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Electron Spin Resonance of the Lowest Excited Triplet States of α-Oxo[1.n]paracyclophanes [Cyclophanobenzophenones]. Effect of Molecular Geometry on the Electronic Character of the Triplet State

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Received: March 25, 1994[®]

We report a low-temperature electron spin resonance (ESR) investigation of the first triplet excited states of a series of cyclophanobenzophenones, the α-oxo[1.n]paracyclophanes ($n = 8–12$). The zero-field D splitting parameters for the series range from about -0.12 cm^{-1} for $n = 12$ to about -0.05 cm^{-1} for $n = 8$. Relative triplet sublevel populating rates range from about 90% P_z and 0% P_x for $n = 12$ to about 50% P_z and 40% P_x for $n = 8$. The results for $n = 12$ are comparable to those for benzophenone and 4,4'-dimethylbenzophenone. Molecular mechanics show that as the methylene tether that connects the two phenyl rings is shortened, the phenyl rings are forced to rotate away from conjugation with the carbonyl π system. We propose that as this conformational change occurs, unpaired electron density in the n orbital of oxygen is transferred to the phenyl rings. This proposal is supported by semiempirical quantum mechanical calculations. Interpretation of our spectroscopic results show that the 15–20% of nominal ππ* character found in the lowest triplet of the $n = 12$ cyclophane increases to around 90% for the $n = 8$ cyclophane. The extreme conformational sensitivity of the phosphorescence lifetimes and T_1 ESR spectra of benzophenone, dimethylbenzophenone, and cyclophanes $n = 9–12$ suggests that T_1 changes from nπ* to ππ* character between phenyl ring twist angles of between 40° and 55°.

Introduction

The electronic configuration and energetics of the lowest triplet state of ketones are functions of the geometry around the carbonyl carbon.[1–4] Since ^{3}nπ* and ^{3}ππ* excited electronic states of aryl alkyl and diaryl ketones are known to be close in energy,[5–8] it is easy to imagine that relatively small conformational variations may lead to relatively large changes in excited-state electronic structure and perhaps to relatively large changes in the energy gap between the lowest triplet states. For example, triplet lifetimes measured for benzophenone frozen in a glassy matrix vary widely around a mean of 5 ms due, it is believed, to the existence of multiple conformations of the ketone in the glass.[9,10] The experiments reported here provide further support for the existence of these multiple conformations.

Time-resolved luminescence spectroscopy, photophorescence spectroscopy, triplet–triplet spectroscopy,[11] heavy-atom-induced phosphorescence excitation S_0–T_1 spectroscopy,[12] electron spin resonance (ESR) spectroscopy, and chemical reactivity are all able to probe the lowest triplet state of aromatic ketones. We have recently described picosecond pump–probe experiments which yield the rate of intersystem crossing (ISC) for the same molecules that we describe herein.[13]

We choose the angles θ and α (see Chart 1) to characterize the conformations of diaryl ketones. We define θ as the dihedral angle by which the phenyl rings lie out of the C–C–C plane, where the central C atom refers to the carbonyl C atom. The C–C–C bond angle α reflects the sp hybridization at the carbonyl carbon and, along with θ, influences the electronic communication between the carbonyl orbitals and the ring π systems. The delocalization of the carbonyl π* orbital into the phenyl ring π*

CHART 1: Illustrations of the Conformation Angles θ and α in Benzophenone and the Structure of the C8 Cyclophanobenzophenone

Benzophenone

C8-cyclophane
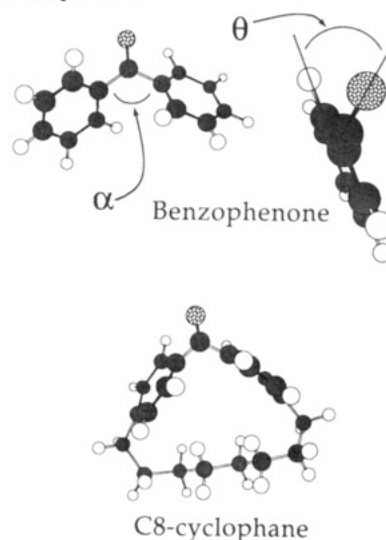
orbital in benzophenone decreases with increasing θ, while that of the oxygen n orbital into the ring π orbital may increase to some extent.[14] Semiempirical calculations[15–17] predict an energy minimum for ^{3}nπ* benzophenone at $\theta = 30°$. The planar structure, in which maximum conjugation of the phenyl rings with the carbonyl π orbital occurs, is of higher energy, largely due to steric interactions between α-protons that prevent further π* stabilization at smaller θ. The same work predicts a ground-state minimum at $\theta = 33°$.[16]

DMBP (p,p'-dimethylbenzophenone) is presumably free to assume the same conformations that are available in BP

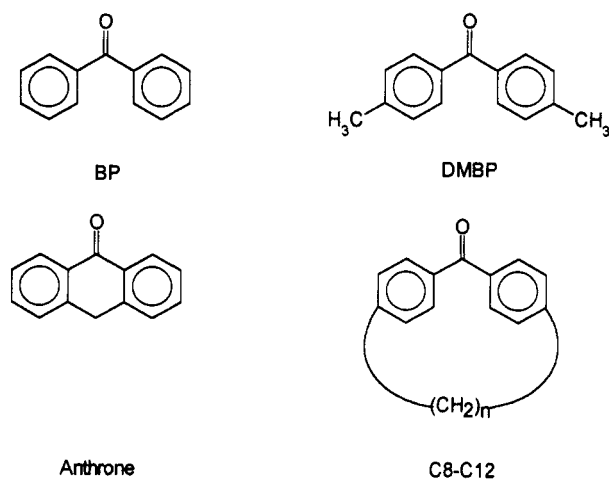(benzophenone)and has the same chemical substitutional char-

BP

DMBP

Anthrone

C8-C12

Figure 1. Schematic orbital energy level diagram of the orbitals of the benzophenone derivatives under discussion. The left-hand part of the diagram represents the delocalization of the π-type carbonyl orbitals onto the phenyl rings. The right-hand part of the diagram represents the mixing of the n- and π-type orbitals when the system looses its π plane of symmetry.

acter and pattern as the cyclophanes C8–C12. We therefore use it as our model compound. Molecular mechanics calculations, the conformation distributions of which are shown in Figure 3, show a gradual increase in θ for the lowest ground-state energy conformation from about 30° in BP, DMBP, and C12, to approximately 60° in C8.[18] The value of α decreases from about 120° in BP and DMBP to about 108° in C8 (Chart 1),[19] a trend confirmed by IR (infrared) carbonyl stretching frequencies and ^{13}C NMR (nuclear magnetic resonance) chemical shifts.[19,20]

We have previously reported a variety of photochemical and photophysical probes of the orbital configuration of T_1 in solution at room temperature and at 77 K for the cyclophanobenzophe-nones.[11] The $n = 12$ cyclophane abstracts hydrogen from 1,4-cyclohexadiene with approximately the same rate constant as benzophenone, $\sim 2 \times 10^8/(\text{mol·s})$. As n is made smaller, this rate constant decreases systematically, and for $n = 8$ the rate constant is $\sim 4 \times 10^6/(\text{mol·s})$. The rate constant for hydrogen abstraction drops most dramatically for the cyclophanes $n < 9$ or 10. The rate of hydrogen abstraction by benzophenone is typical for "pure" nπ* triplets and is similar to that of an alkoxy radical.[21] In contrast ππ* triplets H-abstract orders of magnitude more slowly than nπ* triplets.[21] A straightforward conclusion from these measured rates is that the character of T_1 for these cyclophanobenzophenones changes gradually, gaining ππ* character as the methylene tether is shortened and the geometry about the carbonyl group is modified. The phosphorescence spectra, phosphorescence lifetimes, and phosphorescence excitation spectra provided further support for the conclusion that, for C8, T_1 approaches a "pure" ππ* character.

While these photophysical and photochemical studies of triplet character versus conformation are straightforward and persua-sive,[11] the studies raise certain questions about the nature of the mixed nπ*–ππ* character of the triplet states of C9–C11. For the latter group of cyclophanobenzophenones, the phosphores-cence spectra and the triplet–triplet absorption spectra at room temperature appear to combine the nπ* features of BP, DMBP, and C12 and the ππ* features of C8 to various proportions. The phosphorescence spectra at 77 K, on the other hand, appear to change more abruptly from a progressively less structured, but largely unshifted, nπ* band for BP, DMBP, C12, and C9 to the appearance of a new, broad, red-shifted, ππ*-like band (with some residual nπ* character remaining) in C8. The luminescence decays of the triplet states at 77 K in 3-methylpentane typically display biexponential behavior between C12 and C8. There is a progression from a predominant, short-lived (nπ*) triplet decay component in BP and DMBP to a predominant, longer-lived (ππ*) triplet decay component in C8. Similar effects are observed for the cyclophanes when solvent polarity is increased from that of

3-methylpentane to ethanol, although in ethanol solvent the ππ* decay component is easily visible even for DMBP.

We propose three scenarios which can rationalize the spec-troscopic results:

(a) T_1 is characterized as a mixed electronic state of the type $\psi = a\psi_{n\pi^*} + b\psi_{\pi\pi^*}$, where π and π* may represent linear combinations of ring π or π* and carbonyl π or π* character, as indicated in Figure 1 and as will be discussed later. The coefficient a predominates for BP, DMBP, and C12 and b predominates for C8, while C9–C11 have more nearly comparable values of a and b.

(b) Multiple conformations, of C9–C12, BP, and DMBP, which are of comparable stability in solution, become frozen into place in solid solution. Some of these conformations have pure nπ* T_1 character and others have pure ππ* T_1 character, and some have T_1 of mixed character as described above.

(c) Essentially pure [3]nπ* and pure [3]ππ* states exist and are in thermal equilibrium for C9–C11. The energy separations for BP, DMBP, C12, and C8 are too large for a substantial thermal population of T_2 and thereby establishment of an equilibrium between [3]nπ* and [3]ππ states.

Clearly, all three scenarios could coexist to various degrees. ESR experiments aimed at a distinctly different spectroscopic triplet-state property were performed at lower temperatures than the 77 K temperature of the phosphorescence experiments in an attempt to clarify this picture.

In this paper we employ the common usage of the terms nπ* and ππ*. However, the n or π character of an orbital looses its meaning, strictly speaking, when the molecule has no plane of symmetry, as in most cases under consideration here. The terms nπ* and ππ* ordinarily refer to one-electron excitations between pure n, π, and π* molecular orbitals. The results of the present study appear to indicate substantial mixing[22] of the n orbital with the π orbitals of the phenyl rings (and possibly to a smaller extent with the carbonyl π orbital) (see Figure 1). Thus, when we speak of mixed nπ* and ππ* character, for example, it is in the sense of mixed *orbital character* and not necessarily in the sense of quantum mechanical mixing of well-defined [3]nπ* and [3]ππ* electronic states near an energy level anticrossing geometry.

ESR spectroscopy of the excited triplet states, T_1, of randomly oriented molecules in solids[22–24] yields the energy spacing between the three triplet spin sublevels as well as the relative rates at which they are populated from the singlet. There are two main contributors to the energy spacing, i.e., D and E values.[25] One is the spin–spin magnetic dipole interaction, which is a function of the spatial distribution of the two electrons in the excited state and is positive for carbonyls, as has been shown for BP in detailed calculations.[20] The second contribution is from the spin–orbit coupling interaction whose contribution to the D value is deduced to be large and negative.[26] The contribution is made mainly

from spin–orbit mixing of the $^3n\pi^*$ state with excited states, mainly of the carbonyl and aromatic $^3\pi\pi^*$ types, and to some extent with the singlet ground state.[26,27] Interpretations of experimental g values indicate that the $^3\pi\pi^*$ mixing makes the greatest spin–orbit contribution to the D value,[26] while theory points to interaction with the ground state as the single greatest contributor.[27] It is well established that the singlet–triplet spin–orbit coupling mechanism[21] is one that selectively mixes the z ($\parallel$ CO) sublevel of the lowest excited triplet state, giving it relatively large radiative character and shorter lifetime. It is the latter mixing with the ground state and similar interactions with $^1\pi\pi^*$ states that have the correct symmetry for this selective mixing. It has been frequently assumed that this selective mixing is only with excited singlet states. Experimental and theoretical[27] interpretations show that the spin–spin dipolar contribution to D is positive but somewhat smaller in magnitude than the spin–orbit contribution. As we will explain later, the magnitude of each contributor (i.e., dipolar and spin–orbit) scales inversely to carbonyl electronic orbital delocalization into the phenyl ring, i.e., as the n and/or π^* carbonyl orbitals delocalize, D tends to zero. Calculations of these contributions have been performed for both formaldehyde and benzophenone as a function of such variables as the hybridization of the carbonyl carbon in the excited state.[27,28]

A word of caution to the reader may be useful at this point. The magnitudes of the triplet zero field splitting parameters D presented in this paper are generally relatively small. This *does not* necessarily imply that the triplet electrons are far apart (e.g., as in an aromatic $\pi\pi^*$ triplet state), because the D value is the sum of spin–orbit and dipole–dipole interactions.[25] This small magnitude of the D value may in fact be observed even when the electrons are close, when a comparably large spin–orbit coupling contribution of opposite sign is simultaneously present (e.g., as in some aromatic ketone $n\pi^*$ triplet states).[25]

In favorable cases ESR is able to probe indirectly the dependence of the orbital character of T_1 electronic orbitals on molecular conformation. This includes the conformation dependence of the spin–orbit mixing of other states into T_1 and the conformation dependence of the spin–orbit mixing of the triplet character into S_1 that governs intersystem crossing. The latter should relate to the conformation dependence of the intersystem crossing rates which have recently been directly measured in time-resolved triplet–triplet absorption spectroscopy.[13]

For these reasons we have examined the T_1 ESR of BP, DMBP, and the C8–C12 benzophenone cyclophanes in frozen methylcyclohexane solutions at low (<10 K) temperatures. Experiments on acetone and anthrone were performed for comparison. We perform the experiments near the boiling point of helium to limit spin relaxation and effectively to eliminate any T_1–T_2 thermal equilibria from consideration.

Experimental Section

Approximately 50 mM solutions of the ketones were prepared in Aldrich Spectro Grade methylcyclohexane that had been further purified by distillation. The benzophenone (Aldrich Gold label) was the highest grade available and was used without further purification. The p,p'-dimethylbenzophenone (DMBP) and the cyclophanobenzophenones (C8–C12) were synthesized according to published procedures,[19,20] recrystallized, and checked for purity by gas chromatography. The acetone is Aldrich Spectro Grade and was used as received. The anthrone is Aldrich ACS Reagent Grade and was also used as received. Portions of the solutions were placed in 5-mm-diameter quartz ESR tubes and were frozen without deoxygenation in liquid nitrogen before insertion into a precooled ESR cavity and cryostat.

Low-temperature, direct detection, time-resolved electron spin resonance (TRESR) experiments on molecules in photoexcited
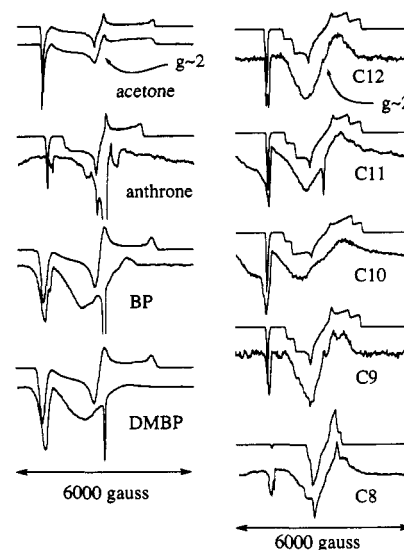
Figure 2. T_1 ESR spectra (bottom) and simulated spectra (top) of the molecules BP, DMBP, C12, C11, C10, C9, and C8. The acetone and anthrone spectra and simulations are likewise shown for comparison.

triplet states at particular delay times after photoexcitation have been described previously.[23,24] The experimental method is called TRESR even when there is only a single delay time and when there is no actual resolution of results at one time from another, in order to distinguish the method from steady-state continuous wave (CW) ESR in which the signal is averaged effectively over all times. We employ a Bruker ESR spectrometer (ESP380) with a dielectric ring cavity (ESP380–1052 DLQ-H) that allows optical irradiation of the samples, tuned to approximately 9.7 GHz. An Oxford cryostat (GFS 300) cools the cavity and sample to 4–30 K. The samples are photoexcited with ∼14-ns (fwhm), 308-nm XeCl excimer laser pulses from a Lambda-Physik excimer laser (LPX 100) fired at 30 Hz. A Princeton Applied Research boxcar averager (Model 4420) averages the EPR signal over a 5-μs period 0.5 μs after the laser pulse. The magnetic field is not modulated, and the microwaves are applied continuously. It should be noted that although the dielectric ring cavity is operated at a Q that is comparable with conventional cavities, its design gives a markedly higher microwave field than conventional cavities do at the same power level. We find the strongest signals with 166 μW of power incident upon the cavity. The detection system of the spectrometer has a rise time of less than 100 ns, making the response time of the instrument a good deal less than the 5-μs time of the experiment. We sweep the magnetic field 6000 G in a period of 1000 s, during which the boxcar acquires 256 points. This means that each point is the average of about 120 laser shots with a field resolution of roughly 25 G. The signal intensity of successive test sweeps does not decrease measurably, indicating that no appreciable chemical degradation of the ketones occurs during the analysis.

Results

The ESR spectra of the triplet ketones frozen in methylcyclohexane glass are displayed in Figure 2. The acetone spectrum measured under similar conditions is included for the purposes of comparison. The spectrum of anthrone, a relatively planar diaryl ketone, is also included for comparison.

All of the spectra display the $\Delta m = 2$ feature[12,29,30] in emission. However, there is considerable variation in the position, width, and height of the feature. For C10 and C11 there is a puzzling but reproducible broad region of emission below the $\Delta m = 2$ feature which we are unable to explain. We note that there exists a cluster of several peaks in the $\Delta m = 2$ feature of the cyclophane T_1 ESR spectra, and we use their existence to conclude that a given cyclophane, even at such low temperatures, can exist in a

TABLE 1: Zero Field Spin Hamiltonian Parameters and Populating Rate Parameters for the Lowest Excited Triplet State of a Series of Diaryl Ketones and Acetone[a]

compd	D/hc (cm^{-1})	E/hc (cm^{-1})	P_x	P_y	P_z	k_{isc}^{-1} (ps)[d]	α (deg)[e]	θ (deg)[e]
BP[b]	−0.1457	+0.05734	c	c	c	18	120	32
	(0.0016)	(0.00082)	c	c	c	(3)		
DMBP[b]	−0.1591	+0.0435	c	c	c	18		
	(0.0011)	(0.0010)				(3)		
C12	−0.12333	+0.01686	0.057	0.023	0.920	16	115	46
	(0.00053)	(0.00045)	(0.026)	(0.026)	(0.037)	(3)		
C11	−0.11966	+0.01592	c	c	c	14	116	43
	(0.00077)	(0.00060)				(3)		
C10	−0.12346	+0.02151	0.274	0.223	0.503	13	112	48
	(0.00093)	(0.00087)	(0.032)	(0.064)	(0.064)	(3)		
C9	−0.11698	+0.01719	0.082	0.122	0.796	11	111	55
	(0.00062)	(0.00047)	(0.019)	(0.024)	(0.031)	(3)		
C8	−0.0531	+0.0087	0.381	0.071	0.547	9	108	62
	(0.0032)	(0.0013)	(0.044)	(0.014)	(0.046)	(3)		
acetone	−0.16189	+0.04461	0.09858	0.3725	0.5317			
	(0.00022)	(0.00020)	(0.0013)	(0.0044)	(0.0045)			
anthrone	−0.1224	+0.0303	c	c	c	f	f	f
	(0.0010)	(0.0009)						

[a] Inverse total intersystem rate constants and ketone conformation angles are given for reference. Standard deviations are given in parentheses. [b] BP and DMBO were fit by assuming a 150-G line width parameter, while all other spectra were fit assuming a 40-G parameter. A single crystal determination gives D/hc = −0.1569, E/hc = 0.0174 cm^{-1}, P_x = 0.04, P_y = 0.05, and P_z = 0.91. See ref 35. [c] Fits converged but P_x, P_y uncertainties rendered values meaningless. [d] From ref 12. [e] See ref 17. Average over multiple conformations, $\theta = \cos^{-1}[(\cos^2 \theta)^{1/2}]$. [f] Molecular mechanics calculations indicate that anthrone is close to planar.

number of conformations, each with its own electronic and magnetic characteristics.

At fields above the $\Delta m = 2$ feature and below $g = 2$, the spectra are generally in emission but the structure and breadth of this region also vary among the ketones. At fields above $g = 2$ the spectra are in absorption and once again the detailed shape depends on the particular ketone. By-and-large the whole range of most of the diaryl ketone ESR spectra, except for the $\Delta m = 2$ feature and the $g = 2$ feature, is lacking in sharp spectral features. This is in marked contrast with the sharp features displayed in the acetone and anthrone spectra of Figure 2 and reported for cyclic alkyl ketones.[23] Only in acetone, anthrone, and benzophenone and to a degree in C8 and C9 can the sharp features normally associated with the canonical axis directions of the spin interactions in T_1 be discerned. Employing the notation of Tominaga et al.,[23] the spectra appear to be mainly of the form E, EEE, AAA (E = emission and A = absorption, from low- to high-field regions), an assignment that will be borne out in spectrum simulations to be discussed in the next section.

For several ketone samples a free radical spectrum at $g = 2$ can be seen in strong emission and this feature has been noted by Murai et al., who suggest that it may be the product of a ketone hydrogen abstraction reaction.[22] We note that the intensity of this feature varies approximately in the order of the solution hydrogen abstraction rate constants[11] discussed above. Although this feature is very pronounced in some of the ketones, its integrated intensity is comparatively small. As noted previously, signal intensity does not decrease with successive scans, indicating that no appreciable chemical degradation occurs during the measurements.

Analysis

We have simulated the spectra with Kottis and Lefebrve's modification[29] of the scheme of Yager et al.[30] In most cases a statistically acceptable least squares fit of the D and E spin Hamiltonian parameters and the x and y zero field sublevel populating rate parameters P_x and P_y, respectively, to the spectra could be obtained. This scheme mixes the molecular frame spin sublevels as a function of both magnetic field and molecular orientation in the field. The molecule's orientation in the field can be described by two polar coordinate angles, θ and ϕ, where θ varies from 0 to π and ϕ varies from 0 to 2π. We solve for 100 angles of θ and 200 angles of ϕ. It is assumed that spin–lattice relaxation and $T_1 \rightarrow S_0$ decay are negligible at the temperature

of the experiments at the time of data acquisition, leaving populations proportional to P_x, P_y, and P_z, and that $P_x + P_y + P_z = 1$. We couple a Levenberg–Marquadt minimization routine to the simulation scheme, and the uncertainties in the D, E, P_x, and P_y parameters are determined according to standard methods.[31] The uncertainty in P_z was determined by propagation from uncertainties in P_x and P_y. We arbitrarily chose a line width of 40 G for all fits except BP and DMBP. For the latter we set the line width at 150 G in order to improve the fit to the broad features observed. The g-factor of the triplet is set at 2.

The simulated spectra are presented in Figure 2 and compared with the experimental spectra. The triplet spin Hamiltonian parameters and intersystem crossing, triplet sublevel populating rate parameters are presented in Table 1. Also presented in Table 1 are the inverse intersystem crossing rates[13] (i.e., triplet rise times) and the conformation angle parameters illustrated in Chart 1. For comparison, Tominaga et al. report D and E values of −0.141 cm^{-1} and 0.056 cm^{-1}, respectively, for acetone.[23]

One of the surprising outcomes of the fitting is how precisely some of the parameters can be determined in the fitting in spite of the large residuals. See Table 1 for the uncertainties in the parameters. One can appreciate the source of the large residuals by observing in Figure 1 how poorly the broad, featureless regions of all of the experimental spectra, except for C8, C9, and acetone, are fit by the well-defined canonical axis features[12,29,30] in the simulated spectra. The precision of the parameters determined from these spectra, which we will show are broadened by conformation distributions, are determined primarily from the minimum in parameter space resulting from the position and shape of the $\Delta m = 2$ region of the spectrum and are not very sensitive to the smeared-out canonical axis regions.

As will be discussed subsequently, molecular mechanics calculations show that the molecules observed in these experiments visit a range of conformations (i.e., different θ, α in Chart 1) in their ground states. Assuming that these become frozen into place in the solutions to some extent at low temperatures, then the experiments report on molecules with a distribution of properties, including the observable D, E, P_x, P_y, and P_z that we have fit with single values to the spectra. This we believe to be the reason why there are large residuals in the fits. The D, E, P_x, P_y, and P_z values in Table 1 are thus *average* values, possibly over significant distributions of conformations. Thus while we report the quantitative parameters and uncertainties obtained
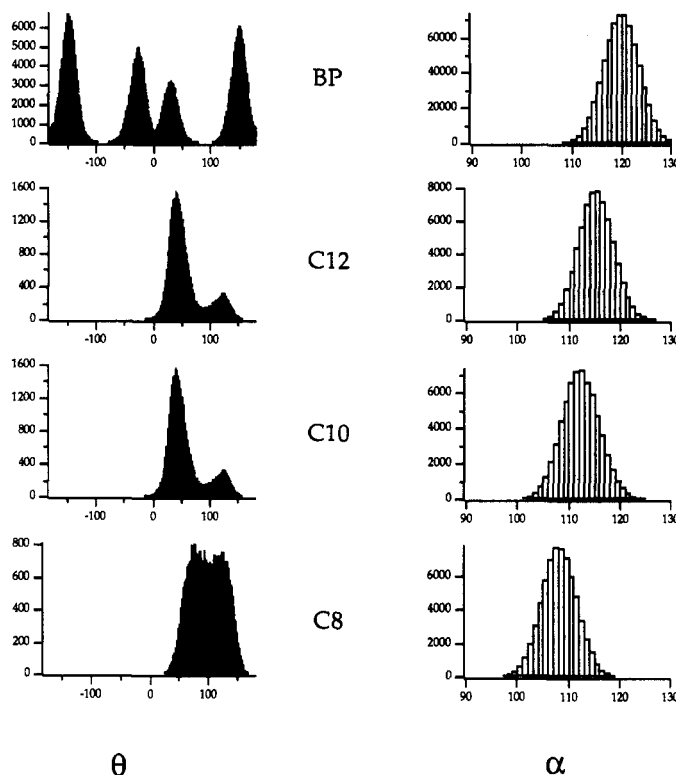
Figure 3. Distributions of the θ and α conformation angle occurrences for four of the molecules investigated experimentally in stochastic dynamics global energy minimum calculations.[18] See text for details. Molecular geometry dictates that the probability distributions be symmetric about $\theta = 90°$. Practical considerations prevented a long enough computer search to achieve equivalent sampling above and below $\theta = 90°$.

from our fits in Table 1, we restrict ourselves to a semiquantitative or qualitative discussion of these results.

We model the ground-state conformations of these molecules using molecular mechanics,[18] first with a Monte Carlo conformational search for the global minima and then with stochastic dynamics on those global minima to find average values for the parameters θ and α. The conformation distributions from these calculations are shown in Figure 3. Both steps are run with an MM2 force field at 300 K in the absence of solvent interactions. For the Monte Carlo conformational search of BP, we process 2000 conformers and find the lowest energy structure 124 times, suggesting that we have sufficiently explored the conformational space of benzophenone. For the C12 cyclophane, we process 12 000 conformers and only find the lowest energy structure once. For C8, we also process 12 000 structures and find each of the two lowest energy structures twice. Although it is clear that we have not completely explored the conformational space of these cyclophanes, we believe the search is sufficient for our qualitative purposes. For BP, we find 85 different conformers in the lowest 3 kcal/mol. For C8, we find 74, and for C12, we find 38. The conformational search for anthrone, not shown in Figure 3, reveals a single conformation.

We run stochastic dynamics on the global energy minimum structure of benzophenone for both 1000 and 10 000 ps, monitoring the parameters θ and α at 25-fs intervals. Both runs yield the same average parameters, but the longer run yields a more symmetrical distribution of θ's. In deference to processor time, we run the cyclophanes for only 1000 ps for dynamics. Figure 3 shows the distribution of θ and α for BP, C12, C10, and C8. Because θ can be found from $-180°$ to $180°$ ($150° = 30° = -30° = -150°$), we calculate the average value of $\cos^2 \theta$ and find the average value of θ from that. Average values of these parameters are listed in Table 1. Because the molecular dynamics calculations did not reach equivalent sampling of the regions $\theta < 90°$ and $\theta > 90°$, the probability distributions in Figure 3 have not achieved the symmetry above and below $90°$ that is dictated by the symmetries of the molecules.

Discussion

We begin our discussion by considering triplet alkenes which assume a twisted conformation, making the p orbitals of the π system orthogonal. Instead of having one electron in a π bonding orbital and the second in a π antibonding orbital in an untwisted conformation, the molecule stabilizes itself by twisting to place the two electrons into nonbonding p orbitals. The excited molecule possesses a driving force to place the electrons in spatially orthogonal orbitals and thereby minimize electron–electron repulsions. The $\pi\pi^*$ state of an aliphatic ketone is analogous to that of an *untwisted* alkene triplet. Moreover the $n\pi^*$ state, normally the lower energy state, is much like the *twisted* triplet alkene in that it has an electron in a nonbonding oxygen p orbital that is orthogonal to the p orbitals of the π^*_{CO} orbital. Normally, little geometry change is required for the $n\pi^*$ triplet carbonyl to achieve its stability. Thus the $n\pi^*$ triplet carbonyl is energetically favored, even though it places an unpaired electron in a highly reactive position on oxygen.

Aromatic ketones are more complex. In benzophenone or DMBP, the π systems of the phenyl rings are twisted about 30° away from the carbonyl π system.[17,32] This allows enough overlap for the phenyl π system to stabilize the $^3n\pi^*$ state's π^* electron. This stabilization is shown schematically in the left-hand side of Figure 1. Our calculations[17] show that the methylene tether of the cyclophanes twists the phenyl π systems out of conjugation with the carbonyl (Chart 1). (These calculations are run for the ground state of these molecules. Although it is clear that excited-state conformations will differ from those of the ground state, we assume that the forces which lead to changes in the ground-state conformation will lead to similar trends in the excited state.) C12 is computed to take the same conformation as DMBP and BP. However, the phenyl π system for C8 is twisted between 50° and 90° from the carbonyl π system. (The average $\theta = \cos^{-1}[(\cos^2 \theta)^{1/2}]$ is given in Table 1.) Clearly, one effect of this twist is to lessen the amount of delocalization possible for the π^* electron of $^3n\pi^*$ and thus to raise the energy of that state. Examination

of the triplet state of BP under conditions of high pressure indicate that θ is reduced and that greater delocalization of the π^* carbonyl electron onto the phenyl rings takes place.[33] We feel there is, in addition, another effect.

As we have previously stated, the $^3n\pi^*$ state is generally lower in energy than the $^3\pi\pi^*$ state because it places the unpaired electrons in spatially orthogonal (i.e., nonbonding/antibonding) orbitals. The twist of the phenyl π system out of conjugation with the carbonyl π system allows for the creation of a $^3\pi\pi^*$ state with some of the characteristics of two electrons resident in orthogonal orbitals: the unpaired π electron localized on the two phenyl rings, the unpaired π^* electron localized on the carbonyl, and no highly reactive unpaired electron on the oxygen. This situation is nominally $^3\pi\pi^*$ in character, but it differs significantly from the $^3\pi\pi^*$ character of planar ketones. One can see that the unpaired electron orbitals on the right-hand side of Figure 1 will have some of this "new" type of $^3\pi\pi^*$ character. Wäckerle *et al.*[14] draw some relevant conclusions from O[17] magnetic resonance studies of the triplet state of BP. They conclude that the unpaired electron on oxygen does not reside in a true "n" orbital, in the plane of the carbonyl, but instead in a linear combination of n and π orbitals which serves to "twist" it 12° out of the plane. See Figure 1. A full 90° twist would convert the $^3n\pi^*$ to $^3\pi\pi^*$. Wäckerle *et al.*[14] feel that the 12° provides enough $\pi\pi^*$ character to the lowest triplet state of BP to explain the fast $S_1 \rightarrow T_1$ ISC observed for the molecule. Another fact that is consistent with a "charge-transfer state" resonance form is that we have previously reported[1] a large (much larger than for BP) change in the triplet–triplet absorption spectrum for the cyclophanes in going from isooctane to acetonitrile.

Electronic excitation to the triplet state involves partial transfer of an electron from the π orbital of a phenyl ring to either a π^* orbital of a phenyl ring or the π^* orbitals of the carbonyl. It seems to us that the relative energies of the two possible π^* orbitals is extremely sensitive to conformation and solvent. One resonance form of the latter state ($\pi_{phenyl}\pi^*_{CO}$) would essentially be a charge-transfer state in which one phenyl ring is a cation radical, a negative charge is on the oxygen, and the second unpaired electron is localized on the carbonyl carbon.

We feel we can qualitatively use this form to explain much of the behavior we observe experimentally, but to put it on firmer ground, we ran unrestricted Hartree–Fock calculations, optimized with AM1, on the triplet states of our molecules. We input for the calculations various low-energy structures that we found from our stochastic dynamics search of the ground state, allowed the computer to optimize these structures for the triplet state with various degrees of freedom, and looked to see where the computer placed the unpaired spin density.

If we allow the computer to optimize the structures of the triplets of any of our molecules fully, starting from any conformation, it rotates the phenyl rings nearly orthogonal to the carbonyl ($\theta \sim 90°$), leaves the carbonyl fully planar, and places all of the unpaired spin density on the phenyl rings. Only when we constrain the molecule to be perfectly planar do we find a pure $n\pi^*$ triplet.

Clearly these calculations are not properly parametrized for our molecules. Among other variables, they do not include factors such as solvent effects. Perhaps what they show us, though, is that the triplet states of aromatic ketones can mix with $\pi\pi^*$ triplet character which can assist in processes such as S–T intersystem crossing merely via rotation around the CO–phenyl bond.

Our TRESR experiments on the triplet states of the cyclophanobenzophenones allow us to connect the conformation of aromatic ketones to their zero field splitting parameters. The limited but qualitative agreement between the simulated and experimental spectra of Figure 2 preclude the use of the parameters of Table 1 in a quantitative manner. However, we believe that the trends are correctly identified in the series C9–C12 to allow

the use of the parameters of Table 1 in the discussion, with fully recognition of their limited accuracy.

The trend in the width of the spectra in Figure 2 is consistent with a decrease in the magnitude of the D splitting parameter (known to be negative for BP) with increasing θ and decreasing angle α. The trend is reflected in the parameters given in Table 1, obtained from our attempts to fit the data. One may safely assume that, for the pure $^3n\pi^*$ state, one unpaired electron resides almost entirely in the n oxygen orbital, consistent with a detailed analysis of the BP spin density which puts 0.48 of the total spin of the triplet state in this orbital.[14] We also assume for simplicity that the degree of delocalization depends approximately on the overlap between the central C p orbital part of the carbonyl π^* orbital and the ring π^* orbitals as would be implied if the π^*_{ring} and π^*_{CO} orbital of the left-hand side of Figure 1 were degenerate. In addition, we assume that there is an equal distribution over all of the atoms of the π^* system (averaging C and O atoms of the CO π^* system). Since the overlap is proportional to cos θ, the wave function of the π^* orbital system can be expressed in the form give in eq 1. Here $\Phi_{\pi^*_{CO}}$ is a normalized carbonyl π^*

$$\psi_{\pi^*} = \frac{1}{[1 + 3 \cos^2 \theta]^{1/2}}\Phi_{\pi^*_{CO}} + \frac{3^{1/2} \cos \theta}{[1 + 3 \cos^2 \theta]^{1/2}}\Phi_{\pi^*_{ring}} \quad (1)$$

wave function and $\Phi_{\pi^*_{ring}}$ is a normalized π^* wavefunction of both rings.[34] To a first approximation, the electron magnetic dipole and spin–orbit coupling interaction contributions to the zero field splitting parameters, e.g., D, are one- or two-center interactions in a $^3n\pi^*$ state. Because the n electron resides entirely on the O atom, within the present approximation, only the contribution of the CO part of the π^* system will make a significant contribution to D. Thus one would expect D to depend on θ in the following way: derived from eq 1 by taking the matrix element of the spin–orbit and dipole operators corresponding to the D parameter[12,25] over the spatial coordinates between the nonbonding oxygen p orbital p_o and ψ_{π^*} and making the assumption discussed above that the p_o–$\Phi_{\pi^*_{ring}}$ matrix element is negligible,

$$D = \frac{D°}{[1 + 3 \cos^2 \theta]^{1/2}} \quad (2)$$

where $D°$ is a parameter that represents the limiting value of D in the absence of any delocalization into the rings; i.e., $\theta = 0$. It is clear that the effect of π^* delocalization in the $n\pi^*$ triplet would lead to *increasing* $|D|$ values with increased θ, rather than the observed decreasing values presented in Table 1. Less delocalization means more negative values of D.

By similar arguments, as the angle α decreases from 120° and approaches the tetrahedral angle of 109° and the central C hybridization changes from sp² and incorporates more sp³ character, the overlap of the resulting C pπ + C s hybrid with the ring π system decreases. The result would be that as α decreases, the delocalization decreases. Consequently, as α decreases $|D|$ would increase, also in conflict with the trend displayed in Table 1. In other words, to a first approximation the magnitude of the magnetic dipole contribution and of the spin–orbit contribution from the carbonyl group scale equally as a function of π^* delocalization. The larger the delocalization, the smaller this scaling factor becomes. Since the magnetic dipole contribution is positive and since current experimental and theoretical considerations of the spin–orbit coupling contribution to the zero field splitting in the $n\pi^*$ T_1 state of BP show that the main spin–orbit interactions have negative contributions to the D parameter,[26,27] any loss of electronic delocalization will scale these two contributions pretty much equally and thus also scale the magnitude of the D value.

Therefore, a suitable explanation of the observed trend in D values necessarily involves some character in the T_1 states of these molecules other than $^3n\pi^*$. We are not, however, simply

dealing with essentially pure $^3n\pi^*$ and $^3\pi\pi^*$ states that cross over one another in energy at a particular molecular conformation with little quantum mechanical mixing. If this were the case, the arguments above would predict the D parameter to become increasingly more negative as one goes from BP, DMBP, and C12 toward C8 uyntil the crossover conformation. At the crossover, D would *suddenly* take on a relatively smaller *positive* value characteristic of a $^3\pi\pi^*$ state. This is also clearly not the trend observed in Table 1. The arguments that follow are intended to show that a change in orbital configurational character results from a progressive rotation of the phenyl rings away from the plane in which the carbonyl group lies.

BP displays independent triplet sublevel phosphorescence decays in doped single crystals at liquid helium temperatures.[35] The authors demonstrate that at 77 K the BP decays with a single exponential whose rate constant closely approximates the average sublevel decay rate that would be expected for fast spin–lattice relaxation between the sublevels.[35] We will assume that a spin-lattice relaxation average of the sublevel rate constants has likewise been observed for each BP, DMBP, and cyclophane conformation in our previous 77 K phosphorescence studies in frozen solution.[11] (We make this widely–accepted generalization with a slight reservation, because in unpublished studies of related carbonyl compounds, Professor D. W. Dwyer has observed non-Boltzmann sublevel populations with microwave-induced-delayed phosphorescence in aromatic–carboxylic acid salts in a polymer matrix in the laboratory at Binghamton.) Our biexponential fits to the phosphorescence decays of the cyclophanobenzophenones at 77 K yield lifetimes of 2.0–6.6 ms for the short-lived component (τ_s) and, for C9–C12, 10–25 ms for the long-lived component (τ_l).[11] For the C8 the τ_s are 5.7 and 6.1 ms and the τ_l are 44.5 and 46.5 ms.

The shortest of these two lifetimes[11] resembles the lifetime of BP in a single crystal, a lifetime attributed to the $n\pi^*$ character of the BP T_1 state.[35] The τ_s cyclophane lifetime remains in the neighborhood, 4 ± 2 ms, but its relative intensity drops from 100% in BP and DMBP to 5% in C8. As the cyclophane tether tightens on the BP rings, a long lifetime decay τ_l appears, at first weakly and then with greater intensity, eventually reaching 95% of the emission in C8. Unlike τ_s, the lifetime τ_l of the long-lived emission also increases from the neighborhood of τ_s in C12 to almost 45 ms in C8. It is well-known[36] that the decay times of pure aromatic hydrocarbon $^3\pi\pi^*$ states, such as triplet benzene or naphthalene, are 2–3 orders of magnitude longer than those of $^3n\pi^*$ states of ketones and aldehydes. Thus, a dilution of the $^3n\pi^*$ character of BP by up to a factor of 6–7.5 times more $^3\pi\pi^*$ character in the triplet state of the C8 conformers with the long decays τ_l,

$$^3\Psi_{C8} \approx 0.37 \; ^3n\pi^* + 0.93 \; ^3\pi\pi^* \tag{3}$$

would be sufficient to explain the degree to which τ_l has been lengthened. We wish to repeat that we only use the terms $n\pi^*$ and $\pi\pi^*$ to denote behavior, not that there is necessarily a quantum mechanical mixing of two states that are pure one-electron excitations between well-defined n, π, and π^* molecular orbitals. The luminescence decay behavior does not allow us to specify how much phenyl ring π or π^* or carbonyl π or π^* character is involved, and it is to be understood that the π and π^* orbitals referred to here are linear combinations of π_{ring} and π^*_{ring} or π_{CO} and π^*_{CO}, respectively.

Because of the nature of spin–orbit coupling on the CO group, the predominant populating pathway P_z is to the z sublevel and the predominant decay pathway, associated with τ_s, is from the z sublevel also. On the other hand, in aromatic hydrocarbon $^3\pi\pi^*$ states, the populating pathways are P_x and P_y into the triplet sublevels x and y, respectively, quantized in planes perpendicular to the ring π plane. We were unable to determine populating rates for the triplets of these ketones with enough confidence to

draw anything but qualitative conclusions. However, there appears to be a trend from the predominantly P_z populating pathway of C12 toward C8 in which relatively more P_x and P_y pathways are involved. This is also in agreement with the trend in the zero field splitting parameters to be discussed next.

Zero field splitting parameters for pure $^3\pi\pi^*$ states have been reported.[36] D and E for triplet benzene are +0.16 and –0.0064 cm^{-1}, respectively. Perhaps more relevant, D and E for biphenyl are +0.1 and –0.036 cm^{-1}.[36] These values vary rather distinctly from the –0.06 and 0.009 cm^{-1} of C8, the most $\pi\pi^*$-like ketone. We therefore once again stress that the $^3\pi\pi^*$ characteristic that we claim for the C8 cyclophane triplet state is fundamentally different from the norm. Wäckerle et al.[14] state that even for benzophenone "the [n, π, and π^*] orbital designations are not truly applicable...[due to] its low molecular symmetry." One of their experimental conclusions is that the n orbital becomes mixed with the π systems of the phenyl rings, as we have implied in the right-hand side of Figure 1. On the basis of the rotation of the axes of the ^{17}O nuclear hyperfine interaction that results from this mixing, Wäckerkle et al.[14] present evidence that the T_1 state of BP already has about 12% $^3\pi\pi^*$ character that is achieved by mixing the "n" character of the oxygen unpaired electron with the phenyl ring π character. Of the –0.1569-cm^{-1} value of D observed for BP,[35] –0.180 cm^{-1} would be that of the pure carbonyl $n\pi^*$ character, and if the effect of the carbonyl π^* electron delocalization into ring π^* orbitals on the D value were ignored, the data would imply that the C8 T_1 state has at least 60% $^3\pi\pi^*$ (i.e., π ring, π^* carbonyl) character. If the π^* delocalization accompanying the change in θ from 32° in BP to (a $\cos^2\theta$ average) $\theta = 62°$ in C8 and the change from sp^2 hybridization in BP toward sp^3 in C8, according to eq 2, are taken into account, then there must be 62% $^3\pi\pi^*$ character, respectively, in order to account for the observed D value of C8.

It has been suggested[14] that there is a substantial mixing of $^3\pi\pi^*$ character into the T_1 state of BP that is responsible for the unusually fast intersystem crossing rate in BP. The mixing is capable of breaking down El-Sayed's rule[37–39] that forbids ISC between the initial S_1 and final T_1 state in which there is no one-orbital occupancy change. The mixing is thought[14] to occur via the interaction that mixes the n and π orbitals, as depicted in Figure 1, when a carbonyl compound has no molecular planes of symmetry through the CO group. In the series of cyclophanobenzophenone compounds under present consideration, we have shown that there is a clear progression of photophysical and photochemical properties[11] that imply a progressive increase in the T_1 $^3\pi\pi^*$ character from 10 to 20% in C12 (based on considerations for BP[14]) to at least 60% in C8. The intersystem crossing rates, measured by time-resolved growth of the T_1–T_n absorption spectrum for these compounds[13] and whose reciprocals are presented in Table 1, exhibit a clear change in the expected direction. If the ISC rate, k_{isc}, depends on the square of the $^1n\pi^*$–$^3\pi\pi^*$ matrix element[37–39] and if all other factors that contribute to k_{isc} remain constant, then k_{isc} will be proportional to the extent of $^3\pi\pi^*$ character in T_1. Thus k_{isc}^{-1} will decrease inversely proportional to the $^3\pi\pi^*$ character. However, the rate of ISC is not only dependent on the T_1 $^3\pi\pi^*$ character but also on such factors as the S_1 $^1n\pi^*$ character, the S_1–T_1 energy gap ΔE_{ST}, and vibronic factors. Thus the measured k_{isc}, which doubles in going from C12 to C8, is consistent qualitatively, if not quantitatively, with the increases in the T_1 $^3\pi\pi^*$ character estimated from the D values and the phosphorescence decay times.

The case of quantum mechanical mixing of $^3n\pi^*$ and $^3\pi\pi^*$ character in the T_1 states of the series of cyclophanobenzophenones appears to be a relatively strong, if a semiquantitative one. The model, however mixed it may be quantum mechanically, predicts an unique set of triplet zero field splitting parameters and triplet sublevel populating rates for a given molecular conformation. Thus there are two experimental observations that the model is

incapable of predicting. One of these is the *absence* of sharp spectral features at the resonance fields at the canonical axes of the anisotropic spin interactions in the T_1 states perhaps of all but anthrone, BP, and the C8 and C9 compounds. Unless the homogeneous line widths of the ESR transitions are chosen to be unreasonably large, discernible features can be found near the high- and low-field transitions associated with the fields directed parallel to the x, y, and z axes of the spin Hamiltonian of T_1.[29,30] These can be seen in all of the simulations shown in Figure 2, as well as in the acetone T_1 ESR spectrum which has been presented for the purpose of discussing this point. The other observation is the *presence* of multiple transitions in the $\Delta m = 2$ region of the spectrum. This transition is be predicted to occur at a field[38]

$$H = [(h\nu/2)^2 - (1/3)(D^2 + 3E^2)]^{1/2}/g\beta \qquad (4)$$

This suggests that there are sets of clusters of molecules with different D, E values present in the samples. Apparently the distribution of D, E values is sufficient to "wash out" the high-field features but not the distinct $\Delta m = 2$ transitions. We suggest that the distributions and/or clusters of D, E values arise from multiple conformations of the molecules in solution, perhaps from multiple energy minima in the θ space of the ring twists, shown in Figure 3. In the C8 cyclophane with the tightest tether, there is relatively little broadening. While the quality of the spectrum is not high, there appears to be little broadening in the anthrone spectrum. In the BP spectrum and in the C9 spectrum, there is considerable broadening but some evidence of the sharp canonical axis features can also be found on top of the broad background feature. In the cyclophanes C10–C12 and DMBP, no sharp features appear to be present at all.

The existence of multiple conformations for some or all of the series C8–C12, as well as in BP and DMBP, is not of great interest in itself. However, many photochemical and photophysical properties[11,20] depend on the degree of $\pi\pi^*$ and $n\pi^*$ character in T_1, which in turn has been shown here to be a relatively sensitive function of molecular conformation. We have noted parallel changes in the phosphorescence.[11] Some of the nontethered systems exhibit pure $n\pi^*$ phosphorescence and some nontethered systems exhibit a mix of molecules, some with pure $n\pi^*$ emission and others with mixed $n\pi^*$ and $\pi\pi^*$ emission. As the tether becomes tighter, the proportion of pure $n\pi^*$ emission decreases in favor of the mixed emission and the degree of $\pi\pi^*$ character in the mixed emission increases. In the C8 extreme, only a small amount of $n\pi^*$ emission remains, and the $n\pi^*$ character in the mixed emission becomes negligible. A hint of similar behavior exists in the photochemistry where the cyclophane hydrogen abstraction rate constant drops abruptly for $n < 9$, 10.[11]

These trends in triplet zero field parameters and phosphorescence lifetimes can be rationalized in terms of the anticrossing of the $^3n\pi^*$ and $^3\pi\pi^*$ levels and the characteristics of the resulting states depicted in Figure 4. The unmixed energy level dependences on twist angle θ in Figure 4 have been determined from the anthrone phosphorescence 0–0 band,[36] the assumed (2000 cm^{-1}) hc interval between the states in BP[14] and the shift between the DMBP $^3n\pi^*$ and C8 $^3\pi\pi^*$ phosphorescence in frozen 3-methylpentane solvent.[11] The unmixed $^3n\pi^*$ and $^3\pi\pi^*$ energy levels were assumed to vary approximately as $\cos\theta$. This would follow from the $\cos\theta$ dependence of the π_{ring}–π_{CO} and π^*_{ring}–π^*_{CO} overlap and delocalization discussed above. A π_{ring}–n_O interaction of the type discussed by Wächerle *et al.*,[14] varying according to the $\sin\theta$ dependent overlap, was employed to mix the two states near the crossing. The 800-cm^{-1} interaction constant of Wächerle *et al.*[14] was adjusted to a value of 600 cm^{-1} in order to give better agreement with the results to be discussed subsequently.

In Figure 5 we compare the θ distributions, predicted by the molecular dynamics calculations for the C8, C10, C12, and BP conformations (see Figure 3), with the percentage $n\pi^*$ character and percentage $\pi\pi^*$ character in the lowest triplet state of the
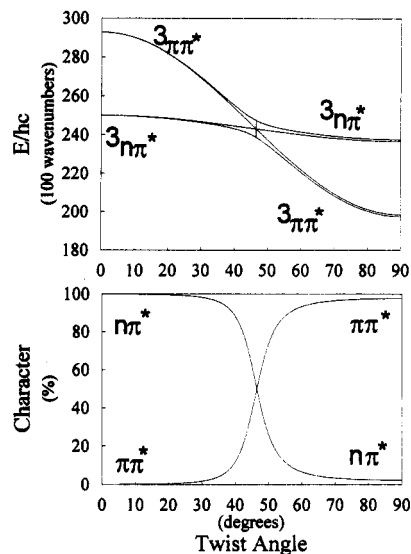

Figure 4. Model of the anticrossing and mixing of the $^3n\pi^*$ and $^3\pi\pi^*$ states of benzophenone and related compounds, as functions of the ring twist angle θ. The states are mixed via an interaction between the n_O and π_{ring} orbitals.[14] The energy levels of the unmixed (crossing) and mixed (anticrossing) states are depicted at the top. The percentages of $n\pi^*$ and $\pi\pi^*$ character in the lowest triplet state corresponding to the avoided crossing are shown at the bottom. See text for the detailed construction of the curves.
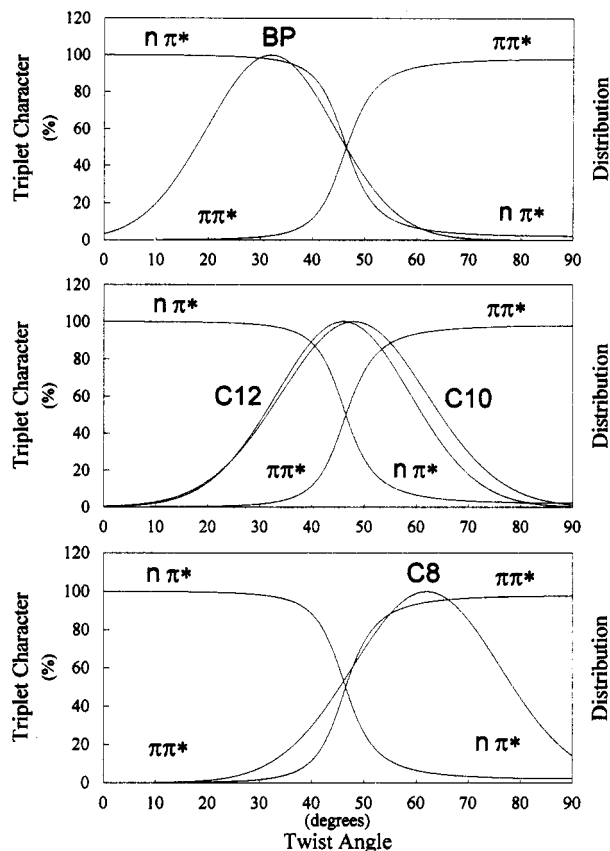

Figure 5. Overlay of the conformation distributions from the molecular dynamics calculations on the electronic character of the lowest triplet state, as functions of the ring twist angle θ, for BP (top), C10 and C12 (middle), and C8 (bottom). (The calculated distributions have been approximated by Gaussian curves here for the purpose of graphing.)

system, as a function of ring twist angle θ. These comparisons predict the observed phosphorescence and TRESR characteristics. Most of the BP distribution lies in a region of predominantly $n\pi^*$ character. This agrees with the predominant intensity of the τ_s emission in BP and DMBP and with the existence of some sharp

(nπ*) structure in the TRESR of BP. The existence of the broad regions of the TRESR is from the remaining small part of the distribution spanning the rapidly changing region of nπ* and $\pi\pi$* character. The existence of the weak τ_1 emission with relatively short (mostly nπ*) decay is also an average of the τ_1 of individual conformers in this region of rapidly changing character. The C10 and C12 distributions straddle the region of rapidly changing character. This is in agreement with the presence of little, if any, sharp TRESR structure characteristic of either nπ* or $\pi\pi$* character. It also predicts a smaller proportion of τ_s emission because of the smaller region of essentially pure nπ* conformations. Correspondingly it predicts a larger proportion of τ_1 emission with longer decay times, characteristic of the average over the remainder of the distribution with its somewhat more $\pi\pi$* character. In the case of C8 most of the distribution lies in the purely $\pi\pi$* region and a smaller part lies in the region of rapidly changing character. This is in agreement with a predominant τ_1 emission of $\pi\pi$* character and with a very small nπ* τ_s component. The distribution also predicts a predominantly structured TRESR spectrum of $\pi\pi$* character, as observed.

Conclusions

The main conclusion of this work is that out-of-plane twisting of the phenyl rings in benzophenone derivatives mixes the n carbonyl orbital with the ring π orbitals, so as to increase the $^3\pi\pi$* (π ring, π*$_{CO}$) character observed in the T_1 states of benzophenone cyclophanes from C12 to C8. The phosphorescence and TRESR behavior suggests that this is accompanied by an energy level anticrossing of $^3\pi\pi$* and ^{3}nπ* states with change in conformation. Chemical evidence suggests that this n$_{CO}$–π_{ring} mixing is such that it dilutes appreciably the chemical reactivity that is usually associated with a localized n$_{CO}$ orbital. In other words, the T_1 character of C8 appears to have one electron in the π*$_{CO}$ orbital and the other mainly on a π_{ring} orbital that may be slightly admixed with n$_{CO}$ character. The trends in the spin Hamiltonian D parameters, the phosphorescence decay times,[11] magnitudes of the phosphorescence decay components,[11] the relative triplet sublevel populating rates, and the ISC rates to T_1[13] are all in the directions expected from the progression of changes in T_1 character. The D values and phosphorescence decay times indicate an increase in $^3\pi\pi$* character of between 5 and 7.5 times from C12, with its estimated 10–20% $^3\pi\pi$* character, to C8. The ISC rates increase by a factor of 2 from C12 to C8, which is in qualitative agreement with the increasing nπ*–$\pi\pi$* allowedness of the ISC process afforded by the progressive mixing of $\pi\pi$* character into T_1.

However, the unrestricted Hartree–Fock calculations do not predict the charge-transfer resonance structure implied by the present results for the lowest triplet state but rather a ring-localized $\pi\pi$* triplet excitation. The calculations also put the ^{3}nπ* and $^3\pi\pi$* states very close in energy.

The ESR spectra show that multiple conformations of the molecule are present in the samples of C10–C12, BP, and DMBP. Molecular mechanics calculations[18] suggest that these may be molecular conformational heterogeneities and not necessarily a result of multiple environments in frozen solution. As a result of the conformational sensitivity of the T_1 electronic character

demonstrated here, these conformations have significantly different photochemical or photophysical properties.

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