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SCF MO Calculations of Tropone, Tropolone and Related Compounds

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The variable-β procedure of the semiempirical SCF MO method was applied to tropone, tropolone and related compounds. Although the bond alternation in the heptagonal ring is neglected in the initial molecular geometry, the predicted transition energies show a good agreement with experiment, indicating the utility of this method for the calculation of the electronic spectra of non-benzenoid aromatic compounds. Discussions are given on the assignments of the absorption bands of tropone and tropolone.

Die Methode der variablen β wurde auf Tropon, Tropolon und verwandte Verbindungen angewandt. Obwohl die Bindungsalternierung in Siebenerringen in der für die Rechnung benutzten molekularen Geometrie vernachlässigt worden ist, zeigen die vorausgesagten Anregungsenergien gute Übereinstimmung mit dem Experiment, womit die Nützlichkeit der Methode für nicht-benzolartige aromatische Verbindungen demonstriert worden ist. Über die Zuordnung von Absorptionsbanden in Tropon und Tropolon wird diskutiert.

La méthode SCF MO semi-empirique à β variable a été appliquée à la tropone, la tropolone et des composés apparentés. Quoique l'alternance des liaisons du cycle heptagonal soit négligée dans la géométrie moléculaire initiale, les énergies de transition prévues sont en bon accord avec l'expérience, montrant ainsi l'utilité de cette méthode pour le calcul du spectre électronique des composés aromatiques non benzéniques. On discute les attributions des bandes d'absorption de la tropone et de la tropolone.

Introduction

A "variable β" procedure of semiempirical SCF MO method within the Pariser-Parr-Pople formalism has been developed by NISHIMOTO and FORSTER [*18*, *19*], who have applied this method with success on the calculation of electronic spectra of aromatic hydrocarbons and their derivatives. For the variable-β calculation, it is not required to specify a precise molecular geometry. We need not assume the alternation of bond distance, even if the molecule is known to have a considerable bond alternation as is in the case of polyenes. In effect FORSTER [*4*] has recently shown that the calculation by this method gives satisfactory results for the transition energies of polyenes.

Nonbenzenoid aromatic compounds are considered to possess an alternation of bond distance within their rings. It has been pointed out that this effect should be taken into account in the theoretical calculation of their electronic states [*17*]. Thus it seems particularly interesting to examine if the variable-β procedure can be successfully applied to the calculation of electronic spectra of nonbenzenoid aromatic compounds without introducing the assumption of bond alternation in the initially assumed molecular geometry.

In the present paper we have calculated by this method the electronic structures of tropone, heptafulvene, troponeimine, tropolone, 3-hydroxytropone and 4-hydroxytropone.

Method

According to the electron diffraction studies [*11*, *12*, *13*], both tropone and tropolone have a regular heptagon, in which the distance of C–C bond is 1.41 and 1.39 Å for tropone and tropolone respectively. The possibility of slight alternation of C–C bond distance, however, has not been ruled out. The observed distance of C=O bond is 1.26 Å for both tropone and tropolone, and that of C–OH bond of tropolone is 1.34 Å. The determination of molecular structure has not been done for the other compounds studied in the present paper. Since it is not necessary for the calculation by the variable-β procedure to specify a precise molecular geometry, we assumed as follows: (i) the molecules always have a regular heptagon with the C–C bond distance of 1.395 Å; (ii) the length of C=O, C=N and C–OH bonds are 1.23, 1.35 and 1.36 Å respectively. The atoms are numbered as shown in Fig. 1. The oxygen atom of hydroxyl group in hydroxytropones was always numbered as 9.

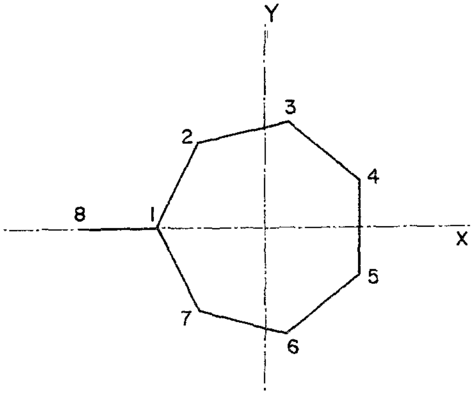

Fig. 1

We used the values given by Nishimoto and Forster [*19*] for the valence-state ionization energies and the one-center repulsion integrals. The core resonance integrals, $\beta_{\mu\nu}$, were adjusted at each iteration by using the following relation,

$$\beta_{\mu\nu} = A_0 + A_1 \, p_{\mu\nu}$$

where $p_{\mu\nu}$ is the bond order. The values of A_0 and A_1 used in the present calculation, are given in Tab. 1. The two-center repulsion integrals, $\gamma_{\mu\nu}$, were kept fixed, which were estimated by using the equation

$$\gamma_{\mu\nu} = 14.397/(a_{\mu\nu} + r_{\mu\nu})$$

where $r_{\mu\nu}$ is the distance between the two atoms, and $a_{\mu\nu}$ is a constant, for which the values proposed by Nishimoto and Forster [*19*] were assumed. The bond

Table 1. *Assumed values of A_0 and A_1*

Bond	A_0 (eV)	A_1 (eV)
C–C	−2.04	−0.51
C–N	−2.24	−0.53
C–O	−2.44	−0.56

lengths were estimated from the final values of bond order by assuming the following relations [*19*];

$$r_{\mathrm{C-C}} = 1.517 - 0.180p \quad (\text{Å})$$
$$r_{\mathrm{C-N}} = 1.451 - 0.180p \quad (\text{Å})$$
$$r_{\mathrm{C-O}} = 1.410 - 0.180p \quad (\text{Å})\,.$$

To calculate the electronic spectra, the configuration interaction was taken into account for all singly excited configurations. The oscillator strength was calculated by the usual procedure. No correction factor was multiplied to the calculated oscillator strengths.

Results and Discussions

I. Tropone, Heptafulvene and Troponeimine

The SCF MO's and their orbital energies are listed in Tab. 2 and the bond orders and bond lengths in the ground state are given in Tab. 3. The charge densities are given in Tab. 4. As can be seen from the values given in Tab. 4 the heptagonal ring has always a positive charge in these compounds. The π-electron contribution to dipole moment was calculated from the charge densities. Total moment was calculated as the sum of π- and σ-moment, where the latter was estimated by using the values of bond moment proposed by ORGEL et al. [*21*]. The results are given in Tab. 5.

The dipole moment of tropone has been experimentally determined, which is 4.30 D according to GIACOMO and SMYTH [*5*] and 4.17 D according to KURITA et al. [*14*]. Our calculation predicts a total moment of 5.9 D, which is appreciably larger than the experimental value. The dipole moment of heptafulvene has not been observed, although it has been theoretically discussed by several authors [*1, 9, 10, 16*]. A calculation by simple LCAO MO method predicted a moment of 4.6 D with the ring positive [*1*]. Evidently this is too large. A small moment, 0.14 D, in the opposite direction was predicted by SCF MO method of ROOTHAAN [*9*], whereas a semiempirical SCF MO method with Pariser-Parr approximation gave a theoretical moment of 0.6 D with the ring positive [*10*]. Recently NAKAJIMA and KATAGIRI [*16*] calculated the electronic structure of heptafulvene taking into account the effect of bond alternation, and predicted a moment of 0.71 D again with the ring positive. The moment predicted in the present calculation is slightly larger than the one given by NAKAJIMA and KATAGIRI.

The calculated transition energies and oscillator strengths are summarized in Tab. 6. The ultra-violet absorption spectrum of heptafulvene exhibits three bands with the maxima respectively located at 427 mμ (2.91 eV), 280 mμ (4.43 eV) and

Table 2. SCF MO's *of tropone, heptafulvene and troponeimine*

MO	Symmetry	Orbital energy (eV)	Coefficients				
			χ_1	$(\chi_2 \pm \chi_7)^a$	$(\chi_3 \pm \chi_6)^a$	$(\chi_4 \pm \chi_5)^a$	χ_8
	Tropone						
1	b_2	−14.1624	0.51065	0.33687	0.28557	0.25269	0.47061
2	b_2	−12.6925	−0.34425	0.01307	0.27824	0.48572	−0.50445
3	a_2	−11.4823	0	−0.42362	−0.52613	−0.20914	0
4	b_2	− 9.4660	0.04724	0.42838	0.20673	−0.37786	−0.50964
5	a_2	− 2.6150	0	−0.49922	0.22389	0.44794	0
6	b_2	− 1.9101	0.44500	0.17979	−0.48897	0.22900	−0.39277
7	a_2	1.0408	0	−0.26708	0.41601	−0.50557	0
8	b_2	1.9090	0.64844	−0.41294	0.24333	−0.07076	−0.33175
	Heptafulvene						
1	b_2	−13.4796	0.41663	0.37182	0.36046	0.34978	0.21300
2	b_2	−11.5955	−0.51951	−0.19372	0.14689	0.48131	−0.38547
3	a_2	−11.2186	0	0.43946	0.51873	0.19442	0
4	b_2	− 8.2667	−0.24945	0.33940	0.27836	−0.31935	−0.59030
5	a_2	− 2.2789	0	0.48984	−0.24798	−0.44560	0
6	b_2	− 1.4825	−0.37202	−0.19998	0.44504	−0.19406	0.55694
7	a_2	1.3588	0	0.25871	−0.41162	0.51346	0
8	b_2	1.8828	−0.59658	0.41114	−0.27009	0.07969	0.38395
	Troponeimine						
1	b_2	−13.8645	0.44519	0.36277	0.34408	0.32828	0.29374
2	b_2	−12.1731	0.47541	0.12370	−0.19093	−0.47152	0.47519
3	a_2	−11.4686	0	−0.43051	−0.52283	−0.20326	0
4	b_2	− 9.0015	−0.09492	0.38430	0.23511	−0.34125	−0.59342
5	a_2	− 2.5818	0	−0.49576	0.23474	0.44623	0
6	b_2	− 1.9220	0.43254	0.17222	−0.46911	0.21742	−0.46790
7	a_2	1.0793	0	−0.26246	0.41419	−0.50948	0
8	b_2	1.7016	0.61619	−0.41922	0.26422	−0.07857	−0.34181

[a] $\chi_2 + \chi_7$, $\chi_3 + \chi_6$, $\chi_4 + \chi_5$ for b_2; $\chi_2 - \chi_7$, $\chi_3 - \chi_6$, $\chi_4 - \chi_5$ for a_2.

212 mμ (5.84 eV) [*3*]. Seemingly the first and second bands are associated with the lowest two transitions predicted in the present calculation, namely the ${}^1B_1 \leftarrow {}^1A_1$ transition of 2.60 eV and the ${}^1A_1 \leftarrow {}^1A_1$ transition of 4.10 eV, and the third band is composed of two bands associated with the next two transition, the ${}^1B_1 \leftarrow {}^1A_1$

Table 3. *Calculated bond order and bond length of the tropone, heptafulvene and troponeimine*

Bond	Tropone		Heptafulvene		Troponeimine	
	Bond order	Bond length (Å)	Bond order	Bond length (Å)	Bond order	Bond length (Å)
1—2	0.37551	1.449	0.34177	1.456	0.36766	1.451
2—3	0.82254	1.369	0.85601	1.363	0.83328	1.367
3—4	0.47845	1.431	0.41748	1.442	0.45804	1.435
4—5	0.79762	1.373	0.83638	1.367	0.81049	1.371
1—8	0.77890	1.270	0.87249	1.360	0.82601	1.302

Table 4. *Charge densities of tropone, heptafulvene and troponeimine*

Atom	Tropone	Heptafulvene	Troponeimine
1	0.7630	1.0114	0.8664
2	0.9532	0.9682	0.9599
3	0.9570	0.9961	0.9669
4	0.9726	0.9876	0.9757
8	1.4714	1.0848	1.3285

transition of 5.87 eV and the $^1A_1 \leftarrow {}^1A_1$ transition of 5.95 eV. The agreement between the calculated and observed transition energies looks quite satisfactory. By the SCF MO method of Roothaan's formalism, JULG [*9*] predicted the $^1B_1 \leftarrow {}^1A_1$ transition at 2.95 eV and the $^1A_1 \leftarrow {}^1A_1$ transition at 5.11 eV. He assumed that the heptagonal ring possesses alternation of single and double bonds with the bond distances 1.46 and 1.35 Å respectively. The calculation by the Pariser-Parr method on the assumption of the same molecular geometry, predicted the two transitions at 2.75 and 3.40 eV [*10*]. Recently INUZUKA and YOKOTA [*3*] made a SCF MO calculation by assuming a regular heptagon structure with the C–C bond distance of 1.41 Å, and predicted the $^1B_1 \leftarrow {}^1A_1$ transition at 2.29 and the $^1A_1 \leftarrow {}^1A_1$ transition at 4.00 eV. As compared with these calculations, the agreement between the calculated and observed transition energies has been considerably improved in the present calculation. A better agreement as regards the energies of the lowest two transitions can be found in the calculation by NAKAJIMA and KATAGIRI [*16*] who carefully took into account the effect of bond alternation. The transition energies predicted by them are 2.82 and 4.53 eV.

The ultra-violet absorption spectrum of tropone was studied by HOSOYA, TANAKA and NAGAKURA [*6*]. They assigned the 305 mμ band (4.17 eV) to the $^1B_1 \leftarrow {}^1A_1$ transition and the 229 mμ band (5.51 eV) to the $^1A_1 \leftarrow {}^1A_1$ transition according to their calculation by the method of "molecules in molecule", where these transitions were predicted at 4.98 and 5.86 eV respectively. Later, however, WELTIN et al. [*22*] have shown that the 305 mμ band does not correspond to a single transition, but is composed of two different transitions, $^1B_1 \leftarrow {}^1A_1$, and $^1A_1 \leftarrow {}^1A_1$. They have also suggested that the 229 mμ band is again composed of $^1B_1 \leftarrow {}^1A_1$ and $^1A_1 \leftarrow {}^1A_1$ transitions. As shown in Tab. 6, the results of our calculation support this interpretation for the spectrum of tropone. The same assignment has been made by INUZUKA and YOKOTA [*7*]. Their calculation predicted the transitions as follows: 2.97 eV ($^1B_1 \leftarrow {}^1A_1$), 3.78 eV ($^1A_1 \leftarrow {}^1A_1$), 5.42 eV ($^1B_1 \leftarrow {}^1A_1$) and 5.81 eV ($^1A_1 \leftarrow {}^1A_1$).

Table 5. *Dipole moments of tropone, heptafulvene and troponeimine*

	Calculated moment		Observed moment (D)
	π-moment (D)	Total (D)	
Tropone	4.68	5.88	4.3 [*5*], 4.17 [*14*]
Heptafulvene	1.24	1.24	(~ 0.7)
Troponeimine	3.71	3.21	—

Table 6. *Calculated transition energies and oscillator strengths for tropone, heptafulvene and troponeimine*

Transition	Calculated		Observed		
	E (eV)	f	E (eV)	f	Ref.
Tropone					
$^1B_1 \leftarrow {}^1A_1$	3.73	0.16	4.17	0.13	[6]
$^1A_1 \leftarrow {}^1A_1$	4.20	0.20			
$^1B_1 \leftarrow {}^1A_1$	6.11	0.04	5.51	0.37	
$^1A_1 \leftarrow {}^1A_1$	6.21	1.57			
$^1B_1 \leftarrow {}^1A_1$	6.67	0.26			
$^1A_1 \leftarrow {}^1A_1$	7.22	0.56			
($^3B_1 \leftarrow {}^1A_1$	1.24)				
Heptafulvene					
$^1B_1 \leftarrow {}^1A_1$	2.60	0.04	2.91	0.02	[3]
$^1A_1 \leftarrow {}^1A_1$	4.10	0.45	4.43	0.3	
$^1B_1 \leftarrow {}^1A_1$	5.87	0.10	5.84	—	
$^1A_1 \leftarrow {}^1A_1$	5.95	1.35			
$^1B_1 \leftarrow {}^1A_1$	6.26	0.004			
$^1A_1 \leftarrow {}^1A_1$	6.44	0.07			
($^3B_1 \leftarrow {}^1A_1$	0.80)				
Troponeimine[a]					
$^1B_1 \leftarrow {}^1A_1$	3.21	0.09	3.44	(0.02)	
$^1A_1 \leftarrow {}^1A_1$	4.10	0.34	4.28	(0.13)	
$^1B_1 \leftarrow {}^1A_1$	5.94	0.01	5.51	(0.4)	
$^1A_1 \leftarrow {}^1A_1$	6.03	1.50			
$^1B_1 \leftarrow {}^1A_1$	6.45	0.21			
$^1A_1 \leftarrow {}^1A_1$	6.88	0.04			
($^3B_1 \leftarrow {}^1A_1$	1.08)				

[a] Observed by Y. KITAHARA.

In the case of troponeimine, the absorption bands are observed at 360 mμ (3.44 eV), 290 mμ (4.28 eV) and 225 mμ (5.51 eV)*. We can assign the first band to a $^1B_1 \leftarrow {}^1A_1$ transition, the second to a $^1A_1 \leftarrow {}^1A_1$ transition and the third to a band composed of $^1B_1 \leftarrow {}^1A_1$ and $^1A_1 \leftarrow {}^1A_1$ transitions.

II. Tropolone, 3-Hydroxytropone and 4-Hydroxytropone

The bond orders and bond distances calculated for the ground states of these molecules are given in Tab. 7. The charge density and the dipole moment are shown in Tab. 8. The dipole moment of tropolone predicted by the present calculation is considerably larger compared with the observed value, 3.72 D [*15*].

The transition energies and oscillator strengths are listed in Tab. 9. In every case, the agreement between the calculated and observed transition energies is satisfactory.

The electronic spectrum of tropolone has been studied by HOSOYA, TANAKA and NAGAKURA [*6*]. The ultra-violet spectrum composed of three bands; the first

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* Observed by Y. KITAHARA.

Table 7. *Calculated bond orders and bond lengths of hydroxytropones*

Bond	Tropolone		3-Hydroxytropone		4-Hydroxytropone	
	Bond order	Bond length (Å)	Bond order	Bond length (Å)	Bond order	Bond length (Å)
1—2	0.35158	1.454	0.41782	1.442	0.36680	1.451
2—3	0.70691	1.390	0.74460	1.383	0.83691	1.366
3—4	0.54374	1.419	0.43512	1.439	0.43906	1.438
4—5	0.75370	1.381	0.81287	1.371	0.72230	1.387
5—6	0.52411	1.423	0.46784	1.433	0.51050	1.425
6—7	0.78470	1.376	0.83141	1.367	0.80137	1.373
7—1	0.42933	1.440	0.36449	1.451	0.39974	1.445
1—8	0.74618	1.276	0.76435	1.272	0.77029	1.271
n[a]—9	0.46670	1.326	0.41215	1.336	0.40716	1.337

[a] $n = 2$, 3 and 4 respectively for tropolone, 3-hydroxytropone, and 4-hydroxytropone.

band in the 340—380 mμ region with vibrational peaks at 374, 356 and 338 mμ, the second one with the maximum at 320 mμ, and the third one of high intensity at 230 mμ. It has been shown by the observation of polarized absorption spectra of a single crystal [*6*], that the first band is associated with a transition polarized in the direction nearly perpendicular to the C=O bond, and the second one is associated with a transition polarized parallel to the C–OH bond. The direction of transition moment derived from the present calculation is shown in Fig. 2, which are in good agreement with the observed polarizations. From the fact that the 320 mμ band is polarized parallel to the direction of the C–OH bond, HOSOYA et al. [*6*] assigned this band to a charge-transfer band associated with the electron transfer from the hydroxyl group to the heptagonal ring. However this interpretation seems questionable according to the present calculation. The energies of the SCF MO's of tropone and tropolone are shown in Fig. 3. It is the orbital 1 of tropolone that has a character highly localized on the oxygen atom of hydroxyl group. The others can be correlated to the orbitals of tropone. Therefore the intramolecular charge transfer band should be associated with an excitation of an

Table 8. *Charge densities and dipole moments of hydroxytropones*

Atom	Tropolone	3-Hydroxytropone	4-Hydroxytropone
1	0.7719	0.7665	0.7671
2	0.9259	1.0664	0.9365
3	1.0772	0.9409	1.0008
4	0.9541	1.0168	0.9486
5	1.0230	0.9624	1.0796
6	0.9441	0.9751	0.9473
7	0.9978	0.9422	0.9988
8	1.5160	1.4934	1.4825
9	1.7901	1.8363	1.8387
π-moment (D)	3.72	5.72	6.60
Total moment (D)	4.95	6.56	7.02
Observed moment (D)	3.53	—	—

Table 9. *Transition energies and oscillator strengths of hydroxytropones*

	Calculated		Observed	
	E (eV)	f	E (eV)	Ref.
Tropolone	3.46	0.22	3.4	[*6*, *2*]
	3.95	0.26	3.9	
	5.55	0.31	5.3	
	6.01	1.36		
	6.60	0.04		
	6.92	0.13		
	(T[a]: 1.13 eV)			
3-Hydroxytropone	3.57	0.10	4.01	[*8*]
	4.13	0.07	4.16	
	5.52	1.03	4.86	
	5.59	0.57	5.08	
	6.59	0.46		
	7.03	0.50		
	(T[a]: 1.25 eV)			
4-Hydroxytropone	3.59	0.20	3.68	[*20*]
	3.99	0.30		
	5.72	0.22	5.44	
	6.26	0.91		
	6.28	0.72		
	6.84	0.003		
	7.00	0.54		
	(T[a]: 1.18 eV)			

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[a] Lowest triplet state.

Table 10. CI *wave functions of the lowest two singlet excited states of tropone and tropolone*

Energy (Symmetry)	CI wave function
	Tropone
3.73 eV ($^1B_1$)	$\Phi_1 = 0.98458\,\psi_{4\to5} + 0.07702\,\psi_{3\to6} + 0.12025\,\psi_{2\to5} + 0.06383\,\psi_{4\to7} -$ $- 0.05495\,\psi_{1\to5} + 0.03882\,\psi_{3\to8} + 0.01324\,\psi_{2\to7} - 0.03788\,\psi_{1\to7}$
4.20 eV ($^1A_1$)	$\Phi_2 = 0.85710\,\psi_{4\to6} - 0.49859\,\psi_{3\to5} - 0.10904\,\psi_{2\to6} - 0.00700\,\psi_{4\to8} +$ $+ 0.03210\,\psi_{1\to6} + 0.03738\,\psi_{3\to7} + 0.04478\,\psi_{2\to8} + 0.02048\,\psi_{1\to8}$
	Tropolone
3.46 eV	$\Phi_1 = 0.86258\,\psi_{5\to6} - 0.41525\,\psi_{5\to7} - 0.20296\,\psi_{4\to6} - 0.15012\,\psi_{4\to7} +$ $+ 0.03607\,\psi_{5\to8} - 0.06156\,\psi_{3\to6} + 0.03224\,\psi_{5\to9} - 0.06100\,\psi_{3\to7} +$ $+ 0.05904\,\psi_{2\to6} + 0.04350\,\psi_{2\to7} + 0.02996\,\psi_{4\to8} + 0.01081\,\psi_{4\to9} +$ $+ 0.00434\,\psi_{1\to6} - 0.00566\,\psi_{1\to7} - 0.00912\,\psi_{3\to8} - 0.04572\,\psi_{3\to9} +$ $+ 0.01329\,\psi_{2\to8} - 0.02344\,\psi_{2\to9} + 0.01911\,\psi_{1\to9} + 0.01557\,\psi_{1\to8}$
3.95 eV	$\Phi_2 = 0.46130\,\psi_{5\to6} + 0.77721\,\psi_{5\to7} + 0.40901\,\psi_{4\to6} - 0.02778\,\psi_{4\to7} +$ $+ 0.04257\,\psi_{5\to8} - 0.07557\,\psi_{3\to6} - 0.01202\,\psi_{5\to9} + 0.03761\,\psi_{3\to7} +$ $+ 0.03876\,\psi_{2\to6} - 0.03261\,\psi_{2\to7} - 0.00676\,\psi_{4\to8} + 0.03880\,\psi_{4\to9} +$ $+ 0.01167\,\psi_{1\to6} + 0.00492\,\psi_{1\to7} - 0.00832\,\psi_{3\to8} + 0.02769\,\psi_{3\to9} +$ $+ 0.02283\,\psi_{2\to8} + 0.01173\,\psi_{2\to9} - 0.00106\,\psi_{1\to9} + 0.01529\,\psi_{1\to8}$

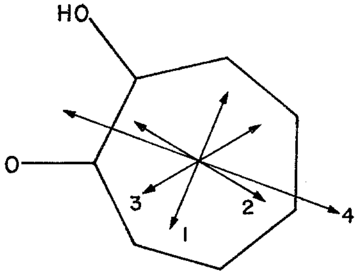

Fig. 2

Fig. 2. Directions of transition moments of the 3.46 eV (1), 3.95 eV (2), 5.55 eV (3) and 6.01 eV (4) transitions of tropolone

Fig. 3
Energies of SCF MO's of tropone and tropolone

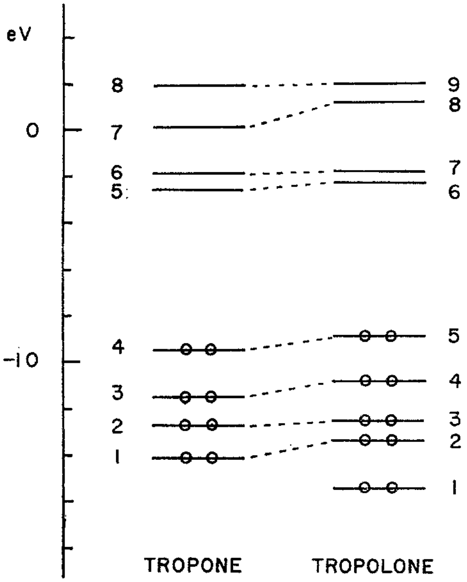

Fig. 3

electron from the orbital 1. However, as can be seen from the CI wavefunctions shown in Tab. 10, the 3.95 eV transition of tropolone is mainly associated with the excitation from the orbital 5 to the orbital 7 which corresponds to the excitation from the orbital 4 to the orbital 6 in the case of tropone. Seemingly the 320 mμ band of tropolone is a band corresponding to the $^1A_1 \leftarrow {}^1A_1$ transition of tropone, and is not a charge transfer band.

Conclusion

As shown above, the calculation by the variable-β procedure can well predict the electronic spectra of tropone, tropolone and related compounds. This may suggest the general utility of this method to nonbenzenoid aromatic compounds.

The present calculation has shown that the 305 mμ band of tropone consists of two different transitions, $^1B_1 \leftarrow {}^1A_1$ and $^1A_1 \leftarrow {}^1A_1$, which correspond respectively to the first and second bands observed in the spectra of heptafulvene or troponeimine. The observed polarizations of the absorption bands of tropolone has been well explained by the present calculation.

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