Tetrahedron Letters No.32, pp.3019-3022, 1971. Pergamon Press. Printed in Great Britain.

A CNDO CI STUDY OF THE ELECTRONIC SPECTRUM OF PHOTOCHROMIC 1,2-DIHYDRONAPHTALENE

B. Tinland and C. Décoret

Section de Recherches de Mécanique Ondulatoire Appliquée
Université de Lyon I . 69 VILLEURBANNE . France

(Received in UK 22 June 1971; accepted in UK for publication 7 July 1971)

Recently several authors[1,2,3] reported their results from the photolysis of 1,2-dihydronaphtalene (I). They proposed that (I), on absorption in its aromatic absorption band, undergoes a photochemical ring opening to the vinyl-o-quinodimethane (II) which isomerises to (III) and finally photocyclises to the benzobicyclohexene (IV) (see Fig. 1). In order to understand the mechanism of photochemical breaking of $C_1 - C_2$ sigma bond on $\pi \rightarrow \pi^*$ excitation, a theoretical knowledge of the electronic structure of 1,2-dihydronaphtalene in its ground and excited states appears of considerable interest. A convenient method for such a study was the all - valence - electrons CNDO CI procedure with the parametrization of Del Bene and Jaffé[4] which proved very successful for the prediction of excited states of organic molecules. Since the geometry of 1,2-dihydronaphtalene is not known, we postulated for the sake of simplicity an ideal naphtalene - like one in which the molecule is planar and both rings are regular hexagons with 1.4 Å bonds and 120 ° angles (see Fig. 2). We do believe that this approximation does not influence significantly the main features of the computed electronic spectrum and structure. A configuration interaction calculation was done over the 30 lowest monoexcited transitions.

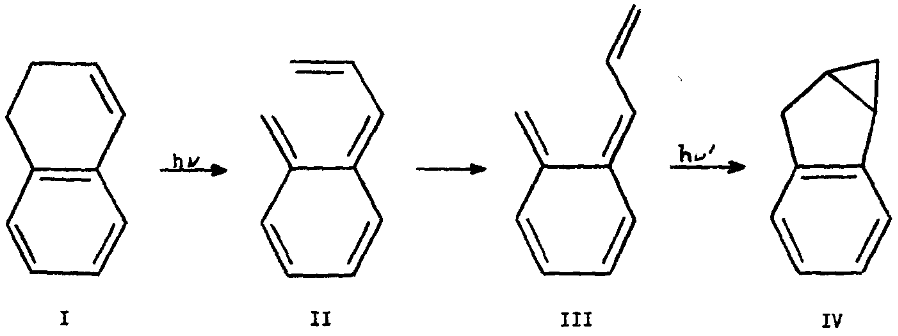

Fig. 1. Photoisomerisation process

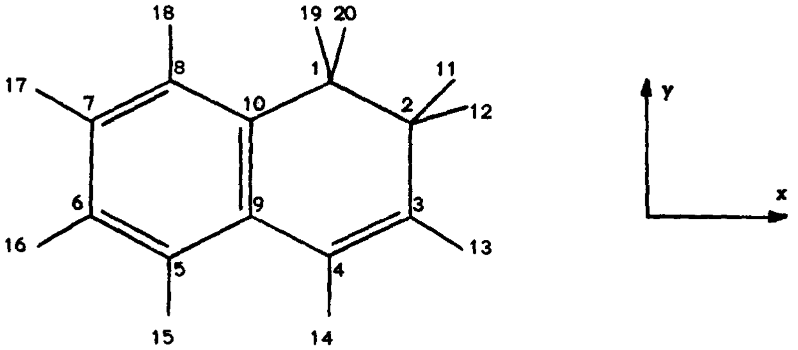

Fig. 2. Co-ordinate axes and numbering scheme

Table 1. Electronic transition energies (ev)

singlet energies	osc. strengths	polarization	type	triplet energies
3.96	0.15	x	$\pi \rightarrow \pi^*$	2.15
4.20	0.001	y	$\pi \rightarrow \pi^*$	3.52
5.33	0.11	x	$\pi \rightarrow \pi^*$	3.75
6.01	0.49	x	$\pi \rightarrow \pi^*$	3.88
6.11	0.0		$\sigma \rightarrow \pi^*$	4.38
6.39	0.19	y	$\pi \rightarrow \pi^*$	5.85

The computed singlet and triplet states are listed in Table 1. We may notice that the four lowest singlet transitions are of $\pi \rightarrow \pi^*$ character and that the first $\sigma \rightarrow \pi^*$ transition appears only at 6.11 ev. It is also apparent that four triplet states lie under the first excited singlet state, which may allow multiple possibilities of intersystem crossing.

The atomic charge densities in the ground and first excited singlet and triplet states are presented in Table 2. The corresponding π bond orders are listed in Table 3. Inspection of these results shows a transfer of 0.085 π electron from the atoms forming the $-CH_2-CH_2-$ group to the rest of the molecule as a result of $S_0 \rightarrow S_1$ excitation. Having lost this quantity of π electrons, these atoms subsequently attract some of the σ bonding electrons, thus weakening the σ bond joining them : $-H_2C \leftarrow\!\rightarrow CH_2-$.

Table 2. Atomic electron charge densities

state	densities	atom number																	
		1	2	3	4	5	6	7	8	9	10	11	13	14	15	16	17	18	19
S_o	π	0.984	0.978	0.964	1.072	1.002	1.023	0.995	1.051	1.010	0.954								
	$\sigma + \pi$	4.022	4.016	4.009	4.075	4.025	4.036	4.016	4.059	3.985	3.958	0.972	0.982	0.985	0.984	0.986	0.985	0.988	0.973
S_1	π	0.970	0.961	1.029	1.045	1.052	0.992	1.053	1.082	1.025	0.902								
	$\sigma + \pi$	4.003	3.996	4.071	4.044	4.073	4.004	4.074	4.088	3.996	3.902	0.961	0.982	0.984	0.983	0.985	0.984	0.987	0.961
T_1	π	0.970	0.963	1.035	1.055	1.038	0.991	1.057	1.067	1.031	0.908								
	$\sigma + \pi$	4.002	3.998	4.078	4.054	4.060	4.002	4.077	4.071	4.000	3.906	0.963	0.982	0.983	0.983	0.985	0.984	0.987	0.962

Table 3. π bond orders

state	1 - 2	2 - 3	3 - 4	4 - 9	5 - 9	5 - 6	6 - 7	7 - 8	8 - 10	1 - 10
S_o	0.061	0.174	0.922	0.327	0.632	0.673	0.660	0.666	0.660	0.149
S_1	0.079	0.209	0.574	0.580	0.440	0.722	0.536	0.574	0.678	0.189
T_1	0.077	0.205	0.595	0.559	0.451	0.694	0.547	0.573	0.654	0.186

At the same time the strong variation of the π bond orders of bonds C_3- C_4 and C_4- C_9 corresponds respectively to a marked lengthening and shortening of these bonds changing from strongly localized bonds to aromatic like ones. All these electronic and geometrical modifications strongly perturb the weakest bond in the molecule, i.e. the C_1- C_2 bond which can therefore more easily be broken than in the ground state.

REFERENCES

1 R.C. COOKSON, S.M. DE B. COSTA and J. HUDEC, Chem. Comm. (1969) 1272
2 H. KLEINHUIS, R.L.C. WIJTING and E. HAVINGA, Tetrahedron Letters n° 3 (1971) 255
3 K. SALISBURY, Tetrahedron Letters n° 10 (1971) 737
4 J. DEL BENE and H.H. JAFFE, J. Chem. Physics 48 (1968) 1807