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Excited States of Phenyl Carbonyl Compounds

Propiophenone

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In an attempt to clarify the origin of the dual phosphorescence in phenyl alkyl ketones, we have made some calculation (within the C.I.P.S.I. method in an excitonic scheme) to elucidate the conformation of both ground states and excited states of propiophenone. Our calculations have shown the presence of two stable isomers in the ground state, first $n \rightarrow \pi^*$ state, and first $\pi \rightarrow \pi^*$ singlet and triplet states. So our work suggests that the origin of the dual phosphorescence of propiophenone could be related to the conformational change of the molecule in the $n \rightarrow \pi^*$ state, because the most stable conformations in the $n \rightarrow \pi^*$ state and in the ground state are different.

Key words: Phenyl alkyl ketones, dual phosphorescence in ~ - Propiophenone

1. Introduction

The spectroscopy and photochemistry of phenyl alkyl ketones are very interesting and have received much recent attention. Several authors [1-11] have reported that most phenyl alkyl ketones display two-component phosphorescence in glassy matrices at 77 °K. The excitation spectra of the two emissions are almost identical, but these two groups of phosphorescence bands have different wavelengths and different life times ($\lambda_1 = 394$ nm, $\tau_1 = 4$–6 ms, $\lambda_2 = 381$ nm, $\tau_2 = 9$–15 ms in P.M and EPA glasses at 77 °K).

The lower-energy (and short-lived) phosphorescence hereafter referred to as the normal emission, is spectrally almost identical to the vapor phase phosphorescence of the molecule.

It is now generally agreed that the major, short-lived component arises from an $n \rightarrow \pi^*$ state: effectively this emission is very ketone-like, consisting of three predominent bands with the 1650 cm^{-1} spacing characteristic of the carbonyl stretch, furthermore this emission band is blue shifted from 2-4-4 trimethyl pentane, when measured in ethanol solution [11].

But the source of the longer-lived minor component remains unclear, most discussions of the problem have been made in terms of emission from two different electronic states. Several reports suggest that the long-lived component is a state of mostly ${}^3\pi \rightarrow \pi^*$ character [1-4]. For such an interpretation to be correct, the two states could not be in equilibrium, but a non-equilibrium distribution would not be expected to occur unless internal conversion between the states were slower than phosphorescence, which seems highly improbable [6].

Kanda and Lim *et al.* [5] have pointed out this problem, and have offered a new interpretation: they have observed the same two-component phosphorescence from 1-indone originally reported in Ref. [1] and they have suggested that the long-lived emission is due to a new chemical species such as an enol or an enolate anion which can be formed by a reversible photochemical reaction.

It is also possible to relate the origin of the dual phosphorescence to the conformational change of the molecule in the lowest triplet state. The hypothesis of two different conformations initially proposed by Gacoin [11] has been adopted by Long [7] and Wagner [8]. A recent study of solvent and substituent effects on the dual phosphorescence of propriophenone and butyrophenone suggests that the prerequisites for the observation of dual emission are the proximity of the lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplet states, and high viscosity of the glassy solvents [8, 10]. The anomalous emission is viscosity dependent, its relative intensity increases with increasing viscosity of the glassy solvent [8, 10]. The conformational change may be due to a valence distortion in the lowest triplet state as suggested by Wagner [8], or due to a pseudo Jahn-Teller distortion of the lowest triplet state resulting from the vibronic interaction between closely spaced $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplet states as proposed by Koyanagi *et al.* [9] to account for a peculiar temperature-dependent phosphorescence in acetophenone. Recently Kanamaru *et al.* [10] have presented a model which combines the pseudo Jahn-Teller distortions of the lowest triplet state and the viscosity-dependent matrix potential which oppose this conformational change. In the model of Kanamaru *et al.* [10] the lowest triplet state of the free molecule is assumed to be distorted along the COR torsional coordinate, since it is the low-frequency mode, for which the double minimum is easily satisfied; but as pointed out by Kanamaru *et al.* [10] the appearance of the COR torsional progression in the spectrum of the normal phosphorescence has not been shown experimentally, neither in the normal emission from glassy solutions, nor in the vapor phase phosphorescence spectrum of propiophenone.

In an attempt to clarify the origin of the duel phosphorescence in phenyl alkyl ketones, we have made some calculations to elucidate the conformations of both ground state and excited states of propiophenone.

When considering that the conformation change in the lowest triplet state could be due to a valence distortion, we may not retain a torsion around the C_6-C_7 axis, since we have shown, in a previous paper, that benzaldehyde and acetophenone are planar in the ground state and in the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states [12]: this result has supported the dynamic

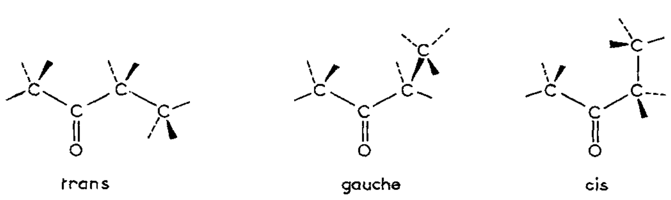


Fig. 1. The three isomers of methyl ethyl ketone are given in Ref. [15]

pseudo Jahn-Teller effect [13]. But when considering propiophenone, it is possible to suppose a rotation around the CO-C_2H_5 axis.

We may *a priori* assume this hypothesis valid with regard to experimental results: a previous infra-red spectrum of methyl ethyl ketone [14] has shown that in the ground state this molecule has two isomers in the vapor and liquid phases as a result of restricted internal rotation about C-C axis adjacent to the C=O bond; one isomer being more stable than the other one by the ΔH of 2.0 kcal/mole and 1.1 kcal/mole in the vapor and liquid phase respectively while only the more stable isomer remains in the solid phase. Then this molecule has been studied by gas electron diffraction [15]. The two isomers shown in Fig. 1 (the *trans* and *gauche* isomers) are present in the ratio 0.95 : 0.05. The dihedral angle for the *gauche* form is 70° (180° for the *trans* isomer).

So we may wonder if: 1. these two conformations of the ground state remain after replacement of the α-methyl group of methyl ethyl ketone by a phenyl group; 2. the excited $n \rightarrow \pi^*$ state also has two stable conformations; if so, do the ground state and the $n \rightarrow \pi^*$ states present identical most stable conformation.

So in this present work we assume the planarity of the benzoyl group and consider the torsion of the ethyl group around the CO-C_2H_5 bond (φ angle).

2. Method

These calculations have been made with the CIPSI method [16] in an excitonic scheme [17–19], within the CNDO/2 parametrization [20]. This method consists in perturbing (up to the second-order correction of the energy) a zeroth-order multiconfigurational wave function which has an adequate overlap with the exact wave function. This multiconfigurational zeroth-order wave function is built up in an iterative way; the iterative process is stopped when the first-order wave function Ψ_m^1 does not contain any component higher than 0.10.

The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states have been calculated separately, since they have not the same symmetry.

1. The zeroth-order wave function chosen for the calculation of the $n \rightarrow \pi^*$ states contains 88 determinants:

The $\Phi\begin{pmatrix}\pi_k^* \\ n\end{pmatrix}$ singly excited determinants $k = 1, 4$

The $\Phi\begin{pmatrix}\pi_{C=O}^* \\ \sigma_l\end{pmatrix}$ singly excited determinants with σ_1 are two σ bonds adjacent to the C=O bond (l = 17 and 19 in Fig. 2).

The $\Phi\begin{pmatrix}\sigma_l^* \\ n\end{pmatrix}$ singly excited determinants, with l = 21, 22 of 23 (see Fig. 2a).

$\Phi\begin{pmatrix}\pi^*_{C=O} & \pi'^*_B \\ n & \pi_B\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi'^*_B & \pi^*_{C=O} \\ n & \pi_B\end{pmatrix}$ where π_B is a π bond of benzene.

$\Phi\begin{pmatrix}\pi^*_1 & \pi^*_{C=O} \\ n & \pi_1\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi^*_{C=O} & \pi^*_1 \\ n & \pi_1\end{pmatrix}$

$\Phi\begin{pmatrix}\pi^*_{C=O} & \pi^*_1 \\ n & \pi_{C=O}\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi^*_1 & \pi^*_{C=O} \\ n & \pi_{C=O}\end{pmatrix}$

$\Phi\begin{pmatrix}\pi^*_{C=O} & \pi^*_{C=O} \\ n & \pi_{C=O}\end{pmatrix}$

$\Phi\begin{pmatrix}\pi^*_{C=O} & \pi^*_{C=O} \\ n & \pi_1\end{pmatrix}$

$\Phi\begin{pmatrix}\pi^*_{C=O} & \pi^*_{C=O} \\ n & \sigma_k\end{pmatrix}$ with $\sigma_k = 21, 22, 23$

$\Phi\begin{pmatrix}\pi^*_{C=O} & \sigma^*_{18} \\ n & \sigma_{20}\end{pmatrix}$ and $\Phi\begin{pmatrix}\sigma^*_{18} & \pi^*_{C=O} \\ n & \sigma_{20}\end{pmatrix}$

doubly excited determinants

$\Phi\begin{pmatrix}\pi^*_{C=O} & \pi^*_B & \bar{\pi}^*_B \\ n & \pi_B & \bar{\pi}_B\end{pmatrix}$ triply excited determinants.

2. The zeroth-order wave function chosen for the calculation of the $\pi \rightarrow \pi^*$ state contains 133 determinants:

- The ground-state fully localized determinant.
- The $\Phi\begin{pmatrix}\pi^*_k \\ \pi_k\end{pmatrix}$ polarization singly excited determinants, $k = 1, 4$.
- The $\Phi\begin{pmatrix}\pi'^*_l \\ \pi_k\end{pmatrix}$ delocalization singly excited determinants, $k \neq l = 1, 4$.
- The $\Phi\begin{pmatrix}\pi^*_i & \bar{\pi}^*_i \\ \pi_i & \bar{\pi}_i\end{pmatrix}$ with $i = 1, 4$

  $\Phi\begin{pmatrix}\pi^*_i & \pi^*_j \\ \pi_i & \pi_j\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi^*_j & \pi^*_i \\ \pi_i & \pi_j\end{pmatrix}$ $i \neq j = 1, 4$

  $\Phi\begin{pmatrix}\pi^*_j & \pi^*_k \\ \pi_i & \pi_k\end{pmatrix}$ and $\Phi\begin{pmatrix}k^* & j^* \\ i & k\end{pmatrix}$ $i \neq j \neq k = 1, 3$

  $\Phi\begin{pmatrix}\pi^*_i & \pi^*_j \\ \pi_i & \pi_i\end{pmatrix}$ $i = 1, 3$
  $j \neq i$ and $j = 1, 3$ when $i \neq 1$
  $j = 2, 4$ when $i = 1$

  $\Phi\begin{pmatrix}\pi^*_j & \pi^*_i \\ \pi_i & \pi_j\end{pmatrix}$ $i = 1, 3$
  $j \neq i$ and $j = 1, 3$ when $i \neq 1$
  $j = 2, 4$ when $i = 1$

  doubly excited determinants

$$\Phi\begin{pmatrix}\pi_1^* & \pi_4^* & \pi_4^* \\ \pi_1 & \pi_4 & \pi_4\end{pmatrix} \text{ triply excited determinants.}$$

The first zeroth-order energy of the ground state (E_1) is the lowest eigenvalue obtained after diagonalization of this excitonic matrix. The second-order energy is given by the perturbation treatment.

We have also given the ground-state second-order energy calculated with the PCILO method [21] : In this method the zeroth-order ground-state energy is the energy of the fully localized determinant representing the ground state, then the second-order energy is calculated by a perturbation treatment.

3. Geometry

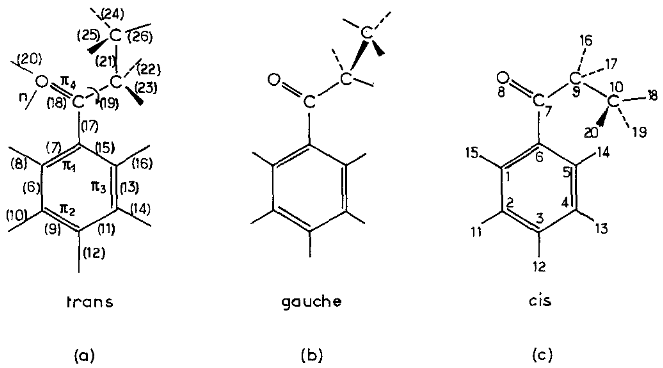
The bond lengths and bond angles of the benzene ring are respectively equal to 1.397 Å and 120°.

The geometry of the $\underset{\underset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}CH_3$ group is the one given by Abe *et al.* [15].

We have made rotations around the C_7C_9 bond (see Fig. 2). The dihedral angle $\tau_{C_6C_7C_9C_{10}}$ is 180° for the *trans* form and 0° for the *cis* form.

4. Results

Table 1 gives the second-order energies of the ground state, first $n \rightarrow \pi^*$ state, first $\pi \rightarrow \pi^*$ triplet and singlet states for different values of the $\tau_{C_6C_7C_9C_{10}}$ dihedral angles (angle φ). φ varies between 0° and 180°. This table also gives the second-order energies of the ground state calculated by the PCILO method [21]. Fig. 3 gives the evolution of the second-order energy of the multiconfigurational ground state, first $n \rightarrow \pi^*$ state, first $\pi \rightarrow \pi^*$ triplet and singlet states with φ.



trans (a) gauche (b) cis (c)

Fig. 2. The three isomers of propiophenone. (a) Gives the numbering of bonds, (c) gives the numbering of atoms

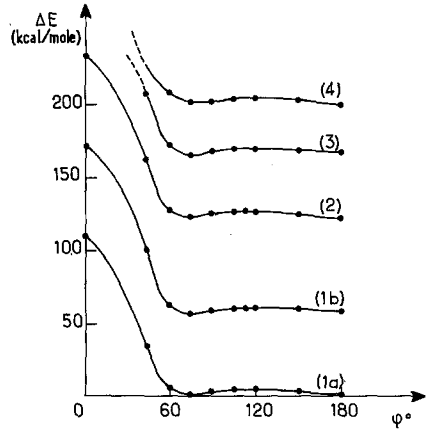


Fig. 3. Evolution with the angle φ (in degrees) of the second order (in kcal/mole) of: (1a) the ground state calculated with the PCILO method, (1b) the ground state calculated with the CIPSI method, (2) the $n \to \pi^*$ state triplet and singlet, (3) the first $\pi \to \pi^*$ triplet state, (4) the first $\pi \to \pi^*$ singlet state

From the results obtained after second-order correction we may notice that:

1. All the electronic states calculated present a double minimum potential energy curve. The two minima are obtained for $\varphi = 180°$ (*trans* form) and $\varphi = 75°$ (*gauche* form).
2. The *cis* conformation is very unstable because of the important nuclear repulsion. Fig. 2 shows that, within the *cis* conformation, one hydrogen of the phenyl group (hydrogen H_{14}) is very near to the two hydrogens of the methyl group.
3. In the ground state (calculated with a multiconfigurational wave function) the *gauche* form ($\varphi = 75°$) is the most stable conformation. The calculation energy difference between the two minima (ΔH) is 1.21 kcal/mole. The calculated energy barrier ($\Delta E_{g,t}$) from the gauche form is 4.23 kcal/mole. We have noticed that the results obtained with the PCILO method are not very different: this method gives also a double minimum potential energy curve. The minima are also obtained for

Table 1. CIPSI second-order energies (in kcal/mole) of the ground state (calculated also by PCILO), $n \to \pi^*$ state) and of first $\pi \to \pi^*$ singlet and triplet state as a function of the rotation angle φ (in degrees)

Angle φ [°]	Ground State (PCILO)	Ground State (CIPSI)	$n \to \pi^*$ (S and T)	$S_{\pi\to\pi^*}$	$T_{\pi\to\pi^*}$
180	−56647.06	−56702.62	−56583.03	−56514.13	−56538.20
150	−56645.62	−56701.34	−56581.49	−56512.51	−56537.08
135	−56644.00		−56579.52		
120	−56643.46	−56699.18	−56578.69	−56510.83	−56535.04
112.5	−56644.46		−56578.48		
105	−56644.81	−56700.29	−56579.52	−56511.95	−56538.08
90	−56646.34	−56701.58	−56580.59	−56513.27	−56537.25
75	−56648.50	−56703.43	−56582.38	−56515.14	−56538.91
67.5	−56648.41		−56582.32		
60	−56645.08	−56700.07	−56579.12	−56511.91	−56535.30
45	−56610.84	−56666.71	−56545.85	−56478.54	−56501.52
0	−56533.09	−56591.58	−56470.90	−56402.46	−56425.08

Table 2. Percentage of molecules in the *gauche* and *trans* form at 77 °K, in the ground state, $n \rightarrow \pi^*$ state and first $\pi \rightarrow \pi^*$ triplet state

	Gauche Form (%)	*Trans* Form (%)
Φ_0	99.99	0.01
$T_{n\pi^*}(S_{n\pi^*})$	3.00	97.00
$T_{\pi\pi^*}$	98.97	1.03

$\varphi = 75°$ and $\varphi = 180°$, and the *gauche* form is the most stable conformation. The calculated ΔH and $\Delta E_{g,t}$ values are quite equivalent to those previous ($\Delta H = 1.45$ kcal/mole, $\Delta E_{g,t} = 5.04$ kcal/mole).

4. In the $n \rightarrow \pi^*$ state, the *trans* form ($\varphi = 180°$) is the most stable one. The calculated energy difference between the two conformations (ΔH) is 0.67 kcal/mole. The calculated energy barrier existing between the *trans* form and the *gauche* form $\Delta E_{t,g}$ is 4.88 kcal/mole. The energy barrier between the *gauche* form and the *trans* form is 3.88 kcal/mole. The calculated $n \rightarrow \pi^*$ transition energy of the *trans* isomer is 5.2 eV. The calculated $n \rightarrow \pi^*$ transition energy of the *gauche* isomer is 5.3 eV. So these two transition energies are separated by 0.1 eV.
5. In the first $T_{\pi \rightarrow \pi^*}$ and $S_{\pi \rightarrow \pi^*}$ the *gauche* form is the most stable conformation. The ΔH between the *gauche* form and the *trans* form is 0.70 kcal/mole and 1.00 kcal respectively. The calculated energy barrier from the *gauche* form to the *trans* form is 3.87 kcal/mole in the first triplet $T_{\pi \rightarrow \pi^*}$ and 4.34 kcal/mole in the first singlet state.

An analysis of our results has shown that:

1. When considering the zeroth-order energy of the ground state, as a function of the rotation angle φ, within the PCILO method, and the first-order energy of the ground state, as a function of the rotation angle φ, within the CIPSI method, the *trans* isomer is the most stable conformation. The stabilization of the *gauche* isomer is due to the second-order delocalization correction within the PCILO method and to the second-order correction due to the singly excited configurations within the CIPSI method.
2. When considering the zeroth-order energy of the $n \rightarrow \pi^*$ state as a function of the rotation angle φ, the *trans* form is still the stable conformation (by 0.58 kcal/mole). The second-order correction does not make any important change.
3. When considering the zeroth-order energy of the first $\pi \rightarrow \pi^*$ triplet and singlet ($T_{\pi\pi^*}$ and $S_{\pi\pi^*}$) the *trans* form is the more stable form. The stabilization of the *gauche* form after the second-order correction originates from the correction due to the doubly excited determinants.

5. Discussion

In order to propose a model which rationalizes the two emission characteristics in propiophenone, we have calculated the repartition of the conformations about the potential minimum of a free propiophenone molecule.

We have used the following partition function:

$$Z = \sum_i \exp(-E_i/KT)$$

where E_i is the calculated energy of each point i of the potential curve.

The probability of finding the molecule with the value E_i of the energy is given by

$$P_i = \exp(-E_i/KT)/Z$$

Since the experimental measures of phosphorescence have been made at 77 °K, our calculations have been made at $T = 77$ °K.

Table 2 gives the percentage of molecules in the two stable conformations of the ground state and of the $n \rightarrow \pi^*$ state. At 77 °K in the ground state, all the molecules are in the *gauche* form (the more stable conformation) and in the $n \rightarrow \pi^*$ state only 3% of the molecules are in the *gauche* form.

So we can propose the following model to try to rationalize the emission characteristics in propiophenone.

Let us consider the optical excitation of molecules in the *gauche* conformation of the ground state. Because of the Franck-Condon principle and the rapid singlet-triplet intersystem crossing, the *gauche* conformation of the lowest $n \rightarrow \pi^*$ triplet is populated. Since this is not a favorable conformation, in the lowest $n \rightarrow \pi^*$ triplet state the molecule will tend to go over to the more stable conformation (the *trans* conformation). Such a conversion will be rapid in the vapor phase, but very slow in high viscosity solvents since it requires the displacement of solvent molecules. So in the $n \rightarrow \pi^*$ state there is competition between the radiative decay of molecules in the *gauche* form with the conversion to the *trans* form.

Within the assumption of this model, the lower energy spectrum (i.e. the normal emission) which occurs in the vapor phase and in relatively fluid isopentane at 77 °K presumably arises from the conformationally relaxed $n \rightarrow \pi^*$ state (in the *trans* conformation) and the higher energy spectrum (the anomalous emission) probably arises from a $n \rightarrow \pi^*$ state held rigidly (by solvent) in the most favorable ground state conformation (see Fig. 4).

From our calculation the $n \rightarrow \pi^*$ and first $\pi \rightarrow \pi^*$ triplet states are separated by 1.90 eV in the *gauche* form and by 1.35 eV in the *trans* form.

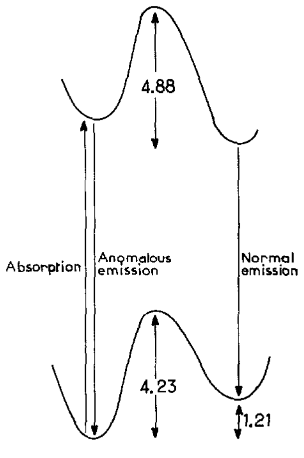


Fig. 4. Our proposed model to try to explain the dual phosphorescence of propiophenone. The energy values are given in kcal/mole

The separation between the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplet states is too large because of the CNDO parametrization; in fact these two states are nearly degenerate, but qualitatively our results suggest that the mixing between the first $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplet state would be a little more important in the *gauche* conformation than in the *trans* conformation: so our model suggests that the anomalous emission has a somewhat more mixed ($n\pi^*$-$\pi\pi^*$) character than the normal one: this result is in agreement with those of [1-4] but in disagreement with the result of Kanamaru *et al.* [10].

6. Conclusion

This work suggests that the origin of the dual phosphorescence of propiophenone could be related to the conformational change of the molecule in the lowest triplet state. This conformational change is due to a valence distortion in the $n \rightarrow \pi^*$ triplet state because the most stable conformations in the $n \rightarrow \pi^*$ triplet state and in the ground state are different. Our model accounts for solvent viscosity dependence of the anomalous emission. In low solvent viscosity the valence distortion dominates over the solvent molecules effect so that the phosphorescence spectrum is essentially that of the gaseous molecule. Our interpretation does not prohibit a torsion of the COC_2H_5 group about the phenyl ring, but this distortion would be induced by a Jahn-Teller dynamical effect [13]. Presently we are lacking experimental evidence of our invoked conformation effect.

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