5.3	6.5
DM-BZ	542	534	7.1	7.0
12	413, 539	416, 542	3.7	3.9
11	530	414, 534	5.2	4.0
10	520	382	7.4	8.9
9	384, 495	390	7.5	(*a*)
8	380, 481	363, 408	24	40

[a] Shows nonexponential decay, which could be approximately fit with a biexponential of ca. 10 and 30 μs.

As the degree of $n\pi^*$ character in an initially pure or model $n\pi^*$ state decreases in a systematic variation of structure, the vibrational structure of phosphorescence is expected to blur, the inherent phosphorescence lifetime is expected to increase, and the phosphorescence excitation spectrum is expected to become more sensitive to external heavy-atom effects. We suggest that the changes in geometry of the cyclophanobenzophenones cause a transition in the configuration of the lowest triplet state from a dominant $^3n\pi^*$ to a dominant $^3\pi\pi^*$ as the size of the cyclophane ring decreases and the geometry of the system varies. In the middle of the series, where the energy levels of the triplet states are very close, mixed behavior is observed. In some instances, we have observed phosphorescence from two active states, T_1 and T_2.

Since the triplet levels are so close for some of the ketones, the exact configurations of those states are of course functions of solvent, temperature, and so on, but the trend toward increasing $\pi\pi^*$ behavior with decreasing ring size is the same for each of the criteria used. We now test this generalization in more detail for the cyclophane family against the paradigms for identification of T_1 as either a $^3n\pi^*$ or $^3\pi\pi^*$ state.

1. **Phosphorescence Spectra.** The phosphorescence spectra shown in Figures 1 and 2 are consistent with the hypothesis that as the cyclophane ring size is decreased the degree of $n\pi^*$ character of T_1 is also decreased. In Figure 1 (room temperature, freon solvent) the vibrational structure typical of a $T_1(n\pi^*)$ state is broadened but distinct for **12** and is almost gone for **10** and **11**. For **8** and **9** the forms of the spectra are clearly different from those of **11** and **12**. In Figure 2 (77 K, 3-methylpentane solvent) the 1700-cm^{-1} vibrational features are more clearly evident for **11** and **12** and are blurred for the smaller rings.

Phosphorescence Lifetimes and Time-Resolved Emission Spectra. The phosphorescence lifetimes of **8–12** at 77 K are also consistent with the increasing importance of a nominally $^3\pi\pi^*$ state as the cyclophane ring size decreases. Here we observed, in most instances, emission from two (or more) states, which did not equilibrate on the time scale of the experiment. In 3-methylpentane glass, BZ, DM-BZ, and **11** emission decays were monoexponential. Emission decays from **8**, **9**, and **12** could be fit to biexponentials, while **10** could only be fit to a triexponential. In ethanol glass, all decays could be fit to a biexponential, except BZ, which was monoexponential.

Favaro[14] has summarized the possible mechanisms for multiple-exponential emission from aromatic ketones as follows:

(1) Emissions may result from nonequilibrating or slowly equilibrating excited states of the ketone, typically $n\pi^*$ and $\pi\pi^*$ states.

(2) Emissions may result from differing solvation sites. For example, there may be site effects in some solvents such that a finite fraction of the ketone molecules are hydrogen bonded or are in particularly polar environments. These ketones have their $\pi\pi^*$ states stabilized, relative to their $n\pi^*$ states, and may produce more than one emission.

(3) Emissions may occur from different conformations. For example, if the ketones are not inherently rigid, two or more discrete conformations that have different emission spectra and/or lifetimes may be frozen on the time scale of measurement.

(4) Photochemistry may occur, leading to excited products, which may emit themselves, along with the ketone.

We consider the possibility of multiple emission in our systems to be likely due to one or more of the first three of these mechanisms. We do not believe there is evidence suggestive for the fourth mechanism in our case.

There is specific evidence for mechanism three in which two or more different conformations are frozen on the time scale of the measurements. The phosphorescence of **12** shows a doubling of each vibrational band in 3-methylpentane glass, where mechanism two, differing solvent sites, is implausible. The relative areas of the "lines" in the vibrational bands vary with excitation wavelength, such that higher energy excitation leads to higher energy emission. We believe that mechanism three is also responsible for at least one of the extra exponentials required to fit to the emission of **10** in 3-methylpentane and may also contribute to the nonexponential behavior observed in ethanol glass, but we believe that mechanism two, differing solvent sites, is very important in ethanol, as well.

Mechanism one, emission from both $n\pi^*$ and $\pi\pi^*$ states, is likely to be operative for the smaller ketones, which show at least partial $\pi\pi^*$ behavior by every other measure.[15] Each shows a short-lived emission (<10 ms), typical of $n\pi^*$ phosphorescence, and a longer lived component, typical of $\pi\pi^*$ states. We propose that the $^3n\pi^*$ and $^3\pi\pi^*$ states invert somewhere in the middle of the series (depending on the conditions) and that T_1 becomes increasingly pure $\pi\pi^*$ in nature, leading to the increase in the longer lifetime. This suggestion is supported by the increase in percentage of the longer lived component in the 3-methylpentane data as the cyclophane size decreases, although the ethanol data are more ambiguous.

Time-resolved emission spectra support the hypothesis of nonequilibrating $n\pi^*$ and $\pi\pi^*$ state emissions in the smaller ketones. Emission spectra collected at 1- and 50-ms delay were identical and structured for BZ and **10–12**. Those collected at 1 ms were relatively structured for **8** and **9**, while the spectra

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[14] Favaro, G. *J. Photochem.* **1982**, *20*, 33.

[15] See, for example: (a) Murai, H.; Minami, M.; I'Haya, Y. J. *J. Phys. Chem.* **1988**, *92*, 2120. (b) Maciejewski, A.; Szymanski, M.; Steer, R. P. *Chem. Phys. Lett.* **1988**, *143*, 559. (c) Connors, R. E.; Christian, W. R. *J. Phys. Chem.* **1982**, *86*, 1524. Amrein, W.; Larsson, J. M.; Schaffner, K. *Helv. Chim. Acta* **1979**, *57*, 2519. (d) Pownall, H. J.; Huber, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 6429. (e) Wagner, P. J.; May, M. J.; Haug, A.; Graber, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 5629. (f) Case, W. A.; Kearns, D. R. *J. Chem. Phys.* **1970**, *52*, 2175. (g) Yang, N. C.; Dusenbury, R. L. *Mol. Photochem.* **1969**, *1*, 159. (h) Rauh, R. D.; Leermakers, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 2246. (i) Griffin, R. N. *Photochem. Photobiol.* **1968**, *7*, 159, 175. (j) Lamola, A. A. *J. Chem. Phys.* **1967**, *47*, 4810. (k) Yang, N. C.; Murov, S. *J. Chem. Phys.* **1966**, *45*, 4358.

Table V. Chemical Quenching Rates at 300 K

quencher (solvent)	BZ	DM-BZ	**12**	**11**	**10**	**9**	**8**
1,4-cyclohexadiene (Freon)	2.8×10^8	1.9×10^8	1.6×10^8	9.3×10^7	3.0×10^7	$6.0 \times 10^{6\,a}$	3.8×10^6
1,4-cyclohexadiene (acetonitrile)	3.3×10^8	1.7×10^8	1.1×10^8	3.7×10^7	3.5×10^6	2.5×10^6	$<5 \times 10^4$
tert-butylamine (Freon)	5.6×10^7	2.2×10^7	3.0×10^7	2.3×10^7	$6.3 \times 10^{6\,a}$	4.1×10^6	$<5 \times 10^4$
isopropyl alcohol (acetonitrile)	1.9×10^6	9.0×10^5	5.4×10^5	1.7×10^5	*b*	$<1 \times 10^5$	$<5 \times 10^4$

[a] Measured at two wavelengths. [b] Curved Stern–Volmer plot.

collected at 50-ms delay were unstructured and red-shifted. The early spectra are attributed to the fast-decaying $n\pi^*$ state and show a progressive blurring similar to the steady-state emissions, suggesting that there is progressively more $\pi\pi^*$ character in the nominally $n\pi^*$ states. The red-shifted broad emissions then can be attributed to slower decaying nominally $\pi\pi^*$ states, which lie slightly below the corresponding $n\pi^*$ states.

2. Triplet–Triplet Absorption Spectra. Little research has been published concerning the correlation of the manifestation of state mixing in triplet–triplet absorption spectra.[12] However, solvent effects have been shown to influence the features of these spectra in a manner consistent with significant change in the shape of the spectrum of a nominal $T_1(n\pi^*)$ with decreasing $n\pi^*$ character.

The triplet–triplet absorption spectra shown in Figure 4 are consistent with a change in electronic character as the size of the cyclophane is decreased. It should be noted that the triplet–triplet absorption spectra of BZ and DM-BZ (Figure 3) are quite similar in shape and spectral maxima and are essentially the same in nonpolar (isooctane) or polar (acetonitrile) solvent. For **12**, the spectral shapes and maxima remain the same as solvent polarity is changed, but the relative intensities of the maxima change. Inspection of the spectra in Figure 4 reveals a remarkable combined effect of ring size and solvent polarity change for the family of cyclophanes. *Decreasing the ring size by one methylene group has an effect on the spectrum that is very similar to increasing the solvent polarity*! Since increasing solvent polarity has been shown to increase the extent of $\pi\pi^*$ character of nominal $T_1(n\pi^*)$ states, we conclude that decreasing the ring size of the cyclophane has the same effect.

3. Phosphorescence Excitation Spectra. Phosphorescence excitation spectra in the S_0 to S_n region are characteristic of the absorption of the corresponding S_n state. The familiar trend of loss of spectral structure with decreasing ring size in the triplet manifold is paralleled in the singlet manifold by the phosphorescence excitation spectra. These results are interpreted to mean that the character of the lowest *singlet* excited state of the cyclophanobenzophenones shows decreasing $n\pi^*$ character with decreasing ring size similar to that exhibited by the triplets.

Significantly, the S_0 to T_1 region of the phosphorescence excitation spectrum of **8** shows a significant enhancement on addition of iodoethane to an EET (ether/ethanol/toluene) glass. Triplet states are expected not to show such an external heavy-atom effect if they contain any significant $n\pi^*$ character, since it is assumed that the external spin–orbit coupling enhancement will be small compared to the inherent spin–orbit coupling of the $n\pi^*$ state. We thus conclude that the lowest triplet of **8** has lost its $n\pi^*$ character under these conditions.

4. Photochemical Reactivity. The rate constants for hydrogen abstraction and electron abstraction by triplet ketones have been intensively investigated and correlated with structure. In general, $n\pi^*$ states are more reactive toward a given substrate than $\pi\pi^*$ states. In systematic structure–reactivity investigations, the rate constant hydrogen atom abstraction for a bench mark $n\pi^*$ state is compared to that for a probe structure, and inferences are then made concerning the electronic structure of the reactive probe state. Decreasing reactivity is considered indicative of increasing $\pi\pi^*$ character of the excited state (in the absence of equilibrium effects between two excited states). It has been shown, in some cases, that virtually all the reactivity of some nominally $\pi\pi^*$ (T_1) ketones is actually due to reactivity of the thermally populated $n\pi^*$ (T_2) level![9]

The data in Table V show a significant and consistent dependence of excited-state reactivity on structure and solvent. The rate constants for a given quencher and solvent vary by as much as 3 orders of magnitude over the series **8–12** where the smaller rates are found for the smaller ketones. For example, in acetonitrile, the rate constants for hydrogen abstraction from 1,4-cyclohexadiene vary from 1.6×10^8 M^{-1} s^{-1} for **12** to $<5 \times 10^4$ M^{-1} s^{-1} for **8**. Considering that the major structural variation is conformational, the range of the structural effect on reactivity is quite significant. The consistency of the rate constant profile as a function of structure and solvent for several substrates argues for related and similar structures in the rate-determining quenching step.[9]

Employing DM-BZ as the model $n\pi^*$ compound, **12** exhibits nearly identical behavior in terms of the absolute values of rate constants and for the solvent effect on quenching by 1,4-cyclohexadiene. The mechanism of quenching by *tert*-butylamine in freon-113 is probably not by full electron abstraction but rather by a related partial charge-transfer mechanism. Charge-transfer quenching rates of $\pi\pi^*$ triplets by amines are often comparable to rates for $n\pi^*$ triplets. We, in fact, observe rate constants within 1 order of magnitude for ketones **9–12** but observe a precipitous drop for ketone **8**. Thus, it is tempting to speculate that the severe twisting in **8** is such a perturbation that even the $\pi\pi^*$ triplet is not the standard sort observed in such molecules as *p*-methoxyacetophenone or acenaphthone.[13]

The salient feature of the structure–reactivity correlations is the monotonic decrease in the rate constant for quenching with a decrease in the number of methylene carbons of the cyclophane structure. We postulate first that the structural connection with reactivity occurs through an indirect modification of the electronic structure of the reacting triplet state, which occurs as a function of the dependence of the geometry of the benzene rings on the cyclophane ring size. We postulate next that the changing geometry "mixes" more $\pi\pi^*$ character into the reacting triplet as the ring size gets smaller, until the lowest triplet is virtually pure $\pi\pi^*$ in **8**. In the spirit of this model, increasing solvent polarity upon going from freon to acetonitrile further increases the $\pi\pi^*$ character of the reacting triplet. We cannot at this point distinguish whether the residual reactivity is due to T_1 or T_2 for the smaller ketones. While our results do not rule out the possibility of involvement of equilibrating triplets at room temperature, this mechanism does not seem to be required by our data. Temperature dependences of the photochemical reactivity would be particularly useful in establishing the role of equilibrating states.[9]

To the extent that the α-oxo[1.*n*]paracyclophanes can be considered twisted benzophenones, our results appear to agree better with the extended Hückel calculations of Hoffmann and Swenson[6c] than the semiempirical calculations of Weitzel and Baessler.[6a,b] The disappearance of $n\pi^*$ behavior with increasing θ can be interpreted as the effect of the raising of the $^3n\pi^*$ energy. We certainly do not observe, as implied in Weitzel and Baessler's work, a pure, localized $n\pi^*$ state as the lowest triplet.

It is also interesting to compare the present results to the known 1-keto[2.2]paracyclophane ([2.2]KPC).[16] Though formally a substituted acetophenone, rather than benzophenone, its geometry also precludes conjugation of the aromatic rings with the carbonyl. The absorption spectrum of [2.2]KPC shows its S_0–$^1\pi\pi^*$ absorption at 224 nm,[16a] similar to **8**; it shows only a broad emission with a 20-ms lifetime at 77 K and has a very low hydrogen abstraction reactivity at room temperature.[16b] Moreover, the S_0–$n\pi^*$ band at ca. 250 nm returns for the higher homologues.[16a]

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(16) (a) Cram, D. J.; Helgeson, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 3515. (b) Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806. We thank a reviewer for bringing this molecule to our attention.

Conclusion

We have shown that the character of the T_1 state of a series of paracyclophane benzophenones loses its $n\pi^*$ character as a function of decreasing cyclophane ring size for the series **8–12** until the nominal character of the lowest triplet is $\pi\pi^*$-like in the smallest and most strained compound. Physically, the increasing $\pi\pi^*$ character is manifest clearly in the form of the phosphorescence spectrum, the decay parameters of phosphorescence, and the triplet–triplet absorption spectrum. Chemically, the increasing $\pi\pi^*$ character is manifested as a decreasing rate constant for hydrogen abstraction.[17] A sharp drop in the charge-transfer quenching rate constant for ketone **8** relative to the other ketones suggests that the character of its lowest triplet may not even be adequately described by the standard $\pi\pi^*$ triplet of other aromatic ketones.

In addition to the studies reported here, other tests of these ideas are possible. For example, the influence of temperature and pressure on the photophysics of the cyclophane family would be interesting to compare to the influence of solvent. Variation in strength of the $n\pi^*$–$\pi\pi^*$ coupling should influence the triplet sublevels, so that ESR analysis should be a useful probe of mixing. In particular, the sublevel selectivity of intersystem crossing (both S_1 to T_1 and T_1 to S_0) should be very sensitive to mixing. Finally, the rate (picosecond) of intersystem crossing from S_1 to T_1 should be significantly influenced by state mixing and the position of various states. Results of such investigations will be reported at a future date.

Experimental Section

General Procedures. Benzophenone was purchased from Aldrich and was recrystallized several times from ethanol. 4,4′-Dimethylbenzophenone was prepared by Grignard reaction of *p*-tolylmagnesium bromide and *p*-tolualdehyde, followed by CrO_3 oxidation in 85% overall yield, and then recrystallized several times from ethanol. The preparation of **8–12** has been reported previously.[8a]

All solvents used in spectroscopic studies were the highest purity commercially available and used as received. Isooctane, isopropyl alcohol, 3-methylpentane, and 1,1,2-trichlorotrifluoroethane (Freon-113) were purchased from Aldrich. Acetonitrile (Kodak), diethyl ether (Mallinkrodt), and ethanol (Pharmco) were used as received. Ethyl iodide (Aldrich) was distilled and stored over mercury. *tert*-Butylamine and 1,4-cyclohexadiene (both from Aldrich) were purified by distillation and passage through alumina, respectively.

Absorption spectra were collected on a Perkin-Elmer 559A spectrophotometer at concentrations such that the peak of interest had an optical density of 0.3–1.0.

Phosphorescence excitation spectra were taken on a Perkin-Elmer LS-5 and a Spex Fluorolog. Solutions were prepared in 3-methylpentane, EET (ether/ethanol/toluene 2:1:1), and EEET (ethyl iodide/ether/ethanol/toluene 1:4:2:2) at concentrations of 1 mM for each ketone. Solutions were placed in a quartz NMR tube and immersed in a liquid-nitrogen Dewar whose bottom section is the same shape as a 1-cm fluorescence cell and made of quartz. Each ketone was monitored at its emission maximum. Spectra obtained in EET and 3-methylpentane glasses showed the same features for excitation wavelengths of 250–400 nm. Spectra obtained in EET and EEET were identical from 375 to 425 nm for all ketones, except **8**, which showed almost 1 order of magnitude signal enhancement.

Phosphorescence emission spectra were taken on a Spex Fluorolog. Room temperature spectra were collected from solutions made in freon with optical densities of 0.10 at 320 nm (the excitation wavelength). The solutions were freeze–pump–thaw degassed for at least five cycles. Spectra obtained at 77 K were from solutions identical with those used for phosphorescence excitation spectra (3-methylpentane and EET only). Spectra were collected with excitation at 300, 320, 340, and 360 nm. Aside from the intensity of emission, the spectra for each ketone were identical, except for **12**, which showed a splitting of several hundred reciprocal centimeters in each main vibrational band. The intensity of each line of the split band was related to the excitation wavelength, with higher energy excitation favoring the higher energy emission line.

Time-resolved emission spectra were collected using the same Dewar assembly as described above. Excitation was provided by a Lambda Physik EMG 201 MSC excimer laser operating at 308 nm. Spectra were obtained using a Parc OMA III optical multichannel analyzer, calibrated with a mercury lamp, operating in the CW mode. A 1-ms "open time" mechanical shutter was used to gate the detector. Timing and control were provided by a PDP 11/23 computer, and spectra were collected at 1- and 50-ms delays.

Phosphorescence decays were obtained, again using the same Dewar system described above, at 77 K using a PRA single-photon-counting unit. Triggering was provided by a Global Specialties Corp. 4001 pulse generator, which triggered both an EG&G PS 302 nanosecond flashlamp power supply and a Tracor Northern TN 1710 with a TN 1736 multichannel scaler unit. The signal from the single-photon counter was run through a PRA 1740 delay box before being sent to the TN 1710. The TN 1710 was interfaced to a PDP 11/03 computer, which performed the fits. All fits had $0.90 < \chi^2 < 1.2$ and flat autocorrelation functions. Solutions were again 1 mM in ethanol and in 3-methylpentane. An interference filter centered about 310 nm was placed in front of the exciting lamp and a 400-nm cutoff filter was placed in front of the monochromator leading to the single-photon counter.

Triplet–triplet absorption spectra were obtained employing an OMA III detector. Solutions had optical densities of 0.3–0.5 at 266 nm in acetonitrile and isooctane and were deoxygenated by bubbling with Ar. Excitation was provided by the 4th harmonic of a Quanta Ray Nd:Yag laser (ca. 8 ns, 2 mJ). The detector was used in the gated mode with an EG&G 1302 fast pulser. Spectra were obtained with ca. 100-ns delay and 10-ns gate.

Chemical quenching rates and room temperature lifetimes were obtained using a standard flash photolysis apparatus,[8b] monitoring absorption at 400 or 530 nm, as appropriate. Excitation was provided either by a Lambda Physik EMG 101 excimer laser operating at 308 nm or by the 4th harmonic of a Quanta Ray Nd:Yag laser (266 nm). Solutions had optical densities of 0.3–0.5 at the appropriate exciting wavelength and were deoxygenated by bubbling with Ar. Quenching rate constants were measured by measuring the decay of T_1 to T_n absorption, making use of the equation $k_{obs} = k_0 + k_q[Q]$. Each rate was measured for at least five concentrations, with at least three points at each concentration. The rates reported generally have a precision of ±10%.

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