

A FRONTIER MOLECULAR ORBITAL TREATMENT OF FULVENE CYCLOADDITIONS

MOLECULAR ORBITAL CALCULATIONS AND PHOTOELECTRON SPECTRA OF SUBSTITUTED FULVENES

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Abstract—MO calculations have been carried out on substituted fulvenes by several semiempirical methods. The results of these calculations are compared with those by other methods, and with photoelectron spectroscopic data obtained here for several substituted fulvenes. Predictions about the periselectivity ([6+4] or [4+2]) of fulvene cycloadditions with dienes, 1,3-dipoles, and ketenes are made and compared with experimental data, where available.

INTRODUCTION

Fulvenes are non-aromatic cyclic polyolefins which undergo the gamut of radical, electrophilic, nucleophilic and concerted reactions.⁴ Because the various types of fulvene carbons are in sterically similar, but electronically dissimilar, environments, fulvenes serve as excellent models for testing of electronic theories of organic reactivity.

Our studies of the cycloadditions of substituted fulvenes to tropone,⁵ 1,3-dipoles,^{6,7} and a variety of conjugated dienes,⁷ and the resulting discoveries of widely differing periselectivity (formation of one of the thermally allowed adducts) resulting from apparently minor variations in substituents on the fulvene or the second addend led us to consider the reactivity of fulvenes in cycloadditions by perturbation MO theory. In the course of these studies, a qualitative method for the rationalization of periselectivity in competing cycloadditions has appeared,⁸ and the results of perturbation calculations on periselectivity in several fulvene cycloadditions have been reported.⁹

As in our treatments of 1,3-dipolar cycloadditions,¹⁰⁻¹² Diels-Alder regioselectivity (orientational selectivity),¹³ Diels-Alder reaction catalysis,¹⁴ and ketene and sulfene cycloadditions,¹⁵ we have attempted to glean the essential features of the frontier molecular orbitals of the species under study from MO calculations and from experimental data, where available. This information can then be used in a qualitative perturbation treatment¹⁶ of reactivity, regioselectivity, and periselectivity, which not only gives reliable rationalizations and predictions, but also provides an explanation for the observed phenomena.

A comparison of MO calculations on fulvenes. The π orbital system of fulvene may be considered a perturbed hexatriene system as shown in Fig 1.

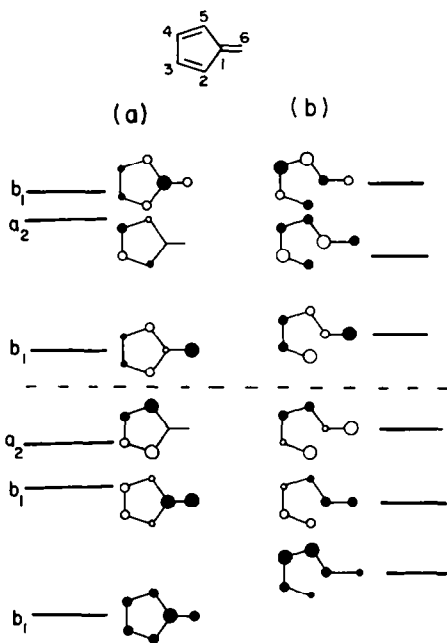


Fig 1. π Molecular orbitals of fulvene and hexatriene.

Union of atoms 1 and 5 of hexatriene causes a lowering or raising of π MO energies depending on whether the new interaction is bonding or antibonding. Alternatively, the π MO's may be built up from those of butadiene and ethylene.¹⁷ The MO's shown in Fig 1 can be obtained from essentially any type of calculation, as shown below.

MO calculations for fulvenes and substituted fulvenes were carried out here by EH,¹⁸ CNDO/2,¹⁹ and CNDO/S²⁰ methods.

In order to insure that the MO coefficients and

energies used in the PMO treatment were not particularly sensitive to the type of calculation employed, fulvene calculations, which have been carried out by essentially all the MO methods, were compared. As shown by the orbital energies given in Table 1 and Fig 2, calculations ranging in sophistication from the qualitative, or "Simplified Molecular Orbital" (SMO) method of Heilbronner and Bock¹⁷ and of Herndon²¹ to the *ab initio* calculations of Praud, *et al.*,²² or Christoffersen,²³ as well as a number of intermediate methods,^{24,26} give qualitatively similar results. If the energy units in these calculations are treated as adjustable parameters, then the ordering of orbital energies and relative separations are quite similar in all methods of calculation and in the experimental photoelectron spectrum.²⁷ The eigenvectors in all calculations are similar. That is, the MO is an antisymmetric orbital (a_2) resembling that of butadiene with $C_2/C_3 = 1$

(SMO) to 1.62 (HMO, $S=O$). The LUMO is symmetric (b_1) with $|C_6| > |C_2| > |C_3| > |C_1|$ and a node between atoms 1 and 6 and atoms 2 and 3 (Fig 1).

Calculations and photoelectron spectroscopy of fulvenes. The quantities of interest in a perturbation treatment of reactivity—calculated here by CNDO/2 or EH—are shown in Tables 2–5 and Figs 3 and 4. Table 2 gives the CNDO/2 calculated eigenvectors and eigenvalues for the two highest occupied π and the lowest unoccupied π orbitals of six fulvenes. Fig 3 diagrammatically shows the correlations between orbitals in different molecules. The geometry chosen for the fulvene nucleus was that determined by microwave spectroscopy for dimethylfulvene.²⁸ Standard bond lengths and angles were used for substituents,¹⁷ and the phenyl groups were rotated 30° out of the fulvene plane. Although only the parent compound has C_{2v} symmetry, Table 3 shows that the local symmetry of the π orbitals is

Table 1. Comparison of selected fulvene calculations: (π MO's) eigenvalues

Calculation	b_1	b_1	a_2	b_1	a_2	b_1	Ref
HMO ($S=0$) ^b	2.12β	1.00β	0.62β	-0.25β	-1.62β	-1.86β	24
HMO ($S=0.25$) ^b	1.38β	0.80β	0.54β	-0.27β	-2.72β	-3.48β	24
SMO ^c	2.00β	1.00β	0.50β	0.00	-1.50β	-1.33β	17, 21
EHT	-14.61 eV	-12.88 eV	-12.26 eV	-9.95 eV	-6.37 eV	-5.68 eV	a
PPP	-17.34 eV	-14.31 eV	-13.68 eV	-4.49 eV	-0.77 eV	-0.47 eV	25
CNDO/2	-23.60 eV	-14.11 eV	-12.41 eV	1.50 eV	7.40 eV	7.84 eV	a
CNDO/S ^d	-14.25 eV	-9.85 eV	-8.94 eV	-1.63 eV	1.14 eV	1.29 eV	a
<i>ab initio</i> (A)	-10.23 eV	-5.87 eV	-4.33 eV	5.49 eV	11.68 eV	13.09 eV	23
<i>ab initio</i> (B)	-16.31 eV	-11.83 eV	-10.74 eV	-0.13 eV	—	—	22
Photoelectron spectrum	$12.8(\pi?)$	9.54	8.55	—	—	—	27
I.P. (vertical)							

^a This work.

^b Overlap integral.

^c "Simplified MO".²¹

^d CNDO/S is a CNDO method with β 's for σ and π overlap treated differently.²⁰

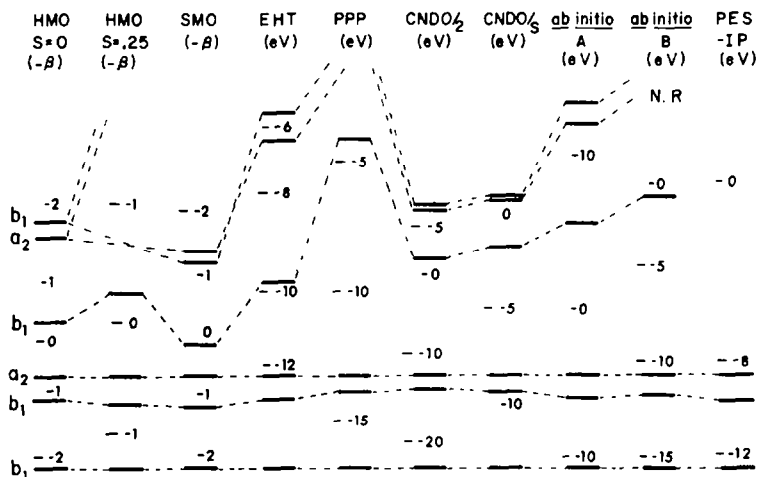


Fig 2. Fulvene π eigenvalues from various methods of calculation.

Table 2. CNDO/2 eigenvalues and eigenvectors for the NHO, HO and LU π orbitals of fulvenes

R	R'	NHO						HO						LU					
		C ₄ C ₃	C ₅ C ₂	C ₁	C ₆	ϵ (eV)	C ₄ C ₃	C ₅ C ₂	C ₁	C ₆	ϵ (eV)	C ₄ C ₃	C ₅ C ₂	C ₁	C ₆	ϵ (eV)			
H	H	0.407	0.110	-0.511	-0.620	-14.108	0.408	0.577	0	0	-12.405	0.365	-0.381	-0.303	0.593	1.500			
		0.407	0.110	-0.511	-0.620	-14.108	-0.408	-0.577	0	0	-12.405	0.365	-0.381	-0.303	0.593	1.500			
Me	H	0.368	0.049	-0.535	-0.523	-12.979	0.421	0.578	-0.016	-0.013	-12.182	0.347	-0.364	-0.298	0.591	1.562			
		0.393	0.088	-0.535	-0.523	-12.979	-0.395	-0.577	-0.016	-0.013	-12.182	0.350	-0.363	-0.298	0.591	1.562			
Me	Me	0.378	0.050	-0.566	-0.478	-12.348	0.408	0.578	0	0	-11.994	0.334	-0.347	-0.295	0.584	1.603			
		0.378	0.050	-0.566	-0.478	-12.348	-0.408	-0.578	0	0	-11.994	0.334	-0.347	-0.295	0.584	1.603			
Ph	H	0.351	0.536	-0.035	0.017	-12.019	0.332	0.079	-0.452	-0.360	-11.913	0.321	-0.315	-0.321	0.522	1.083			
		-0.421	-0.540	-0.035	0.017	-12.019	-0.257	-0.028	-0.452	-0.360	-11.913	0.320	-0.315	-0.321	0.522	1.083			
Cl	H	0.252	-0.015	-0.432	-0.392	-12.971	0.429	0.580	-0.043	-0.037	-12.726	0.357	-0.338	-0.354	0.541	0.618			
		0.336	0.105	-0.432	-0.392	-12.971	-0.380	-0.571	-0.043	-0.037	-12.726	0.348	-0.339	-0.354	0.541	0.618			
NH ₂	H	0.376	0.573	0.047	0.033	-11.839	0.392	0.067	-0.555	-0.357	-11.554	0.332	-0.375	-0.233	0.619	2.226			
		-0.435	-0.579	0.047	0.033	-11.839	0.324	-0.028	-0.555	-0.357	-11.554	0.337	-0.374	-0.233	0.619	2.226			

Table 3. EH eigenvalues and eigenvectors for NHO, HO, and LU π orbitals of fulvenes


R	R'	NHO						HO						LU					
		C ₄ C ₃	C ₅ C ₂	C ₁	C ₆	ϵ (eV)	C ₄ C ₃	C ₅ C ₂	C ₁	C ₆	ϵ (eV)	C ₄ C ₃	C ₅ C ₂	C ₁	C ₆	ϵ (eV)			
H	H	0.387	0.053	-0.452	-0.566	-12.883	0.374	0.556	0	0	-12.258	0.381	0.406	-0.294	0.681	-9.949			
		0.387	0.023	-0.522	-0.468	-12.539	-0.374	-0.556				0.381	-0.406						
Me	H	0.379	-0.023	-0.522	-0.468	-12.539	0.389	0.554	-0.021	-0.013	-12.257	0.357	0.427	-0.193	0.709	-9.640			
		0.405	0.019	-0.522	-0.468	-12.539	-0.360	-0.558				0.364	-0.425						
Me	Me	0.403	-0.030	-0.559	-0.416	-12.386	0.375	0.556	0	0	-12.287	0.347	0.443	-0.114	0.748	-9.375			
		0.403	0.030	-0.559	-0.416	-12.386	-0.375	-0.556				0.347	-0.443						
Ph	H	0.365	0.068	-0.410	-0.266	-12.279	0.238	0.434	0.027	-0.032	-12.083	0.349	0.359	-0.275	0.606	-9.951			
		0.373	-0.139	-0.410	-0.266	-12.279	-0.362	-0.401				0.333	-0.366						
Ph	Me	0.309	-0.098	-0.488	-0.288	-12.207	0.234	0.418	0.016	0.039	-12.072	0.329	0.363	-0.200	0.612	-9.720			
		0.330	0.063	-0.477	-0.245	-12.116	-0.345	-0.386				0.308	-0.369						
Ph	Ph	0.330	-0.063	-0.477	-0.245	-12.116	0.277	0.365	0	0	-11.939	0.313	0.330	-0.261	0.552	-9.960			
		0.330	0.063	-0.477	-0.245	-12.116	-0.277	-0.365				0.313	-0.330						
		-0.273	0.548	-0.102	-0.031	-12.184	0.442	0.032	-0.545	-0.254	-12.049	0.327	0.408	-0.121	0.670	-9.413			
		0.462	0.513	-0.102	-0.031	-12.184	0.281	0.188				0.319	-0.410						
Cl	H	0.375	-0.035	-0.526	-0.453	-12.507	0.394	0.553	-0.027	-0.017	-12.257	0.354	0.427	-0.188	0.706	-9.623			
		0.409	0.020	-0.526	-0.453	-12.507	-0.355	-0.558				0.362	-0.425						
NH ₂	H	0.339	-0.123	-0.550	-0.370	-12.330	0.431	0.542	-0.085	-0.051	-12.256	0.341	0.441	-0.116	0.705	-9.389			
		0.449	0.045	-0.550	-0.370	-12.330	-0.311	-0.558				0.349	-0.439						

Table 4. CNDO/2 π and total charges and dipole moments for fulvenes

		π				Total				μ (Debye)	
R	R'	Atom				Atom				Calcd	Exptl
		4 3	5 2	1	6	4 3	5 2	1	6		
H	H	+0.004	-0.045	+0.015	+0.067	+0.006	-0.036	+0.049	+0.002	0.649	0.44 \pm 0.02 ^a
Me	H	-0.009	-0.049	-0.031	+0.105	0	-0.038	+0.019	+0.042	1.497	1.1 ^b
Me	Me	-0.004	-0.050	-0.066	+0.134	-0.003	-0.038	-0.019	+0.042	1.497	1.1 ^b
Me	Me	-0.016	-0.047	-0.066	+0.134	-0.004	-0.039	-0.004	+0.088	2.193	1.44 \pm 0.03 ^c
Ph	H	-0.006	-0.046	-0.017	+0.093	+0.002	-0.041	+0.026	+0.030	1.323	1.19, 1.22 ^d
Ph	H	-0.006	-0.050	-0.017	+0.093	0	-0.037	+0.026	+0.030	1.323	1.34 \pm 0.04 ^{e, f}
Cl	H	+0.019	-0.058	+0.040	+0.045	+0.015	-0.040	+0.066	+0.059	1.325	—
Cl	H	+0.009	-0.034	+0.040	+0.045	+0.009	-0.034	+0.066	+0.059	1.325	—
NH ₂	H	-0.033	-0.045	-0.126	+0.134	-0.013	-0.029	-0.049	+0.166	3.195	4.48 ^f
NH ₂	H	-0.028	-0.052	-0.126	+0.134	-0.010	-0.031	-0.049	+0.166	3.195	4.48 ^f

^aR. D. Brown, F. R. Burden and J. E. Kent, *J. Chem. Phys.* **49**, 45542 (1968). ^bJ. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr* 207 (1958). ^cG. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949). ^d6-Methyl, 6-Phenyl: G. Kresze and H. Goetz, *Chem. Ber.* **90**, 2161 (1957). ^e6,6-Diphenyl. ^f6-Dimethylamino: K. Hafner, K. H. Vöpel, G. Ploss and C. König, *Liebigs Ann.* **661**, 52 (1963).

Table 5. Calculated and experimental vertical ionization potentials (eV) of fulvenes

	I.(exptl)	I.(CNDO/2) ^a	I.(EH) ^a
Fulvene	8.55 ²⁷	8.4	8.3
	9.54	10.1	8.9
Dimethylfulvene	8.03 ^b (8.08 ^c)	8.0	8.3
	8.73 ^b (8.75 ^c)	8.3	8.4
Diphenylfulvene	7.96 (2 bands?) ^b	7.9 ^c	7.9
	9.0	8.0	8.1
Dimethylaminofulvene	7.43 (2 bands?) ^b	7.5 ^d	8.3 ^d
		7.8	8.3

^aI.(calcd) - 4 eV.

^bThis work.

^cPhenylfulvene calculation.

^dAminofulvene calculation.

^eSee footnote † on next page.

only slightly altered by asymmetric substitution of C-6. Only the lowest unoccupied (LU), highest occupied (HO), and next to highest occupied (NHO) π orbitals are shown here, since these will be the most important orbitals in a perturbation treatment of reactivity. Table 3 and Fig 4 show these same quantities obtained from EH calculations on ten fulvenes. As with the CNDO/2 calculations, local symmetry is rather well preserved even in the highly substituted fulvenes.

Table 4 shows the π charges and total charges at the six atoms of the fulvene nucleus calculated by the CNDO/2 method. With the exception of the 6-amino substituent, which donates significant electron density to the ring, most substituents have a minor effect on the charges at the ring atoms. The small changes in charge densities produced by substituents in the CNDO/2 calculations contrast with the large charge polarization in Hückel calcula-

tions. Table 5 also tabulates the calculated and experimental dipole moments. Satisfactory agreement is found in light of the lack of geometrical optimization in the fulvene calculations. The eigenvectors and charges are affected to only a minor extent by 6-substitution, so that the predominant effect of 6-substitution is alteration of orbital energies.

Substituent effects on orbital energies. A simple model for substituent effects may be constructed from perturbation arguments.^{17,29} Mixing of a methyl pseudo- π orbital formed from CH bond orbitals of the appropriate symmetry with a fulvene π orbital of higher energy will raise the π orbital energy to an extent which is dependent on the magnitude of the coefficient of the π orbital at the site of Me attachment. This effect is clearly shown in both the CNDO/2 and the EH calculations for the occupied orbitals of fulvene, 6-methylfulvene, and 6,6-dimethylfulvene. In both calculations, the

NHOMO is raised to a large extent and the LUMO somewhat less so by the attachment of a Me substituent, since the coefficients in both of these orbitals at C-6 are quite large. The energy of the HOMO is affected to a much smaller extent than that of the NHOMO because the former has a node at C-6. As shown in Table 5, the photoelectron spectroscopic studies of fulvene by Heilbronner, *et al.*,²⁷ and those reported here for dimethylfulvene, 6,6-diphenylfulvene, and 6-methylaminofulvene*† are in qualitative accord with this reasoning. Thus, the HOMO of fulvene is destabilized by 0.52 eV on 6,6-dimethylation, while the NHOMO is destabilized by 0.81 eV.‡

Phenyl substitution has a similar effect on the occupied orbital energies. The destabilization of the

*K. N. Houk, unpublished results using a Perkin-Elmer PS-18 Photoelectron Spectrometer. This work was discontinued when it was learned that Professor Heilbronner had obtained extensive data on substituted fulvenes. We thank Professor Heilbronner for informing us of his work.

†An empirical correction factor of 4 eV has been subtracted from the calculated ionization potentials: S. D. Worley, *Chem. Rev.* **71**, 295 (1971)

‡Since the completion of this work, photoelectron spectra of eleven 6-alkyl and 6,6-dialkylfulvenes have been reported: F. Brogli, P. A. Clark, E. Heilbronner and M. Nueunschwander, *Angew. Chemie Int. Ed. Engl.* **12**, 122 (1973). These authors also refer to unpublished EHT, MINDO/2, INDO, and SPINDO calculations which suggest that the fulvene NHOMO is unaffected by 6-alkyl substitution, in agreement with first-order perturbation considerations. The calculations reported here are in qualitative agreement with those cited by Brogli *et al.* Furthermore, the deviations from Koopmans' theorem for fulvenes noted by these authors suggest that the crossover in a_2 and b_1 levels does occur as indicated by CNDO/2 calculations (Fig 3), in spite of the lack of definitive evidence from the pes spectra.

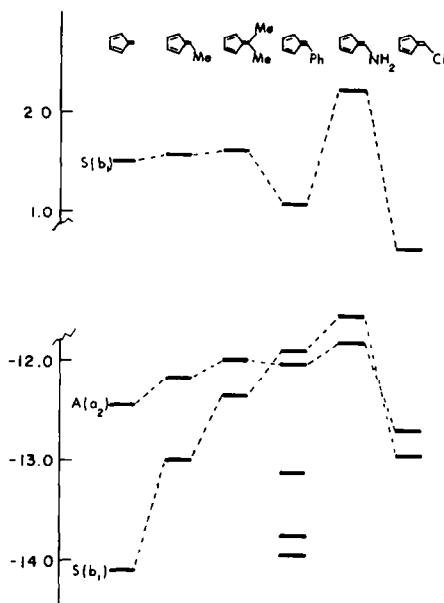


Fig 3. Frontier orbital energies of substituted fulvenes (CNDO/2).

"S" orbital is sufficiently large in the CNDO/2 calculation that this orbital becomes the HOMO while the EH calculation does not predict this crossover.

Whether crossover is achieved is a moot point, since the photoelectron spectrum shows a broad band at 7.96 eV probably due to ionization from two orbitals. That is, the HO and NHO orbitals are nearly degenerate in diphenylfulvene and both types of calculations predict this near degeneracy for phenyl- or diphenyl-fulvenes. The LUMO has been lowered in both calculations due to mixing of

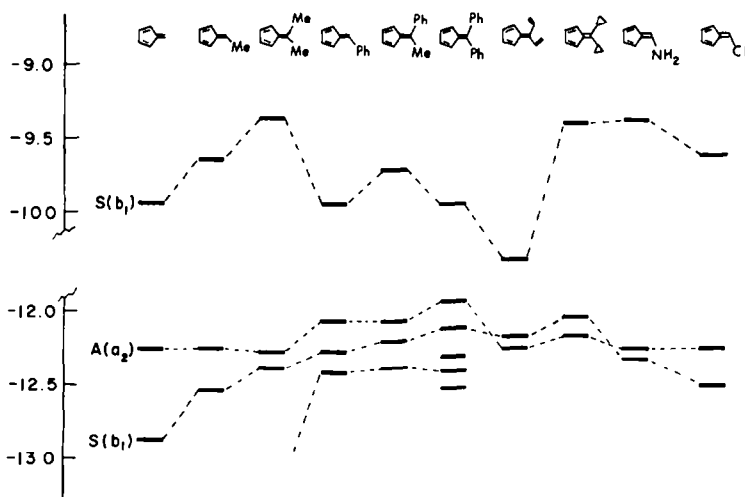


Fig 4. Frontier orbital energies of substituted fulvenes (EH).

phenyl π^* orbitals with the lower-lying fulvene LUMO. Similar patterns may be seen in the remaining EH calculations for fulvenes with conjugating substituents. A perturbation calculation for diphenylfulvene at the Hückel level has been reported³⁰ which differs rather significantly from the results reported here.

Calculations for two hetero-substituted fulvenes have also been carried out. As expected on the basis of dipolar resonance contributions, electron-releasing substituents are expected to stabilize fulvenes to a great extent. Thus, 6-amino or 6-hydroxyl substitution produces aromatic-like behavior in fulvenes.³¹ The 6-amino group raises the energies of NHO, HO, and LU orbitals to a great extent, and, as discussed below, the inertness of 6-aminofulvenes toward cycloaddition may be attributed to the destabilization of the LU. By contrast, the LUMO of 6-chlorofulvene is very low in energy, compatible with the high reactivity of this species toward nucleophilic attack at C-6.³²

The photoelectron spectrum of 6-dimethylamino-

fulvene has a broad band at 7.43 eV indicating the HO and NHO orbitals are nearly degenerate, once again in agreement with both types of calculations.

Spectroscopic calculations. The absorption spectra of fulvenes have been of considerable interest, in part due to the rather intense visible absorptions observed for these benzene isomers. Table 6 gives the first few singlet-singlet transition energies for several fulvene isomers calculated by the CNDO/S method, including limited configuration interaction between the 10 lowest energy singly excited configurations. The Table shows that CI only slightly mixes electronic configurations except for the non-planar phenylfulvene model. These assignments agree with those found for fulvene by a PPP calculation, except that the latter, which used a single CC distance, gave much lower transition energies.³³ The table also gives experimental values for the principal long wavelength absorptions in several fulvenes. The absorption spectroscopy of fulvenes has recently been analyzed by a "molecules in molecules" approach by Heilbronner, *et al.*³⁴ The identification of excited states made there agrees with the CNDO/S calculations where comparisons are available.

Estimates of LUMO energies of fulvenes. One goal of the excited state calculations was to gain more information about the LUMO energies of fulvenes to use in the perturbation treatment of fulvene cycloaddition reactivity.* Since the CNDO/S calculations indicate that the lowest singlet involves predominantly promotion of an elec-

*The attempted estimation of LUMO energies may appear to be somewhat akin to the measurement of the length of a unicorn's horn. The energies of excited states (estimated from electronic transition energies) or of radical anions estimated from electron affinities) do have experimentally definable meaning, and can be used to estimate the top-most occupied orbital energies of such species. This, in turn, can be used as a basis orbital in a perturbation scheme to approximate the change in energy which occurs upon interaction of two molecules.^{11, 12, 16, 17}

Table 6. Calculated (CNDO/S) and observed transition energies

	Calculated			Observed		
	Energy (eV)	CI Composition	f ^a	Energy (eV)	log ϵ	Ref
H	3.63	0.99 (HO \rightarrow LU)	0.018	3.44	2.31	c
	5.37	0.91 (NHO \rightarrow LU)	0.245	5.13	4.14	
Me	3.60	0.99 (HO \rightarrow LU)	0.020	3.47	2.50	d
	4.96	0.90 (NHO \rightarrow LU)	0.257	4.86	4.24	
Ph (30°)	3.41	0.99 (HO \rightarrow LU)	0.018	4.13	—	e
	4.18	0.97 (NHO \rightarrow LU)	0.423	5.06-5.39	—	
	4.54	a	0.047			
	5.31	b	0.028			
NH ₂ (planar)	3.66	0.99 (HO \rightarrow LU)	0.019	3.92 (Me ₂ N)	4.49	f
	4.49	0.95 (NHO \rightarrow LU)	0.330			

^a 0.66 (NNHO \rightarrow LU) + 0.61 (NHO \rightarrow NLU).

^b 0.54 (NNHO \rightarrow LU) + 0.52 (NHO \rightarrow NLS).

^c H. Schaltegger, M. Neuenschwander and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

^d E. Sturm and K. Hafner, *Angew. Chem.*, **76**, 862 (1964).

^e J. H. Day and J. C. Lukman, *Ohio J. Sci.*, **52**, 335 (1952); *Chem. Abst.*, **47**, 8658 (1953).

^f Ref 31.

The oscillator strengths calculated by the CNDO/S method involve terms of the form $C_r C_r'$, where C_r is the coefficient of basis AO r in the ground state orbital and C_r' of the excited state orbital involved in the transition.³⁰ Since all of the transitions calculated here are of the $\pi\pi^$ type, the f 's should be equally accurate (or inaccurate) for all transitions reported and differ mainly in the low values for 1B_2 (in C_{2v}) transitions (e.g., HO(a_2) \rightarrow LU(b_1)) and higher values for 1A_1 (in C_{2v}) transitions (e.g., NHO(b_1) \rightarrow LU(b_1)), since Ψ_1 overlap with Ψ_1 is low in the former case, and high in the latter case.

tron from HOMO→LUMO and the calculated transition energies are quite satisfactory, the difference between the CNDO/S HO and LU orbital energies should be rather close to the difference between the I.P. and the electron affinity (E.A.), which we have assumed in earlier calculations to be equal to the negatives of the HO and LU orbital energies, respectively¹¹ (Koopmans' theorem). Using this method and -(I.P.) as the HO orbital energy, the LU orbital energies in Column A of Table 7 are obtained. A second estimate can be arrived at purely empirically, by assuming a constant change in electron-repulsion upon $\pi\pi^*$ transition in the whole series.¹¹ These estimates are given in Column B. Thirdly, the E.A. of hexatriene has been calculated as +0.17 eV,³⁵ and that of fulvene should be somewhat higher. Using a value of +0.5 for the E.A. ($\epsilon_{LU} = -0.5$ eV) and estimates of substituent effects made earlier,¹¹ the numbers in Column C are calculated. To be consistent with earlier estimates of alkene energies,¹¹ the values in Column B are used in the subsequent discussion.

Frontier orbital analysis of fulvene cycloaddition reactivity. It has been shown in earlier work that considerations of only frontier orbital interactions can provide good rationalizations of reactivity, regioselectivity, and periselectivity in a variety of cycloaddition reactions.^{10-15, 36-38} Thus, if the HO orbital of one addend is close in energy to the LU orbital of a second addend, substitution on either addend which decreases this frontier orbital separation will increase reactivity, while substitution on either addend which results in an increase in this energy gap will decrease reactivity. Furthermore, from considerations of the magnitudes and signs of the coefficients of these strongly interacting frontier orbitals, the favored regioisomer and peri-

isomer may be predicted. That is, as long as bonding interactions may simultaneously occur at two pairs of centers (orbital symmetry control), then the favored product will be that in which the largest coefficients in each of the frontier orbitals are united.^{12, 39}

Steric and geometrical effects (which affect the amount of overlap possible simultaneously between four centers) can also be of importance, and such effects can be incorporated into a perturbation treatment.^{37, 40} However, we have chosen to neglect these effects, and consider their influence in an *ad hoc* fashion when large substituents are present or when geometrical constraints prevent efficient overlap of four centers in a concerted transition state. Thus, only overlap, or "charge-transfer" interactions are considered explicitly here.

The LU orbital of fulvene and its derivatives has the largest coefficient on the exocyclic carbon (C-6) and smaller coefficients, all of roughly the same magnitude, at the ring atoms. This, combined with the small positive charge at this position, results in preferential attack by nucleophiles at C-6 of fulvenes. The HO of fulvene and its simple alkyl derivatives is antisymmetric and has its largest coefficients at C-2 and C-5. That is, it resembles the HOMO of butadiene. Because of this and the relatively high negative charge at these positions, electrophilic attack occurs at C-1 of fulvene and its simple derivatives.⁴¹

In cycloaddition reactions, the local symmetries of the HO and LU orbitals of the alkene (S, A), diene (A, S), and triene (-, A) fragments of fulvene are those expected for concerted reactions to be allowed with $4n$, $4n + 2$, and $4n \pi$ electron systems, respectively. However, whether dienes will cycloadd by one of the allowed [4 + 2] or the [6 + 4] modes, or whether trienes will cycloadd to fulvenes in one of the [4 + 2] or one of the [6 + 4] modes, are more subtle questions, the answers to which require at least qualitative frontier orbital energies and coefficients.

The fulvene frontier orbital energies estimated here, and those estimated for typical substituted alkenes¹¹ are given in Fig 5. As shown by the calculations, the HO and LU orbital coefficients of all fulvenes are closely approximated by those represented schematically in Fig 1, with the exception that phenyl- and amino-fulvenes have a second high-lying occupied orbital (NHOMO in Fig 1) nearly degenerate with the HO represented in Fig 1.

Alkenes. The Diels-Alder reactions of fulvenes are well known, although these are often reversible.^{4, 7} As shown in Fig 5, fulvenes should and do react readily in Diels-Alder reactions with electron-deficient dienophiles due to the strong interaction between the fulvene HO and dienophile LU orbitals. With the very electron-rich 6-dialkylaminofulvenes, concerted reaction has been found to give way to a (presumably) stepwise sub-

Table 7. Estimated LU orbital energies (eV) of fulvenes

	Method		
	A	B	C
Fulvene	-1.3	-0.9	-0.5
6,6-Dimethylfulvene ^a	-0.8	-0.2	+0.5
6-Phenylfulvene ^b	-1.1	-0.5	-1.0
6-Dimethylaminofulvene	-0.1	+0.8	+1.5

^a Methylfulvene or dimethylfulvene numbers are used from Tables 5 and 6.

^b Phenylfulvene or diphenylfulvene numbers are used from Tables 5 and 6.

^c Dimethylaminofulvene or aminofulvene numbers are used from Tables 5 and 6.

A Calculated from exptl. I_v 's (Table 5) and $|\epsilon_{HO} - \epsilon_{LU}|$ obtained from CNDO/S calculations.

B Calculated by assuming $\epsilon_{LU} = I_v - \epsilon_{\text{ref}} - 4.3$ eV.¹¹

C Estimated by extrapolations from the E.A. (+0.17 eV) of hexatriene to $\epsilon_{LU} = -0.4$ eV for fulvene and using substituent effects in Ref 11.

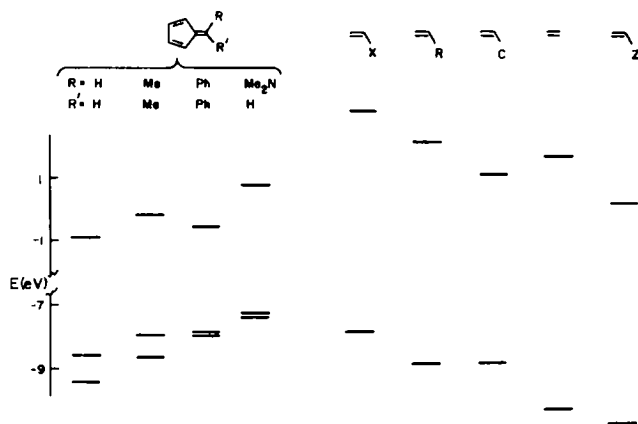
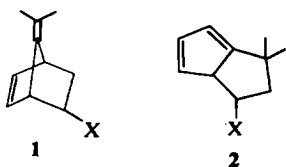


Fig 5. Estimated frontier orbital energies of fulvenes and alkenes. ($X = \text{OR}, \text{NR}_2$, etc.; $R = \text{alkyl}, C = \text{vinyl}, \text{phenyl}$, etc., $Z = -\text{COR}, -\text{CN}$, etc.).¹¹

stitution at C-1 with the very electrophilic dimethyl acetylenedicarboxylate.³¹

Fulvenes should also react readily with electron-rich alkenes such as enamines, since the fulvene LU-alkene HO interaction is strong. Two reaction types are possible, although neither has apparently been studied. The first, a concerted [4 + 2] cycloaddition, is favored by possibilities for simultaneous overlap of the diene termini of fulvene with the alkene termini and would lead to usual Diels-Alder adducts 1. The second, a stepwise [6 + 2] cycloaddition involving a zwitterionic intermediate will be favored both by the electrostatic interactions between the C-6 fulvene atom (+) and the unsubstituted terminus of the enamine (-) or other electron-rich species, and will lead to 2 or a [2 + 2] adduct. Qualitatively, very electron-rich species should favor the latter mode of reaction, while moderately electron-rich species should give [4 + 2] adducts. In favorable cases, competition between the two modes of reaction may be controlled by means of varying solvent polarity. These predictions are the subject of planned experimental tests.



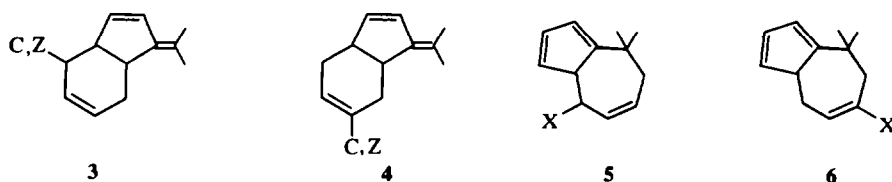
The expected relative reactivities of substituted fulvenes based on frontier orbital arguments are of interest. Thus, based on the calculations, spectra, and data summarized in Fig 5, the relative reactivities of fulvenes toward electron-deficient alkenes should increase in the order: $R = R' = \text{H} < R = \text{Me}, R' = \text{H} < R = R' = \text{Me} < R = \text{Ph}, R' = \text{H} < R = \text{Me}_2\text{N}, R' = \text{H}$. Reactions of tetrayanoethylene

with 6-phenyl-6-(X-phenyl) fulvene decrease in the order $X = p\text{-MeO} > \text{H} > p\text{-Br} > p\text{-Cl} > m\text{-NO}_2$, in accord with this analysis.⁴² Increasing the size of the alkyl group in dialkylfulvenes also accelerates reaction.⁴²

With electron-rich alkenes, the relative reactivity order should be: $R = \text{Me}_2\text{N}, R' = \text{H} < R = R' = \text{Me} < R = \text{Ph}, R' = \text{H} < R = R' = \text{H}$. This reactivity order has not been experimentally verified as yet.

Dienes. Since the HO orbital of fulvene is approximately the same as that of cyclopentadiene, qualitative similarities in reactivity between the two compounds are expected. However, the decrease in energy separating the fulvene HOMO and LUMO as compared to that for cyclopentadiene indicates the former should be more reactive in cycloadditions, including dimerizations. That this is not experimentally observed must be due to the strain present in fulvene adducts and dimers, due to the 7-methylenenorbornene unit present in these adducts. This effect probably accounts for the fact that fulvene reacts preferentially as a dienophile in Diels-Alder reactions with dienes, rather than as a diene. However, the experimental fact must be tempered by the realization that fulvene-diene Diels-Alder adducts can undergo Cope rearrangements to form the thermodynamically more stable adduct. Thus, a variety of fulvenes react with cyclopentadiene, cyclopentadienones, α -pyrone, and 2,4-cycloheptadienone to give *endo* Diels-Alder adducts where the fulvene acts as the dienophile (3 or 4).⁷ Although none of the other Diels-Alder adducts are observed in these reactions, kinetic control has not been proven.

A second symmetry-allowed mode of reaction—a [6 + 4]—to give 5 or 6 where fulvene acts as a triene was initially observed only in the reactions of tropone with fulvenes (see below).⁵ This puzzling observation can be rationalized by using frontier orbital arguments. Cyclopent-



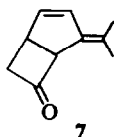
tadienones and 2,4-cycloheptadienone are both "electron-deficient dienes", characterized by low-energy frontier orbitals. With these species, the fulvene HOMO-diene LUMO interaction predominates, and this interaction favors the [4+2] mode of reaction, since there is a node or near-node through C-6. Cyclopentadiene and α -pyrone are less electron-deficient, but still add in a [4+2] fashion. Only when the fulvene LUMO-diene HOMO interaction becomes much stronger than the other interaction will [6+4] addition be observed, since then the largest fulvene coefficient is at C-6 and a diene can simultaneously bond to C-2 in a concerted fashion.¹² Based on this prediction, the study of reactions of fulvenes with 1-aminobutadienes was undertaken, and preliminary results indicate that only [6+4] adducts are formed.⁴³ Other examples of this type are under investigation.

Regiochemical predictions follow from considerations of coefficients of controlling orbitals. Thus, with conjugated or electron-deficient 1-substituted dienes (which have largest LU coefficients at the unsubstituted termini)¹¹ the adducts 3 are favored with simple fulvenes (which have largest HOMO coefficient at C-2). 2-Substituted dienes should give adducts 4. For phenyl and 6-dimethylamino-fulvenes, this preference should be diminished somewhat due to the near degeneracy of the top-most occupied MO's, which have opposite orienting preferences.

For [6+4] cycloadditions with electron-rich 1-substituted or 2-substituted dienes, adducts 5 and 6 should be favored. No direct evidence to support these predictions is available.

1,3-Dipoles. Arguments about regioselectivity, reactivity and periselectivity in reactions of fulvenes with 1,3-dipoles follow those given above for dienes. Examples have been cited earlier.¹²

Ketenes. Ketene cycloadditions with electron-rich species are dominated by the low energy vacant in-plane orbital on the central carbon and the simultaneous [$\pi^2a + \pi^2s$] interaction of the alkene LU and ketene HO.^{15,38} For fulvenes, these interactions lead to formation of adducts 7. Several examples of reactions of this type are known.⁴⁴



Trienes. The previous discussions apply to reactions of trienes also, except that one additional reaction, the [6+4] in which the triene is the 6 electron component and fulvene the 4 electron, can occur. As long as the triene termini are held in reasonably close proximity, the latter will be favored for fulvene HO control, while the [6 (fulvene) + 4 (triene)] will be favored for fulvene LU control. However, secondary orbital interactions can also play a role, which will be described in a forthcoming paper on the fulvene cycloadditions to tropone.

CONCLUSION

MO calculations and photoelectron spectroscopy of fulvenes have led to qualitative generalizations about fulvene frontier molecular orbitals. These have been used to rationalize or predict modes and mechanisms of fulvene cycloadditions as a function of substituents on the fulvene and the second addend. These results differ from the few theoretical treatments of isolated examples of fulvene periselectivity^{8,9} in that no explicit calculations are required, and the varieties of cycloaddition behavior expected upon reactions of fulvenes with compounds varying in electron availability have been revealed.

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