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Dipole Moments of 1-Cyclopentadienylidene-2-cycloheptatrienylidene-ethylene and its Related Compounds

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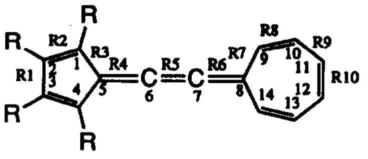
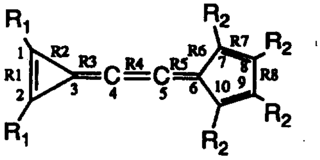
Abstract: The dipole moments of 1-cyclopentadienylidene-2-cycloheptatrienylidene-ethylene 1a and its related compounds are calculated by MNDO and ab initio methods. The calculated dipole moment of 1a (μ(1a)=3.39D) is compared with the value 3.71D which is estimated from our experimental dipole moment of 1-tetraphenyl-cyclopentadienylidene-2-cycloheptatrienylidene-ethylene.

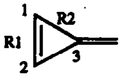
Non-benzenoid aromatic hydrocarbons have been one of fascinating targets for organic chemists since its stability had been suggested by simple Hückel molecular orbital method (HMO). Yoshida et.al tried to synthesized the π-system 2a, i.e., two different cross-conjugated systems are bound with two sp-hybrid carbons (push-pull type compound).[1)] They succeeded to synthesize 2b, the derivative of 2a, and reported the results of IR, UV and NMR spectra. Toda et.al, recently, succeeded to synthesize same type of push-pull compound 1b.[2)]



1a R=H
1b R=Ph



2a R₁=H, R₂=H
2b R₁=N(i-pr)₂, R₂=Ph



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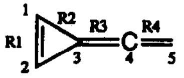

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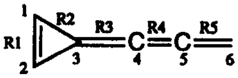

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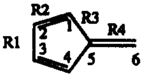

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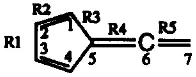

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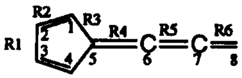

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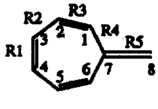

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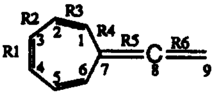

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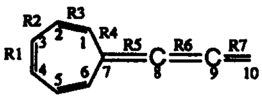

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Norden et. al and Prinzbach et. al had discussed on the nature of cross-conjugation and dipole moments of triafulvene 3, calicene and sesquifulvalene, respectively.3), 4)

Here we examined electronic structures of 1a, 2a and some cross-conjugated non-benzenoid hydrocarbons (3 - 11) by the MO methods (MNDO and ab initio methods). The geometrical parameters of all molecules are optimized by using STO-3G minimal basis sets.[5] The molecular symmetry is fixed to be C_{2v} in all molecules. The optimized bond lengths are given in Table 1.

Table 1. The Optimized Bond Lengths by STO-3G a)

	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
1a	1.482	1.329	1.484	1.321	1.240	1.327	1.484	1.329	1.472	1.328
2a	1.309	1.442	1.296	1.243	1.321	1.480	1.330	1.477	—	—
3	1.303	1.446	1.303	—	—	—	—	—	—	—
4	1.298	1.457	1.274	1.289	—	—	—	—	—	—
5	1.305	1.448	1.287	1.251	1.298	—	—	—	—	—
6	1.492	1.323	1.495	1.319	—	—	—	—	—	—
7	1.487	1.325	1.493	1.302	1.287	—	—	—	—	—
8	1.489	1.326	1.492	1.311	1.252	1.300	—	—	—	—
9	1.325	1.477	1.324	1.494	1.325	—	—	—	—	—
10	1.324	1.479	1.323	1.497	1.306	1.285	—	—	—	—
11	1.326	1.475	1.326	1.490	1.319	1.248	1.301	—	—	—

a) in Å unit ; 1Å = 10^{-10}m

Table 2. The π-Electron Densities by STO-3G Calculations

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
1a	1.038	1.016	1.016	1.038	1.048	0.919	1.030	0.977	0.985	0.986	0.987
2a	0.894	0.894	0.924	1.154	0.886	1.108	1.036	1.033	—	—	—
3	0.921	0.921	0.950	1.209	—	—	—	—	—	—	—
4	0.932	0.932	1.019	1.115	0.992	—	—	—	—	—	—
5	0.911	0.911	0.962	1.143	0.938	1.136	—	—	—	—	—
6	1.027	1.001	1.001	1.027	0.981	0.965	—	—	—	—	—
7	1.030	1.008	1.008	1.030	1.006	0.891	1.013	—	—	—	—
8	1.034	1.002	1.002	1.034	1.010	0.931	0.975	1.012	—	—	—
9	0.983	1.001	0.996	0.996	1.001	0.983	0.985	1.045	—	—	—
10	0.985	1.012	0.997	0.997	1.012	0.997	1.058	0.969	1.004	—	—
11	0.983	1.001	0.993	0.993	1.001	0.983	1.009	1.010	0.960	1.068	—

The bond alternations are found clearly in all odd-membered rings. The central C=C bonds of cummulene parts of molecules 1a , 2a , 3, 8 and 9 are shortest in length among all other bonds, respectively. Especially R5(C_5-C_6) = 1.243Å of 1a , and R4(C_4-C_5) = 1.240Å of 2a are shorter than that of the cummulene bond length of about 1.31Å.[6] The stretching vibrations due to these bonds of 1b and 2b are reported to be ν = 2036 cm^{-1} and ν = 2110 cm^{-1}, respectively.[1),2)] The latter resembles the absorption of acetylenic C≡C vibrations and the former those of tri- and tetra-arylbutatrienes whose absorptions were reported at about ν = 2032 cm^{-1} .[7)] Between two molecules 1a and 2a, the contribution of ionic structure (acetylenic structure) to the ground states is more important in 2a than in 1a. The large contribution of ionic structure 2a' was also suggested from ^{13}C NMR spectra.[2)]

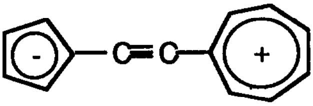
The total π-electron densities calculated by Mulliken population analysis are given in Table 2. The 4n+2 Hückel rule is satisfied in all rings, i.e., three- and seve-membered rings are positively charged and five membered rings are negatively , respectively. From these π-electron densities we can see that the push-out ability of π-electron of three-membered ring is stronger than that of seven-membered one. This fact corresponds to the magnitude of the dipole moments of each molecules given below. Of interest is the existence of charge alternations in the seven membered rings of 6 , 7 and 8 .

The dipole moment of a molecule reflects the electronic structure of the ground state directly. The molecules 1a and 2a are expected to have large dipole moments from the previous mentions about IR spectra. The calculated dipole moments are given in Table 3.

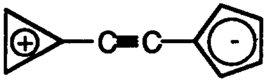
Table 3. Calculated Dipole Moment[a)]

Molecule	STO-3G	MNDO	expl.
1a	3.39 (3.86)[c]	2.55	3.91[b]
2a	5.88	3.88	
3	1.88	1.26	1.90
4	2.15	1.41	
5	3.25	1.86	
6	0.43	0.70	0.44
7	0.73	0.74	
8	0.78	1.14	
9	0.38 (0.42)[c]	0.07	
10	0.26	0.12	
11	1.10	0.36	

a) in Debye unit ; 1 D = 3.336×10^{-3} Cm
b) estimated from 1b (μ=4.19D)
c) 3-21G Calculation



1a'



2a'

The MNDO method gives smaller values than that of STO-3G ab initio calculations in all molecules. The agreements of the calculated dipole moments with the experimental ones are good in the case of triafulvene 3 and fulvene 6, respectively. The dipole moment of 1a calculated by STO-3G agrees also with μ=3.91D which is estimated from our experimental value μ=4.19D of 1b .[8)] Among the molecules considered here the dipole moment of 2a is the largest μ=5.88D, and 1a has the next μ=3.39D. As expected by Yoshida et.al and Toda et.al, these large dipole moments suggest that the contribution of resonance structures 1a' and 2a' is appreciable in the ground states of both molecules, respectively. The contribution of resonance structure 2a' to the ground state is estimated to be about 13% as follows; We express the ground state wavefunction as

$$\Psi_g = a\Psi_N + b\Psi_{ion} \qquad (1)$$

where Ψ_N and Ψ_{ion} express the wavefunctions which correspond to the resonance structures 2a and 2a', respectively. We assume that $\mu = \langle\Psi_g|er|\Psi_g\rangle$ is equal to the calculated value, $\langle\Psi_N|er|\Psi_N\rangle$ is equal to $\mu(3)+\mu(4)$, i.e., the sum of two cross-conjugated moieties, $\langle\Psi_g|er|\Psi_{ion}\rangle=0$ and $\langle\Psi_{ion}|er|\Psi_{ion}\rangle=29.01\mathrm{D}$ which is calculated from the model that a point charge is located at the center of each terminal rings. Using the normalization condition $a^2 + b^2 = 1$, we obtain the contribution of ionic structure 2a' to be $b^2 = 0.13$. This contribution for the molecule 1a is estimated to be about 3% from the same procedure. These results explain the difference of the C=C stretching vibrations and short bond lengths of 1a and 2a very well, respectively.

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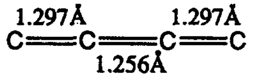
5) The calculation was performed by ACOS-850 at Hirosaki University. The extended 3-21G calculations of 2a and 9 were done by the SX-2 super computer at Tohoku University, using the optimized molecular structure by STO-3G calculations.

6) The optimized bond lengths of $H_2C{=}C{=}C{=}CH_2$ by STO-3G are as follows:



$$\mathrm{C}\overset{1.297\,\text{Å}}{=\!=\!=}\mathrm{C}\underset{1.256\,\text{Å}}{=\!=\!=\!=}\mathrm{C}\overset{1.297\,\text{Å}}{=\!=\!=}\mathrm{C}$$

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