CROATICA CHEMICA ACTA CCACAA **59** (3) 745—756 (1986)

CCA-1685

YU ISSN 0011 1643
UDC 541
Original Scientific Paper

Molecular Geometry and Electronic Structure of Heptalentropones and Heptalendiones*

Giuseppe Buemi and Felice Zuccarello

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6,
95125 Catania, Italy

Received February 3, 1986

The molecular geometries of 8-H-cycloheptatropone (I), 8-H-cycloheptatropolone (II), 2-methoxy-8-H-cycloheptatropone (III), heptalen-1,8-dione (IV), 7-methoxy-heptalen-1,8-dione (V), 9-methoxy-heptalen-1,8-dione (VI) were fully optimized at MINDO/3 level. Heptalen-2,3-dione was also taken into account. The electronic structures of the above molecules were studied by means of INDO/S method and the importance of doubly excited configurations was tested at CNDO/S level.

In all compounds a remarkable »single« and »double« bond alternation was found. Hydroxy and methoxy substitution affects the geometry of the ring where the substitution occurs whilst the unsubstituted ring undergoes minor or negligible changes.

The electronic transitions agree well enough with the experimentally available absorption maxima; a strong transition is predicted in the neighborood of 200 nm. Several of these transitions can be correlated with those of tropone and tropolone: on the whole they are not, or negligibly, affected by double excitations except those lying in the range of 5 eV and the ones at 4.29 eV and 4.82 eV of heptalen-2,3-dione.

INTRODUCTION

Heptalentropones and heptalendiones can be considered as either derived from heptalene (since they mantain the same C atoms skeleton but one or two H atom(s) are replaced by one or two oxygen(s)) or derived from two tropone (or one tropone and one cycloheptatriene) molecules variously condensed with each other. Their study is, therefore, very important because the increased π-system size could produce interesting changes or evidence analogies with the electronic structures of the component parent compounds, also in connection with the electronic transitions. Indeed, in a previous paper on heptalen-3,8-dione and its dimethyl and 2-methoxyderivatives[1] we pointed out that several electronic transitions can be correlated with those of tropone and tropolone and also with those of heptalene[2]; moreover, a correlation between some MOs of these molecules is possible. The title compounds are generally not known as free molecules, but several hydroxy and methoxy

---

* Paper presented at the International Symposium on Applications of Mathematical Concepts to Chemistry held in Dubrovnik, Croatia, September 2—5 1985.

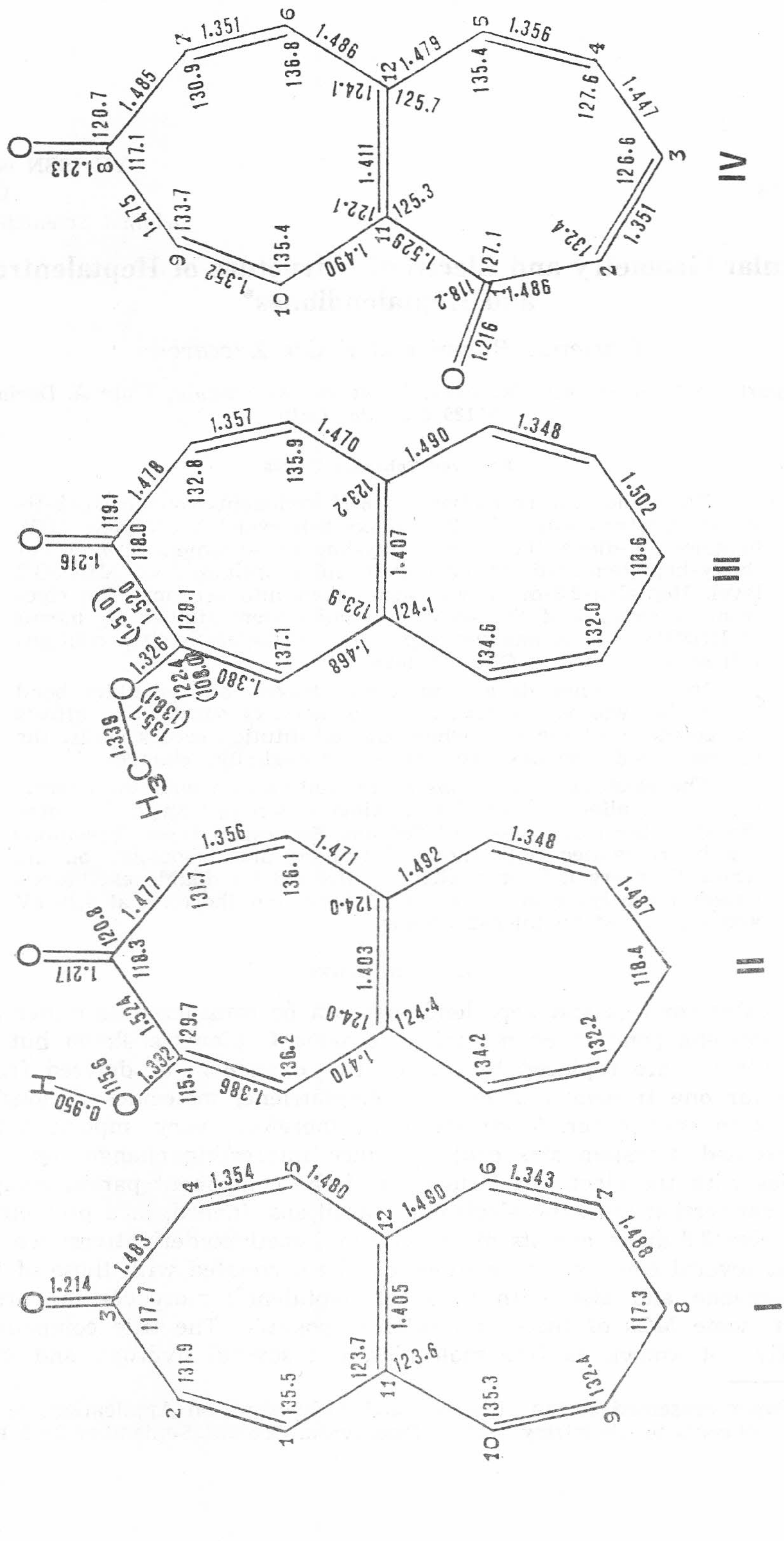

Figure 1. to be continued

Figure 1. continued

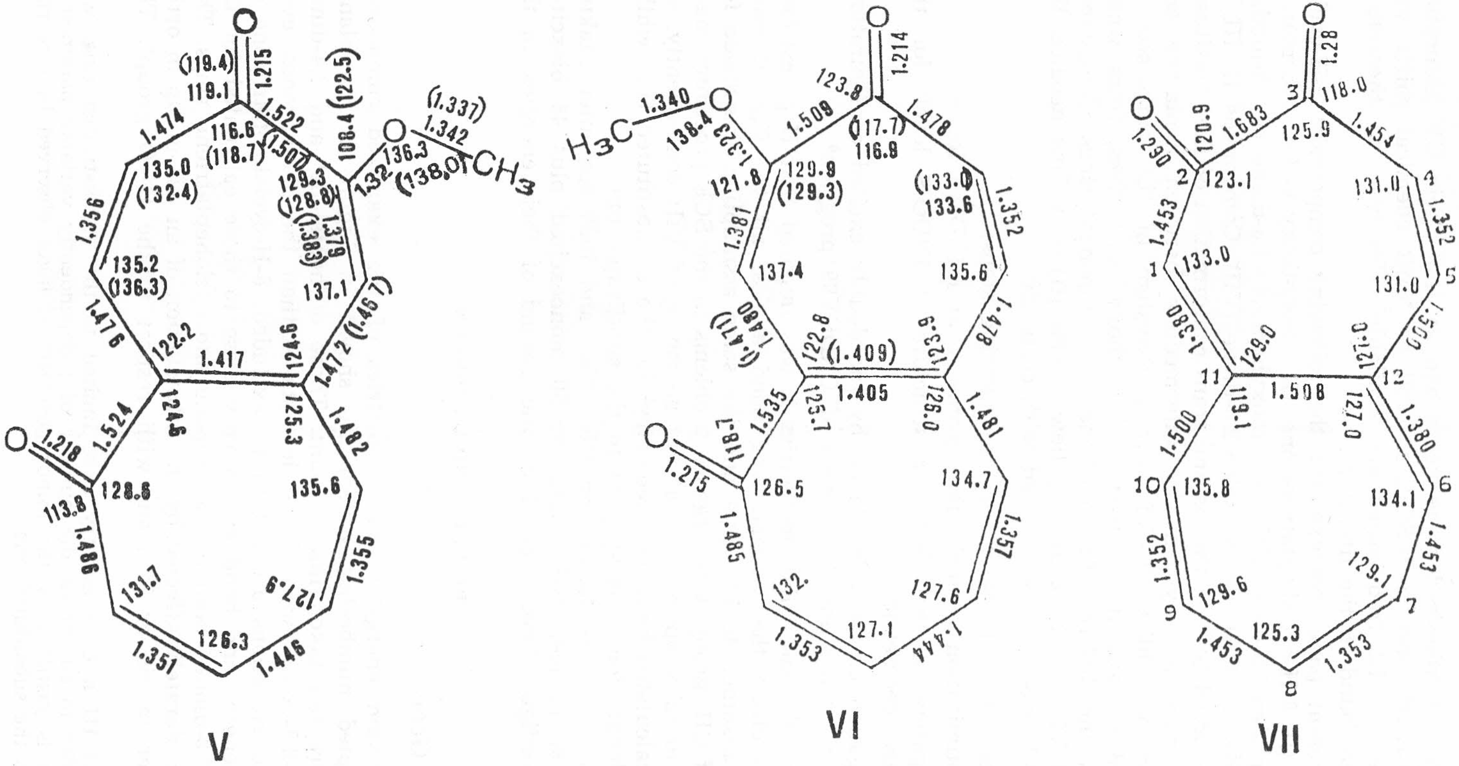

Figure 1. Geometries of the studied compounds. All structures come from the full optimization procedure at MINDO/3 level except the one of VII (see Text). Values in parentheses refer to the cis isomer. Only the most important changes are shown. I. 8-H-cycloheptatropone; II. 8-H-cycloheptatropolone; III. 2-methoxycycloheptatropone; IV. Heptalen-1,8-dione; V. 7-methoxyheptalen-1,8-dione; VI. 9-methoxyheptalen-1,8-dione; VII. Heptalen-2,3-dione. The calculated C—H bond lengths, in all compounds, range from 1.111 to 1.113 Å. The H—C—H bond angles of methyl group are 113.3°. In I, II and III, $r_{\mathrm{C-H}}$ for hydrogens bonded to C_8 is 1.115 Å, H—C—C angle is 107.1° and the torsion angle $w_{\mathrm{H-C_8-C_7-C_6}}$ is 121.2° (all these are optimized values, too).

derivatives were synthesized some years ago so that their UV absorption maxima (in CH_3OH and in H_2SO_4), as well as NMR chemical shifts, and some characteristic IR frequencies are available[3]. However, no theoretical study has been found in the literature.

In the present paper we examine the following compounds: 8-H-cycloheptatropone (I) 8-H-cycloheptatropolone (II), 2-methoxy-8-H-cycloheptatropone (III), heptalen-1,8-dione (IV), 7-methoxyheptalen-1,8-dione (V), 9-methoxyheptalen-1,8-dione (VI) and heptalen-2,3-dione (VII). Compounds II, III, V and VI were studied both in the cis and trans conformation of the substituent group. I—III have a π-system size intermediate between heptalene and heptalene-3,8-dione whilst IV—VI have a π-system of the same size of heptalene-3,8-dione and its hydroxy and methoxy derivatives, from which they differ by the different fusion of the two component rings. Compounds II, III, V and VI were isolated as yellow prisms (II) or yellow needles, the existence of VII has not been proved with certainty.

The present study is based on the following steps:

a) full optimization of molecular geometry at MINDO/3 level[4]:

b) investigation of the electronic structure at INDO/S level[5] for the above optimized geometries;

c) investigation of the role played by the doubly excited configurations on the electronic transitions by means of CNDUV99 program[6].

In defining the molecular geometries it was imposed that H atoms (and O atom in I) bisect the internal ring bond angles; all the C_{sp^2}—H bond lengths were assumed to be equal and the same assumption was made for the C_{sp^3}—H of CH_3 group. Convergence problems in the SCF procedure made it impossible to fully optimize whatever geometry of VII; consequently, we imposed the calculated heptalene geometry[2] for the unsubstituted ring whilst that of tropolonate ion[7] was adapted to the substituted one.

Calculations were performed on CDC 6600 and 7600 computers, taking into account 80 monoexcited (INDO) or 50 monoexcited plus 45 biexcited (CNDUV99) configurations, selected on the ground of their energies, in the CI procedure.

RESULTS AND DISCUSSION

i) Molecular Geometry

The minimum energy planar geometries of the examined compounds and the adopted numbering system are shown in Figure 1. Non-planar structures were not taken into account. Those of heptalene[1] and 2,4-dimethylheptalene-3,8-dione[1] were found less stable than the planar ones, even if out-of-plane vibrations are not to be excluded. 8-H-cycloheptatropone (I) shows bond lengths and bond angles very close to those calculated for the D_{2h} heptalen-3,8-dione[1], both in the tropone and cycloheptatriene rings. This geometry is moderately affected by the introduction of an OH group in ortho position, either in cis or in trans with respect to the C=O group*. The

---

* In I and III a C_2 symmetry axis, limited to the unsubstituted ring, was imposed in order to cut down the number of independently variable parameters. This limitation is justified by the minor geometry changes observed in this ring with respect to the substituted one.

greatest variation is noted in the bond length joining OH and C=O groups (longer than in I, as found also in tropolone[1]) and in the consequent moderate rearrangement of the bond angles at C_1, C_2 and C_3. Both in cis and trans conformers, the OH group lies coplanar to the C atoms skeleton and the two structures appear to be practically isoenergetic. However, we are aware that MINDO/3 generally underestimates hydrogen bonding and that spectroscopic analyses[8,9] of the near UV spectrum of the parent molecule tropolone indicated the cis isomer as the most stable. Then we think that also the cis form of II is more stable than the trans one. The rotation barrier (0—90°) was calculated to be 2.44 kcal/mol, a value not significantly different from the OH barrier in phenol coming from IR spectra (3.26 kcal/mol[10]). Substitution of OH with OCH_3 group causes principally a large widening of $H_3C—O—C_2$ and $O—C_2—C_1$ bond angles, as a consequence of the increased steric effect. The largest changes in the rings occur in the bond angles at C_1 and C_4 (larger than in II) and in the $C_7—C_8$ bond length (longer than in II). The trans isomer was found 1.54 kcal/mol more stable than the cis one.

In heptalen-1,8-dione, IV, where the fusion of the two component tropone systems occurs along the basis of a ring and the $C_2—C_3$ side of the other, appreciable geometry changes, mainly in the latter ring, can be observed. In particular, the internal bond angle at C_1 is about 10 degrees larger than the bond angle at C_8 and about 7 degrees larger than the corresponding angle of tropone[1]; moreover, the $C_1—C_{11}$ bond is the longest one and its length is comparable with that of an isolated »single« bond. As noted for I, also in IV the introduction of OCH_3 group in ortho position to C=O of the upper ring causes (isomers V and VI) a lengthening of the bond joining these two groups and a remarkable widening of $H_3C—O—C$ and O—C—C angles. It is interesting to note that methoxy substitution modifies the geometry of the upper ring of IV, making it very similar to that of the corresponding ring of III. When the methoxy group is bonded in position 7 (V), the $H_3C—O—C$ angle is ~ 2 degrees lower than in VI and the internal ring bond angle at the substituted C atoms (C_7 in V, C_9 in VI) is lower than in the unsubstituted parent dione IV.

Both in V and VI the trans form is more stable than the cis one by about 1.5 kcal/mol (i. e. the same ΔE found for the same isomer of III) and in any case the 7-methoxy is more stable than the 9-methoxyderivative ($\Delta E_{7cis—9cis}$ is 1.64 kcal/mol; $\Delta E_{7trans—9trans}$ is 2.04 kcal/mol). From analysis of single energy contributions one can deduce that in V there is a lower repulsion than in VI. In V the variation in energy accompanying the OCH_3 rotation was calculated with full optimization of all the independently variable geometrical parameters. It was found that the energy profile suggests the possibility of a quasi-complete free rotation, showing a narrow (about 60°) barrier of about 2.6 kcal/mol with a saddle point at 0° (cis form).

In all I—VI compounds the internal central double bond lies in the range 1.40—1.42 Å, i. e. it is nearly equal to the analogous bond of naphthalene (1.412 Å)[11]. Thus, in these molecules the strain energy would not be remarkable. Finally, it is important to point out that the bonds are strongly localized and the remarkable »single« and »double« bond lengths alternation predicted by calculations resembles that of the antiaromatic[12] heptalene and of heptalen-3,8-dione.

ii) Dipole Moments

The dipole moments of the title compounds, calculated at MINDO/3 level, are collected in Table I. Experimental data are not known except for those concerning the monocyclic parent compounds tropone ($\mu = 4.30$ D[13]) and ortho-methoxytropone ($\mu = 4.72$ D[14])). Our theoretical values for I and for the trans conformer of III are of the same order, which would mean that the unsubstituted ring system scarcely contributes to the total moment and that the equilibrium between cis and trans forms of III is expected to be displaced towards the latter isomer, as also suggested by the relative energies.

TABLE I

Dipole Moments (Debyes) of the Studied Compounds[a] as Obtained by MINDO/3 Method

Compound		μ_x	μ_y	μ_{tot}
I		—	—4.990 (—0.665)	4.990
II	cis	0.542 (0.276)	—3.071 (0.071)	3.119
	trans	—0.897 (—0.519)	—5.186 (—1.030)	5.263
III	cis	—0.136 (0.147)	—3.295 (—0.231)	3.297
	trans	—0.919 (—0.320)	—4.392 (—0.874)	4.487
IV		3.898 (0.764)	—5.113 (—0.760)	6.429
V[b]	cis	4.257 (0.630)	—3.278 (—0.346)	5.373
	trans	4.926 (1.065)	—4.491 (—0.988)	6.666
VI	cis	3.788 (0.935)	—3.184 (—0.272)	4.949
	trans	3.042 (0.476)	—4.292 (—0.907)	5.261

[a] Values in parentheses are the s-p polarization contributions.

[b] In the conformation having OCH_3 rotated by 90° the calculated dipole moment is 6.083 D ($\mu_x = 3.974$; $\mu_y = -4.507$; $\mu_z = 0.947$).

On the whole, the data in Table I indicate that the examined molecules are highly polar, the main contribution being the one coming from charge densities. Only in II and III the s-p polarization contribution along the short molecular axis is comparable with the charge density dipole value. Obviously, the greatest contributions are given by the oxygens and by the C atoms bonded to them, where charge densities ranging from $0.2 \div 0.35$ (C atoms) to $-0.4 \div -0.5$ (oxygens) are found.

iii) Electronic Spectra

In the literature only the UV absorption maxima of II, III, V, and VI are reported.[3] They are compared with the theoretically obtained electronic transitions in Tables II—III. From the data in Table II it can be seen that the lowest energy electronic transition of I is $n \rightarrow \pi^*$ in nature and it is followed by a practically degenerate $\pi \rightarrow \pi^*$ (HOMO → LUMO) transition which undergoes a red shift by introducing an OH (II) or OCH_3 (III) group in position 2. The $n \rightarrow \pi^*$ transition lies in the same energy range (3.2 3.3 eV) as found in tropone, tropolone, heptalen-3,8-dione and its 2-methoxy-derivative[1], as well as in the other diones studied: i. e., it appears to be independent of the position of the C=O groups in the molecule, although the characteristics of the involved n-orbital(s) are not the same on passing from one compound to another*. The $\pi_1 \rightarrow \pi_1^*$ transition implies promotion of an electron from a molecular orbital spanning on the whole molecule to another having a nodal plane along the C=O bond. The lowest energy absorption spectra of both II and III are characterized by a band centered at 3.56 eV and a shoulder at about 3.2 eV; they originate from the above discussed transitions.

The band centered at 4.3 eV originates from the HOMO → NLUMO transition (NLUMO is the Next to the Lowest Unoccupied Molecular Orbital), predicted at 4.11 eV in I and at 3.85 eV in II and III; it is polarized along the y axis (coincident with the C_2 symmetry axis of I). Once again, this transition was found in heptalen-3,8-dione, in tropone and in tropolone.[1] It is to be noted that the HOMO, LUMO and NLUMO, involved in the transitions analysed so far, are scarcely affected by ortho-hydroxy or ortho-methoxy substitution.

In the energy range 4.7—5.7 eV four $\pi \rightarrow \pi^*$ transitions are calculated. Two of them, both involving NHOMO, are very weak and x-polarized in I but become strong in II and III where they modify remarkably their polarization and appear directed almost along the long molecular axis owing to modifications in NHOMO (π_2) due to substitution (in fact the greatest coefficients of these orbitals are now located on the substituted molecular side (C_9—C_{10}—C_{11}—C_1—C_2OCH_3 fragment)) and the energy is increased with respect to the corresponding orbital of the unsubstituted cycloheptatropone I. A similar trend was observed in the transition involving π_2 and π_3 orbitals of heptalen-3,8-dione and 2-methoxy-heptalen-3,8-dione.[1]

---

* In IV—VII one can distinguish two n-orbitals originating mainly from the negative (n_-) and positive (n_+) combination of the n orbitals of each carbonyl oxygen atoms, even if this combination appears to be poorer in VI.

TABLE II

Electronic Transitions of 8-Cycloheptatropone (I), 8-H-cycloheptatropolone (II) and 2-Methoxy-8-H-Cycloheptatropone (III) Energies in eV.

I				II			III				Experimental[c]	
ΔE	Sym.	f	Pol.[a]	ΔE	f	Pol.[a]	ΔE	f	Pol.[a]	Nature[b]	E	log ε
3.29	$^1A_2$	0	—	3.37	0	—	3.30	0	—	$n \rightarrow \pi_2^*$	$(3.16\ 3.24)_{sh}$	(3.68 3.78)
3.30	$^1B_1$	0.22	x	3.19	0.25	x	3.16	0.26	—1	$\pi_1 \rightarrow \pi_1^*$	3.56	3.96 4.01
4.11	$^1A_1$	0.35	y	3.85	0.27	—87	3.85	0.25	—87	$\pi_1 \rightarrow \pi_2^*$	4.29 4.27	4.43 4.41
4.53	$^1B_2$	$5 \cdot 10^{-3}$	z	4.66	$4 \cdot 10^{-3}$	z	4.49	$4 \cdot 10^{-3}$	z	$n \rightarrow \pi_1^*$		
4.95	$^1B_1$	0.03	x	4.73	0.35	—73	4.68	0.37	—72	$\pi_2 \rightarrow \pi_1^*$	4.96	4.35 4.39
5.21	$^1B_1$	$2 \cdot 10^{-3}$	x	4.96	0.23	85	4.92	0.23	85	$\pi_1 \rightarrow \pi_3^*$		
5.25	$^1A_1$	0.26	y	5.21	0.07	78	5.18	0.06	81	$\pi_1 \rightarrow \pi_4^*$	$(5.06\ 5.32)_{sh}$	4.30 4.12
5.71	$^1A_1$	1.41	y	5.55	1.18	77	5.49	1.26	—89	$\pi_3 \rightarrow \pi_1^*$		

[a] Angle between transition moment vector and x axis. [b] Only the dominating configuration is reported. [c] Ref. 3, the first figure refers to II, the second to III.

TABLE III

Electronic Transitions (Energies in eV) of Compounds IV—VII.

IV				V			Experimental[c]		VI				Experimental[c]		VII			
ΔE	f	Pol.[a]	Nature[b]	ΔE	f	Pol.[a]	E	log. ε	ΔE	f	Pol.[a]	Nature[b]	E	log. ε	ΔE	f	Pol.[a]	Nature[b]
3.14	$7\cdot 10^{-6}$	z	$n\rightarrow\pi^*$	3.13	~ 0	z			3.15	~ 0	z	$n\rightarrow\pi^*$			2.57	10^{-6}	—	$n\rightarrow\pi^*$
3.27	~ 0	—	$n\rightarrow\pi^*$	3.30	~ 0	z			3.28	~ 0	z	$n'\rightarrow\pi^*$	3.01_{sh}	3.73	2.94	0.25	75	$\pi_1\rightarrow\pi_1^*$
3.72	0.31	—62	$\pi_1\rightarrow\pi_1^*$	3.57	0.22	—46	3.54_{sh}	3.66	3.46	0.35	—49	$\pi_1\rightarrow\pi_1^*$	3.31	4.03	3.15	10^{-6}	—	$n\rightarrow\pi^*$
4.12	0.19	42	$\pi_1\rightarrow\pi_2^*$	3.96	0.06	13			3.81	0.36	58	$\pi_1\rightarrow\pi_2^*$	3.93_{sh}	3.85	3.50	0.55	—53	$\pi_1\rightarrow\pi_1^*$
4.29	$3\cdot 10^{-5}$	z	$n_-\rightarrow\pi_1^*$	4.33	10^{-4}	z			4.36	0.18	—78	$\pi_1\rightarrow\pi_3^*$	4.38	4.10	4.29	0.05	—83	$\pi_1\rightarrow\pi_3^*$
4.63	$8\cdot 10^{-3}$	z	$n_+\rightarrow\pi_1^*$	4.48	$5\cdot 10^{-3}$	z			4.43	10^{-3}	z	$n\rightarrow\pi_1^*$			4.82	0.49	—68	$\pi_2\rightarrow\pi_1^*$
4.65	0.40	67	$\pi_2\rightarrow\pi_1^*$	4.38	0.98	57	4.13	4.21	4.62	$7\cdot 10^{-3}$	z	$n'\rightarrow\pi_1^*$			5.15	$3\cdot 10^{4}$	z	$n\rightarrow\pi^*$
4.81	0.26	18	$\pi_1\rightarrow\pi_3^*$	4.56	0.20	—81	4.80_{sh}	4.08	4.72	0.23	28	$\pi_2\rightarrow\pi_1^*$			5.17	0.04	—84	$\pi_1\rightarrow\pi_4^*$
5.58	0.23	—32	$\pi_2\rightarrow\pi_2^*$	5.15	0.26	—27	4.94	4.14	5.40	0.13	58	$\pi_1\rightarrow\pi_4^*$	4.80	4.39	5.39	$7\cdot 10^{-4}$	z	$\pi_1\rightarrow\sigma^*$
5.78	0.04	x	$\pi_1\rightarrow\pi_4^*$	5.56	0.12	7			5.51	0.65	—61	$\pi_2\rightarrow\pi_2^*$			5.50	$4\cdot 10^{-4}$	z	$n\rightarrow\pi^*$
5.88	0.73	—74	$\pi_3\rightarrow\pi_1^*$	5.79	0.78	—70			5.56	0.15	32	$\pi_1\rightarrow\pi_4^*$			5.54	1.25	—82	$\pi_2\rightarrow\pi_2^*$

[a] Angle between the transition moment vector and x axis. [b] Only the dominating configuration is reported. [c] Ref. 3.

The other two transitions (both y-polarized) were calculated at 5.25 eV and 5.71 eV in I. In II and III they undergo a red shift (the former less than the latter) and an oscillator strength weakening with respect to the parent compound; in any case the latter remains the strongest whilst the former becomes very feeble. The first three of these transitions would be responsible for the absorption band observed at 4.96 eV in II and III and the shoulders at 5.06 eV in II and at 5.32 eV in III. Unfortunately, the shape of the experimental spectrum up to 200 nm is not available, so that we cannot discuss the assignment of the neighbouring very strong transition calculated in the range of 5.5 eV. An INDO/S calculation carried out on the trans form of II gave practically the same results as those reported for the cis one.

As it can be seen from data collected in Table III, two feeble $n \rightarrow \pi^*$ transitions are predicted for IV, V and VI on the borderline of UV and the visible region. HOMO → LUMO and HOMO → NLUMO, $\pi \rightarrow \pi^*$ transitions are calculated at 3.72 eV and 4.12 eV in heptalene-1,8-dione. The former lies at a higher energy than in 8-H-cycloheptatropone owing to the increased stability of HOMO (—7.88 eV in I, —8.56 eV in IV), while the latter is practically unchanged; both energies are nearly equal to those of the corresponding transitions of heptalen-3,8-dione.[1] A red shift of 0.15 eV and a lowering of the oscillator strength are predicted for the first $\pi \rightarrow \pi^*$ transition as a consequence of methoxysubstitution in position 7 (V); a larger red shift occurs when substitution is made in position 9 (VI). HOMO→NLUMO transition appears to be red shifted and weakened also in V; in VI it is even more red shifted and enhanced in intensity because NLUMO involves a charge transfer from the methoxy oxygen atom.

The two transitions calculated at 4.65 eV and at 4.81 eV in IV imply electron promotion from HOMO to the orbital next to NLUMO (π_3^*) and from NHOMO (π_2) to LUMO. The latter configuration is the most important in the former transition and vice versa. Both of these transitions shift towards lower energies in V. The strong intensity of the former transition is once again due to charge transfer from the methoxy oxygen atom. On the whole, the present results agree acceptably with experimental data.

Different from previous diones, the two $n \rightarrow \pi^*$ transitions of heptalen-2,3-dione (VII) are separated by 0.5 eV, with the HOMO → LUMO, $\pi \rightarrow \pi^*$, transition lying in the middle. This large ΔE is principally due to the stabilization of n_+ orbital, the energy of which is about 1 eV lower than in IV—VI. The HOMO → LUMO transition (2.94 eV) is red shifted by 0.22 eV and 0.36 eV in comparison with the one of III and I, respectively, thus suggesting an increased conjugation. We think it is interesting to compare the behaviour of $\pi_1 \rightarrow \pi_1^*$ transition and the involved MOs in the various compounds studied here and in the parent monocyclic tropone. From the data in Table IV it can be noted that HOMO undergoes destabilization whilst LUMO becomes more stable on going from tropone to heptalen-3,8-dione and heptalene-1,8-dione and, above all, to 8-H-cycloheptatropone I and heptalen-2,3-dione, VII. This trend causes a red shift of the HOMO → LUMO transition, which is maximal in I and VII. It is noteworthy that, notwithstanding the greater extension of the π-system, heptalen-3,8-dione and heptalen-1,8-dione, where two C=O groups are present, seem to be less conjugated

TABLE IV

Energies (in eV) of HOMO, LUMO and HOMO → LUMO Transition in the Parent Molecules and in the Corresponding Methoxyderivatives

	E_{π_1}	E_{π_1*}	$E_{\pi_1 \to \pi_1*}$	f	$E'^{a}_{\pi_1 \to \pi_1*}$	f
Tropone	—8.77	—1.38	4.31	0.19	3.86[b]	0.20[b]
Heptalen-3,8-dione	—8.61	—2.19	3.74	0.27	3.45	0.28
Heptalen-1,8-dione	—8.56	—2.08	3.72	0.31	3.57(V) 3.46(VI)	0.22 0.35
8-H-Cycloheptatropone	—7.88	—1.77	3.30	0.22	3.16	0.26
Heptalen-2,3-dione	—8.04	—2.28	2.94	0.25	—	—

[a] This column refers to the methoxyderivatives. [b] Value of tropolone.

than 8-H-cycloheptatropone. The OCH_3 group also produces a red shift of the same transition caused mainly by its inductive effect. Also the $\pi_1 \to \pi_2^*$ and subsequent $\pi \to \pi^*$ transitions of VII are red shifted but a comparison with those of the previous compounds is not straightforward, firstly because the dominating configurations in the higher energy transitions change in nature and percentage, secondly because the molecular geometry of VII is approximate. Unfortunately, experimental information on this molecule is much more scarce than for I—IV.

CNDO/S calculations with inclusion of doubly excited configurations were carried out in order to test the importance of double excitations on the electronic spectrum. The obtained transitions are practically coincident with those of INDO/S apart from the $n \to \pi^*$ ones, which are predicted at higher energies. Moderate doubly excited configuration contributions, involving mainly HOMO and LUMO, are found only in some transitions lying at energies near or higher than 5 eV. Only in the I a transition essentially originating from $V_{\mathrm{HOMO,\,HOMO}}^{\mathrm{LUMO,\,LUMO}}$ (70%) the configuration is calculated at 4.66 eV. In II it disappears and the only transition strongly affected by the above double excitation (47%) is predicted at 4.83 eV. Also in VII the transitions containing appreciable doubly excited configuration percentage lie at 4.29 eV and 4.82 eV.

CONCLUSION

By comparing the optimized geometries of I—VI it can be observed that the main geometrical changes due to hydroxy and methoxy substitution take place in the neighbourohod of the substituting group whilst the remaining molecular fragment is much less affected. Anyway, the strong »single« and »double« bond length alternation indicates a small conjugation.

As far as the electronic transitions are concerned, theoretical results on the whole match sufficiently well the available experimental absorption maxima. On the ground of the calculated energy of HOMO → LUMO transitions in the various compounds, the π-system conjugation increases on going from heptalene-1,8-dione to 8-H-cycloheptatropone and heptalene-2,3-dione. In the methoxyderivatives the electronic transitions calculated for the cis isomers do not differ appreciably from those of the more stable trans isomers; slightly more significant changes occur in some oscillator strengths. Inclusion of double excited configurations does not modify appreciably the $\pi \longrightarrow \pi^*$ transition energies; moderate percentages of double excitations are present in few transitions lying generally near 5 eV or higher energies.

Since the calculated spectra refer to the gas phase and the available experimental maxima were taken in CH_3OH it would be interesting to test the importance of the environment effect taking into account both static and dynamic polarization properties, as well as dispersion forces, which have shown to play an important role in the electronic transition shifts.[15] For this purpose, however, new experimental measurements, possibly in different solvents, and a knowledge of the shape of the entire absorption curves (yet not available) are desirable.

Acknowledgment. — Financial support by the Italian Ministero della Pubblica Istruzione is acknowledged.

REFERENCES

1. G Bumemi and F. Zuccarello, *J. Mol. Struct. Theochem*, **137** (1986) 55.
2. G. Buemi and F. Zuccarello, *Gazz. Chim. It.*, **115** (1985) 103.
3. S. Kuroda and T. Asao, *Tetrahedron Lett.*, (1977) 285 and 289.
4. a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.* **97** (1975) 1285.
   b) Q. C. P. E. Program nr. 279.
5. V. Galasso and G. Pappalardo, *J. Chem. Soc. Perkin Trans.* **2** (1976) 574.
6. H. Baumann, (CNDUV99), Q. C. P. E. Program nr. 333 (1977).
7. *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Special Publication nr. 18; The Chemical Society, London, 1965.
8. A. C. P. Alves and J. M. Hollas, *Mol. Phys.* **23** (1973) 927.
9. A. C. P. Alves and J. M. Hollas, *Mol. Phys.* **25** (1973) 1305.
10. G. Allen and S. Fewster in *Internal Rotation in Molecules;* W. J. Orville-Thomas Ed., J. Wiley and Sons, London, 1974, pag. 275.
11. S. N. Ketkar and M. Fink, *J. Mol. Struct.* **77** (1981) 139.
12. M. Randić, *J. Am. Chem. Soc.* **99** (1977) 444.
13. A. L. McClellan, *Tables of Experimental Dipole Moments*, Rahara Enterprises, El Cerrito, 1974.
14. Y. Kurita, S. Seto, T. Nozoe, and M. Kubo, *Bull. Chem. Soc. Jpn.* **26** (1953) 272.
15. F. Zuccarello, G. Buemi, and A. Raudino, *J. Chem. Soc. Faraday Trans. II*, **82** (1986), in press.

SAŽETAK

Molekularna geometrija i elektronska struktura heptalentropona i heptalendiona

G. Buemi and F. Zuccarello

Određene su geometrije nekih heptalentropona i heptalendiona s pomoću semiempirijske MINDO/3 metode. Elektronska struktura je razmatrana primjenom INDO/S i CNDO/S metoda, pri čemu je ova posljednja korištena u svrhu ocjene važnosti dvostruko-pobuđenih konfiguracija. Osnovna karakeristika izračunanih geometrija je alternacija jednostrukih i dvostrukih veza. Ocjenjeni elektronski prijelazi nalaze se u dobrom slaganju s raspoloživim eksperimentalnim podacima. Dvostruko eksitirane konfiguracije igraju značajniju ulogu samo kod heptalen-2,3-diona.