

## PHOTODISSOCIATION OF $\beta$ -CARBOLINE

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### Summary

An explanation for the photochemical homolytic self-dissociation of  $\beta$ -carboline has been found by means of intermediate neglect of differential overlap (INDO) and complete neglect of differential overlap/spectroscopic parametrization (CNDO/S) molecular orbital calculations. The need to excite to the  $n\pi^*$  triplet state to produce the homolytic cleavage of the N—H bond has been explained. A spin-orbital coupling that causes an important  $^1\Sigma$  contamination on this triplet state is invoked to explain its population. Finally, the role of the pyrrolic ring of  $\beta$ -carboline on such a photochemical process is discussed.

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### 1. Introduction

The photoexcitation of a polycyclic aromatic compound results in the formation of neutral radicals. Thus, the indolyl radical is produced on irradiation of indole [1]. The double-flash technique has been used to show that the N—H bond of carbazole breaks when the molecule is in a highly excited triplet state to yield the carbazyl radical [2]. This behaviour has been theoretically explained by means of molecular orbital (MO) calculations [3] showing that a triplet state of  $\Pi$  symmetry is involved in the homolytic self-dissociation. Such a  $\Pi$  triplet state is contaminated by  $\Sigma$  symmetry states through spin-orbital coupling which enables it to be populated.

The growing interest in the photochemical behaviour of  $\beta$ -carboline (9*H*-pyrido(3,4-*b*)indole) and its derivatives originates from their biological importance. Thus, the photocytotoxic activity of  $\beta$ -carboline has recently been reported [4, 5]. Also, it has been indicated [6] that light could be responsible for the inhibitory [7] or the catalytic [8] character of  $\beta$ -carboline or for the mutagenic activity of benzapyrene.

Balsells and Frasca [9] have shown that  $\beta$ -carboline yields dimers on irradiation using a mercury lamp. In particular,  $\beta$ -carboline only yields a product that contains an N—N bond between pyrrolic rings. These researchers suggest a mechanism involving the population of an  $n\pi^*$  triplet state and self-dissociation from it.

The purpose of the present work is to interpret, from a theoretical point of view, such photochemical behaviour of  $\beta$ -carboline.

## 2. Molecular orbital calculations

The molecular energy was calculated by the intermediate neglect of differential overlap (INDO) method [10] with a closed-shell restriction for the ground state  $S_0$ . For the doublet and triplet states, an open-shell treatment was used. The search for the minimum energy structures was carried out using Rinaldi's version [11] of the Murtagh-Sargent method [12].

Likewise, the calculation of the INDO energy profiles was achieved by varying the  $r_{\text{NH}}$  distance. All the other geometric parameters were optimized at each point.

The energy of the excited triplet states  $T_n$  was computed using the complete neglect of differential overlap/spectroscopic parametrization (CNDO/S) method [13]. The Pariser-Parr approach [14] was employed to calculate the Coulomb integrals for the triplet and doublet states and the Nishimoto-Mataga approach [15] was employed for the singlet case, as was suggested previously [16]. The configuration interaction (CI) involved the 90 mono-excited configurations lowest in energy in all cases.

All calculations were performed by using the programs CNDO/M [17] and GEOMO [18].

## 3. Results and discussion

### 3.1. Photodissociation mechanism

The MO calculations must be preceded by a knowledge of the molecular geometry. No structural data on  $\beta$ -carboline (norharmane) are available from the literature. Thus, the geometry of the isolated molecule has been approximated by finding the minimum stationary point on its potential-energy hypersurface.

From the INDO-optimized energies for the  $\beta$ -carboline ground state ( $S_0$ ), triplet state ( $T_1$ ) and  $\beta$ -carbonyl radical ground state ( $D_0$ ), it can be inferred that the most important differences between these molecular structures concern the pyrrolic ring and the neighbourhood of the pyridinic nitrogen. (For the sake of conciseness the data is not reported in this paper, but this information is available from the authors on request.)

However, the  $\sigma$ -localized electronic population on  $\beta$ -carboline  $S_0$  and the  $\pi$ -localized electronic population on  $\beta$ -carbonyl radical  $D_0$  (see Table 1) suggest that the  $\beta$ -carboline ( $S_0$ )- $\beta$ -carbonyl radical ( $D_0$ ) interaction must involve the two pyrrolic nitrogen atoms. This suggestion correlates with the experimental finding that only a dimer which involves the formation of an N-N bond is detected on photoexcitation of  $\beta$ -carboline [9].

However, such a dimerization can be preceded by the formation of the  $\beta$ -carbonyl radical. Figure 2 shows the INDO energy profile *versus* the  $r_{\text{NH}}$

TABLE 1

$\pi$  and  $\sigma$  net atomic charges corresponding to the  $\beta$ -carboline singlet ( $S_0$ ) and  $\beta$ -carbolinyl radical doublet ( $D_0$ ) ground states respectively

	$q_\sigma (S_0)$	$q_\pi (D_0)$
C <sub>1</sub>	-0.01	-0.01
C <sub>2</sub>	-0.07	0.00
C <sub>3</sub>	0.02	0.11
C <sub>4</sub>	-0.06	0.00
C <sub>5</sub>	0.01	0.03
C <sub>6</sub>	-0.05	0.02
C <sub>7</sub>	0.02	0.02
N <sub>8</sub>	0.25	-0.16
C <sub>9</sub>	-0.02	0.10
C <sub>10</sub>	-0.01	0.09
N <sub>11</sub>	-0.07	-0.10
C <sub>12</sub>	0.00	0.11
C <sub>13</sub>	-0.02	0.01

The numbering of the atoms is shown in Fig. 1.

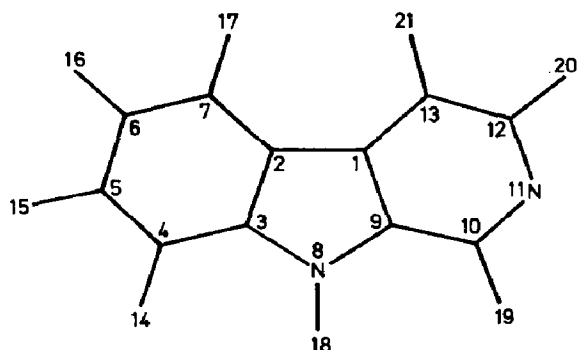


Fig. 1. Numbering system for the studied molecules.

distance for the  $\beta$ -carboline singlet ground state; it indicates that thermal dissociation cannot occur. Indeed, CNDO/S studies on the singlet excited states reveal that no photodissociations, via singlet states, can be expected. (As above, the data is not reported in this paper.)

Consequently, the self-dissociation must start from a triplet state. Then, a previous problem, *i.e.* the possibility of triplet population, must be considered. We have performed calculations on  $\beta$ -carboline concerning the contamination of triplet states by singlet states arising from spin-orbital coupling [19, 20]. (The corresponding subroutines of the CNDO/M program [17] have been used.)

A methodological consideration should be made in relation to the spin-orbital coupling calculation. As previously stated, it has been shown [16] that Coulomb integrals calculated by the Mataga-Nishimoto method [15] give the best results for singlet-singlet transition energies while Pariser-Parr integrals [14] give better results for the calculation of triplet states. In

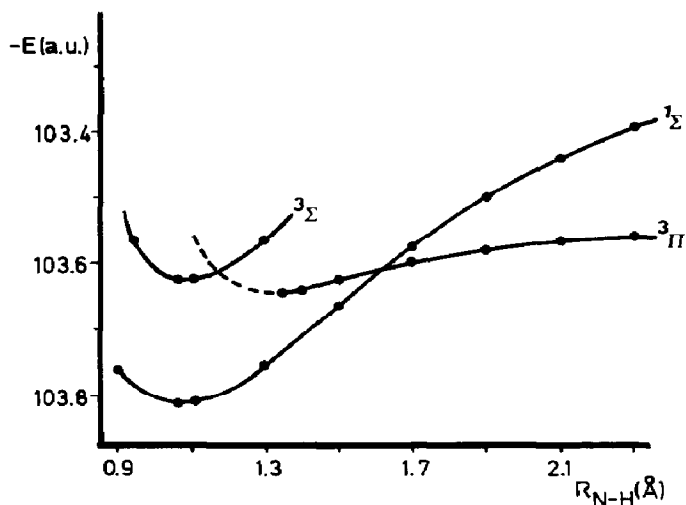


Fig. 2.  $\beta$ -carboline: ground state ( $S_0$ ) and triplet state ( $T_1$ ) INDO energy profiles vs. the N—H bond distance.

the spin-orbital coupling calculation both singlet and triplet states are involved. This fact has led to the arbitrary choice of the Coulomb integral calculation method. Both the Mataga-Nishimoto and the Pariser-Parr method have been used without specification in the literature [20, 21].

We have carried out two calculations making use of the two approaches for the Coulomb integrals. The molecular geometry adopted is the INDO-optimized ground state geometry. Both calculations lead to the more contaminated triplet states being those of  $\Pi$  symmetry, with the triplet states of  $\Sigma$  symmetry being less contaminated.

Table 2 shows the major terms of the spin-orbital coupling between the lowest triplet state of  $\Pi$  symmetry ( $T_\pi$ ) and all the singlet states. Moreover, it must be pointed out that  $T_\pi$  correlates with the ground state  $D_0$  of the  $\beta$ -carbonyl radical because of symmetry rules. Furthermore,  $T_\pi$  has  $n\pi^*$  character.

Figure 2 shows the INDO open-shell energy profile that corresponds to the lowest triplet state for each distance  $r_{NH}$ . It can be seen that a crossing takes place in the vicinity of  $r_{NH} = 1.3$  Å. In fact, for  $r_{NH} < 1.3$  Å the lowest triplet state wave function belongs to  $\Sigma$  symmetry. However, for  $r_{NH} > 1.3$  Å the lowest triplet state wave function belongs to  $\Pi$  symmetry. Similar behaviour has been reported for carbazole [3]. This fact is further evidence for the close similarity between the electronic properties of  $\beta$ -carboline and carbazole.

Table 3 summarizes the dependence of a number of parameters on  $r_{NH}$ . It can be seen that at  $r_{NH} \approx 1.3$  Å the Wiberg index [22] associated with the NH bond of the pyrrolic ring undergoes a sudden descent. At  $r_{NH} > 1.35$  Å the Wiberg index continuously tends to zero. Similar trends occur for the total charge population and the spin density on the pyrrolic hydrogen which tend to unity as  $r_{NH}$  increases. The limiting values of all these indexes are those expected for a homolytic dissociation.

TABLE 2

$\beta$ -Carboline spin-orbital coupling: singlets perturbing the lowest  $\Pi$ -symmetry triplet state  $T_\pi$

Component	Singlet	Symmetry	$\Delta E$ (cm <sup>-1</sup> )	Spin-orbital coupling (cm <sup>-1</sup> )
$\Gamma_-$	0		34823	-24.085
	1		1628	-1.256
	3	A'	-1405	3.407
	4		-4224	4.134
	5		-8869	1.821
$\Gamma_+$	0		34823	-5.589
	1		1628	-0.314
	3	A'	-1405	0.495
	4		-4224	0.994
	5		-8869	0.429
$\Gamma_z$	8		-12367	0.188
	10		-13834	-5.604
	13	A''	-15438	-4.808
	14		-17592	0.656
	17		-20756	-7.316

The Mataga-Nishimoto method [15] was used to calculate the Coulomb integrals.

TABLE 3

Symmetry (wave function), total energy  $E$ , Wiberg index, total charge population  $q_Q(\text{H})$  on the pyrrolic hydrogen and spin density  $q_S(\text{H})$  on the pyrrolic hydrogen, versus  $r_{\text{NH}}$  (Å), for the more stable  $\beta$ -carboline triplet state

$r_{\text{NH}}$	Symmetry	$E$ (atomic units)	Wiberg index	$q_Q(\text{H})$	$q_S(\text{H})$
0.9	$\Sigma$	-103.56717804	0.9608	0.8830	-0.0046
1.1	$\Sigma$	-103.62458502	0.9490	0.9077	-0.0094
1.3	$\Sigma$	-103.56489545	0.9270	0.9340	-0.0304
1.35	$\Pi$	-103.64432982	0.2260	1.2326	0.7186
1.5	$\Pi$	-103.62458232	0.1750	1.1868	0.7893
1.7	$\Pi$	-103.59720367	0.1140	1.1200	0.8701
1.9	$\Pi$	-103.57711087	0.0649	1.0663	0.9293
2.1	$\Pi$	-103.56492994	0.0332	1.0333	0.9647
2.3	$\Pi$	-103.55831880	0.0159	1.0157	0.9834

The triplet state that crosses  $T_1$  has been located by performing CNDO/S calculations of triplet states as  $r_{\text{NH}}$  increases. At each  $r_{\text{NH}}$  the previously optimized INDO geometries for the lowest triplet state and the Pariser-Parr integrals [14] were adopted.

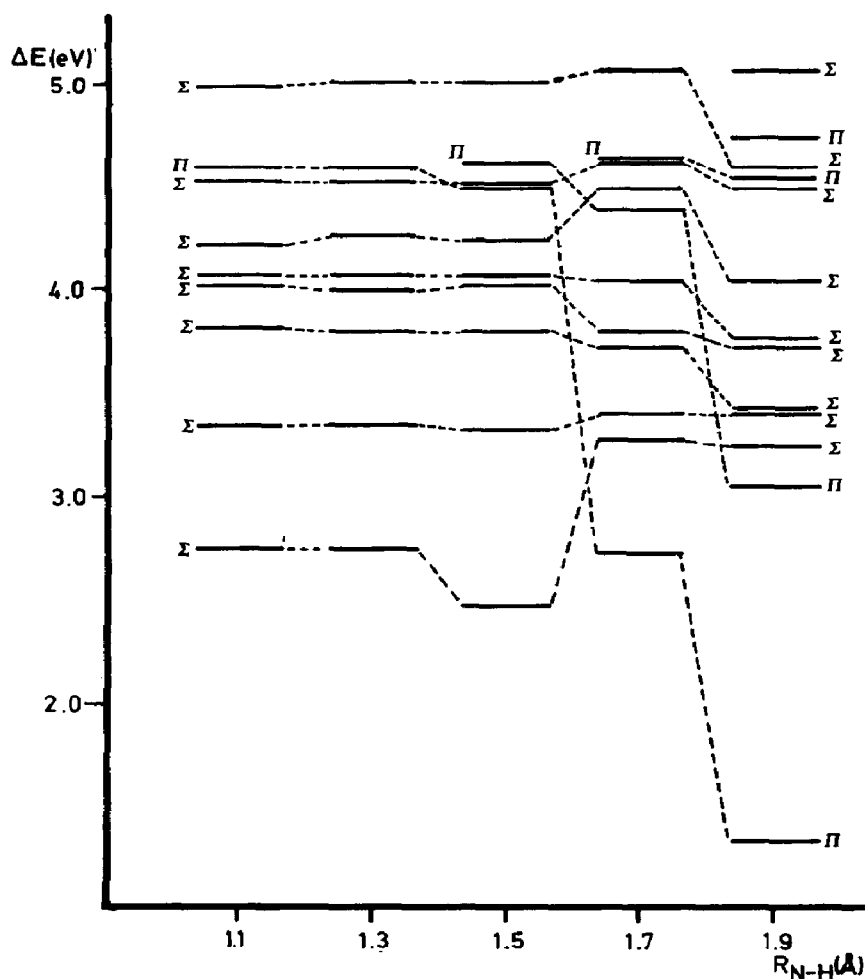


Fig. 3. CNDO/S relative energies, referred to the ground state, for the  $\beta$ -carboline triplet states vs. the N—H bond distance.

Figure 3 shows the evolution of the CNDO/S triplet energies, relative to the ground state  $S_0$ , with  $r_{NH}$ . This figure reveals that the energy of  $T_\pi$  falls dramatically and that  $T_\pi$  crosses the  $T_1$  level as  $r_{NH}$  increases.

The population of  $T_\pi$  can arise from two possible mechanisms: (i) direct population from  $S_0$  that is allowed because of  $^1\Sigma$  contamination of  $T_\pi$  (derived from spin-orbital coupling); (ii) intersystem crossing with a singlet state, also aided by  $^1\Sigma$  contamination of  $T_\pi$ .

Figure 2 allows us to establish that a vertical transition from  $S_0$  and/or an indirect mechanism involving intersystem crossing with  $S_3$  (at equilibrium, the energy gap between  $T_\pi$  and  $S_3$  is small (about 0.17 eV) (see Table 2)) yield a vibrational level in  $T_\pi$  more energetic than the energy barrier for  $T_\pi$  dissociation.

These results enable an interpretation of the experimental data from the photochemical reaction that yields a  $\beta$ -carboline solution in a quartz flask on irradiation for 15 h using a mercury lamp [9]. Moreover, the

reaction occurs when the container is a Pyrex flask [9]. Pyrex is transparent to a wide range of wavelengths but below about 320 nm it begins to lose its transparency and can be considered to be opaque for light of wavelength shorter than 265 nm [23]. For wavelengths longer than 265 nm the first and second bands in the  $\beta$ -carboline absorption spectrum appear (350 nm and 290 nm respectively [24]). The band at 350 nm has been assigned to the  $S_1 \leftarrow S_0$  transition [25], whereas the band at 290 nm comprises a strong  $\pi\pi^*$  transition ( $S_3 \leftarrow S_0$ ) that masks the weak  $n\pi^*$  transition [25].

INDO calculations (see Fig. 2) show that  $T_\pi$  crosses  $S_0$  when  $r_{NH} = 1.6$  Å. Symmetry rules lead us to predict a  $T_\pi-S_1$  crossing for  $r_{NH} < 1.6$  Å. This may be a  $T_\pi-S_1$  intersystem crossing. However,  $T_\pi$  must be populated on some dissociative vibrational level for a photochemical reaction to occur.

We can estimate the energy corresponding to the  $T_\pi$  dissociation barrier by using INDO calculations. The INDO method has not been parametrized to reproduce the spectral transitions. In fact, INDO calculations lead to the  $T_1 \leftarrow S_0$  transition being 0.095 atomic units more energetic than the more suitable CNDO/S result. If we assign this value as a "correction" for the INDO triplet energies, the energy gap between the minimum ground state  $S_0$  and the top of the barrier for  $T_\pi$  dissociation can be established to be 0.165 atomic units (about 280 nm). This result, which can only be considered to be approximate, seems to exclude the  $S_1 \leftarrow S_0$  transition (350 nm) as being the starting point of the photochemical reaction. The band at 290 nm, which has been theoretically computed to be at 276 nm (see Table 2), cannot be excluded.

In relation to the results stated above it must be kept in mind that it has been found experimentally that no photochemical reaction occurs when the light source is a tungsten lamp [9]. This kind of lamp is used to illuminate the 350 - 800 nm wavelength range. This experimental data conclusively excludes the  $S_1 \leftarrow S_0$  transition as being responsible for the beginning of the photochemical reaction.

All the experimental data [9] agree with the theoretical results calculated here and the range of wavelengths able to induce photochemical phenomena correspond to the 290 nm absorption band of  $\beta$ -carboline.

In summary, our calculations reveal that the first  $n\pi^*$  triplet state must be responsible for the self-dissociation of the N-H bond in  $\beta$ -carboline, in accord with the suggestions of Balsells and Frasca [9], and confirm the mechanism proposed by these researchers to explain the photochemical behaviour of  $\beta$ -carboline. The spin-orbital coupling enables  $T_\pi$  to be populated by  $T_\pi-S_3$  intersystem crossing and to a lesser extent through direct population from  $S_0$  in parallel.

### 3.2. Role of the pyrrolic ring

An extension of the mechanism discussed above to polycyclic aromatic compounds containing a pyrrolic ring can be expected to be possible because of the similar photochemical behaviour of  $\beta$ -carboline and carbazole involving self-dissociation, from experimental evidence that photochemical

substitution reactions of pyrrole proceed via triplet states [26] and because pyrrole-anthracene addition implies the formation of a pyrrolyl radical through N-H homolytic cleavage [27]. For this reason, we have performed some calculations on the triplet states of pyrrole.

Despite the report [28] of the pyramidalization about the nitrogen atom in the first triplet state of pyrrole, we have forced the molecule to be planar in our calculation because we are interested in the generalization to polycyclic aromatic compounds whose annular strengths prevent the pyramidalization in the first triplet state that occurs in  $\beta$ -carboline and carbazole systems.

The study performed on the pyrrole ( $C_{2v}$ ) is similar to that described above for  $\beta$ -carboline. The major spin-orbital coupling is found for the  $\Pi$  triplet states ( $A_2$  and  $B_1$  symmetries). Indeed, the lowest  $A_2$  triplet state ( $T_5$ ) correlates, by non-crossing symmetry rules, with the ground state  $D_0$  of the radical, while the lowest  $B_1$  triplet state ( $T_6$ ) correlates with  $D_1$ .

In Fig. 4 and Table 4 are summarized the more important results for pyrrole. A crossing similar to that found in  $\beta$ -carboline is obtained. The

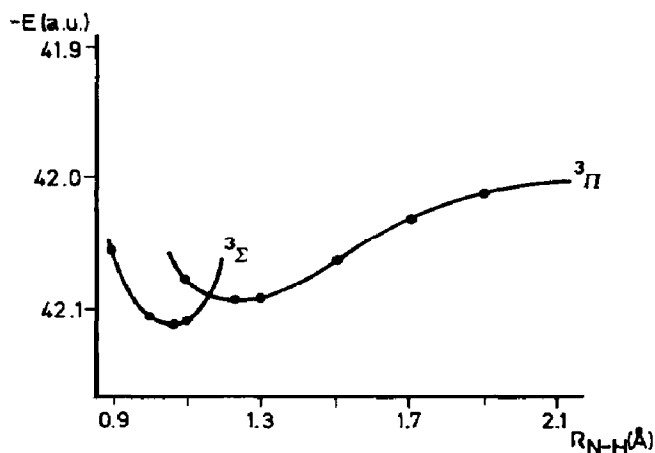


Fig. 4. Pyrrole:  $T_1$  triplet state INDO energy profile vs. the N-H bond distance.

TABLE 4

Symmetry (wave function), total energy  $E$ , Wiberg index, total charge population  $q_Q(H)$  on the pyrrolic hydrogen and spin density  $q_S(H)$  on the pyrrolic hydrogen, versus  $r_{NH}$  (Å), for the more stable pyrrole triplet state

$r_{NH}$	Symmetry	$E$ (atomic units)	Wiberg index	$q_Q(H)$	$q_S(H)$
0.9	$\Sigma$	-42.05486463	0.9619	0.8807	-0.0105
1.1	$\Sigma$	-42.10917625	0.9520	0.9031	-0.0170
1.1	$\Pi$	-42.07817897	0.3474	1.2534	0.5706
1.3	$\Pi$	-42.08964751	0.2365	1.2210	0.7152
1.5	$\Pi$	-42.06327228	0.1707	1.1818	0.7955
1.7	$\Pi$	-42.03639879	0.1105	1.1154	0.8751
1.9	$\Pi$	-42.01670906	0.0626	1.0633	0.9325



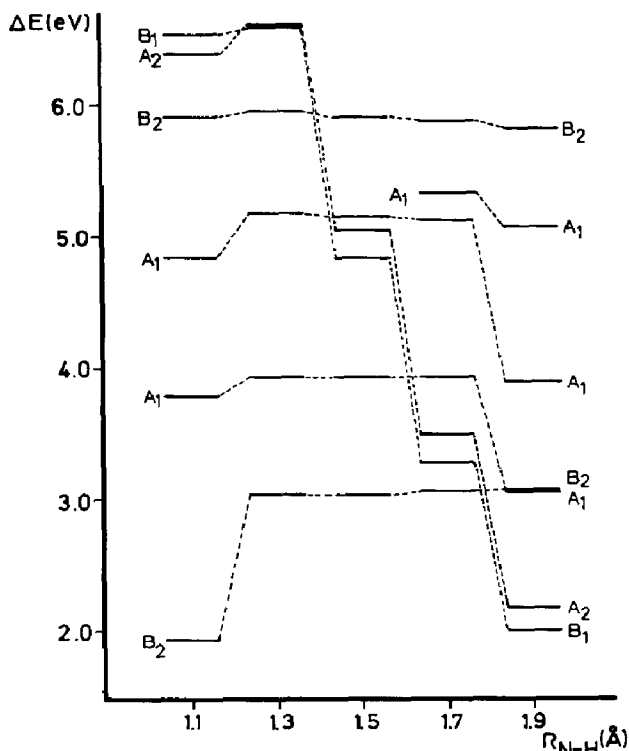


Fig. 5. CNDO/S relative energies, referred to the ground state, for the pyrrole triplet states vs. the N-H bond distance.

CNDO/S results of Fig. 5 show that  $T_5$  and  $T_6$ , belonging to  $\Pi$  symmetry, are the triplet states that undergo stabilization as the homolytic breakage of the N-H bond progresses.

In summary, our calculations indicate that the properties found for the triplet states of  $\beta$ -carboline and carbazole [3] are characteristic of the pyrrolic ring, and so similar photochemical behaviour can be reasonably expected for polycyclic aromatic compounds provided that the aromatic structure stabilizes the radical produced.

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