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Pentatriafulvalenes [1]

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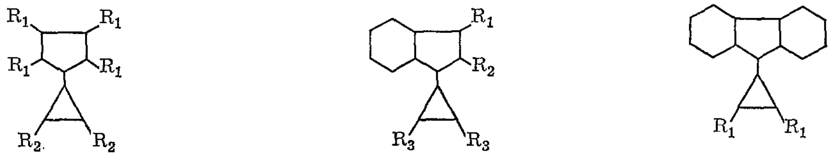
Recent interest in the pentatriafulvalenes (calicenes, Fig. 1) has led to several projects of theoretical calculations, based upon variants of the SCF method [2, 3], In order to study the usefulness, in this domain, of the simple Hückel approach.

Table. *Longest wavelength electronic transitions of pentatriafulvalenes*

Calculated			Found			
A Compd.	*B* (beta units)	*C* (mμ)	Compd.	(mμ)	solvent	Ref.
Ia	1.4893	244				
Ib	1.3078	271				
IIa	1.1698	295	IIa	335	C_6H_{14}	[*10*]
IIb	1.1626	297	IIc	363	MeOH	[*11*]
IId	1.1567	298	IIe	365	MeOH	[*11*]
Ic	1.0710	312	Ic	338	MeOH	[*12*]
				345	MeCN	[*13*]
				349	C_6H_{12}	[*13*]
IIIa	1.0463	320	IIIa	353	C_6H_{12}	[*14*]
IIf	1.0168	328	IIg	355	MeOH	[*15*]
IIh	0.8486	373	IIh			[*9*]
Id	0.8406	375	Id	371	MeCN	[*7*]
				377	C_6H_{12}	[*7*]
IIIb	0.7732	397	IIIb	437	MeCN	[*9*]
				478	C_6H_{12}	[*9*]



Ia $R_1 = H, R_2 = H$
Ib $R_1 = CH_3, R_2 = CH_3$
Ic $R_1 = Cl, R_2 = C_6H_6$
Id $R_1 = C_6H_5, R_2 = C_5H_5$

IIa $R_1 = H, R_2 = H, R_3 = CH_3$
IIb $R_1 = COOCH_3, R_2 = H, R_3 = CH_3$
IIc $R_1 = COOCH_3, R_2 = H, R_3 = CH_2CH_2CH_3$
IId $R_1 = COOCH_3, R_2 = Br, R_3 = CH_3$
IIe $R_1 = COOCH_3, R_2 = Br, R_3 = CH_2CH_2CH_3$
IIf $R_1 = CN, R_2 = H, R_3 = CH_3$
IIg $R_1 = CN, R_2 = H, R_3 = CH_2CH_2CH_3$
IIh $R_1 = H, R_2 = H, R_3 = C_6H_5$

IIIa $R_1 = CH_3$
IIIb $R_1 = C_6H_5$

Fig. 1. Pentatriafulvalenes

we have applied it to the calculation of the longest wavelength electronic transition of a number of pentatriafulvalenes. The results, in beta units, are summarized (column *B*) and compared with the experiment in the table.

The parameters used were [*4*]:

for methyl substitution (C_{ar}–C_{al} H_3): $\delta(C_{ar}) = -0.1$, $\eta(C_{ar}\text{–}C_{al}) = 0.7$, $\delta(C_{al}) = 0.0$, $\eta(C_{al}\text{–}H_3) = 2.0$;

for substitution by chlorine: $\delta(C) = 0.15$, $\eta(C\text{–}Cl) = 0.5$, $\delta(Cl) = 2.0$;

for substitution by bromine: $\delta(C) = 0.2$, $\eta(C\text{–}Br) = 0.7$, $\delta(Br) = 2.0$;

for the C=O grouping: $\eta(C{=}O) = 2.0$, $\delta(O) = 0.7$;

for the C–O bond: $\eta(C\text{–}O) = 0.9$, $\delta(O) = 1.9$.

In spite of the large variation in substitution and the number of parameters introduced, the results predict correctly the trend of the bathochromic shifts observed in the series.

In order to obtain absolute wavelengths from the results, further relations are needed. It has been shown [*5*] that the first ultraviolet transition band of fulvene can be fairly well reproduced from Hückel theory in conjunction with an empirical relation developed for the ^1L_a transition of catacondensed hydrocarbons. Applying this approach to the pentatriafulvalenes, we get the results reproduced in column *C* of the table. The agreement seems satisfactory.

Ground-state dipole-moments, directed from the three- to the five-membered ring, have also been calculated in this study. Not unexpectedly, the results are too high [*6*]; thus, a moment of about 13D is calculated for the parent compound (Ia), and of about 10 D (as compared with the experimental value 6.3 D [7]) for the hexaphenyl derivative (Id). In addition, there exist σ dipole-moments of the same direction; a calculation by the semiempirical method of Del Re [*8*] yields 0.03 D for the σ dipole-moment of the parent compound.

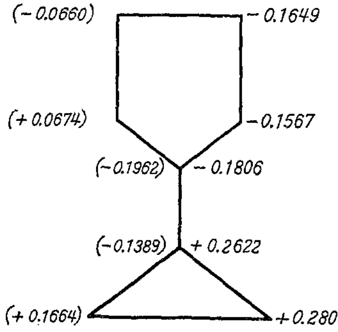


Fig. 2. π-electronic charges of the ground (excited) state of pentatriafulvalene

On $N \rightarrow V_1$ excitation, dipole moments diminish, as exemplified by the molecular diagram (Fig. 2: ground-state π-electronic charges; in parentheses — excited state charges). This relation corroborates the arguments used [*9*] to explain the spectral solvent-shifts observed in several cases.

Note added in proof. Recently, the π-electronic properties of Ia and Id have been investigated by the modified Hückel approach which takes into account the effect of bond alternation on the resonance integral (T. Nakajima, S. Kohda, A. Tajiri and S. Karasawa: Tetrahedron **23,** 2189 (1967)). The dipole moment thus calculated for the *π-conjugated all-carbon* compound Id, is in very good agreement with the experimental value.

References

1. Fulvenes and Thermochromic Ethylenes, Part 45. (Part 44: Rabinovitz, M., I. Agranat, and E. D. Bergmann: J. chem. Soc. (London) **1967**. (In press).

2. Dewar, M. J. S., and G. J. Gleicher: Tetrahedron **21**, 3423 (1965).

3. KENDE, A. S., P. T. IZZO, and P. T. MACGREGOR: J. Amer. chem. Soc. 88, 3359 (1966). See also ZAHRADNIK, R.: Angew. Chem. Internat. Ed. 4, 1039 (1965).
4. PULLMAN, B.: Private communication.
5. MURRELL, J. N.: The theory of the electronic spectra of organic molecules. London: Methuen & Co., Ltd. 1963.
6. See BERGMANN, E. D.: Progress in organic chemistry 3, 81 (1955).
7. —, and I. AGRANAT: Chem. Communic. **1965,** 512.
8. DEL RE, G.: J. chem. Soc. (London) **1958**, 4031.
9. JONES, W. M., and R. SCOTT PYRON: J. Amer. chem. Soc. 86, 1608 (1965).
10. PRINZBACH, H., D. SEIP und U. FICHER: Angew. Chem. Internat. Ed. 4, 242 (1965).
11. KENDE, A. S., and P. T. IZZO: J. Amer. chem. Soc. 87, 1609 (1965).
12. UENO, M., I. MURATA, and Y. KITAHARA: Tetrahedron Letters **1965,** 2967.
13. BERGMANN, E. D., and I. AGRANAT: Tetrahedron 22, 1275 (1966).
14. PRINZBACH, H., and U. FISCHER: Angew. Chem. Internat. Ed. 4, 598 (1965).
15. KENDE, A. S., and P. T. IZZO: J. Amer. chem. Soc. 87, 4162 (1965).

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