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CNDO/2 Calculations of Ionization Potentials of Some Fluorosubstituted Conjugated Hydrocarbons

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The ionization potentials of the fluorosubstituted derivatives of ethylene, *trans*-1,3-butadiene, and benzene were calculated by using the modified CNDO/2 method. In agreement with the available experimental facts, the ionization potentials due to the π-electron were predicted to change little on fluorination, while those due to the σ-electron were predicted to suffer a more or less large change on fluorination. An explanation for this fact, called the perfluoro effect, can be given by a simple perturbational treatment.

One of the methods which can be of great help in the assignment of the photoelectron spectra of conjugated molecules is the perfluoro effect first studied by Robin *et al.*;[1] the substitution of the hydrogen atoms in a planar conjugated molecule by fluorine atoms will increase the ionization potentials (*IP*'s) of the σ-MO's by 2.5—5 eV, whereas the π-MO's are stabilized by only 0—1 eV.

Most of the molecular orbital calculations thus far made of ionization potentials of fluorosubstituted planar conjugated molecules have been confined to levels due to π-electrons. There have been very few systematic and quantitative studies of ionization potentials due to σ-electrons.

In order to identify the photoelectron spectra of monofluoro- and tetrafluoroethylene, Robin *et al.*[1] and Meza and Wahlgren[2] have performed the GTO calculations of ionization potentials due to π- and σ-electrons and compared the results with those for ethylene in order to examine the effect of fluorination on ionization potentials.

In this paper, we study systematically and quantitatively the fluorosubstituent effects by using a modified CNDO/2 method proposed in a previous paper.[3] In order to examine how the perfluoro effect holds for ethylene in particular, we draw a diagram showing the correlation of ionization potentials at various degrees of fluorination. The calculated ionization potentials are compared with the available experimental values and those obtained by other SCF MO methods. Further, we show that a simple perturbational treatment can give a satisfactory explanation of the perfluoro effect that the ionization potentials due to π-electrons of conjugated hydrocarbons suffer no substitutional change on fluorination.

Method of Calculation

Tajiri *et al.*[4] and Ohmichi *et al.*[5] have calculated the electronic spectra of a number of saturated and unsaturated compounds using a modified CNDO/2 method which is a compromise between the methods of Bene-Jaffé[6] and of Sichel-Whitehead.[7] Our method differs from those above in the following point; the local core matrix element, $U_{\mu\mu}$, of the atomic orbital, μ, is estimated as an additional empirical parameter and adjusted, together with selected values of the bonding parameters, β^0_A, and the separation constant, k, so that a wide range of ionization potentials of a certain molecule may be reproduced. The details of the method were described in a previous paper,[3] in which a good agreement between the calculated ionization potentials and electronic spectra and the experimental ones for several unsaturated hydrocarbons was obtained. The parameter values for the fluorine atom are determined so that they may reproduce a wide range of observed ionization potentials for mono-, 1,1-di-, and tetrafluoroethylene. The new parameter values, together with those of earlier workers, are given in Table 1.

Table 1. Parameter values[a)]

Parameter	Method	H	C	F
U_{ss}	CNDO/2[b)]	−17.38	−70.30	−199.3
	Ohmichi *et al.*[c)]	−13.60	−50.69	−130.1
	This method	−13.60	−42.0	−112.0
U_{pp}	CNDO/2		−61.8	−178.1
	Ohmichi *et al.*		−41.53	−108.9
	This method		−40.0	−110.0
β^0_A	CNDO/2	9	21	39
	Ohmichi *et al.*	8	15	
	This method	9	15	29
k	Ohmichi *et al.*		0.75	0.75
	This method		0.70	0.70

a) Values for U_{ss}, U_{pp}, and β^0_A are in eV units.
b) Ref. 18. c) Ref. 5.

The geometrical structure of tetrafluoroethylene was taken from Sutton's tables.[8] For the other fluoroderivatives, the bond lengths of C–F and C–H are assumed to be 1.33 and 1.08 Å respectively, and all the bond angles are taken to be 120°. The bond lengths of all the formal C=C and C–C bonds are assumed to be 1.34 and 1.47 Å respectively. For the benzene derivatives, the C–C bond lengths of the benzene ring are assumed to be the same as those of benzene.

The calculations were carried out on the NEAC 2200, model 700, computer of Tohoku University.

Results and Discussion

The CNDO/2 Calculations for Fluoroderivatives. The high-resolution photoelectron spectra of ethylene, monofluoroethylene, 1,1-difluoroethylene, and tetrafluoroethylene have been investigated by Robin *et al.*[1] and by Lake and Thompson.[9] From the facts that the vibrational progression of the C=C bond stretching mode appears in the first bands observed at about 10.6 eV in these fluoroderivatives, and that in the second bands no such progression is observed, it seems that the first *IP*'s are due to a π-electron, and the second *IP*'s, to a σ-electron. It is noted that the first *IP*'s of these fluoroderivatives are almost the same as that of ethylene, while the second *IP*'s suffer a large shift to a higher energy.

TABLE 2. IONIZATION POTENTIALS OF MONOFLUOROETHYLENE (eV)

Vertical *IP*10)	This work	*ab initio*2)
10.58	10.58 πa''	10.27 a''
13.79	13.63 a'	14.85 a'
14.51	14.97 a'	15.71 a'
16.77	17.49 a'	18.09 a''
17.97	18.05 πa''	18.17 a'
	18.32 a'	19.71 a'
	20.22 a'	22.38 a'
	23.80 a'	28.86 a'
	28.18 a'	44.19 a'

TABLE 3. IONIZATION POTENTIALS OF 1,1-DIFLUOROETHYLENE (eV)

Vertical *IP*10)	This work
10.72	10.60 πb_1
14.79	14.92 a_1
15.73	15.17 b_2
	17.53 b_2
	17.75 πa_2
18.22	18.32 a_1
	18.56 b_2
19.68	18.71 a_1
	18.93 πb_1
	24.03 a_1
	25.94 b_2
	28.89 a_1

TABLE 4. IONIZATION POTENTIALS OF TETRAFLUOROETHYLENE (eV)

Obsd1)	Calcd	
	This work	Robin *et al.*
10.52	10.55 $\pi 2b_{1u}$	10.86 $\pi 2b_{1u}$
15.95	15.53 $6a_g$	17.15 $6a_g$
16.4	17.68 $4b_{1g}$	17.40 $4b_{1g}$
16.6	17.68 $4b_{2u}$	17.77 $4b_{2u}$
16.9	18.05 $\pi 1a_u$	18.15 $\pi 1a_u$
17.60	18.08 $\pi 1b_{3g}$	18.32 $\pi 1b_{3g}$
18.21	18.21 $5b_{3u}$	18.82 $5b_{3u}$
	18.65 $3b_{1g}$	19.60 $\pi 1b_{2g}$
	18.89 $3b_{2u}$	19.90 $3b_{1g}$
	18.89 $\pi 1b_{2g}$	20.83 $\pi 1b_{1u}$
19.46	19.05 $5a_g$	21.50 $3b_{2u}$
21.0	19.05 $4b_{3u}$	22.15 $5a_g$
22.5	19.87 $\pi 1b_{1u}$	23.26 $4b_{3u}$
	22.29 $4a_g$	28.66 $4a_g$
	23.28 $2b_{1g}$	
	27.78 $2b_{2u}$	
	28.51 $3b_{3u}$	
	30.21 $3a_g$	

Tables 2, 3, and 4 show the calculated and observe ionization potentials of mono-, 1,1-di-, and tetrafluoroethylene respectively. It may be seen that the calculated ionization potentials of monofluoro- and difluoroderivatives and the calculated lower ionization potentials (<18.5 eV) of tetrafluoroethylene are in fairly good agreement with the experimental values. For the first seven levels of tetrafluoroethylene, the order of energy and the atomic populations are in good agreement with those obtained by a GTO calculation.1)

Figure 1 shows the correlations of the MO's of ethylene with those of various fluoroderivatives of ethylene. The correlation diagram was drawn on the basis of the atomic and overlap population analyses and of the correspondence among the irreducible representations of various point groups. Comparing the atomic and overlap populations of ethylene with those of tetrafluoroethylene, we can correlate the $1b_{1u}$ π orbital and the $1b_{1g}$, $1b_{2u}$, $2b_{3u}$, and $2a_g$ σ orbitals of ethylene with the $2b_{1u}$ π orbital and the $2b_{1g}$, $2b_{2u}$, $3b_{3u}$, and $3a_g$ σ orbitals of tetrafluoroethylene respectively. This is because, in this correlation, the atomic populations on the carbon atoms in these orbitals of ethylene are least affected on fluorination. The $3a_g$ σ orbital of ethylene may be correlated with the $6a_g$ or $4a_g$ orbital of tetrafluoroethylene. The two other symmetrically possible correlations, $3a_g$ (ethylene)-$5a_g$ or $3a_g$ (tetrafluoroethylene), can be rejected, because the atomic population on carbon atoms in the $5a_g$ or $3a_g$ orbital of tetrafluoroethylene are substantially different from those in the $3a_g$ orbital of ethylene.

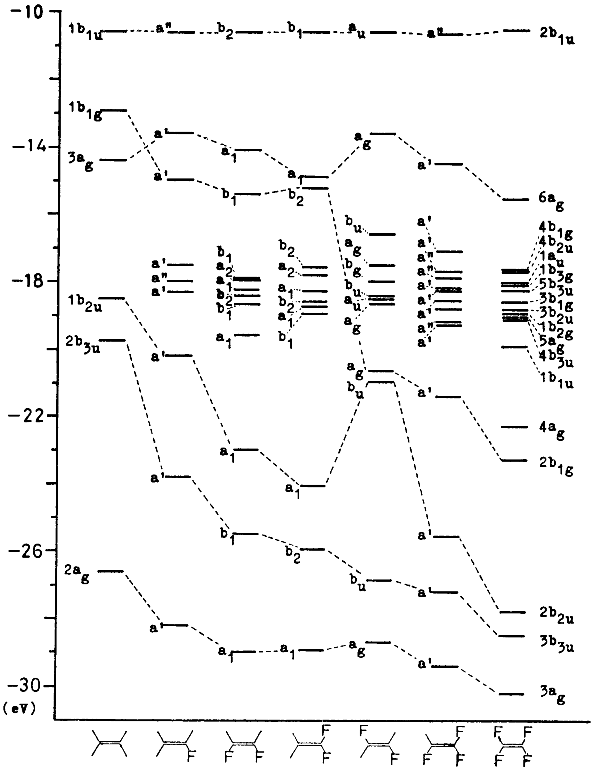

Fig. 1. MO correlation diagram of ethylene and its fluoro-derivatives.

Of the two possible correlations, we prefer the $3a_g$ (ethylene)-$6a_g$(tetrafluoroethylene) correlation. The reason for this preference is as follows; in the mono-, di- and tri-fluoroethylene examined, the orbitals related to the $3a_g$ orbital of ethylene turned out to have negative overlap populations on the C–F bonds, while in tetrafluoroethylene only the $6a_g$ orbitals has the negative overlap populations on the C–F bonds. The correlations of the σ-orbitals of ethylene with those of tetrafluoroethylene proposed by Robin *et al.*[1] are considerably different from the present correlations. For monofluoro- and trifluoroethylene, the correlations are less unambiguous because, for these molecules, the population analyses do not give sufficient information and their molecular symmetries are low.

It may be seen in Fig. 1 that the energy of the MO ($1b_{1u}$) due to π-electrons of carbon atoms of ethylene remains almost constant on fluorination, while the MO's due to σ-electrons are more or less markedly lowered in energy on fluorination, with the exception of the $3a_g$ σ orbital. This orbital is raised in energy in some fluoroderivatives and is lowered in some others, the change in energy being in all cases considerably small compared with those of other σ orbitals. It should be noted that the σ orbitals related to the $3a_g$ orbital of ethylene are characterized by the fact that, in these orbitals, the overlap population between the carbon and fluorine atoms is negative; that is, these orbitals are antibonding between the carbon and fluorine atoms. Furthermore, in these orbitals the atomic population on the fluorine atom is relatively small. On the other hand, all the other σ orbitals of the fluoroderivatives are bonding between the carbon and fluorine atoms, and in these orbitals the atomic populations on the fluorine atoms are relatively large.

TABLE 5. IONIZATION POTENTIALS OF 1,1,4,4-TETRAFLUOROBUTADIENE (eV)

Obsd[10]	This work
9.30	9.33 πb_g
12.04	12.34 πa_u
14.5	13.39 a_g
15.3	14.15 a_g
16.0	15.89 b_u
	17.37 b_u
	17.51 a_g
	17.75 πb_g
	17.76 πa_u
	17.93 a_g
18.0	18.08 b_u
19.6	18.58 a_g
21.0	18.68 b_u
21.9	18.73 a_g
	18.87 πb_g
	18.88 b_u
	19.03 πa_u
	22.09 b_u
	24.84 a_g
	26.40 b_u
	26.48 a_g
	28.67 b_u
	30.35 a_g

The assignment of the ionization potentials of *trans*-1,3-butadiene has not been uniquely determined. There remains the problem of where the two π *IP*'s lie. The earlier study by Robin *et al.*[10] of the photoelectron spectra of the fluorinated derivatives of this molecule indicated that the first three ionization potentials are due to π, σ, and π electrons respectively, but recent investigations[19–20] have suggested that the π, π, and σ sequence is also acceptable.

In order to examine this point, we calculated the ionization potentials of 1,1,4,4-tetrafluorobutadiene (Table 5) and compared them with those of the parent hydrocarbon calculated previously using the same method. In a previous paper[3] the experimental ionization potentials of 9.07, 11.27 and 12.17 eV were assigned to the calculated 9.07 (π), 11.75 (σ), and 12, 39 (π) eV respectively. The ionization potential calculated from the lowest π orbital of 1,3-butadiene (12.39 eV) shifts, though slightly, to a lower energy in its tetrafluoro derivative (12.34 eV). This result suggests that the third band observed at 12.17 eV in 1,3-butadiene corresponds to the second band observed at 12.04 eV in its tetrafluoro derivative, both the bands being due to π-electrons, because, in our calculations, the other two lower ionization potentials of the parent hydrocarbon shift to higher energies on tetrafluorination. Moreover, such an assignment is supported by the results of a simple perturbational treatment (*vide infra*).

Experimentally the intense bands observed at about 16 eV of the tetrafluobutadiene was attributed to the fluorine lone-pair electron. In our calculation this band is assigned to the b_u σ level, and the ionization potentials due to the fluorine lone-pair electrons are predicted to be 17—19 eV.

The photoelectron spectra of fluorobenzene, *p*-difluorobenzene, and 1,2,4-trifluorobenzene have been reported by Turner *et al.*[11] and Clark and Frost.[12] The absorption spectra of the lower energy region (9—14 eV) of fluorobenzene have also been investigated by other authors.[13–15] The calculated ionization potentials of monofluoro-, *p*-difluoro-, and 1,2,4-trifluorobenzene are listed in Tables 6, 7, and 8, together with the experimental values. In these tables the observed third bands are assigned to the calculated fifth ionization potentials (at about 13.8 eV) due to a π-electron. The reason for this assignment will be given below. The first three observed bands in these molecules are predicted to be due to π-electrons, the first two being related to the e_{1g} π levels of benzene observed at 9.3 eV, and the third one, to the a_{2u} π level of benzene observed at 12.1 eV. This assignment is in agreement with those proposed by Turner *et al.*,[11] Clark and Frost,[12] and Gilbert and Sandorfy.[13] On the other hand, Narayan and Murrell[16] have suggested that, in fluoro- and *p*-difluorobenzene, the π level, which is related to the a_{2u} level of benzene, should be preceded by a σ level, as in benzene itself, and that in the higher fluorides the highest σ level would lie below the third π level.

TABLE 6. IONIZATION POTENTIALS OF FLUOROBENZENE (eV)

Obsd		This work
Clark[12]	Turner[11]	
9.21	9.19	9.40 πb_1
9.87	9.82	9.54 πa_2
11.83	11.77	13.83 πb_1
12.98	12.8	11.37 b_2
13.89	13.68	12.00 a_1
14.55	14.2	14.07 b_2
	14.8	14.45 a_1
16.24	15.9	14.68 b_2
17.77	17.3	16.52 a_1
		17.74 b_2
19.02		18.11 πb_1
19.55		18.30 a_1
20.69		20.75 a_1
		21.53 b_2
		23.33 a_1
		25.46 b_2
		27.89 a_1
		33.23 a_1

TABLE 7. IONIZATION POTENTIAL OF p-DIFLUOROBENZENE (eV)

Obsd		This work
Clark[12]	Turner[11]	
9.15	9.33	9.41 πb_{3g}
10.04	10.10	9.67 πb_{2g}
12.16	(12.3)	13.73 πb_{1u}
		11.42 b_{1g}
13.55	(13.6)	13.31 a_g
14.24	(14.3)	14.16 b_{3u}
15.01	(15.0)	14.37 b_{3u}
(15.44)	(15.3)	14.58 b_{2u}
(16.79)		16.87 b_{1g}
17.12	17.09	17.86 b_{2u}
		18.09 πb_{3g}
		18.27 a_g
17.93		18.31 πb_{1u}
19.74		18.73 b_{3u}
20.03		19.79 b_{2u}
		20.88 a_g
		22.12 b_{1g}
		25.70 b_{3u}
		26.92 a_g
		28.51 b_{2u}
		33.33 a_g

Table 9 lists the calculated energy shifts, measured from the corresponding *IP*'s of benzene, of the first *IP*'s of the fluorobenzenes brought about on fluorination, together with the observed ones. In obtaining the observed shifts we have assumed that the observed third bands are related to the a_{2u} π-orbital of benzene, since the shifts of this band on fluorination are always very small. The energy shifts of the calculated fifth band are also quite small, so that the observed third band should be assigned to the calculated fifth one. The calculated third and fourth levels, predicted to be related to the e_{2g} σ orbitals of benzene, undergo relatively large blue shifts, and the observed fourth and fifth levels should be assigned to these levels.

TABLE 8. IONIZATION POTENTIAL OF 1,2,4-TRIFLUOROBENZENE (eV)

Obsd[12]	This work
9.30	9.50 $\pi a''$
10.05	9.72 $\pi a''$
12.26	13.67 $\pi a''$
12.93	11.84 a'
13.64	13.32 a'
14.35	14.18 a'
15.26	14.47 a'
(15.93)	16.04 a'
(16.92)	17.21 a'
	17.55 a'
	17.96 $\pi a''$
	18.13 a'
	18.23 $\pi a''$
17.05	18.35 a'
17.92	18.67 $\pi a''$
20.5	18.74 a'
	19.26 a'
	20.23 a'
	22.10 a'
	24.10 a'
	27.06 a'
	27.69 a'
	29.02 a'
	33.43 a'

TABLE 9. DIFFERENCES OF IONIZATION POTENTIALS BETWEEN BENZENE AND ITS FLUORO-DERIVATIVES

Calcd			
FB	PDFB	TFB	Symmetry of benzene
−0.01	0.00	0.09	$e_{1g}(\pi)$
0.13	0.26	0.31	
0.03	0.08	0.50	e_{2g}
0.66	1.97	1.98	
−0.10	−0.20	−0.09	$a_{2u}(\pi)$
Obsd			
FB	PDFB	TFB	Symmetry of benzene
−0.06	−0.12	0.03	$e_{1g}(\pi)$
0.6	0.77	0.78	
−0.1	−0.04	0.06	$a_{2u}(\pi)$
1.51	?	1.46	e_{2g}
2.42	2.08	2.17	

FB=Fluorobenzene, PDFB=p-Difluorobenzene, TFB=1,2,4-Trifluorobenzene.

Thus, the characteristic bands of the photoelectron spectra observed at 13.89 eV in fluorobenzene and at 13.55 eV in p-difluorobenzene should be assigned to the bands due to σ electrons. On the other hand, from a nonempirical LCAO MO SCF calculation, Clark *et al.*[17] have assigned these bands to a fluorine 2p(σ) lone-pair orbital mixed with a benzene σ orbital. In our calculation, the ionization potentials due to fluorine lone-pair electrons are predicted to lie in the 15.5—18.5 eV range in fluorobenzene, the 16.5—19 eV range in *p*-difluorobenzene, and the 17.0—19.5 eV range in 1,2,4-trifluorobenzene.

A Perturbational Treatment of the Perfluoro Effect. In order to understand the origin of the perfluoro effect, we now use a simple perturbation theory in the framework of the Hückel MO approximation in calculating the energy change, due to fluorination, of π molecular orbitals. The energy change, brought about by a fluoro-substituent, of the *i*-th π molecular orbital of a conjugated molecule can be expressed as;

$$\Delta\varepsilon_i = C_{ir}^2\delta\alpha_C + \frac{C_{ir}^2}{\varepsilon_i-\varepsilon_F}\beta_{CF}^2$$

where C_{ir} is the molecular orbital coefficient of the carbon atom on which the fluoro-substituent is introduced; $\delta\alpha_C$, the change in the Coulomb integral brought about by the inductive effect of a fluorine atom on the attached carbon, and β_{CF}, the resonance integral between the carbon and fluorine 2p π orbitals.

In the Hückel MO approximation, for a fluoro-substituent $\delta\alpha_C$ and β_{CF} are taken usually to be 0.15—0.30 and 0.5—0.7 respectively in β (the standard resonance integral) units. The value of ε_F, the energy of the fluorine 2pπ atomic orbital, is taken to be about 3β (measured from the standard Coulomb integral, α), which corresponds to the ionization potential of the fluorine 2p electron, 17.34 eV. These parameter values indicate that, in case of fluorination, while the inductive effect gives rise to a lowering in the energy of the π molecular orbitals of the parent hydrocarbon, these orbitals are always raised by the conjugative (or mesomeric) effect, and suggest that, for π molecular orbitals which lie within a certain energy range of the parent hydrocarbon, the conjugative and inductive effects may cancel each other, with the result that these orbitals suffer no substantial energy change on fluorination. Actually, if we use $\delta\alpha_C=0.28$, $\beta_{CF}=0.7$, and $\varepsilon_F=2.8$, the sum, $\delta\alpha_C+\beta^2{}_{CF}/(\varepsilon_i-\varepsilon_F)$, is approximately equal to zero for π molecular orbitals which lie at about $\alpha+\beta$, *i.e.*, about 10 eV. The energies of the b_{1u} π orbital of ethylene and the e_{1g} π orbitals of benzene are equal to $\alpha+\beta$ in the Hückel MO approximation; thus, they can be predicted not to change on fluorination.

Table 10. Differences of π-ionization potentials between ethylene and its halogeno-derivatives (eV)[a)]

	Mono-			Tetra-		
	F	Cl	Br	F	Cl	Br
Calcd[b)]	0.012	−0.269	−0.722	0.049	−1.06	−2.89
Obsd	0.003	−0.34	−0.52	0.02	−1.01	

a) The standard β value is taken to be 3.1 eV.

b) Values for various parameters are taken as follows; $\delta\alpha(\mathrm{Cl})=0.18$, $\delta\alpha(\mathrm{Br})=0.14$, $\beta(\mathrm{C\text{-}Cl})=0.6$, $\beta(\mathrm{C\text{-}Br})=0.5$, $\varepsilon_{\mathrm{Cl}}=1.8$, $\varepsilon_{\mathrm{Br}}=1.4$.

The π molecular orbitals which are higher or lower in energy than $\alpha+\beta$ should, in principle, shift to a lower or a higher energy respectively on fluorination. For example, the b_g π orbital of butadiene, whose energy is $\alpha+0.618\beta$, is predicted to be lowered on fluorination, whereas the a_u π orbital, which lies at $\alpha+1.618\beta$, should be raised. This prediction is in qualitative agreement with the results obtained by the present calculation[3)] and the experimental fact.[10)]

On the basis of the simple perturbation theory, it is expected that, on halogenations other than fluorination, the π molecular orbitals which lie at about 10 eV of a conjugated hydrocarbon will be raised in energy. In the case, for example, of chlorination, the ionization potential of the chlorine 3p electron (12.95 eV) is considerably smaller than that of the fluorine 2p electron, and the chlorine atom is less electronegative than the fluorine atom, so that the conjugative effect overcomes the inductive effect, with the result that the π MO's of the parent hydrocarbon are raised in energy. In the case of bromination, the π MO's are predicted to be shifted further to a higher energy. Table 10 presents the differences, calculated by using the simple perturbation theory, of the π ionization potential between ethylene and its halogeno-derivatives. The predicted values are in fairly good agreement with the experimental ones[11)] listed also in Table 10.

Finally, it may be added that, as for the σ MO's, there seems not to exist any simple way for predicting the amounts of energy change brought about by fluorination.

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