EXTERNAL SPIN–ORBIT COUPLING ON THE ^{3}n,π* STATE OF SEVERAL CYCLOALKANONES

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Summary

The results of a study on the external spin–orbit coupling on the triplet state of several cyclic aliphatic ketones by optically detected magnetic resonance are reported.

1. Introduction

The effect of spin–orbit coupling on the phosphorescent triplet state of organic molecules has been of interest to researchers for some time, particularly because of its importance in photochemistry. The effect, in which the perturbing atom is a halogen, has been studied with respect to phosphorescent lifetimes, energies of the phosphorescent triplet state and quantum yields. Much of the work in the earliest studies was on the intramolecular spin–orbit effect, primarily on aromatic molecules [1 - 15]. Recently, studies have included the intermolecular spin–orbit coupling effect for heavy atoms on host or solvent molecules [16 - 24]. In addition to the heavy-atom studies, deuterium effects have also been investigated [25 - 28].

The sensitivity of the triplet state to molecular perturbations makes it an ideal probe for the spin–orbit coupling effect. The distortion in the triplet state caused by spin–orbit interactions can then be monitored by optically detected magnetic resonance (ODMR) techniques. Although ODMR is an extremely sensitive and powerful method with which intermolecular perturbations can be studied, the full potential has not been realized, because the theory on external spin–orbit coupling contributions to zero-field parameters with respect to distance and angles to the perturber, for example, have not been throughly substantiated by experimental data. Turro and coworkers have studied the effects of halogen perturbers on aromatic chromophores in naphthonorbornanes [29 - 31]. Others have attempted to correlate zero-field

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splittings with intramolecular spin–orbit interaction, particularly in aromatic carbonyls [32 - 39]. However, the analyses have been particularly difficult, because the phosphorescent states are perturbed by the energetically adjacent triplet and singlet states of the aromatic group.

The molecular systems chosen for this study were cyclic aliphatic ketones (cyclohexanes) in which the carbon on the 4-position had heavy-atom substituents. These perturbing atoms were oxygen, sulfur and another carbonyl carbon. Since the perturbing atom and the emitting chromophore were on the same molecule, the distance and the angular orientations could be predicted from simple molecular models. In addition, in the analyses of the data, perturbations on the $^3n,\pi^*$ state resulting from close-lying π,π^* states could be safely ignored.

In a previous study, isotopic substitution of the α-hydrogens was employed to examine the contribution to the relaxation rates from the coupling of certain vibrational modes to the electronic states [39, 40]. The results of this study indicated that the α-hydrogens play a significant role in the relaxation of the phosphorescent triplet state of this ketone. To examine further this deuterium effect on the $^3n,\pi^*$ state, the α-protons of each of the cyclic ketones in this study were deuterated and the results of the ODMR study were compared with the previous work.

2. Experimental details

The protonated aliphatic cyclic ketones cyclohexanone (CHN), tetrahydro-4H-pyran-4-one (THP), tetrahydrothiopyan-4-one (THTP) and 1,4-cyclohexanedione (CHD) were purchased commercially and purified by fractional distillation or multiple vacuum sublimation. Figure 1 shows the structure of these molecules. The samples were degassed and stored in ampoules sealed under vacuum.
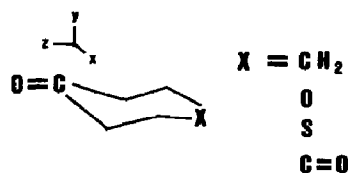

Fig. 1. Axis system for the phosphorescent $^3n,\pi^*$ carbonyl state: z is along the C=O bond and y is perpendicular to the plane containing C=O. The cycloalkanones studied were those cases where X $\equiv$ CH$_2$, O, S and C=O.

The deuterated compounds were prepared using a new procedure which will be reported in detail elsewhere [41]. A typical procedure involved dissolving 3 g of the ketone in 10 ml acetone-d_6 (AC-d_6) (99.5% D) followed by 10 ml deuterium oxide (99.8% D). Additional AC-d_6 was added to maintain a clear solution (not more than 3 ml). Trifluoroacetic acid-d_1 (0.5 ml, 99% D) was added and the mixture was left stirring at room temperature.

The progress of the reaction was conveniently followed using nuclear magnetic resonance (NMR) spectroscopy by removing an aliquot, recording the spectrum and returning the sample to the reaction flask. Equilibrium was usually reached after 3 - 4 days. The solvents were removed by vacuum distillation and the exchange was repeated. The deuterium incorporation at the α-positions was always in the range 96% - 98% after the two exchange reactions, as determined by integration of the NMR spectrum. The products were purified and prepared for analysis as described above.

Single crystals of molecules which were solids at room temperature were grown by the standard Bridgeman method. Liquid samples were placed in specially made thin-walled ampoules, degassed and sealed under vacuum. The sample was then placed in a helical microwave antenna made of flattened silver wire. The antenna was then connected to one of the ends of a semi-rigid stainless steel coaxial cable and the entire assembly was immersed in liquid helium.

Optical excitation was accomplished by focusing the light from a well-filtered 100 W high pressure mercury lamp onto the sample. The phosphorescence was monitored using a monochromator equipped with a thermoelectrically cooled photomultiplier. The details of the ODMR apparatus have been discussed in a previous paper [11]. Briefly, the microwave power was impinged on the sample via the helix. The microwave frequency was slowly swept while modulating the microwave power. At resonance, the modulation in the phosphorescence intensity was phase-sensitive detected, resulting in the ODMR spectrum. The dynamic parameters of the triplet state were recorded by adiabatic rapid passage of the zero-field transitions as first described by Winscom and Maki [42]. Signal averaging was performed on a Tracor–Northern instrument and the data were transferred to a Hewlett–Packard model 216 microcomputer and stored on disk for later analysis by an interactive multiple linear regression program.

3. Results and discussion

The zero-field transitions and dynamic parameters for the phosphorescence decay from the three sublevels of the triplet state in all of the cyclic ketones which were studied are shown in Table 1. The axis system used here is such that z lies along the carbonyl group and x is perpendicular to the plane formed by the carbonyl and the methylene groups (cf. Fig. 1). The data for cyclopentanone (CPN) [43, 44] and AC [38] are also given for comparison.

Using the perturbation approach, the depopulation rate constants from the magnetic sublevels of the triplet state can be shown to be roughly proportional to the square of the corresponding spin–orbit matrix element. If the overlap integrals are assumed to be relatively constant for the series CHN, THP and THTP, then to a very rough approximation the spin–orbit contribution is proportional to the square of the ratio of the effective nuclear

TABLE 1

Zero-field splittings ZFS, zero-field transitions, total phosphorescence rate constants and relative radiative rate constants (in parentheses) for several aliphatic ketones as determined by ODMR at 1.4 K

Compound	ZFS (MHz)		Zero-field transitions (MHz)	Total phosphorescence rate constants (s^{-1})		
	D	E		K_x	K_y	K_z
AC[a]	4738	1343	— 3395 2685	860 (1.0)	210 (0.049)	1720 (1.4)
CPN[b]	4210	813	5022 3397 1625	725 (1.0)	79.4 (0.017)	775 (0.47)
CHN	4243	876	5076 3367 1752	500 (1.0)	30 (<0.005)	604 (1.3)
THP	4388	938	5325 3450 1875	620 (1.0)	30 (0.020)	720 (1.4)
THTP	4553	944	5498 3609 1887	880 (1.0)	33 (0.070)	1170 (1.8)
CHD	4057	1112	— 2945 2223	360 (1.0)	37 (0.053)	440 (0.60)
THP-d_4			— 3450 —	340	26	540
THTP-d_4	4576	944	5519 3632 1888	471 (1.0)	25 (0.080)	725 (1.4)
CHD-d_8	4091	1104	— 2987 2207	240 (1.0)	11 (0.0030)	290 (0.55)

[a]Data from ref. 38.
[b]Data from refs. 43 and 44.

charge on the perturbing atom to the cube of the distance to the chromophore. These ratios were derived using bond distances from crystallographic data [45] and Slater charges and are shown in Table 2. Although the results appear to be in good agreement with the phosphorescence rate constant ratios, the inverse sixth power of the distance factor makes the ratio extremely sensitive to the distance.

Referring to Table 2, it is noteworthy that both K_x and K_z are affected to approximately the same degree while K_y remains relatively constant, even with the inclusion of CHD, which is a special case in this series (vide infra). A tentative explanation is that the expected distortion of the carbonyl geometry in the excited state is sufficiently large to result in a roughly equal distribution of the spin–orbit interaction over the two perpendicular axes. A similar argument has been used by Schmidt et al. to explain the

TABLE 2

Total rate constants, zero-field splittings ZFS and spin–orbit coupling factors for THP and THTP relative to CHN

Compound	ZFS		R	Z^*	$(Z^*/R^3)^2$	SO	K_x	K_y	K_z
	D	E							
CHN	1.0	1.0	2.9	3.25	0.0177	1.0	1.0	1.0	1.0
THP	1.034	1.071	3.0	4.55	0.0284	1.6	1.24	1.0	1.19
THTP	1.073	1.078	3.1	5.45	0.0334	1.9	1.76	1.1	1.94

R is the approximate distance between the carbonyl carbon and the heavy-atom perturber and SO is the relative spin–orbit coupling factor.

results for isoquinoline [46]. Gerhtz *et al.* have shown that for simple aliphatic ketones the distortion angle is approximately 38°, as compared with 35.6° for formaldehyde [38]. However, in larger aliphatic carbonyls such as those studied here, this distortion angle is expected to decrease significantly.

In the absence of an external magnetic field, the total magnetic hamiltonian can be written as a sum of the spin–spin dipolar and spin–orbit interaction hamiltonians:

$$H_{tot} = H_{ss} + H_{so}$$

in which the spin–spin interaction can be described by

$$DS_z{}^2 + E(S_x{}^2 - S_y{}^2)$$

where D and E are the spatial integrals involving spin–spin dipolar interaction and are termed the zero-field splitting parameters and S_x, S_y and S_z are the triplet state spin operators. In aromatic carbonyl molecules, such as benzophenones and benzaldehydes, the spin–orbit contribution to the zero-field splitting is dominant and the strong coupling of the closely lying n,π^* and π,π^* states induces a nearly planar geometry for the triplet state of the carbonyl group [37, 38]. The same is no longer true in the case of aliphatic ketones, in which the coupling between the nearest ^{1}n,π^* and ^{3}n,π^* states is expected to be weak. Hence, in contrast to the large spin–orbit contribution to the zero-field splittings which have been observed in the aromatic ketones, the spin–orbit contribution to the magnetic interaction hamiltonian is predicted to be small (*cf.* Table 2).

It is known that the spin–orbit contribution to the zero-field splitting is opposite in sign to the spin–spin interaction [32]. The energy shifts caused by such spin–orbit interaction will be proportional to $-\langle H_{so}\rangle^2$ where terms involving admixtures of other states with the well-isolated lowest excited states can be ignored, because of the energy denominator. As stated earlier, in these ketones the spin–orbit contribution to the zero-field splitting is relatively small. More importantly, however, the observed *increase* in the relative zero-field splittings must mean that the signs of D and E must be *reversed* from those for AC. The differences in the relative zero-field splittings in the protonated and deuterated cyclic ketones as compared with AC add support to this conclusion (*cf.* Table 3).

In formaldehyde, various values of D have been calculated, depending upon the geometry, with a smaller D value of approximately 5.7 GHz for a bent T_1 [47]. The even smaller D value observed for AC has been argued by Gehrtz *et al.* to be due to interaction of the π^* orbital with the methyl groups via hyperconjugation [38]. Their conclusions that the triplet wavefunction is delocalized entirely over the two methyl groups in AC and that the low frequency torsional modes cause the triplet state energy to be considerably broadened are consistent with the interpretation of the data found for these cyclic ketones.

The E value in the zero-field splitting defines the anisotropy in the triplet wavefunction. If, as argued above, the sign of E is positive, since

TABLE 3

Effect of deuteration on the zero-field splittings ZFS and the total phosphorescence rate constants for AC, THTP and CHD

Compound	ZFS		K_x	K_y	K_z
	D	E			
AC-d_6:AC[a]	0.9979	1.0149	1.0	0.60	0.96
THTP-d_4:THTP	1.0050	1.0000	0.71	1.0	0.82
CHD-d_8:CHD	1.0084	0.9929	1.0	0.45	0.66

The data are ratios of the values for the deuterated vs. the protonated molecules.
[a]From ref. 38.

$$E_{ss} \propto \left\langle \frac{y^2 - x^2}{r^5} \right\rangle$$

where r is the distance between the two electrons and x and y are the vectorial components of r, the triplet delocalization is more extensive in the y direction than in the x. Such delocalization can occur via hyperconjugation with the methylene groups.

Group theoretical analysis has shown that the T_z sublevel decays via radiationless processes by the electronic part of the adiabatic spin–orbit interaction. T_x and T_y, in contrast, decay via vibrationally induced spin–orbit coupling mechanisms: T_x by b_1 and T_y by b_2 modes respectively [38]. If we make the approximation that there is a zero vibronic contribution to the purely electronically allowed deactivation from T_z, then spin-specific deuterium effects on the other sublevels may be found. This is shown in Table 3. It has been noted that C—H vibrationally induced adiabatic spin–orbit coupling should give an isotope factor of 0.56 [48, 49]. The isotope effect on CHD shows good agreement with a vibrationally induced coupling mechanism for T_y, in contrast to THTP. Tentatively, the explanation might be that the relatively rigid structure of CHD does not allow for skeletal vibrations which are possible for the other cyclic ketones. For T_x, the large rates for the deactivation process must be the result of mixing with the electronically allowed T_x. In a study of the phosphorescent triplet state of AC, Gehrtz *et al.* have argued that the matrix element coupling the $^3B_1(n,\pi^*)$ with $^1B_1(\pi,\pi^*)$ via spin–orbit interaction is negligible [38]. In AC, it is the b_1 vibrational mode (pyramidal out-of-plane bending) which induces intersystem crossing into T_y, whereas population of T_z is induced by spin–orbit coupling mechanisms. In all of the molecules studied here, except for CHD, the phosphorescence intensity of the $T_z \langle \sim \rangle T_y$ and $T_y \langle \sim \rangle T_x$ transitions decreased upon saturation with microwave field. This implies that except for CHD the adiabatic coupling of T_z is dominant. In contrast, the rigid structure of the CHD ring causes the carbonyl bending mode to be the primary populating route to T_y for that molecule.

In this series of molecules, CHD is a special case owing to the possibility that either of the carbonyl groups may be electronically excited while the other carbonyl then becomes the perturber. The enhanced anisotropy in the triplet wavefunction resulting from hyperconjugation can be seen from the increase in the E value (cf. Table 1). The dramatically lower total phosphorescence rate constants might be evidence for narrower non-radiative pathways for depopulation, perhaps owing to the rigidity of the cyclic ring and the depressed involvement of ring modes in the vibronically induced spin−orbit coupling mechanism, especially with respect to T_x.

Further work along the following directions is in progress. The magnetic spin axes for the spin−orbit and spin−spin tensors do not coincide, owing the expected distortion in the triplet state geometry. The full tensor contribution to the zero-field transitions has to be determined. Such an analysis will yield a better estimate of the carbonyl distortion angle in the triplet excited state of these cyclic aliphatic ketones. In addition, the role of non-radiative depopulation from the triplet state sublevels needs to be more precisely addressed. Finally, CHD is a molecular system worthy of further investigation because of its potential as an excellent model for energetically resonant molecular complexes, in which the angle and distance between the two chromophores are well defined.

4. Conclusions

Although this work is preliminary, the following conclusions can be drawn regarding the phosphorescent triplet state of these cyclic aliphatic ketones.

(1) The signs of the zero-field splitting parameters D and E are negative and positive respectively.

(2) The depopulation routes from the triplet state are parallel to those for AC.

(3) CHD promises to be an excellent model for a resonant bimolecular complex.

Acknowledgments

References

1 D. S. McClure, J. Chem. Phys., 17 (1949) 905.
2 J. Sidman, J. Chem. Phys., 29 (1958) 644.
3 N. K. Chaudhuri and M. A. El-Sayed, J. Chem. Phys., 45 (1966) 1358.
4 E. T. Harrigan, T. C. Wong and N. Hirota, Chem. Phys. Lett., 14 (1972) 549.

5 G. Kothandaraman and D. S. Tinti, *Chem. Phys. Lett.*, *19* (1973) 225.
6 J. Friedrich, F. Metz and F. Dorr, *Mol. Phys.*, *30* (1975) 289.
7 P. A. Szerenyi and L. Shia, *Chem. Phys. Lett.*, *39* (1976) 593.
8 C. T. Lin, *J. Lumin.*, *12/13* (1976) 375.
9 K. A. Martin, G. Moller and A. M. Nishimura, *J. Phys. Chem.*, *80* (1976) 2788.
10 T. Akasheh, *Chem. Phys. Lett.*, *59* (1978) 392.
11 K. J. Latas and A. M. Nishimura, *J. Phys. Chem.*, *82* (1978) 491.
12 H. Saigusa and T. Azumi, *J. Chem. Phys.*, *71* (1979) 1408; *72* (1980) 1713.
13 H. Shinohara and N. Hirota, *J. Chem. Phys.*, *72* (1980) 4445.
14 J. Najbar, W. Jarzeba and Z. H. Urbanek, *Chem. Phys.*, *79* (1983) 245.
15 S. G. Hilburn, R. K. Power, K. A. Martin and A. M. Nishimura, *Chem. Phys. Lett.*, *100* (1983) 429.
16 T. H. Cheng, N. Hirota and S. W. Mao, *Chem. Phys. Lett.*, *15* (1972) 274.
17 D. Schweitzer, J. Zuclich and A. H. Maki, *Chem. Phys. Lett.*, *18* (1973) 24.
18 T. Azumi, *Chem. Phys. Lett.*, *19* (1973) 580.
19 J. Najbar, *J. Lumin.*, *11* (75/76) 207.
20 J. Najbar and A. Chodkowska, *J. Lumin.*, *11* (1975/76) 215.
21 S. Yamauchi, K. Matsuzaki and T. Azumi, *J. Lumin.*, *12/13* (1976) 369.
22 G. Weinzierl and J. Friedrich, *Chem. Phys. Lett.*, *80* (1981) 55.
23 S. Yamauchi, Y. Komada and N. Hirota, *Chem. Phys. Lett.*, *93* (1982) 133.
24 Y. Komada, S. Yamauchi and N. Hirota, *J. Chem. Phys.*, *82* (1985) 1651.
25 P. M. Johnson and M. C. Studer, *Chem. Phys. Lett.*, *18* (1973) 341.
26 J. Friedrich, J. Vogel, W. Windhager and F. Dorr, *Z. Naturforsch., Teil A*, *31* (1976) 61.
27 J. B. Birks, T. D. S. Hamilton and J. Najbar, *Chem. Phys. Lett.*, *39* (1976) 445.
28 B. Dzhargarov, R. H. Hofeldt, G. L. Findley and S. P. McGlynn, *Chem. Phys.*, *37* (1979) 195.
29 N. J. Turro, G. Kavarnos, V. Fung, A. L. Lyons, Jr., T. Cole, Jr., *J. Am. Chem. Soc.*, *93* (1971) 1032.
30 G. Kavarnos, T. Cole, P. Scribe, J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.*, *95* (1972) 1392.
31 A. K. Chandra, N. J. Turro, A. L. Lyons, Jr. and P. Stone, *J. Am. Chem. Soc.*, *100* (1978) 4964.
32 S. P. McGlynn, T. Azumi and M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Prentice–Hall, New York, 1969, pp. 345 · 349.
33 S. J. Fogel and H. F. Hameka, *J. Chem. Phys.*, *42* (1965) 132.
34 J. W. McIver, Jr. and H. F. Hameka, *J. Chem. Phys.*, *45* (1966) 767.
35 H. Hayashi and S. Nagakura, *Chem. Phys. Lett.*, *18* (1973) 63.
36 A. M. Nishimura and D. S. Tinti, *Chem. Phys. Lett.*, *13* (1972) 278.
37 E. T. Harrigan and N. Hirota, *Mol. Phys.*, *31* (1976) 663; *31* (1976) 681.
38 M. Gehrtz, C. Brauchle and J. Voitlander, *Mol. Phys.*, *53* (1984) 769.
39 R. K. Power and A. M. Nishimura, *J. Photochem.*, *8* (1978) 263.
40 R. K. Power, K. A. Martin, D. G. Frank and A. M. Nishimura, *J. Photochem.*, *23* (1983) 335.
41 N. J. Tro and D. F. Marten, to be published.
42 C. J. Winscom and A. H. Maki, *Chem. Phys. Lett.*, *12* (1971) 264.
43 A. L. Shain, W. T. Chiang and M. Sharnoff, *Chem. Phys. Lett.*, *16* (1972) 206.
44 A. L. Shain and M. Sharnoff, *Chem. Phys. Lett.*, *13* (1972) 278.
45 K. Ramalingam, K. D. Berlin, R. A. Loghry, D. van der Helm and N. Satyamurthy, *J. Org. Chem.*, *44* (1979) 477.
46 J. Schmidt, W. S. Veeman and J. H. van der Waals, *Chem. Phys. Lett.*, *4* (1969) 341.
47 E. R. Davidson and J. C. Ellenbogen, *J. Chem. Phys.*, *73* (1980) 865.
48 B. R. Henry and W. Siebrand, in J. B. Birks (ed.), *Organic Molecular Photophysics*, Wiley, 1973.
49 B. R. Henry and W. Siebrand, *J. Chem. Phys.*, *54* (1971) 1072.