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Theoretical Study of Triafulvene, Fulvene, Heptafulvene, and Their *O*- and *N*-Heteroanalogs

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The geometry, electronic structure, and the aromatic stability of triafulvene, fulvene, heptafulvene, and their *O*- and *N*-heteroanalogs have been investigated by the PPP-CI MO method. Energy minimization with respect to bond lengths has been carried out in order to find the optimal geometry of the studied compounds. Aromatic stability predictions are based on the topological resonance energy, TRE, approach. Theoretical results are in very good agreement with experimental measurements.

INTRODUCTION

The structure and properties of the title compounds have attracted considerable theoretical interest, particularly in connection with the Hückel 4n+2 rule[1]. Triafulvene (methylenecyclopropene), fulvene and heptafulvene have quite different properties than their valence isomers cyclobutadiene, benzene and cyclooctatetraene which are typical representatives of aromatic and antiaromatic compounds. There also has been a great synthetic interest in the title compounds[2,3]. In recent years the importance of cyclopropenones in organic chemistry has been demonstrated by their utilization in a wide variety of organic reactions[4–7] which may be classified into four categories: decarbonylation reactions[4], addition reactions[5], oxidation reactions[6], and substitution reactions[7]. These compounds have been also studied by various MO methods[3,8–13]. Here we wish to extend these studies to their isoelectronic heteroanalogues in order to investigate the influence of heterosubstitution on the π-electron skeleton and consequently on their properties. Atomic skeletal structures of the studied compounds are given in Figure 1.

METHOD OF CALCULATION

Here we have used the Lo-Whitehead (variable β) variant[14a] of the PPP CI method[14b] in which the π-electron energy, E_{π}, is minimized with respect to geometrical parameters: bond lengths and bond angles. The Fletcher-Powell gradient technique for localization of minima[15], in which E_{π} and the gradient with respect to all variables at each point are evaluated, was used for this minimization procedure. The gradient was calculated numerically. Proper input geometries of compounds **1—9**, based on the recommended[16] standard bond lengths and bond angles, have been used. Aromatic stibility predictions are based on the topological resonance energy, TRE, approach.[17,18].

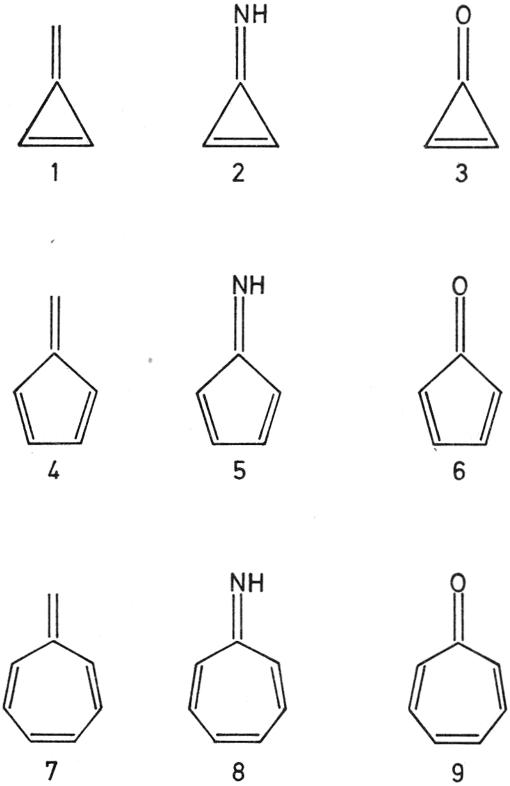

Figure 1. Atomic skeletal structures of studied compounds.
1 Methylenecyclopropene (triafulvene); 2 Iminocyclopropenone; 3 Cyclopropenone; 4 Methylenecyclopentadiene (fulvene); 5 Iminocyclopentadienone; 6 Cyclopentadienone; 7 Methylenecycloheptatriene (heptafulvene); 8 Iminocycloheptatrienone (8-azaheptafulvene); 9 Cycloheptatrienone (tropone).

Topological resonance energy is calculated using the following expresion:

$$\mathrm{TRE} = \sum_{j} g_j \, (x_j - x_j^{\mathrm{ac}})$$

where g_j is orbital occupancy number, x_j are Hückel eigenvalues, and $x_j^{\mathrm{ac.}}$ are eigenvalues obtained by solving the acyclic polynomial[18]. TRE index has been shown to be a good theoretical index for predicting the aromatic stability of conjugated systems.[17–19]

Calculations were carried out on the UNIVAC 1110 computer of the University of Zagreb.

RESULTS AND DISCUSSION

In Figure 2. calculated bond lengths for the studied compounds **1—9** are given.

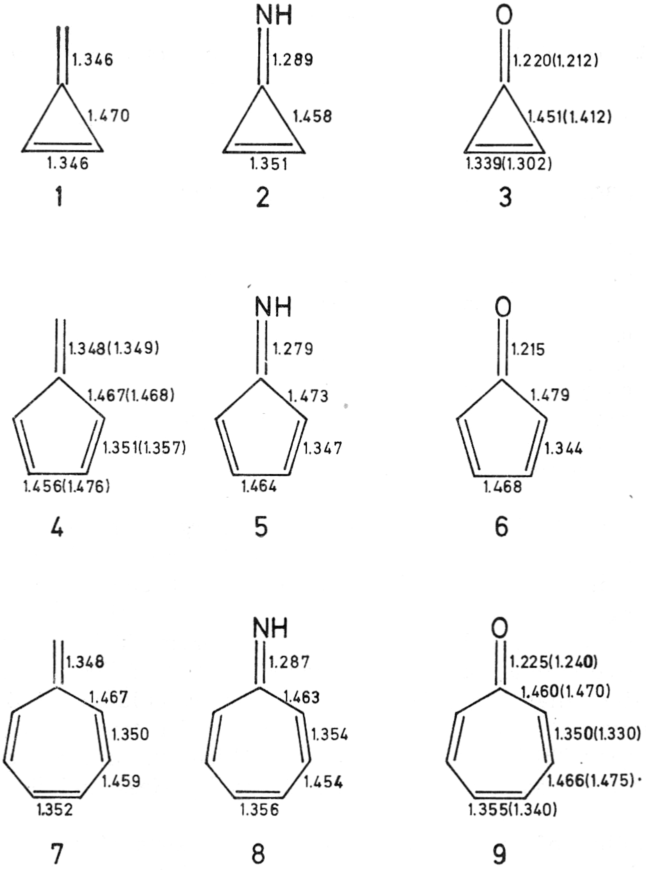

Figure 2. Predicted bond lengths. The experimental results, where available, are given in brackets.

In the brackets we give experimental results, obtained from microwave spectra, of cyclopropenone[20], fulvene[21,22] and tropone[23].

Theoretical results are in very good agreement with experimental findings especially for fulvene[21,22] where the difference in the bond lengths is within few hundreds of an angström. In the case of cyclopropenone[20] our calculation predicts slightly longer bond lengths (average deviation from experimental values being 0.028 Å). The calculated result for the ring angle $C_3C_1C_2$ in cyclopropenone is 62.52^0, and the experimental value[20] is 62.55^0. It is gratifying that the tropone ring system is predicted to have alternanting bond lengths. Until very recently[42] the tropone ring system was believed to be similar to the tropylium ring with all bonds of equal length. Such a good correlation between calculated and experimental results suggests that the optimized geometries of other investigated compounds in this work, where there are no experimental results, are reasonably good and are very near the true ones.

In Table I results for aromatic stability for compounds **1**—**9** are presented.

TABLE I

TRE and TREPE Indices of Studied Compounds (in β units)

Compound	TRE	TREPE	REPE[10,24,25]*	RE[11]	DE[8]	Number of π-electrons in the ring
1	0.063	0.016	0.005	0.718	0.241	2
2	0.303	0.076				2
3	0.163	0.041		3.126		2
4	0.020	0.003	— 0.002	0.228	0.244	4
5	— 0.198	— 0.033	— 0.032			4
6	— 0.070	— 0.012		— 1.769		4
7	0.009	0.001	— 0.002	0.104	0.249	6
8	0.142	0.018				6
9	0.071	0.009		1.606		6

* REPE = resonance energy per electron

TRE and TREPE (topological resonance energy per electron) indices are compared with the earlier work of Zahradník[8], Hess and Schaad[10,24,25], and Aihara.[11] Zahradník et al.[26] tried to amend the defficiencies of classical delocalization energy, DE, model by dividing DE with m the number of σ-bonds over which the conjugated systems extends, DE/m. This attempt, however, was not as successful as later amendments (e. g.[10]) of DE approach. Thus, it is not surprising, that delocalization energies[26], calculated by Zahradník and coworkers[8], give the opposite trend in stability for triafulvene, fulvene and heptafulvene than TRE and TREPE indices which are in good agreement with recent results for resonance energy published by Hess and Schaad[10,24,25] and Aihara[11].

Total stability of the studied compounds consists of three different contributions: (*a*) aromatic stability gained by cyclization and conjugation, (*b*) strain energy which is most pronounced in the compouds with the three membered ring, and (*c*) reactivity of the exocyclic double bond. On the basis of our TRE and TREPE values we classify all the studied compounds in three groups: aromatic, nonaromatic and antiaromatic. Iminocyclopentadienone and cyclopentadienone having negative TRE values belong to the antiaromatic group. This is in agreement with experimental findings. Iminocyclopentadiene has not yet been prepared, and cyclopentadienone is stable only below 77 K[27] and under spectroscopic conditions has life-time of ~15 s.[28] Fulvene and heptafulvene have TREPE value very near zero and belong to the group of nonaromatic compounds. They are stable under nitrogen at 200 K.[29,30] Tropone is also marginally nonaromatic compound, though it appears that it is stable at room temperature[31] under normal conditions. Triafulvene, iminocyclopropenone, and iminocycloheptatrienone are aromatic compounds. Iminocycloheptatrianone is destabilized by the imino group and is known as the *N*-methyl substituted derivative which is stable in dilute solution at 273 K.[32] Molecules **1**—**3** with a three membered ring have large strain energies which destabilize them so they are more unstable than it would be expected on the basis of their TREPE values. Cyclopropenone is a stable crystalline compound below 243 K,[33] and only derivatives of triafulvene and iminocyclopropenone[35] are known. If the studied compounds are grouped according to the size of the ring it can be seen that compounds with three-membered rings bearing 2π electrons within the ring belong to the class of molecules with an 4n+2 perimeter and they are all aromatic compounds. Five-membered ring compounds have 4π electrons within the ring system and are of the 4n-type perimeter, and they are either antiaromatic and nonaromatic.[39] Compounds with a seven membered ring have an 4n+2 perimeter and they are either aromatic or nonaromatic species. This is in very good agreement with the perimeter rule[36]. Especially interesting cases are hydrocarbons: triafulvene, fulvene and heptafulvene. Here we have a very simple rule. When the size of the ring increases the aromaticity of the compound decreaseses. The MO energies (in eV) for all occupied π-orbitals are given in Table II together with experimental vertical ionization energies deter-

TABLE II

*Orbital Energies ε_i (eV) and Vertical Ionization Energies IP_i (eV)**

Compound	Band	$-\varepsilon_i$/eV	Orbital assignment	IP_i/eV
1	1	8.58 (b_1)		
	2	13.97 (b_1)		
2	1	9.87 (b_1)		
	2	14.50 (b_1)		
3	1	10.76 (b_1)		
	2	14.94 (b_1)		
4	1	9.53 (a_2)	a_2	8.55
	2	10.50 (b_1)	b_1	9.54
	3	13.51 (b_1)	b_1	12.1
5	1	9.97 (a_2)		
	2	11.52 (b_1)		
	3	14.20 (b_1)		
6	1	10.14 (a_2)		
	2	12.20 (b_1)		
	3	14.99 (b_1)		
7	1	8.35 (b_1)	b_1	7.69
	2	11.48 (a_2)	a_2	10.22
	3	11.79 (b_1)	b_1	10.50
	4	13.71 (b_1)	b_1	12.30
8	1	9.16 (b_1)		
	2	11.74 (a_2)		
	3	12.37 (b_1)		
	4	14.09 (b_1)		
9	1	9.59 (b_1)	b_1	8.90
	2	11.77 (a_2)	a_2	10.67
	3	12.89 (b_1)	b_1	11.54
	4	14.46 (b_1)		

* 1 eV $\approx$ 1.60219 $\times$ 10^{-19} J

mined from the UVPE spectra of fulvene[37], heptafulvene[13] and tropone.[38] For the interpretation of the PE spectrum Koopmans' theorem was used. Our assignments of the spectra based on the calculation are in agreement with earlier experimental findings. Calculated MO energies are approximately 1 eV higher than the experimental vertical ionization energies, but there is a linear correlation between them as can be seen from Figure 3.

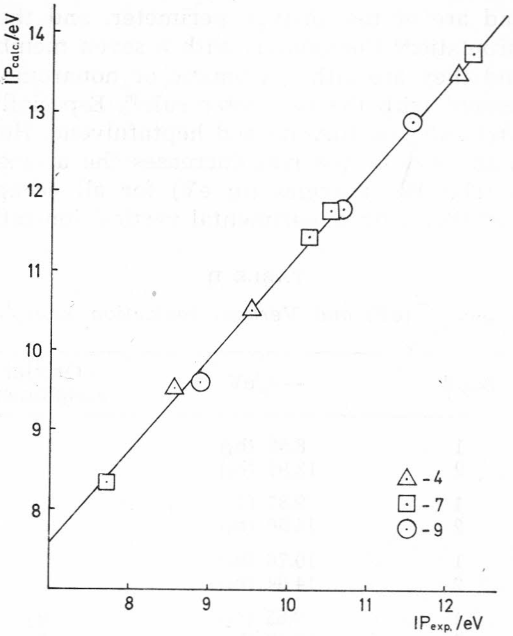

Figure 3. Least-squares regression of the observed-ionization energies vs. PPP calculation results.

The least-squares equation which relates the calculated and experimental results is given below:

$$(-\varepsilon_i)_{\mathrm{cacl.}} = 1.167\ (IP)_i - 0.597$$

The correlation coefficient is 0.996.

Such a correlation supports the suggestion that the optimized molecular structures are very accurate for all studied compounds in the gas phase.

Calculated and experimental singlet-singlet transitions from UV spectra are given in Table III. Calculated electronic absorption spectra are obtained with PPP-CI method where all single excited states are used. In the Table III, calculated oscilator strenghts (f) are correlated with extinction coefficient (log ε) and transition assignments are also given.

Calculated transitions in fulvene, cyclopentadienone, heptafulvene, iminocycloheptatrienone and tropone are in good agreement with experimental results[13,31,32]. Our transition assignments, based on the PPP-CI method, for fulvene and heptafulvene confirm earlier work by Heilbronner and co-workers[40,41]. In Figure 4. experimental transition energies are plotted against

TABLE III

Observed and Calculated Electronic Absorption Spectra of all Studied Compounds (eV)[a]

Compound	$^1\Delta E_{calc.}$	f	Symm.	$^1E_{obs.}$	log ε	Symm.
1	4.33	0.048	$^1B_2$			
	6.43	0.751	$^1A_1$			
2	5.39	0.085	$^1B_2$			
	6.72	0.733	$^1A_1$			
3	6.73	0.133	$^1B_2$			
	7.85	0.823	$^1A_1$			
4	3.67	0.037	$^1B_2$	3.42	2.4	$^1B_2$
	5.35	0.461	$^1A_1$	5.12	4.1	$^1A_1$
5	3.30	0.021	$^1B_2$			
	5.57	0.505	$^1A_1$			
6	3.39	0.025	$^1B_2$	3.27	1.9	
	6.17	0.305	$^1A_1$	6.21	4.7	
7	3.17	0.037	$^1B_2$	2.93—3.26		$^1B_2$
	4.81	0.461	$^1A_1$	4.44—5.08		$^1A_1$
	5.63	0.086	$^1B_2$	5.93		$^1B_2$
8[b]	3.88	0.087	$^1B_2$	4.00		
	5.61	1.375	$^1A_1$	5.30		
	6.76	0.769	$^1B_2$			
9	3.98	0.155	$^1B_2$	3.97	3.92	
	5.85	1.436	$^1A_1$	5.40	4.34	
	6.44	0.193	$^1B_2$			

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[a] 1 eV ≈ 1.60219×10^{-19} J

[b] Experimental results are for *N*-methyliminocycloheptatrienone.

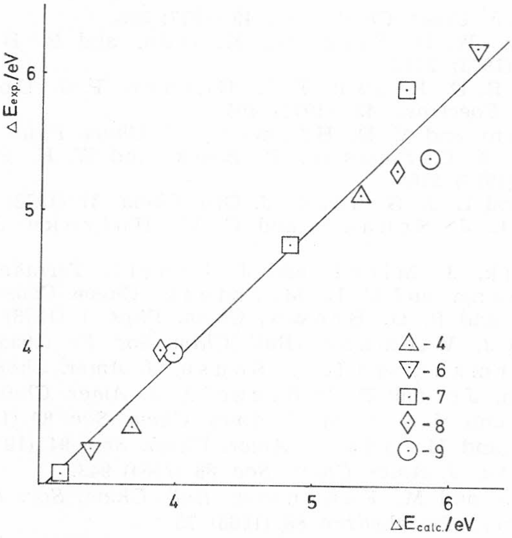

Figure 4. Least-squares regression of the observed $\pi^* \leftarrow \pi$ electronic transitions vs. PPP CI calculation results.

our calculated values. The linear equation correlating the experimental and calculated results is given below; the correlation coefficient being 0.963.

$$\Delta E_{\text{obs:}} = 0.997 \cdot \Delta E_{\text{calc.}} + 0.012$$

One can see from Figure 4. that there is a good linear correlation between experimental and calculated transitions.

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SAŽETAK

Teorijski studij triafulvena, fulvena, heptafulvena i njihovih *O*- i *N*- heteroanaloga

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Struktura i svojstva spojeva, u naslovu ispitivani su metodom PPP-CI. Računski određene geometrije molekula vrlo se dobro slažu s poznatim eksperimentalnim rezultatima. Postoji linearna ovisnost računskih MO energija o energijama $\pi^* \leftarrow \pi$ prijelaza te s rezultatima dobivenim iz fotoelektronskih i ultraljubičastih spektara. Pokazano je da stabilnost ispitivanih molekula ovisi o tri čimbenika: (*a*) o aromatskoj stabilnosti prstena, (*b*) o energiji napetosti u prstenu i (*c*) o reaktivnosti eksociklične dvostruke veze.

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