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A MOLECULAR ORBITAL STUDY OF THE PHOTOTROPISM OF 2 - (2',4' - DINITROBENZYL) PYRIDINE

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I. INTRODUCTION

2 - (2',4'- dinitrobenzyl) pyridine is known to undergo a photochemical isomerization involving the displacement of a hydrogen atom. Studies by Chichibabin et al.[1] of the phototropism of this molecule led to the proposal that a hydrogen transfer took place from the methylene bridge to the nitrogen of the pyridine ring. A more recent work[2] suggested an alternate mechanism in which this hydrogen transfers to the oxygen of the nitro group. In their study of the phototropic properties of various nitrobenzyl derivatives, J.D. Margerum et al.[3] observed that no compound was found to be phototropic which did not have a nitro group ortho to a benzyl hydrogen. Their results were consistent with the photochemical production of an excited species in which hydrogen is transferred from the methylene carbon to the oxygen of the ortho nitro group, producing a colored aci quinoid structure in equilibrium with its anion. The present quantum mechanical study was undertaken in order to predict which of the two suggested photochemical processes is theoretically favoured.

II. METHOD and PARAMETERS

We used the classical Pariser - Parr - Pople semiempirical SCF ASMO CI method treating π electrons only[4,5]. All rings were assumed regular hexagonal structures with equal bond lengths (1.4 Å) and all angles equal to 120°. For the sake of simplicity, the calculations were made assuming planar conformations, although steric requirements obviously exist in the quinoid form. The two-center repulsion integrals were computed in the Nishimoto - Mataga approximation[6]. The valence state ionization energies and one - center repulsion integrals used are listed in Table 1. The configuration interaction calculation included the four highest occupied molecular orbitals and the four lowest vacant ones.

Table 1. Parameter summary (ev)

atoms or groups	I_μ	$\gamma_{\mu\mu}$
C	11.16	11.13
CH_2	21.46	15.73
$\dot{N}$	14.12	12.34
$\ddot{N}$	26.70	17.44
$\dot{O}$	17.70	15.23
$\ddot{O}$	32.90	21.53

III. RESULTS

We studied the A,B and C species (see Fig. 1) in their ground and excited states. The computed energies of the lowest singlet and triplet states are listed in Table 2 and indicate a bathochromic shift when going from A to B or C but do not permit choosing between the two proposed processes. The only experimental transition available for comparison was the absorption band at 2.16 ev quoted in ref. 7 for the final product (B or C) in ethanol solution. This value appears to be in moderate agreement with the computed ones (~ 2.6 ev). This discrepancy may be related to the difficulty of choosing suitable parameters for the $-CH_2$ group in the PPP scheme. In Table 3 are summarized the π electron densities on atoms possibly involved in the photoisomerization processes. If one looks at the π electron densities of A, the density at C_7 decreases, at N decreases slightly and at O increases. It seems therefore likely for a proton to go from C_7 to O. We may also remark that the π density on atom N decreases upon singlet excitation of A and exhibits therefore no tendency to become equal to that in B . On the contrary, the densities on atom N in the lowest states of A and C are quite similar. The process

$$A \xrightarrow{h\nu} A^* \longrightarrow B^* \longrightarrow B$$

appears therefore to be very unlikely. This is confirmed by the marked tendency of the density on atom O_{19} to increase upon excitation, thus tending to resemble that of species C and allowing π electrons to enter in a O – H bond, while the corresponding density on O_{19} in the ground state of B is lower than that in A. On the basis of these remarks we may conclude that our theory undoubtedly predicts that the process

$$A \xrightarrow{h\nu} A^* \longrightarrow C^* \longrightarrow C$$

is responsible for the observed isomerization in good agreement with the experimental results of Margerum et al.[3].

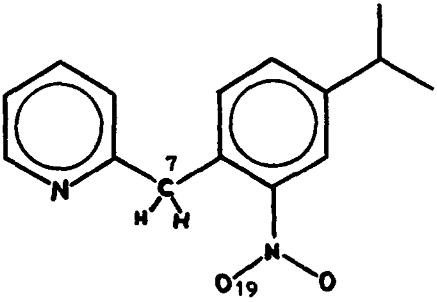
Finally the question arises whether excited singlet or triplet states are postulated as intermediates. Our feeling is that it may be hazardous to suggest too precise a pathway via the excited states of the involved species simply on the basis of the actual PPP treatment. More elaborate calculations using for example a CNDO CI type method may be of better value for such a detailed study.

Table 2. Computed transition energies (ev) and oscillator strengths

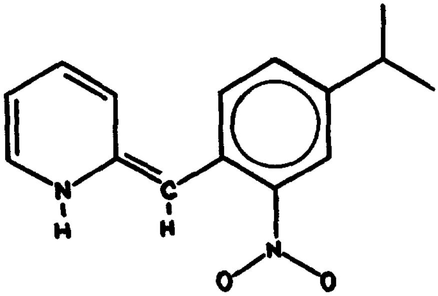
A		B		C	
Singlets	Triplets	Singlets	Triplets	Singlets	Triplets
2.81 (0.53)	1.51	2.66 (0.85)	1.39	2.64 (0.64)	0.20
3.26 (0.77)	1.71	3.17 (0.36)	1.50	3.32 (0.81)	1.69
4.40 (0.08)	2.46	3.33 (0.03)	2.20	4.22 (0.03)	2.54
4.55 (0.09)	3.34	4.45 (0.15)	2.40	4.26 (0.03)	3.57
5.02 (0.34)	3.46	4.82 (0.32)	2.78	4.57 (0.07)	3.90
5.14 (0.08)	3.74	5.16 (0.20)	3.50	4.82 (0.38)	4.12
5.42 (0.14)	4.57	5.42 (0.15)	3.79	4.93 (0.41)	5.14
5.47 (0.00)	4.65	5.56 (0.16)	4.26	5.59 (0.08)	5.18
5.65 (0.23)	5.44	5.73 (0.09)	5.42	5.71 (0.10)	5.30
5.85 (0.41)	5.47	5.83 (0.51)	5.69	6.06 (0.38)	5.54

Table 3. π electron densities in the ground and excited states

molecule	state	(ev)	charge on atom C_7	charge on atom N	charge on atom O_{19}
A	S_0	0.	1.419	1.263	1.542
	S_1	2.81	1.148	1.244	1.609
	S_2	3.26	1.093	1.213	1.593
	T_1	1.51	1.405	1.310	1.613
	T_2	1.71	1.139	1.248	1.649
B	S_0	0.	1.179	1.613	1.502
	S_1	2.66	0.857	1.583	1.502
	S_2	3.17	0.859	1.518	1.589
	T_1	1.39	1.186	1.667	1.628
	T_2	1.50	0.854	1.541	1.540
C	S_0	0.	1.060	1.234	1.871
	S_1	2.64	0.967	1.221	1.900
	S_2	3.32	0.895	1.219	1.848
	T_1	0.20	0.922	1.240	1.886
	T_2	1.69	1.221	1.298	1.888



structure A



structure B

structure C

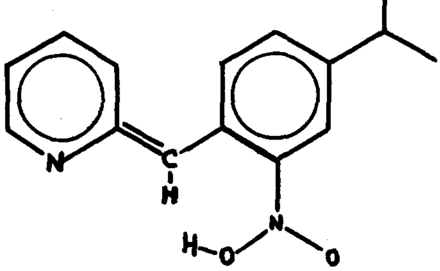


Fig. 1. Species A, B and C.

Perhaps the most significant finding is that a triplet state only 0.2 ev above the ground state is calculated for structure C. This would of course be a good way to distinguish B from C after the appropriate experiments are run.

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