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Theoretical Study of the Photochemical Isomerism of Oximes

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Photochemical syn-anti isomerism of oximes is approached by both semi-empirical and *ab initio* calculations. The geometry and the energy of different intermediate species are evaluated by optimization. The results agree with available experimental data.

A mechanism is proposed which involves the peculiar form of the energy surface in the triplet state.

Key words: Oximes – Photochemical isomerism

1. Introduction

In a previous paper [1] the syn-anti isomerism of the formaldoxime molecule was found to occur in the molecular plane with a high inversion barrier.

On the other hand several workers [2–9] presented experimental evidence for the fact that oxime inversion is easier under U.V. irradiation. This paper presents a study of the essential features of the energy surface of this state for formaldoxime and benzaldoxime molecules and a mechanism is proposed.

Table 1. First triplet state of formaldoxime (experimental geometry)

	Form I (Fig. 1)		Form II	
	Fundamental	First triplet state	Fundamental	First triplet state
Ab initio	- 168,330204	- 168,16111 (a) - 168,197649 (b)	- 168,16306	- 168,22842 (a) - 168,256436 (b)
C.N.D.O.	- 39,3322	- 39,04669 (a) - 39,0838 (c) - 39,0876 (d)	- 39,1668	- 39,1446 (a) - 39,1507 (c) - 39,19192 (d)

Energies in A. U.

[a] Virtual orbital method.
[b] Roothaan SCF theory.
[c] Interaction of twenty first monoexcited configurations.
[d] UHF theory.

2. Computational Details

Calculations were carried out according to the CNDO/2 scheme [12]. The geometry was optimized [1–13] in both first singlet and triplet states. The experimental geometry of the formaldoxime molecule [10] is used as a test point to compare the energy obtained by CNDO/2 calculation (IC method and UHF theory [12b]) and that obtained by the *ab initio* method [15] (Virtual Orbital and Roothaan theory [11]). For the last, the Gaussian basis set is that of Ref. [1]. Results are reported in Table 1 and show reasonable cohesion between relative stabilities.

3. Results and Discussion

3.1. Fundamental Singlet State of Benzaldoxime

Optimized geometries (Table 3) lead to very similar energy values (Table 4) for both the α and β planar forms, which is in agreement with experimentals results [5, 6]. An inversion about the nitrogen atom (41.5 kcal/mole) is much easier

Table 2. Optimized geometries of formaldoxime for first singlet and triplet states

ϕ	C-N Å	N-O Å	H_1-C-N degrees	H_2-$\hat{C}$-N degrees	C-$\hat{N}$-O degrees	E a.u.
90° triplet Form II	1,363	1,263	121,0	121,0	110,1	- 39,2728
0° triplet Form I	1,422	1,250	122,7	118,2	110,0	- 39,2200
0° fundamental (1)	1.286	1,275	123,6	120,3	115,3	- 39,39319

Table 3. Quasi optimized geometries of benzaldoxime

GROUP	Å and degrees
Phenyl (a)	C-C = 1,384 C-H = 1,117
Oxime (b)	(C-H) = 1,10 (C=N) = 1,286 (N-O) = 1,275 (H-C-N) = 121,0 (N-O-H) = 107,4
(c)	(C-C) (phenyl-oxime) = 1,453 (N-C-C) = 129,6

[a] Taken from Ref. [14].
[b] Previously obtained in formaldoxime case (1).
[c] Optimized.

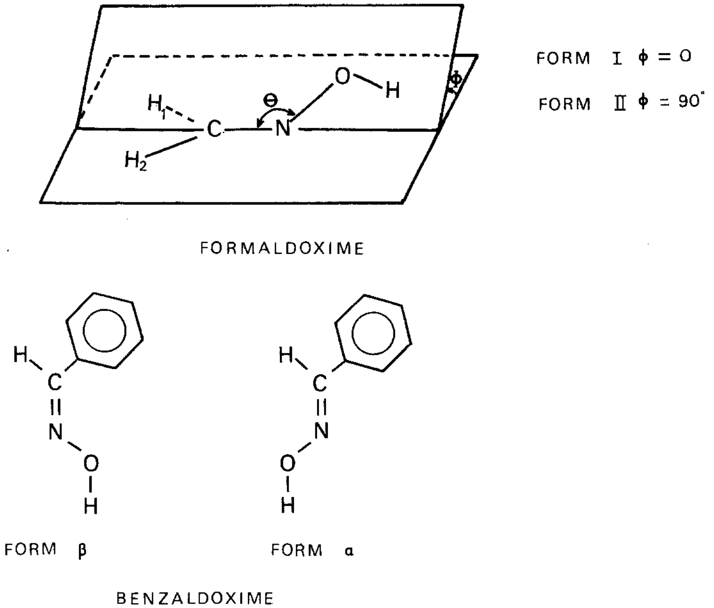

Fig. 1. Conformations and geometrical parameters

than an hypothetical rotation (~96 kcal/mole). These results are very similar to those for the formaldoxime molecule in spite of the phenyl group contribution: the inversion mechanism is controlled by the hybridization change at the nitrogen atom.

3.2. First Triplet State of Oxime and Benzaldoxime

For both molecules, the most stable conformation is obtained for $\Phi = 90°$ (form II, Fig. 1). No secondary minimum was found. Moving the OH group out of the plane lead to a biradical stable as suggested by the shortening of the CN bond (Table 2) and by Π spin density (e.g. C : 0.879; N : 0.633; O : 0.488 for the formaldoxime molecule).

The calculated (0, 0) transition energy of the benzaldoxime molecule (62.4 kcal/mole, Table 4) agrees with the photosensibilization determination (55–60 kcal/mole [2]).

The relative stability of both α and β isomers increases slightly in this triplet state.

4. Conclusion

These results show that substituents have little effect on the isomerism properties of the oximes.

The first triplet state can be obtained via the first excited singlet state or directly by photosensibilization [2–4]. After triplet relaxation leading the OH group out of the molecular plane, the singlet fundamental state cannot be reached

Table 4. Stationary point of singlet and triplet states of benzaldoxime

geometry (figure 1)		Energy of electronic state (a.u.)			
θ	ϕ	Singlet		Triplet	
115,2	0	- 85,10140	β form (minima)	- 84,96106	β form (saddle point)
244,8	0	- 85,10130	α form (minima)	- 84,95940	α form (saddle point)
180	0	- 85,03522	Inversion (saddle point)		
115,2	90	- 84,94522	Rotation	- 85,00090	Rotation (minima)

by vertical transition (Table 4). We suggest that the desactivation of the triplet state is obtained by a non-radiative process at the intersection of singlet and triplet surfaces. Therefore, the rotation of the OH group is the common feature of the beginning of the most probable paths toward one of the planar forms.

In the case of the benzaldoxime, the slight dissymmetry of the triplet surface favours the β form as experimentally observed ($\beta/\alpha = 1.6$ [2]). The very weak energy involved in the desactivation process may account for the short lifetime observed by several authors.

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