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Nonempirical Quantum-Chemical Calculations of the Structure and Conformations of the 2,2-Dichloroethanal Molecule in the Lowest Excited Singlet State

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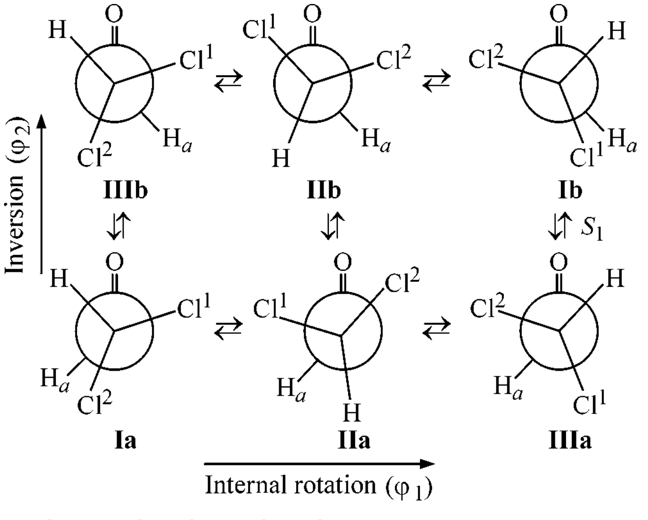
Abstract—The structure of the 2,2-dichloroethanal molecule ($CHCl_2CHO$) in the lowest excited singlet state was calculated by the nonempirical multiconfigurational self-consistent field method. The electron transition of $CHCl_2CHO$ from the ground to lowest excited singlet state is accompanied by rotation of the $CHCl_2$ group, and the carbonyl fragment becomes nonplanar. The potential energy surface for the excited $CHCl_2CHO$ molecule contains six minima corresponding to three pairs of enantiomers. This surface was used to solve torsion and inversion motion problems in the one-dimensional approximation and also two-dimensional torsion–inversion problem. Comparison of the results showed a relation between torsion and inversion motions.

This work is a part of our systematic experimental and theoretical studies on the structure of conformationally nonrigid molecules of carbonyl compounds in the ground and excited electronic states (see [1, 2] and references therein). Previous theoretical investigation [3] of the 2,2-dichloroethanal molecule ($CHCl_2CHO$) in the ground (S_0) and lowest excited triplet (T_1) states showed that the $S_0 \rightarrow T_1$ excitation essentially changes the shape of the potential energy surface (PES): instead of the *cis* (∠HCCO = 0°) and *gauche* conformers (∠HCCO ≈ 111°) with planar (or nearly planar) CCHO carbonyl fragment, minima on the PES for the T_1 state correspond to the structure having a pyramidal carbonyl fragment and turned $CHCl_2$ top. In the T_1 state of 2,2-dichloroethanal, the torsion vibrations and inversion vibrations of the nonplanar carbonyl fragment are appreciably coupled.

In this work we studied the structure and conformations of the 2,2-dichloroethanal molecule in the lowest singlet excited state (S_1); here, the torsion and inversion motions of nuclei were considered both in the one-dimensional approximation and in terms of the two-dimensional torsion–inversion model.

The calculations were performed using the multiconfiguration complete active space self-consistent field procedure (CASSCF). This procedure previously gave reliable results for related molecules of carbonyl compounds in lowest electronically excited states [2]. The singlet excited state was calculated with full optimization of the second root of the secular equation. In the examined region of potential energy surface, there was no problem of variation collapse of the ground and excited states when we used (as initial approximation) molecular orbitals corresponding to the symmetric configuration of nuclei. In this case, the S_1 state has a symmetry different from that of the ground state. Our experience in studying molecules of carbonyl compounds in electronically excited states shows [2, 3] that correct description of such systems can be achieved with the use of active space including five molecular orbitals: σ_{CO}, π_{CO}, n_O, π^*_{CO}, and σ^*_{CO} and populated by six electrons and of two-exponent basis of atomic orbitals supplemented by polarization functions on all atoms (like 6-31G**). The main calculations were performed just in this way with the aid of GAMESS software [4] (PC GAMESS version [5]).



The results show that the $S_0 \rightarrow S_1$ excitation is accompanied by considerable changes in the molecular geometry (Table 1). The scheme above shows the

Table 1. Geometric parameters (interatomic distances, Å, and angles, deg) of $CHCl_2CHO$ conformers in the S_0, T_1, and S_1 states and their relative energies ΔE (cm^{-1}), calculated by the CASSCF/6-31G** method

Parameter	S_0 [3]		T_1 [3]			S_1		
	cis	*gauche*	**Ia**	**IIa**	**IIIa**	**Ia**	**IIa**	**IIIa**
r(C=O)	1.218	1.214	1.368	1.363	1.365	1.388	1.383	1.386
r(C–C)	1.515	1.522	1.499	1.489	1.491	1.497	1.487	1.489
r(C–H$_a$)	1.086	1.088	1.077	1.077	1.076	1.076	1.076	1.075
r(C–H)	1.075	1.078	1.078	1.075	1.076	1.078	1.075	1.076
r(C–Cl^1)	1.773	1.758	1.780	1.793	1.773	1.779	1.791	1.773
r(C–Cl^2)	1.773	1.780	1.774	1.776	1.792	1.774	1.776	1.790
$\angle$CCO	121.0	124.0	114.4	116.9	114.3	113.9	116.7	114.0
$\angle$H$_a$CO	122.7	122.1	112.2	112.1	113.0	113.0	112.9	113.7
$\angle$CCH	110.2	109.3	112.3	109.3	111.2	111.9	109.5	111.1
$\angle$CCCl^1	109.4	112.9	111.1	112.2	109.5	111.0	111.8	109.6
$\angle$CCCl^2	109.4	108.5	109.2	111.6	112.2	109.5	111.5	111.9
$\angle$CH$_a$ nonpl.[a]	0.0	–1.3	–38.2	–35.8	–35.1	–36.8	–34.4	–33.8
$\angle$Cl^{1}CH	108.2	107.6	106.0	106.0	107.3	106.1	106.1	107.3
$\angle$Cl^{2}CH	108.2	106.2	106.8	107.0	106.0	107.0	107.1	106.1
$\angle$HCCO	0.0	111.4	59.7	–173.0	–45.8	57.7	–174.3	–46.6
ΔE	0	604	562	252	0	525	298	0

[a] The angle between the CH$_a$ bond and CCO plane.

Table 2. Calculated harmonic frequencies (cm^{-1}) of $CHCl_2CHO$ conformers in the S_0 (MP2/6-31G**), T_1, and S_1 states (CASSCF/6-3G**)

Vibration mode and symmetry	S_0 [3]		T_1 [3]			S_1		
	cis	*gauche*	**I**	**II**	**III**	**I**	**II**	**III**
CH stretch.	3244	3191	3307	3349	3337	3351	3350	3336
CH$_a$ stretch.	3074	3062	3338	3333	3349	3306	3339	3359
CO stretch.	1790	1798	1184	1216	1108	1168	1207	1087
CH$_a$O bend.	1439	1435	1443	1472	1319	1440	1462	1315
CH out-of-pl.	1313	1314	1349	1368	1373	1349	1368	1373
CCH bend.	1264	1287	1396	1402	1496	1394	1404	1492
CC stretch.	1108	1063	1107	1033	1216	1092	1013	1206
Invers.[a]	1037	969	684	723	827	687	723	830
CCl$_2$ stretch. asym.	822	863	890	847	862	894	851	863
CCl$_2$ stretch. sym.	792	676	822	753	716	815	751	715
CCO bend.	448	628	449	608	421	437	608	419
CCl$_2$ wagg.	332	357	416	311	409	416	311	407
CCl$_2$ twist.-bend.	287	229	226	340	234	225	335	231
CCl$_2$ sciss.	267	287	291	218	291	292	215	290
Torsion	74	82	101	104	113	99	105	113

[a] CH$_a$ out-of plane vibrations in the S_0 state.

Newman projections of $CHCl_2CHO$ conformers in the S_1 state.

We have revealed six minima on the PES of 2,2-dichloroethanal in the S_1 state, which correspond to six different conformers. Table 2 contains geometric parameters of three of these conformers (**Ia**, **IIa**, and **IIIa**); the other three conformers are their enantiomers (**Ib**, **IIb**, and **IIIb**). Thus, the $S_1 \leftarrow S_0$ excitation of 2,2-dichloroethanal is accompanied by rotation of the

$CHCl_2$ group and pyramidalization of the carbonyl fragment. In addition, considerable elongation of the C=O distance and decrease of the CCO bond angle are observed, which are typical of $n \rightarrow \pi^*$excitation of carbonyl compounds.

Pyramidalization of the carbonyl fragment and change of orientation of the $CHCl_2$ top also follow from the results of calculations with account taken of configuration interactions (singly excited configurations only) (CIS) using the Dunning–Hay basis set [6] supplemented by polarization functions on all atoms. However, this procedure gives only four minima (two enantiomer pairs) on the examined potential energy surface, which are characterized by HCCO angles of –173.8° and –45.4°. The corresponding geometries are generally similar to those obtained by the CASSCF method for structures **II** and **III**, except for the C=O bond length (1.26 Å) and the angle of declination of the $C-H_a$ bond from the CCO plane (–27°). While analyzing the obtained results, it should be kept in mind that the CIS procedure less reliably reproduces the shape of the potential energy surface for molecules of carbonyl compounds in excited states, as compared to CASSCF [2].

Table 2 contains harmonic vibration frequencies of 2,2-dichloroethanal in the S_0, T_1 [3], and S_1 states. The two examined excited states are characterized by very similar frequencies of vibrations of the same mode. It should be noted that the electronic excitation $S_1 \leftarrow S_0$ (as well as $T_1 \leftarrow S_0$) leads to strong decrease of the C=O vibration frequency, in keeping with the data obtained for the other carbonyl compounds [1]. The frequencies given in Table 2 were determined in terms of the harmonic model which, strictly speaking, is applicable only to vibrations with a small amplitude. Insofar as torsion and inversion vibrations imply moving of nuclei with a large amplitude, we have considered the corresponding models in one- and two-dimensional approximations. The procedures for solving large-amplitude vibrational problems were reported, e.g., in [2, 7–10]. These procedures involve the following vibrational motion Hamiltonian:

$$\hat{H}(\varphi_1, ..., \varphi_n) = -\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial}{\partial\varphi_i}B_{ij}(\varphi_1, ..., \varphi_n)\frac{\partial}{\partial\varphi_j} + V(\varphi_1, ..., \varphi_n). \quad (1)$$

Here, n is the number of vibrational coordinates taken into account; B_{ij} are elements of a symmetric matrix of kinetic parameters, which is selected so as to ensure separation of vibrational and rotational motions according to the Eckart conditions; and V is the potential function. As variables for internal rotation and inversion we took the angle of relative rotation of the CHO and $CHCl_2$ groups (dihedral angle HCCO, φ_1) and declination of the $C-H_a$ bond from the CCO plane (φ_2).

In terms of the one-dimensional internal rotation model, the inversion coordinate φ_2 changes on variation of the angle φ_1; it is determined by geometry optimization. The same is true of the one-dimensional inversion model. Therefore, the “trajectories” corresponding to one-dimensional internal rotation and one-dimensional inversion on the two-dimensional PES are curvilinear. The maximal variation of φ_2 upon internal rotation in the S_1 state is 8.4° (8.8° for T_1); the declination of the $C-H_a$ bond from the CCO plane in the S_0 state is $\pm 3.3°$. The parameters B and potential functions V in the one-dimensional models were approximated as follows:

Internal rotation:

$$B(\varphi_1) = B_0 + \sum_{k=1}^{N} B_k^e \cos k\varphi_1 + \sum_{k=1}^{P} B_k^0 \sin k\varphi_1, \quad (2a)$$

$$V(\varphi_1) = V_0 + \frac{1}{2}\sum_{k=1}^{N} V_k^e(1 - \cos k\varphi_1) + \frac{1}{2}\sum_{k=1}^{L} V_k^0(1 - \sin k\varphi_1). \quad (2b)$$

Inversion:

$$B(Q) = \sum_{k=0}^{N} B_k Q^k = \frac{\hbar^2}{2}\sum_{k=0}^{N} g_{44}^{(k)} Q^k, \quad (3a)$$

$$V(Q) = \sum_{k=0}^{M} V_k Q^k. \quad (3b)$$

Here, $Q = R_{CH_a}\varphi_2$; φ_1 and φ_2 vary within the ranges $0° \le \varphi_1 \le 180°$ and $-60° \le \varphi_2 \le 60°$ with steps of 15° and 10°, respectively; and the other geometric parameters were optimized in the course of nonempirical calculations. Using the calculated values, the functions B_{ij} and V were approximated by the least-squares procedure through linear combinations of trigonometric functions.

$$B(\varphi_1, \varphi_2) = \sum_K\sum_L C_{KL}^{cc} \cos K\varphi_1 \cos L\varphi_2 + \sum_K\sum_L C_{KL}^{ss} \sin K\varphi_1 \sin L\varphi_2, \quad (4a)$$

$$V(\varphi_1, \varphi_2) = \sum_K\sum_L V_{KL}^{cc} \cos K\varphi_1 \cos L\varphi_2 + \sum_K\sum_L V_{KL}^{ss} \sin K\varphi_1 \sin L\varphi_2. \quad (4b)$$

The coefficients in expansions (2)–(4) for 2,2-dichloroethanal in the S_1 state and standard deviations which characterize the accuracy of reproduction of the kinetic parameters and potentials in reference

Table 3. Parameters of kinetic energy function (2a) and one-dimensional internal rotation potential function (2b) for the molecule of $CHCl_2CHO$ in the S_1 state and the corresponding standard deviations σ (cm^{-1})[a]

k	B_k^e	B_k^o	V_k^e	V_k^o
0	1.3745	–	–	–
1	–0.0127	–0.0019	476.8	304.7
2	–0.2230	–0.0212	470.6	148.1
3	0.0378	0.0045	–949.1	347.6
4	0.0213	0.0032	7.2	16.0
5	–0.0066	–0.0039	1.4	–1.5
6	–0.0011	–0.0014	2.3	–12.9
7	–0.0006	–0.0003	–1.8	2.6
8	–0.0014	–0.0009	2.9	1.2
9	–0.0012	–0.0005	1.1	0.2
σ	0.0020		0.3	

[a] In the given approximation, the energies of conformers **I** and **II** relative to **III** are 530 and 309 cm^{-1}, respectively. The heights of potential barriers to the conformational transitions **Ia** → **IIa** → **IIIa** → **Ia** are 1072, 1168, and 914 cm^{-1}, respectively.

Table 4. Parameters of kinetic energy function (3a) and one-dimensional inversion potential function (3b) for the molecule of $CHCl_2CHO$ in the S_1 state and the corresponding standard deviations σ (cm^{-1})[a]

k	**Ia** $\rightleftarrows$ **IIIb** or **Ib** $\rightleftarrows$ **IIIa**		Inversion **IIa** $\rightleftarrows$ **IIb**	
	B_k	V_k	$g_{44}^{(k)}$[b]	V_k
0	1.0297	889.4	1.0309	643.3
1	–0.0201	–1040.3	–	–
2	0.0199	–2956.7	0.0144	–3299.5
3	0.0214	2392.0	–	–
4	–0.0597	3776.2	–0.0177	4843.9
5	–0.0086	–2611.4	–	–
6	0.0369	–644.8	0.0049	–1633.3
7	–	1175.5	–	–
8	–	–	–	289.0
σ	0.0005	5.3	0.0003	5.4

[a] In the given approximation, the energy of conformer **I** relative to **III** is 521 cm^{-1}. The heights of potential barriers to the conformational transitions **IIIb** → **Ia** and **IIa** → **IIb** are 973 and 643 cm^{-1}, respectively. [b] The $g_{44}^{(k)}$ values are given in $(amu)^{-1}$ $Å^{-k}$.

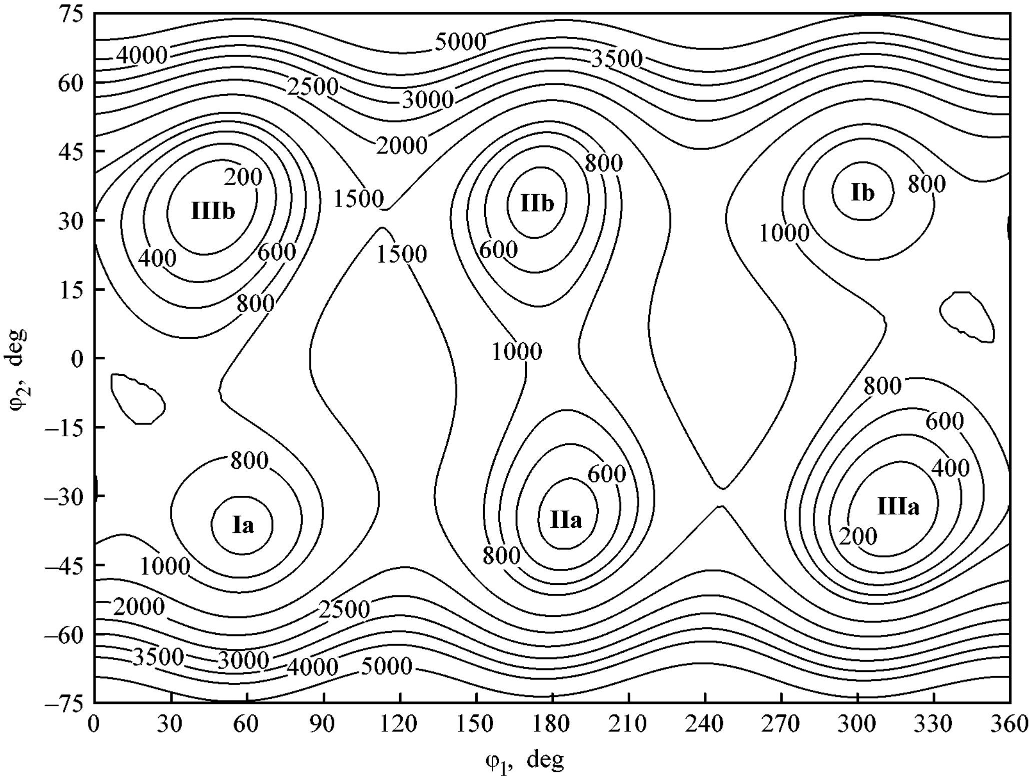
Table 5. Approximation coefficients of the kinetic parameters B_{11}, B_{12}, and B_{22} given by Eqs. (4a) and standard deviations σ (cm^{-1})

K	L	B_{11}	B_{12}	B_{22}
		Coefficients C_{KL}^{cc}		
0	0	2.4068	3.1553	19.3641
0	1	–1.3819	–2.1088	–3.5436
0	2	0.5779	1.0510	2.2009
1	0	–0.0263	–0.0670	–0.1561
2	0	–0.3043	–0.4705	–0.6793
2	2	–0.0536	–0.2045	–0.5864
3	0	0.0469	0.0696	0.1215
3	2	0.0139	0.0351	0.0456
4	0	0.0358	0.0519	0.0669
4	2	0.0079	0.0301	0.0869
5	0	–0.0152	–0.0270	–0.0469
		Coefficients C_{KL}^{ss}		
1	1	0.0099	0.0660	0.1265
2	2	0.0029	–0.1042	–0.3733
3	1	–0.0109	0.0012	0.0173
4	2	0.0009	0.0168	0.0512
σ		0.0063	0.0108	0.0267

Table 6. Approximation coefficients of the potential function V given by Eq. (4b) and standard deviations σ (cm^{-1})

K	L	Coefficients V_{KL}^{cc}	K	L	Coefficients V_{KL}^{ss}
0	0	18242.5	1	1	21.9
0	1	–24021.8	1	3	–170.6
0	2	6907.6	2	1	–53.0
0	4	143.8	2	3	–52.1
1	0	–240.8	2	6	–9.9
1	2	11.6	3	3	–180.6
2	0	–208.6	3	6	–4.6
2	2	–96.9	4	3	11.6
2	6	–13.9	6	3	–3.5
3	1	892.4	σ		6.3
3	2	–655.9			
3	4	43.2			
3	6	–26.0			
4	4	13.2			
6	0	7.9			
6	2	–4.5			

points are collected in Tables 3–6. The corresponding vibrational problems were solved by the variation procedure in the trigonometric basis using one- and two-dimensional B and V surfaces. The figure shows the two-dimensional nonempirical potential energy surface for the 2,2-dichloroethanal molecule in the S_1 state. This surface has a shape similar to that obtained previously [3] for the T_1 state of the same molecule.



Two-dimensional potential energy surface for the CHCl$_2$CHO molecule in the S_1 state (CASSCF/6-31G**).

Table 7. Torsion, inversion, and torsion–inversion energy levels of CHCl$_2$CHO conformers in the S_1 state (cm^{-1})

Energy level		Assignment[a]	Energy level		Assignment[a]
torsion–inversion[b] (n = 2)	torsion and inversion (n = 1)		torsion–inversion[b] (n = 2)	torsion and inversion (n = 1)	
0.0	0.0	**III** (0, 0)+	490.9	522.2	**I** (0, 0)+
0.0	0.0	**III** (0, 0)–	491.0	522.2	**I** (0, 0)–
101.2	110.8	**III** (1, 0)+	534.9	485.8	**III** (0, 1)+
101.2	110.8	**III** (1, 0)–	535.0	485.8	**III** (0, 1)–
199.3	217.9	**III** (2, 0)+	543.7	605.6	**III** (6, 0)+
199.3	217.9	**III** (2, 0)–	554.5	605.6	**III** (6, 0)–
267.6	307.8	**II** (0, 0)+	567.9	642.9	**II** (3, 0)+
276.2	322.2	**II** (0, 0)–	571.4	628.4	**II** (3, 0)–
293.7	321.2	**III** (3, 0)+	589.9	616.7	**I** (1, 0)+
293.7	321.2	**III** (3, 0)–	590.1	616.7	**I** (1, 0)–
370.2	431.8	**II** (1, 0)+	611.4	690.5	**III** (7, 0)+
378.0	417.3	**II** (1, 0)–	628.4	596.6	**III** (1, 1)–
384.1	420.4	**III** (4, 0)+	628.7	596.6	**III** (1, 1)+
384.3	420.4	**III** (4, 0)–	637.4	690.5	**III** (7, 0)–
468.5	515.3	**III** (5, 0)+	662.5	705.5	**I** (2, 0)–
469.3	538.7	**II** (2, 0)–	662.8	729.8	**II** (4, 0)+
470.6	515.3	**III** (5, 0)–	662.9	705.5	**I** (2, 0)+
476.9	524.2	**II** (2, 0)+	663.3	744.3	**II** (4, 0)–

[a] The numbers in parentheses (v_t, v_i) are the torsion and inversion quantum numbers, respectively; the Roman numerals refer to the conformer number; the signs "+" and "–" denote, respectively, the even and odd components of the inversion splitting. [b] In terms of the two-dimensional torsion–inversion model, pairs of mirror-symmetric conformers **a** and **b** (see scheme) are characterized by approximately doubly degenerate levels.

It is seen that the torsion and inversion motions are interrelated: the inversion is accompanied by some rotation of the $CHCl_2$ top.

Analysis of the structure of nodal surfaces and localization areas of the calculated wave functions for vibrational states in the two-dimensional approximation shows that the one-dimensional model is applicable only when the vibrational wave functions are localized in potential wells corresponding to particular conformers. As the torsion and inversion quantum numbers increase, the wave functions rapidly become delocalized so that description of high-lying vibrational states (especially, of those having a joint torsion–inversion character) requires a multidimensional model to be considered.

Table 7 gives the results of calculations in the one- and two-dimensional approximations for a number of low-lying vibrational states of the 2,2-dichloroethanal molecule in the S_1 state. It is seen that the energies of the lowest torsion levels, determined for the $CHCl_2CHO$ conformers in one- and two-dimensional approximation, agree well with each other, but the difference between these energies grows as the torsion quantum number increases.

The $CHCl_2CHO$ molecule is characterized by qualitatively the same conformational behavior in the T_1 and S_1 states. In both cases, there are six conformers with similar geometries for the corresponding pairs. In addition, the vibration modes are quite similar, and many frequencies differ insignificantly. Analogous relations were observed by us in the calculations of potential energy surfaces for $CH_xR_{3-x}CHO$ molecules (R = F, Cl, $x = 0$–3) in electronically excited states [2]. As for the 2-chloroethanal molecule (CH_2ClCHO), analysis of the electronic and vibrational spectra [11] supports theoretical predictions [7] on the PES structure for its T_1 state.

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