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The Electronic Structure of the Fulvene Radical Cation

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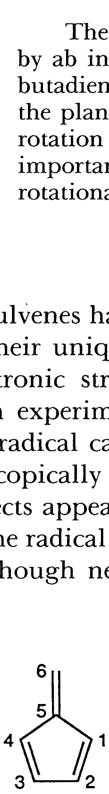
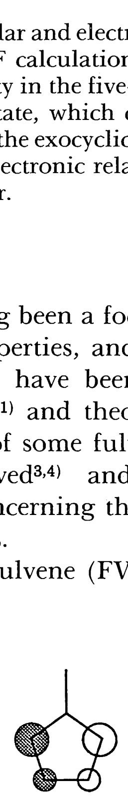
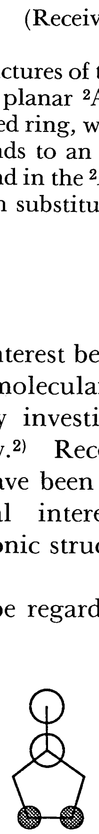
The molecular and electronic structures of the unsubstituted fulvene radical cation, $FV^{+\cdot}$, were investigated by ab initio SCF calculations. The planar $^2A_2$ state, which corresponds to removing an electron from the butadienic moiety in the five-membered ring, was found to be the ground state of $FV^{+\cdot}$, and is more stable than the planar $^2B_1$ state, which corresponds to an olefin radical cation, by about 26 kcal mol^{-1}. The barrier to rotation around the exocyclic C-C bond in the $^2A_2$ radical cation was calculated to be about 63 kcal mol^{-1}. The importance of electronic relaxation in substituted fulvene radical cations is discussed in connection with the rotational barrier.

Fulvenes have long been a focus of interest because of their unique properties, and their molecular and electronic structures have been widely investigated both experimentally[1)] and theoretically.[2)] Recently, the radical cations of some fulvenes have been spectroscopically observed[3,4)] and several interesting aspects appeared concerning the electronic structures of the radical cations.


FV


HOMO($1a_2$)


NHOMO($2b_1$)

Though neutral fulvene (FV) may be regarded as being an olefin, its HOMO ($1a_2$) is not associated with the exocyclic double bond, but extends within the butadienic moiety in the five-membered ring; the HOMO is essentially the HOMO of butadiene. The electrons associated with the exocyclic double bond are in the next to the HOMO (NHOMO), $2b_1$, which is energetically close to the HOMO. This situation of the MO levels of FV can be understood by constructing π MO's of FV from those of butadiene and ethylene, as shown in Fig. 1. The ground state of the fulvene radical cation ($FV^{+\cdot}$) is then expected to correspond to removing a π electron from the butadienic moiety ($^2A_2$ state).

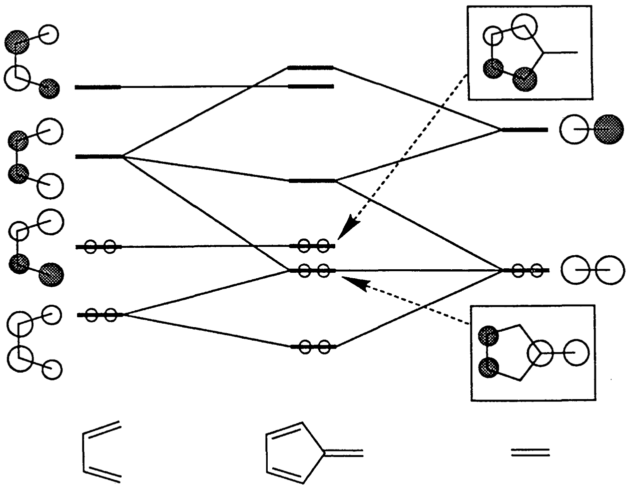
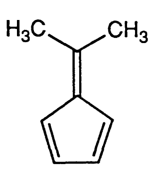


Fig. 1. Construction of π MO's of FV from those of butadiene and ethylene.

Indeed, the freon matrix ESR spectrum of the radical cation of 6,6-dimethylfulvene (**1**),[3)] and CIDNP observed during UV irraddiation of **1**, 6,6-diphenylfulvene (**2**), 6-phenylfulvene (**3**), (*Z*)- and (*E*)-2,6-di-*t*-butylfulvene (**4**), and (*Z*)- and (*E*)-2-*t*-butyl-6-(dimethylamino)fulvene (**5**) in the presence of electron acceptors[4)] have shown that all of the radical cations of these fulvenes have a_2 or a_2-like SOMO.

On the other hand, if the electronic structure of the radical cations merely corresponds to removing an electron from the a_2-like HOMO of the neutral fulvenes, the unpaired electron and positive charge would be constrained to within the butadienic moiety and the double-bond character of the exocyclic double bond would not be reduced. Thus, it is very interesting that (*Z*)-$\mathbf{5}^{+\cdot}$ and (*E*)-$\mathbf{5}^{+\cdot}$ readily interconvert, while (*Z*)-$\mathbf{4}^{+\cdot}$ and (*E*)-$\mathbf{4}^{+\cdot}$ do not show any interconversion.[4)] The electronic relaxation in substituted fulvene radical cations may be important in relation to the rotational barrier around the exocyclic double bond. In this respect, it is important to clarify the electronic structure of the unsubstituted fulvene radical cation, $FV^{+\cdot}$, at both the planar and 90°-twisted forms.

Although a semi-empirical INDO calculation on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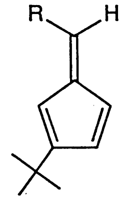
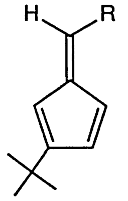
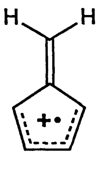
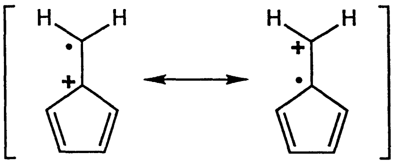

Z-4 R=-C(CH$_3$)$_3$
Z-5 R=-N(CH$_3$)$_2$

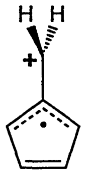

E-4 R=-C(CH$_3$)$_3$
E-5 R=-N(CH$_3$)$_2$



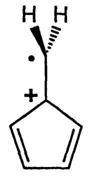
$^2A_2$



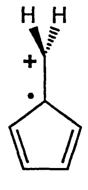
$^2B_1$



$^2A_2$



$^2B_2$



$^2B_1$

$FV^{+\cdot}$ has been carried out in connection with the photoelectron (PE) spectra of a series of alkyl-substituted fulvenes,[5] there are no ab initio level found through theoretical studies on $FV^{+\cdot}$. In this paper the electronic structures of the planar and 90°-twisted forms of $FV^{+\cdot}$ were examined using restricted open-shell Hartree-Fock (ROHF) calculations with the STO-3G[6] and 3-21G[7] basis sets. A C_{2v} symmetry was assumed for both planar and 90°-twisted forms, and the $^2A_2$ and $^2B_1$ states of the planar form and the $^2A_2$, $^2B_2$, and $^2B_1$ states of the 90°-twisted form were examined.

Results and Discussion

Planar $FV^{+\cdot}$. The two lowest energy bands in the PE spectrum of FV have been assigned to formation of the $^2A_2$ (first peak) and $^2B_1$ (second peak) states of $FV^{+\cdot}$.[5] Calculations were carried out for these two states of $FV^{+\cdot}$ using a geometry optimized for FV, so that the calculated relative energies could be compared with the vertical ionization potentials, 8.55 and 9.54 eV for the $^2A_2$ and $^2B_1$ states, respectively, measured for FV.[5] The optimized structures of FV are given in Table 1, and the energies of the two low-lying states of

Table 1. Calculated Molecular Structures of FV[a]

	3-21G	STO-3G	Exp.[b]
Bond lengths			
C_5-C_1	1.485	1.494	1.470
C_1-C_2	1.333	1.324	1.355
C_2-C_3	1.489	1.492	1.476
C_5-C_6	1.321	1.319	1.349
C_1-H_1	1.068	1.079	1.078
C_2-H_2	1.068	1.081	1.080
C_6-H_6	1.073	1.083	1.13
Bond angles			
$C_4C_5C_1$	105.2	104.6	106.6
$C_5C_1C_2$	108.3	108.5	107.7
$C_1C_2C_3$	109.1	109.2	109.0
$C_5C_1H_1$	123.8	123.4	124.7
$C_1C_2H_2$	126.9	127.3	126.4
$C_2C_6H_6$	121.7	122.0	121.5

a) Bond lengths are in Å and bond angles are in degrees. b) Ref. 8.

Table 2. Total Energies of FV and $FV^{+\cdot}$ Calculated at the Geometries Optimized for FV

Species	3-21G	STO-3G	Exp.[a]
FV	−229.35434[b]	−227.82340[b]	—
$FV^{+\cdot}(^2A_2)$	7.50[c]	6.07[c]	8.55
$FV^{+\cdot}(^2B_1)$	8.49	6.99	9.54

a) Vertical ionization potentials in eV. Ref. 5. b) Energy in a.u.. c) Energy relative to FV in eV.

Table 3. Molecular Structures of $FV^{+\cdot}$ Obtained by ROHF/3-21G and ROHF/STO-3G (in Parentheses) Calculations[a]

	C_{2v} planar		C_{2v} perpendicular		
	$^2A_2$	$^2B_1$	$^2A_2$	$^2B_2$	$^2B_1$
Bond lengths					
C_5-C_1	1.457(1.469)	1.471(1.485)	1.401(1.397)	1.472(1.487)	1.472(1.484)
C_1-C_2	1.403(1.410)	1.331(1.329)	1.464(1.469)	1.330(1.330)	1.345(1.334)
C_2-C_3	1.394(1.398)	1.546(1.546)	1.343(1.338)	1.565(1.560)	1.481(1.493)
C_5-C_6	1.333(1.339)	1.409(1.435)	1.435(1.473)	1.440(1.485)	1.411(1.458)
C_1-H_1	1.069(1.091)	1.066(1.080)	1.069(1.086)	1.065(1.080)	1.065(1.080)
C_2-H_2	1.067(1.086)	1.068(1.089)	1.067(1.082)	1.068(1.091)	1.067(1.085)
C_6-H_6	1.073(1.092)	1.072(1.092)	1.080(1.119)	1.075(1.085)	1.081(1.119)
Bond angles					
$C_4C_5C_1$	105.1(104.7)	108.7(108.4)	108.6(109.2)	109.1(108.7)	108.2(107.9)
$C_5C_1C_2$	108.4(108.4)	107.1(106.9)	107.1(106.8)	107.2(106.9)	106.2(106.2)
$C_1C_2C_3$	109.1(109.2)	108.5(109.0)	108.6(108.6)	108.2(108.8)	109.7(109.9)
$C_5C_1H_1$	125.4(125.3)	124.4(123.7)	127.0(127.1)	123.8(123.5)	124.9(124.1)
$C_1C_2H_2$	125.2(125.1)	127.7(127.9)	123.6(123.2)	128.1(128.2)	125.7(126.1)
$C_2C_6H_6$	121.6(121.7)	120.7(120.6)	121.6(122.7)	119.5(118.9)	121.3(115.5)

a) Bond lengths are in Å and bond angles are in degrees.

Table 4. Calculated Total Energies (a.u.) and Relative Energies (kcal mol^{-1}, in Parentheses) of FV$^{+\cdot}$

Structure	State	ROHF/3-21G	ROHF/STO-3G
C_{2v} planar	$^2A_2$	−229.09276(0.0)	−227.62288(0.0)
	$^2B_1$	−229.05143(25.9)	−227.58552(23.4)
C_{2v} perpendicular	$^2A_2$	−228.99294(62.6)	−227.51738(66.2)
	$^2B_2$	−229.02113(44.9)	−227.55711(41.2)
	$^2B_1$	−228.98995(64.5)	−227.51630(66.8)

FV$^{+\cdot}$ calculated using the geometries for FV are given in Table 2 along with the energies of FV and the experimental ionization potentials.[5] The calculated energy differences between the $^2A_2$ and $^2B_1$ states, 0.92 and 0.99 eV at ROHF/STO-3G and ROHF/3-21G levels, respectively, are in good agreement with the experimental value, 0.99 eV, although the ionization potentials are largely underestimated. The vertical ionization potentials estimated by the Koopmans' theorem are 7.07 and 7.96 eV (STO-3G), and 8.53 and 9.46 eV (3-21G) for the $^2A_2$ and $^2B_1$ states, respectively. These values show that the electronic reorganization energies for the $^2A_2$ and $^2B_1$ radical cations are almost the same, although the ionization that produces the $^2A_2$ radical cation is more local.[9]

The structures of the $^2A_2$ and $^2B_1$ states of the planar form of FV$^{+\cdot}$ were then optimized. The optimized structures are shown in Table 3, while the calculated total energies are given in Table 4. The calculated bond lengths well reflect the nodal properties of the MO of FV from which an electron is removed. The $^2A_2$ state is more stable than the $^2B_1$ state by about 26 kcal mol^{-1} (3-21G, 1 cal=4.184 J) when the geometries are optimized for each state, which agrees with spectroscopic observations of the spin distributions of some fulvene radical cations described above. Both the $^2A_2$ and $^2B_1$ states of the planar FV$^{+\cdot}$ correspond to energy minima as confirmed by slight twisting of the radical cations around the exocyclic C–C bond.

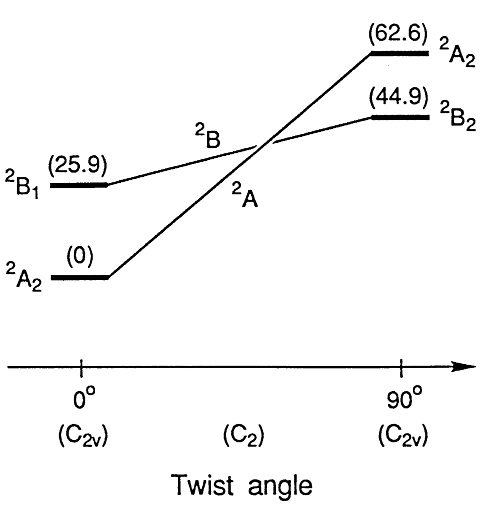
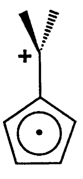


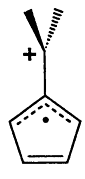
Fig. 2. A state correlation diagram for twisting of FV$^{+\cdot}$. The ROHF/3-21G energies relative to the planar $^2A_2$ state are shown in kcal mol^{-1}.

90°-Twisted FV$^{+\cdot}$. Rigid twisting of the radical cations showed that the $^2A_2$ and $^2B_1$ states of the planar FV$^{+\cdot}$ correlate with the $^2A_2$ and $^2B_2$ states of the 90°-twisted FV$^{+\cdot}$, respectively. The structures of the $^2A_2$ and $^2B_2$ states, as well as the $^2B_1$ state, of the 90°-twisted form were then optimized. The optimized structures are shown in Table 3, while the calculated total energies are given in Table 4. Figure 2 is a state correlation diagram for the double-bond twisting. For the 90°-twisted form, the $^2B_2$ state which correlates with the excited $^2B_1$ state of the planar form is the most stable; the $^2A_2$ state of the 90°-twisted form, which correlates with the $^2A_2$ ground state of the planar form, is higher in energy than the $^2B_2$ state by about 18 kcal mol^{-1} (3-21G). Both the $^2A_2$ and $^2B_2$ states of the 90°-twisted form correspond to the maxima of rotation around the exocyclic C–C bond, as confirmed by the slight untwisting of the 90°-twisted radical cations. Although the $^2B_2$ state is more stable than the $^2A_2$ state at the 90°-twisted form, rotation from the planar $^2A_2$ FV$^{+\cdot}$ is expected to proceed via the $^2A_2$ transition state, since the ^2A and ^2B states of the C_2 twisted forms prefer different molecular structures and, hence, a high barrier exists between the ^2A and ^2B valleys; the energy of the 90°-twisted $^2B_2$ state calculated at the geometry optimized for the 90°-twisted $^2A_2$ state is 88.1 kcal mol^{-1} (3-21G) relative to that of the planar $^2A_2$ ground state. Thus, the rotational barriers estimated for the planar $^2A_2$ and $^2B_1$ states are 62.6 and 19.0(=44.9−25.9) kcal mol^{-1}, respectively (3-21G).

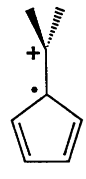
It should be emphasized that an expression such as **I**, which was used in Ref. 4, is not appropriate for the 90°-twisted FV$^{+\cdot}$, since it does not distinguish between the $^2A_2$ and $^2B_1$ states, which are well represented by **II** and **III**, respectively. Both of the two states can be regarded as being a cyclopentadienyl radical attached by a positively charged substituent, -CH$_2$; the SOMO's of the two states stem from the doubly-degenerate SOMO of the ideal D_{5h} cyclopentadienyl



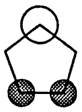
I



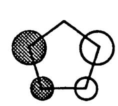
II($^2A_2$)



III($^2B_1$)



S



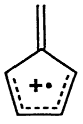
A

radical, the symmetric orbital (S) and the antisymmetric orbital (A).

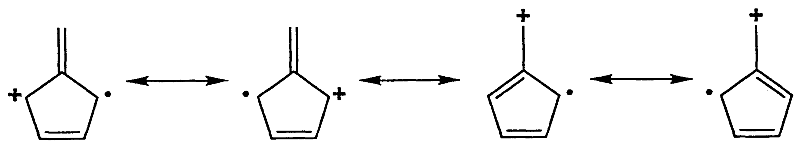
For the 90°-twisted form, the $^2B_2$ state is calculated to be more stable than the $^2B_1$ state by about 20 kcal mol^{-1} (3-21G), although the $^2B_2$ radical cation has an antiaromatic 4π system. This result, however, is not surprising, since the positive charge in the $^2B_1$ radical cation is constrained at the C_6 atom. Furthermore, in the $^2B_2$ radical cation, two C_6-H bonds interact with the π system of the five-membered ring hyperconjugatively to spread positive charge. However, substitution by electron-donating groups at the C_6 position may reverse the relative stability of the two states, since the positive charge at C_6 in the $^2B_1$ or $^2B_1$-like radical cation is largely stabilized.

Electronic Structure of Planar $^2A_2$ State and Rotational Barrier. As described above, both the planar $^2A_2$ and $^2B_1$ FV$^{+\cdot}$ resist twisting around the exocyclic C-C bond especially in the former. Because substitution of *t*-butyl groups is expected not to greatly affect the π electron distribution of FV$^{+\cdot}$, the present computational results concerning the twisting agree with the experimental observation that (*Z*)-**4**$^{+\cdot}$ and (*E*)-**4**$^{+\cdot}$ do not show interconversion.[4] In contrast to (*Z*)-**4**$^{+\cdot}$ and (*E*)-**4**$^{+\cdot}$, (*Z*)-**5**$^{+\cdot}$ and (*E*)-**5**$^{+\cdot}$ showed ready interconversion, in spite of the spin distribution which corresponds to an $^2A_2$-like state.[4] This is partially due to the large stabilization of the 90°-twisted $^2A_2$-like state caused by an electron-donating group at C_6. On the other hand, this result can also be interpreted based on the electronic properties inherently involved in the planar $^2A_2$ state which can be described as follows.

In Table 5 the π electron and unpaired electron populations of the carbon atoms in planar $^2A_2$ and $^2B_1$ FV$^{+\cdot}$ are shown. The unpaired electron distribution in the $^2A_2$ FV$^{+\cdot}$ simply reflects the shape of the SOMO, 1a$_2$; the unpaired electron is located largely on C_1 and C_4 and to a smaller degree on C_2 and C_3. Because the SOMO has a nodal plane perpendicular to the molecular plane and passing through C_5 and C_6, the unpaired electron is not located on C_5 and C_6. This spin distribution seems to correspond to a butadiene radical cation, **IV** or [**V**↔**V′**]. However, as can be seen from Table 5, the π electron density is the most dilute at C_6, which implies a significant contribution of **VI** and **VI′**. Because the SOMO has no coefficient at C_5 or C_6, the electron flow from C_6 can be attributed to π electrons other than the unpaired electron. Namely, the positively charged hole, which is made by removing an electron from the 1a$_2$ HOMO of FV, is partially filled by a reorganization of π electrons other than the unpaired electron. If an electron-donating group, such as the dimethylamino group, is introduced at C_6, the contributions of **VI** and **VI′** become large, which may considerably reduce the double-bond character of the exocyclic C_5-C_6 bond and,



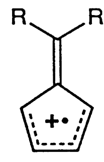
IV



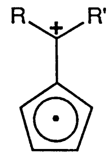
V **V'** **VI** **VI'**

Table 5. The π Electron and Unpaired Electron Populations of the Carbon Atoms in the Planar $^2A_2$ and $^2B_1$ FV$^{+\cdot}$ Obtained by ROHF/3-21G and ROHF/STO-3G (in Parentheses) Calculations

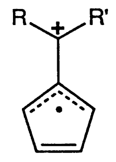
Atom	π Electron population		Unpaired electron population	
	$^2A_2$	$^2B_1$	$^2A_2$	$^2B_1$
C_1, C_4	0.696(0.702)	1.098(1.094)	0.377(0.382)	0.005(0.005)
C_2, C_3	0.896(0.892)	0.781(0.793)	0.123(0.118)	0.065(0.049)
C_5	1.151(1.120)	0.608(0.540)	0.000(0.000)	0.251(0.222)
C_6	0.665(0.693)	0.632(0.687)	0.000(0.000)	0.611(0.668)



VII



VIII



IX

hence, lower the rotational barrier.[10]

On the other hand, the $^2B_1$ state is essentially an olefin radical cation with a weakened C_5–C_6 bond, as can be seen from Tables 3 and 5. Indeed, the rotational barrier for the $^2B_1$ state is relatively small.

In Ref. 4, **VII** and **VIII** were referred to as "localized" and "relaxed" radical cations, respectively, in order to specify the possible electronic structures of the fulvene radical cations. In a "localized" radical cation, the unpaired electron and positive charge are localized in the endocyclic butadienic moiety; in a "relaxed" radical cation, the unpaired electron is located in the ring and the positive charge is located on C_6. As can be seen from the above discussion, however, both **VII** and **VIII** represent an $^2A_2$-like state with similar SOMO; as the substituent attached to the C_6 atom becomes more electron-donating, the radical cation becomes more "relaxed". Note that fulvene radical cations are more or less "relaxed", and that the boundary between the "localized" and "relaxed"radical cations is not distinct. Furthermore, it should be noted that such a representation as **VIII** used in Ref. 4 does not distinguish between the "relaxed" $^2A_2$ radical cation and the $^2B_1$ radical cation. The former may be explicitly described by **IX**. In the $^2A_2$ radical cation, the unpaired electron is not located on C_5 and C_6, while it is located mainly on C_5 and C_6 in the $^2B_1$ radical cation.

Conclusion

Ab initio SCF calculations using the STO-3G and 3-21G basis sets have shown that the ground state of the unsubstituted fulvene radical cation ($FV^{+\cdot}$) is the planar $^2A_2$ state. Though this state corresponds to removing a π electron from the butadienic moiety in the five-membered ring of FV, the positively charged hole is partially filled by a π-electron flow from the exocyclic region without any significant change in the unpaired electron distribution. The planar $^2B_1$ state, which corresponds to an olefin radical cation with a weakened exocyclic C–C bond, is higher in energy than the $^2A_2$ state by about 26 kcal mol^{-1}. Both the planar $^2A_2$ and $^2B_1$ states correspond to the minima of rotation around the exocyclic C–C bond. Although the 90°-twisted $^2A_2$ state is higher than the planar $^2A_2$ state by about 63 kcal mol^{-1}, the rotational barrier for the $^2A_2$ state was predicted to be considerably lowered by the substitution of electron-donating groups at the C_6 position.

References

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9) As to the validity of the Koopmans' theorem in connection with the fulvene radical cations, see Ref. 5.

10) The present discussion on the twisting of $FV^{+\cdot}$ reminds one of the calculations on the trimethylenemethane radical cation ($TMM^{+\cdot}$) by Du and Borden.[11] Indeed, the π system of $FV^{+\cdot}$ may be regarded as that of "$TMM^{+\cdot}$+ethylene", and the SOMO of the planar $^2A_2$ $FV^{+\cdot}$ is an in-phase combination of that of the planar $^2A_2$ $TMM^{+\cdot}$ and the LUMO of ethylene.

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