Electronic Spectra and Structures of Organic π-Systems. V. SCFMO Calculations of Some Fulvenes and Fulvalenes with the Variable Integrals Methods[1)]

Zen-ichi YOSHIDA and Tsunetoshi KOBAYASHI*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University

(Received February 8, 1971)

The electronic states of fulvene, 6-vinylfulvene, 6-aminofulvene, 6,6-dialkoxyfulvene, 6-amino-6-alkoxyfulvene, heptafulvene, 8-vinylheptafulvene, sesquifulvalene, and fulvalene have been investigated with the variable integrals methods. The effect of bond alternation is taken into account in the SCF procedure. Agreement between the calculated and observed transition energies is satisfactory.

The variable integrals methods I and II[2)] are applied to fulvene, 6-vinylfulvene, 6-aminofulvene, 6,6-dialkoxyfulvene, 6-amino-6-alkoxyfulvene, heptafulvene, 8-vinylheptafulvene, sesquifulvalene, and fulvalene in order to check the applicability of these methods. The effect of bond alternation is taken into consideration in the SCF procedure. Agreement between the calculated transition energies and the observed ones is satisfactory.

Methods of Calculation

Methods I and II (VI/2/only NNβ) were described in the previous papers.[2)]

In order to introduce the effect of bond alternations, the bond lengths between two adjacent atoms are reevaluated by the following formulas in each iteration step of the SCF procedures.

$$\text{VI/1} \qquad l_{CC} = 1.515 - 0.177\,P \qquad (1)$$

$$l_{CO} = 1.367 - 0.177\,P \qquad (2)$$

$$l_{CN} = 1.453 - 0.177\,P \qquad (3)$$

$$\text{VI/2} \qquad l_{CC} = 1.515 - 0.177\,P \qquad (4)$$

$$l_{CO} = 1.371 - 0.177\,P \qquad (5)$$

$$l_{CN} = 1.454 - 0.177\,P \qquad (6)$$

Formulas (1)—(6) are obtained on the assumption that bond lengths depend linearly on bond orders. The coefficients of formuals (1) and (4) are obtained using ethylene and benzene as reference standards. Formulas (2) and (5) are obtained with formaldehyde as the standard, and (3) and (6) with pyridine. The difference between double bond length and single bond length of sp^2-hybridized atom is assumed to be equal to that of sp^2-hybridized carbon atom, *viz.*, 0.177 Å.

For the sake of simplicity the variable parameters are reevaluated only in the first five iteration steps of SCF procedures.

In order to check the applicability of formulas (1)—(6), the above methods have been applied also to *trans*-butadiene, *trans*-acrolein, *p*-dimethoxybenzene, benzoic acid, and acetanilide.

For the sake of brevity the numberings of the atomic orbitals in the molecules are given in Fig. 1. The

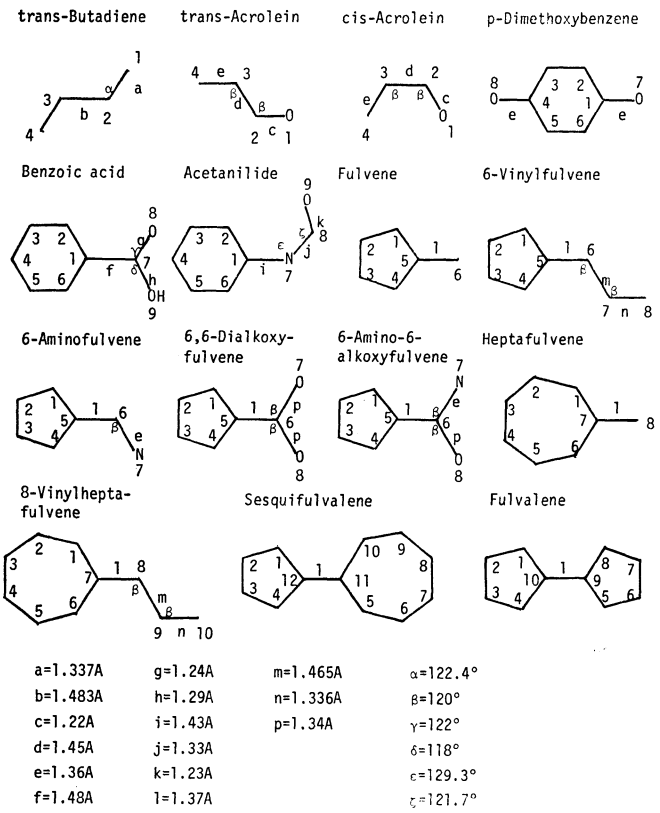

Fig. 1. Assumed structures and numbering systems of molecules.

starting molecular dimensions[3)] are assumed as in Fig. 1, the five-, six-, and seven-membered rings being taken to be regular polygons, the C–C bond lengths of pentagons and heptagons to be 1.40 Å and the C–C bond lengths of benzene rings 1.397 Å.

All the singly excited configurations are taken into account in the configuration interactions.

* Present address: The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo.

1) Presented at the 3rd Symposium on Chemistry of Non-benzenoid Aromatic Compounds, Osaka, November, 1969.

2) a) Z. Yoshida and T. Kobayashi, *Theor. Chim. Acta*, **19**, 377 (1970). b) Z. Yoshida and T. Kobayashi, *J. Chem. Phys.*, **54**, 4538 (1971). c) Z. Yoshida, T. Kobayashi, and A. Konishi, This Bulletin, **45**, 309 (1972). d) Z. Yoshida, T. Kobayashi, and H. Yamada, *ibid.*, **45**, 313 (1972).

3) "Interatomic Distances," Sp. Pub. No. 11, ed. by L. E. Sutton, The Chem. Soc., London (1958). "Interatomic Distances," Sp. Pub. No. 18, ed. by L. E. Sutton, The Chem. Soc., London (1965).

Table 1. π-Electron densities

	VI/1	VI/2	VI/1	VI/2	VI/1	VI/2
	trans-Acrolein		*cis*-Acrolein		*p*-Dimethoxybenzene	
1	1.4206	1.4087	1.4408	1.4249	0.9906	0.9904
2	0.6444	0.6394	0.6454	0.6410	1.0292	1.0301
3	0.9949	0.9932	1.0350	1.0345		
4	0.9401	0.9587	0.8788	0.8996		
7					1.9510	1.9495
	Bonzoic acid		Acetanilide		Fulvene	
1	1.0365	1.0321	1.0275	1.0208	1.0421	1.0364
2	0.9254	0.9368	0.9855	0.9891	1.0103	1.0094
3	1.0033	1.0018	0.9834	0.9866		
4	0.9707	0.9760	1.0034	1.0051		
5	1.0044	1.0031	0.9891	0.9916	0.9992	0.9998
6	0.9998	1.0053	1.0584	1.0505	0.8960	0.9086
7	0.6448	0.6449	1.7338	1.8009		
8	1.5403	1.5028	0.6618	0.6580		
9	1.8749	1.8974	1.5571	1.4974		
	6-Vinylfulvene		6-Aminofulvene		6-Amino-6-alkoxyfulvene	
1	1.0479	1.0413	1.0475	1.0440	1.0737	1.0664
2	1.0138	1.0123	1.0338	1.0291	1.0329	1.0316
3	1.0138	1.0123	1.0218	1.0198	1.0359	1.0330
4	1.0489	1.0420	1.0742	1·0635	1.0652	1.0621
5	1.0027	1.0029	1.1077	1.0881	1.1622	1.1409
6	0.9016	0.9110	0.8760	0.8848	0.8553	0.8597
7	1.0055	1.0051	1.8390	1.8707	1.8538	1.8815
8	0.9659	0.9732			1.9211	1.9247
	6,6-Dialkoxyfulvene		Heptafulvene		Fulvalene	
1	1.0628	1.0596	0.9731	0.9799	1.0454	1.0382
2	1.0282	1.0278	0.9985	0.9986	0.9965	0.9984
3			0.9920	0.9939		
5	1.1347	1.1271				
6	0.8487	0.8520				
7	1.9173	1.9230	1.0022	1.0017		
8			1.0705	1.0535		
9					0.9163	0.9268
	8-Vinylheptafulvene		Sesquifulvalene			
1	0.9695	0.9768	1.0704	1.0620		
2	0.9972	0.9976	1.0346	1.0305		
3	0.9897	0.9922				
4	0.9896	0.9921				
5	0.9971	0.9976	0.9518	0.9623		
6	0.9688	0.9763	0.9719	0.9749		
7	1.0006	1.0006	0.9761	0.9807		
8	1.0681	1.0534				
9	0.9961	0.9968				
10	1.0231	1.0167				
11			0.9146	0.9145		
12			1.0761	1.0649		

Results and Discussion

The π-electron densities are given in Table 1, and π-bond orders and the calculated final bond lengths in Table 2 together with the observed bond lengths.[3] The bond lengths of 6,6-dimethylfulvene observed by Norman and Post[4] are also shown in the column for fulvene in Table 2. The calculated $^1\pi^*$–$^1\pi$ electronic transition energies are given in Table 3.

trans-*Butadiene, Acrolein,* p-*Dimethoxybenzene, Benzoic Acid, and Acetanilide.* Agreement between the finally used bond lengths and the observed ones, and that between the finally calculated bond lengths and the observed ones is good, as shown in Table 2. On the whole both methods give similar γ_{pq}-values and β_{pq}-values in these systems, and similar π-electron

4) N. Norman and B. Post, *Acta Crystallogr.*, **14**, 503 (1961).

Table 2. π-Bond orders and calculated bond lengths

	Bond orders		Bond lengths (Å)		
	VI/1	VI/2	VI/1	VI/2	Obsd.[3]
trans-Butadiene					
1—2	0.9584	0.9643	1.345	1.344	1.337
2—3	0.2854	0.2649	1.464	1.468	1.483
trans-Acrolein					
1—2	0.8633	0.8809	1.214	1.215	1.22
2—3	0.3213	0.2741	1.458	1.466	1.45
3—4	0.9462	0.9610	1.348	1.345	1.36
cis-Acrolein					
1—2	0.8438	0.8646	1.218	1.218	
2—3	0.3630	0.3155	1.451	1.459	
3—4	0.9295	0.9469	1.350	1.347	
p-Dimethoxybenzene					
1—2	0.6499	0.6483	1.400	1.400	1.40
1—7	0.2218	0.2252	1.328	1.331	1.36
2—3	0.6676	0.6698	1.397	1.396	1.37
Benzoic acid					
1—2	0.6380	0.6460	1.402	1.401	1.39
1—6	0.6251	0.6352	1.404	1.403	1.39
1—7	0.3059	0.2648	1.461	1.468	1.48
2—3	0.6666	0.6650	1.397	1.397	1.41
3—4	0.6673	0.6693	1.397	1.397	1.37
4—5	0.6571	0.6576	1.399	1.399	1.36
5—6	0.6813	0.6787	1.394	1.395	1.42
7—8	0.7689	0.8058	1.231	1.228	1.24
7—9	0.4079	0.3703	1.295	1.305	1.29
Acetanilide					
1—2	0.6477	0.6503	1.400	1.400	1.38
1—6	0.6398	0.6454	1.402	1.401	1.37
1—7	0.2479	0.2270	1.409	1.414	1.43
2—3	0.6690	0.6686	1.397	1.397	1.39
3—4	0.6640	0.6653	1.397	1.397	1.40
4—5	0.6646	0.6642	1.397	1.397	1.37
5—6	0.6717	0.6709	1.396	1.396	1.41
7—8	0.5285	0.4479	1.359	1.375	1.33
8—9	0.7679	0.8203	1.231	1.226	1.23
Fulvene					
1—2	0.8863	0.8996	1.358	1.356	1.346[4]
1—5	0.2892	0.2760	1.464	1.466	1.439
2—3	0.3848	0.3583	1.447	1.452	1.435
5—6	0.9108	0.9191	1.354	1.352	1.343
6-Vinylfulvene					
1—2	0.8773	0.8918	1.360	1.357	
1—5	0.3090	0.2940	1.460	1.463	
2—3	0.3935	0.3663	1.445	1.450	
3—4	0.8771	0.8916	1.360	1.357	
4—5	0.3089	0.2941	1.460	1.463	
5—6	0.8539	0.8702	1.364	1.361	
6—7	0.3301	0.3028	1.457	1.461	
7—8	0.9425	0.9520	1.348	1.347	

	Bond orders		Bond lengths (Å)	
	VI/1	VI/2	VI/1	VI/2
6-Aminofulvene				
1—2	0.8574	0.8729	1.364	1.361
1—5	0.3385	0.3233	1.455	1.458
2—3	0.4354	0.4054	1.438	1.443
3—4	0.8579	0.8724	1.363	1.361
4—5	0.3290	0.3197	1.457	1.458
5—6	0.8176	0.8388	1.370	1.367
6—7	0.4226	0.3771	1.378	1.387
6,6-Dialkoxyfulvene				
1—2	0.8557	0.8650	1.364	1.362
1—5	0.3361	0.3339	1.456	1.456
2—3	0.4412	0.4199	1.437	1.441
5—6	0.8083	0.8147	1.372	1.371
6—7	0.3073	0.2961	1.313	1.319
Sesquifulvalene				
1—2	0.8444	0.8601	1.366	1.363
1—12	0.3637	0.3491	1.451	1.453
2—3	0.4410	0.4128	1.437	1.442
5—6	0.8400	0.8608	1.366	1.363
5—11	0.3853	0.3565	1.447	1.452
6—7	0.4261	0.3982	1.440	1.445
7—8	0.8334	0.8531	1.368	1.364
11—12	0.7406	0.7680	1.384	1.379
Fulvalene				
1—2	0.8869	0.9016	1.358	1.355
1—10	0.3014	0.2845	1.462	1.465
2—3	0.3616	0.3362	1.451	1.455
9—10	0.8196	0.8393	1.370	1.366
6-Amino-6-alkoxyfulvene				
1—2	0.8460	0.8577	1.365	1.363
1—5	0.3516	0.3457	1.453	1.454
2—3	0.4552	0.4303	1.434	1.439
3—4	0.8463	0.8580	1.365	1.363
4—5	0.3534	0.3463	1.452	1.454
5—6	0.7735	0.7920	1.378	1.375
6—7	0.4067	0.3653	1.381	1.389
6—8	0.2993	0.2918	1.314	1.319
Heptafulvene				
1—2	0.8864	0.9030	1.358	1.355
1—7	0.3075	0.2817	1.461	1.465
2—3	0.3670	0.3406	1.450	1.455
3—4	0.8728	0.8897	1.361	1.358
7—8	0.8981	0.9155	1.356	1.353
8-Vinylheptafulvene				
1—2	0.8778	0.8952	1.360	1.357
1—7	0.3270	0.3004	1.457	1.462
2—3	0.3742	0.3479	1.449	1.453
3—4	0.8677	0.8849	1.361	1.358
4—5	0.3742	0.3480	1.449	1.453
5—6	0.8771	0.8947	1.360	1.357
6—7	0.3285	0.3017	1.457	1.462
7—8	0.8422	0.8654	1.366	1.362
8—9	0.3261	0.3046	1.457	1.461
9—10	0.9439	0.9513	1.348	1.347

Table 3. Calculated $^1\pi^*$-$^1\pi$ electronic transitions in eV

	VI/1		VI/2		Obsd.		
Sym.	E	f	Sym.	E	f	E	f	Ref.
trans-Butadiene								
^1B_u	5.965	1.042	^1B_u	6.118	1.016	6.0		5)
^1A_g	7.427	0	^1A_g	7.514	0			
^1A_g	7.762	0	^1A_g	7.845	0			
trans-Acrolein								
	6.158	0.935		6.294	0.806	6.41		6)
	7.591	0.017		7.743	0.038			
	8.384	0.077		8.300	0.159			
cis-Acrolein								
	5.612	0.389		5.736	0.353			
	7.558	0.128		7.651	0.058			
	8.427	0.545		8.366	0.636			
Hydroquinone								
$^1B_{2u}$	4.614	0.026	$^1B_{2u}$	4.596	0.028	4.25	(3.43) [b]	7)
$^1B_{1u}$	5.394	0.023	$^1B_{1u}$	5.368	0.035	5.51	(3.71) [b]	
$^1B_{1u}$	7.056	1.353	$^1B_{2u}$	7.038	1.115			
$^1B_{2u}$	7.066	1.129	$^1B_{1u}$	7.068	1.352			
Benzoic acid								
	4.699	0.020		4.660	0.013	4.5	(3) [b]	8)
	5.207	0.289		5.278	0.174	5.28	(4.3) [b]	
	6.118	0.206		6.302	0.414			
	6.915	0.942		6.872	0.891			
Acetanilide								
	4.705	0.016		4.695	0.009	4.53		9)
	5.156	0.204		5.227	0.152	5.18		
	5.990	0.145		5.983	0.181	6.20		
	6.981	1.054		6.985	1.031			
	7.329	1.150		7.267	0.669			

	VI/1				VI/2				Obsd.		
Sym.	E	f	CI Composition[a]		Sym.	E	f	CI Composition[a]		E	f	Ref.
Fulvene												
$^1B_2$	3.425	0.053	3—4	0.998	$^1B_2$	3.663	0.052	3—4	0.999	3.32	0.012	10)
$^1A_1$	5.255	0.507	2—4	0.921	$^1A_1$	5.330	0.524	2—4	0.928	5.13	0.32	
			3—5	0.369				3—5	−0.350			
$^1A_1$	7.083	0.384	1—4	0.825	$^1A_1$	7.117	0.311	1—4	0.831			
			3—5	−0.520				3—5	0.517			
$^1B_2$	7.311	0.163			$^1B_2$	7.357	0.156					
6-Vinylfulvene												
	3.117	0.037	4—5	0.984		3.386	0.038	4—5	0.982	3.12		11)
	4.529	1.108	3—5	0.967		4.636	1.066	3—5	0.968	4.20		
	6.146	0.128	2—5	0.872		6.237	0.092	2—5	0.881			
			4—7	0.443				4—7	0.423			
	6.582	0.365				6.625	0.343					

5) R. S. Mulliken, *Rev. Modern Phys.*, **14**, 265 (1942).
6) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 498 (1945).
7) R. Adams and J. C. Anderson, *J. Amer. Chem. Soc.*, **72**, 5154 (1950).
8) L. Dedel and A. Rosenberg, *Ber.*, **67**, 147 (1934).
9) H. Baba and S. Suzuki, *J. Chem. Phys.*, **32**, 1706 (1960).
10) J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, **23**, 177 (1956).
11) P. A. Straub, Doris Meuche, and E. Heilbronner, *Helv. Chim. Acta*, **49**, 517 (1966).

Table 3. (Continued)

	VI/1				VI/2				Obsd.		
Sym.	E	f	CI Composition[a]		Sym.	E	f	CI Composition[a]	E	f	Ref.
6-Aminofulvene											
	3.483	0.055	4—5	0.998		3.616	0.051	4—5 0.998	3.87	(4.5)[b]	12)
	4.630	0.633	3—5	0.948		4.718	0.654	3—5 0.951			
	6.523	0.222	2—5	0.745		6.577	0.141	2—5 0.764			
			4—6	−0.347				4—6 −0.452			
			4—7	0.458							
	6.860	0.115				7.075	0.095				
6,6-Diethoxyfulvene											
$^1B_2$	3.573	0.061	5—6	0.998	$^1B_2$	3.677	0.055	5—6 0.998	4.28	(4.25)[b]	12)
$^1A_1$	4.724	0.591	4—6	0.941	$^1A_1$	4.785	0.630	4—6 0.946			
$^1A_1$	6.665	0.313	3—6	0.721	$^1A_1$	6.792	0.284	3—6 0.718			
			4—7	0.313				5—7 0.588			
			5—8	0.597				4—8 0.341			
$^1B_2$	6.825	0.098			$^1A_1$	7.015	0.078				
6-Amino-6-ethoxyfulvene											
	3.587	0.059	5—6	0.997		3.657	0.053	5—6 0.998	3.76	(4.4)[b]	12)
	4.510	0.619	4—6	0.948		4.597	0.656	4—6 0.952			
	6.488	0.249	3—6	0.660		6.591	0.177	3—6 0.693			
			4—7	0.418				4—7 0.388			
			5—8	−0.602				5—8 0.567			
	6.691	0.087				6.932	0.067				

	VI/1		VI/2		Obsd.		
Sym.	E	f	Sym.	E	f	E	f	Ref.
Heptafulvene								
$^1B_2$	3.056	0.043	$^1B_2$	3.354	0.049	2.91	0.02	13)
$^1A_1$	4.537	0.460	$^1A_1$	4.731	0.424	4.43	0.3	
$^1B_2$	6.205	0.043	$^1B_2$	6.295	0.037			
$^1A_1$	6.406	1.153	$^1A_1$	6.501	1.182			
8-Vinylheptafulvene								
	2.834	0.030		3.131	0.035	2.79		14)
	4.011	1.031		4.210	0.973	3.81		
	5.646	0.677		5.746	0.725			
	5.839	0.070		5.961	0.046			
	5.912	0.045		6.050	0.045			
Sesquifulvalene								
$^1B_2$	2.761	0.001	$^1B_2$	2.956	0.003	3.07	0.47	15)
$^1B_2$	2.954	0.061	$^1B_2$	3.161	0.064			
$^1A_1$	3.513	1.038	$^1A_1$	3.608	1.013			
$^1A_1$	4.593	0.003	$^1A_1$	5.030	0.003			
$^1A_1$	5.336	0.190	$^1A_1$	5.352	0.265			
Fulvalene								
$^1B_{3g}$	2.534	0	$^1B_{3g}$	2.899	0	2.98		16)
$^1B_{2u}$	2.683	0.033	$^1B_{2u}$	3.043	0.035			
$^1B_{1u}$	4.276	1.087	$^1B_{1u}$	4.376	1.050	3.95	0.4	
^1A_g	5·893	0	^1A_g	6.036	0			
^1A_g	6.498	0	^1A_g	6.456	0			

a) The transition denoted by i-j refers to a one-electron excitation from orbital i to virtual orbital j. The second column gives the CI coefficient of the configuration i-j.
b) $\log \varepsilon$

12) K. Hafner, G. Schulz, and K. Wagner, *Ann.*, **678**, 39 (1964).
13) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).
14) D. J. Bertelli, *J. Amer. Chem. Soc.*, **86**, 3326 (1964).
15) H. Prinzbach, *Angew. Chem.*, **73**, 169 (1961); H. Prinzbach and D. Seip, *ibid.*, **73**, 169 (1961); H. Prinzbach and W. Rosswog, *ibid.*, **73**, 543 (1961).
16) W. von E. Doering, "Theoretical Organic Chemistry, Kekulé Symposium," Butterworths, London (1959), p. 35.

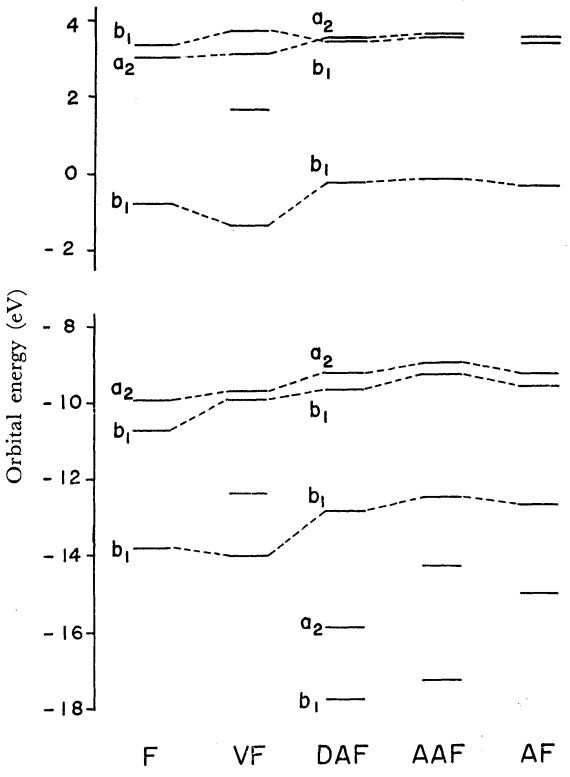

Fig. 2. Correlation diagram for fulvene derivatives with the variable integrals method I.
(F: Fulvene; VF: 6-Vinylfulvene; DAF: 6,6-Dialkoxyfulvene; AAF: 6-Amino-6-alkoxyfulvene; AF: 6-Aminofulvene.)

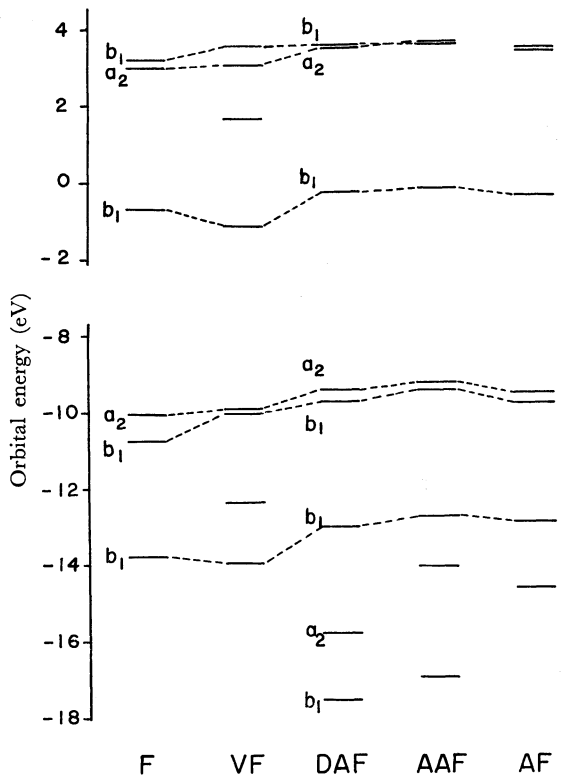

Fig. 3. Correlation diagram for fulvene derivatives with the variable integrals method II.
(F: Fulvene; VF: 6-Vinylfulvene; DAF: 6,6-Dialkoxyfulvene; AAF: 6-Amino-6-alkoxyfulvene; AF: 6-Aminofulvene.)

densities and bond orders (Tables 1 and 2). Agreement between the calculated transition energies by both methods and the observed ones is excellent (Table 3). These results suggest that formulas (1)—(6) can be safely used.

Fulvenes and Fulvalenes. The final parameters or the Coulomb repulsion integrals, γ_{pq}'s, bond lengths, l_{pq}'s, and core resonance integrals, β_{pq}'s, used by both methods are similar to each other except for some cases. In the case of fulvene the finally used bond lengths are in good agreement with the observed bond lengths of 6,6-dimethylfulvene.

The SCF eigenvalues and the eigenvectors given by both methods resemble each other on the whole. The molecular orbitals for fulvene and its derivatives may be approximately correlated as shown in Figs. 2 and 3 for the VI/1 and VI/2 methods, respectively. The correlation diagrams given by the two methods are alike. The lowest occupied orbital of 6-aminofulvene and the two lowest occupied orbitals of 6,6-dialkoxyfulvene or 6-amino-6-alkoxyfulvene are mainly localized on the 6-substituents.

The π-charge densities calculated by both methods are similar to each other (Table 1). The π-bond orders and bond lengths calculated by both methods also resemble each other on the whole (Table 2). The calculated bond lengths of fulvene are in adequate agreement with the bond lengths for 6,6-dimethylfulvene observed by Norman and Post[4] by X-ray crystallographic examination. Both methods reproduce well the bond alternation in the five-membered ring of fulvene. From the table, it is anticipated that slight bond alternations may be present in the five-membered and seven-membered rings of these systems as in fulvene.

The dipolemoment of fulvene calculated by the VI/1 method is 1.231 D and that by the VI/2 method 1.084 D. These values are in good agreement with the observed value (1.1 D) by Thiec and Wiemann[10] in benzene solution. On the other hand the dipolemoment observed by Brown and coworkers[17] by the microwave method is 0.44 D.

The observed transitions are tentatively assigned as in Table 3. Agreement between the calculated transition energies and the observed ones is satisfactory on the whole. The longest wavelength transitions in fulvene, 6-vinylfulvene, 6-aminofulvene, 6,6-diethoxyfulvene and 6-amino-6-ethoxyfulvene are clearly the intramolecular charge-transfer transitions caused by electron transfer from the five-membered rings to the branches.

In conclusion the variable integrals methods I and II are applicable also to these systems.

The calculation was carried out on a HITAC 5020E computer at the Computer Centre of the University of Tokyo.

17) R. D. Brown, F. R. Burden, and J. E. Kent, *J. Chem. Phys.*, **49**, 5542 (1968).