Ab initio studies of tetrafluoroethylene and tetratrifluoromethylethylene molecules in the ground and "twisted" states

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Ab initio calculations with full optimization of geometry have been carried out with the 6-31 G* basis set on tetrafluoroethylene (with the unrestricted Hartree—Fock method — UHF and the second-order Moller—Plesset perturbation theory — MP2) and tetratrifluoromethylethylene (with UHF) molecules in the singlet ground and triplet biradical states. The symmetry of the tetrafluoroethylene molecule in the triplet biradical state was demonstrated to differ from that of ethylene (D_{2d}) due to the deviation of fluorine atoms from CCFF plane. The MP2 optimized geometries of ethylene and tetrafluoroethylene were used for higher level calculations (MP3, MP4, CCSD). The energy of the ground state singlet-biradical triplet splitting decreases in the series: ethylene > tetrafluoroethylene > tetratrifluoromethylethylene. These data on energy splitting explain the increase in reactivity toward the [2+2]-cycloaddition on going from ethylene to tetrafluoroethylene.

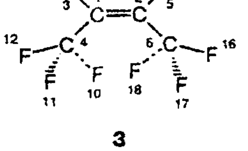
Key words: *ab initio* calculations, tetrafluoroethylene, tetratrifluoromethylethylene, triplet biradical, singlet-triplet splitting.

It is well known[1,2] that tetrafluoroethylene is susceptible to [2+2]-cycloaddition reaction in contrast to ethylene. It has been suggested that a biradical state of the tetrafluoroethylene is an intermediate of this reaction. This was confirmed by the kinetic spectroscopy method.[3] There are other experimental data showing the biradical state of tetrafluoroethylene to be an intermediate of its thermal dissociation.[4]

Theoretically the biradical states of olefins have been studied only in the case of ethylene (**1**). Calculations[5] show the singlet and triplet biradical states of ethylene to be close in energy. Both singlet and triplet biradical states of ethylene have D_{2d} symmetry (the "twisted" states).

1

2



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As the biradical states of fluoroethylenes are important intermediates, the study of its electronic structure is of current interest. This study utilizes *ab initio* calculations to study the geometry and electronic structure of the ground singlet (S) and triplet (T) biradical states of two molecules of fluoroolefins: tetrafluoroethylene (**2**) and tetra(trifluoromethyl)ethylene (**3**). The results of these calculations are compared with that for ethylene.

Procedure of calculation

Calculations of geometric and electronic structure of molecules **1**—**3** were done first at the unrestricted Hartree—Fock method (UHF) level[5] with full optimization of geometry using the 6-31 G* basis set. For **1** and **2** second-order Moller—Plesset perturbation theory (MP2)[6] with full optimization of geometry were done as the second step. The electronic structure of ethylene and tetrafluoroethylene molecules was also studied using higher-level theory (MP3, MP4DQ, MP4SDQ, CCSD, CCSD(T)) with the geometry of the MP2 calculation. The calculations were done using the GAUSSIAN-94 program.[7] The calculations were done on a CRAY J90 supercomputer (Berkeley, California, USA).

The results of calculations of the geometric structure of **1** and **2** in two electronic states S and T are given in Table 1 (MP2/6-31 G* level of the theory). In Table 2 the results of calculations of **3** in the S and T electronic states are given (UHF/6-31 G* level of the theory).

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Table 1. The results of MP2/6-31 G* calculations of bond distances (*d*), valence (φ) and dihedral (ω) angles of **1** and **2** molecules in the S and T electronic states.

Parameter	C_2H_4 (**1**)		C_2F_4 (**2**)	
	S*	T	S*	T
Bond		*d*/Å		
1—2	1.336 (1.339)	1.457	1.328 (1.311)	1.490
1—3	1.085 (1.086)	1.085	1.328 (1.319)	1.341
1—4	1.085 (1.086)	1.085	1.328 (1.319)	1.334
2—5	1.085 (1.086)	1.085	1.328 (1.319)	1.334
2—6	1.085 (1.086)	1.085	1.328 (1.319)	1.341
Angle		φ/deg		
1—2—5	121.70 (121.2)	121.58	122.99 (123.8)	113.45
1—2—6	121.70 (121.2)	121.58	122.99 (123.8)	114.96
2—1—3	121.70 (121.2)	121.58	122.99 (123.8)	114.96
2—1—4	121.70 (121.2)	121.58	122.99 (123.8)	113.45
		ω/deg		
3—1—2—5	0.0 (0.0)	−90.0	0.0 (0.0)	66.45
3—1—2—6	180.0 (180.0)	90.0	180.0 (180.0)	−62.92
4—1—2—5	180.0 (180.0)	90.0	180.0 (180.0)	−164.17
4—1—2—6	0.0 (0.0)	−90.0	0.0 (0.0)	66.45

*The experimental values are given in brackets.[8—11]

Table 2. The results of UHF/6-31 G* calculations of bond distances (*d*), valence (φ) and dihedral (ω) angles of molecule **3** in the T and S electronic states

Parameter	S	T	Parameter	S	T
Bond	*d*/Å		Angle	φ/deg	
1—2	1.334	1.474	1—3—8	108.38	111.26
1—3	1.543	1.505	1—3—9	108.38	110.09
1—4	1.559	1.506	1—4—10	111.31	110.25
2—5	1.543	1.506	1—4—11	111.31	110.96
2—6	1.559	1.505	1—4—12	112.01	111.30
3—7	1.319	1.319	2—6—16	112.01	111.06
3—8	1.319	1.314	2—6—17	111.31	111.27
3—9	1.302	1.318	2—6—18	111.31	110.09
4—10	1.313	1.317		ω/deg	
4—11	1.313	1.317	3—1—2—5	0.0	−91.74
4—12	1.314	1.317	3—1—2—6	180.0	81.98
5—13	1.302	1.317	4—1—2—5	180.0	94.20
5—14	1.319	1.317	4—1—2—6	0.0	−92.08
5—15	1.319	1.317	1—2—5—13	0.0	7.62
6—16	1.314	1.319	1—2—5—14	120.83	127.69
6—17	1.313	1.314	1—2—5—15	−120.83	−112.13
6—18	1.313	1.318	1—2—6—16	−180.00	−81.93
Angle	φ/deg		1—2—6—17	60.83	157.59
1—2—5	129.42	120.94	1—2—6—18	−60.83	37.24
1—2—6	121.99	119.50	2—1—3—7	120.83	−82.41
2—1—3	129.42	119.53	2—1—3—8	−120.83	157.11
2—1—4	121.99	120.94	2—1—3—9	0.00	36.78
2—5—13	117.50	110.24	2—1—4—10	60.83	8.17
2—5—14	108.38	110.97	2—1—4—11	−60.83	128.24
2—5—15	108.38	111.29	2—1—4—12	180.00	−111.52
1—3—7	117.50	111.07			

Results and Discussion

Here we discuss the results of calculations of the geometric structures of molecules **1**—**3** in the S and T states. In the T state "twisted" ethylene has D_{2d} symmetry. In **2** D_{2d} symmetry is broken through passage of the atoms F(3) and F(4) from the F(3)—F(4)—C(1)—C(2) plane and the atoms F(5) and F(6) from the F(5)—F(6)—C(2)—C(1) plane, respectively. This results in the dipole moment of the "twisted" tetrafluoroethylene is different from zero. The value of the dipole moment is equal to 0.90 D at the HF/6-31 G* level of the theory and to 1.01 D at the MP2/6-31 G* level of the theory.

An *ab initio* study of the singlet ground state of **3** has been done for the first time, so we consider the results of these calculations more closely. The length of the C=C bond of **3** at the UHF/6-31 G* level of the theory (1.334 Å) is greater than not only the value of **2** (1.300 Å), but also the value of **1** (1.317 Å).

The geometric structure of **3** in the ground state can be characterized by the following: 1) the bond angles are equal to 129.42° (C(3)—C(1)—C(2), C(1)—C(2)—C(5)) and 121.99° (C(4)—C(1)—C(2), C(1)—C(2)—C(6)), 2) the atoms C(1), C(2), C(3), C(4), C(5), C(6) and the atoms F(9), F(12), F(13), F(16) lie on the same plane, 3) the atoms F(7), F(10), F(15), and F(18) are found on one side from the plane of the C atoms and all lie in one plane, 4) The atoms F(8), F(11), F(14), and F(17) are to be found on one side from the plane of the C atoms and all lie in one plane. The calculated dipole moment of molecule **3** in the singlet ground state is equal 0.42 D.

The "twisted" molecule **3** in the triplet state is characterized by the configuration of the C atoms, which

Table 3. The total energies of **1**—**3** in the S (E_S) and T (E_T) states (au) and the transition energy from the S to the T state (δE/kcal mol^{-1})

Method	C_2H_4 (**1**)			C_2F_4 (**2**)			$C_2(CF_3)_4$ (**3**)		
	E_S	E_T	δE	E_S	E_T	δE	E_S	E_T	δE
UHF	−78.0317	−77.9643	42.3	−473.4157	−473.3764	24.7	−1420.4486	−1420.4320	10.4
MP2	−78.2850	−78.1768	67.9	−474.3409	−474.2603	50.6	–	–	–
MP3	−78.3060	−78.2041	63.9	−474.3388	−474.2605	49.1	–	–	–
MP4 (DQ)	−78.3087	−78.2065	64.1	−474.3440	−474.2665	48.6	–	–	–
MP4 (SDQ)	−78.3114	−78.2080	64.9	−474.3581	−474.2815	48.0	–	–	–
CCSD	−78.3126	−78.2098	64.5	−474.3533	−474.2781	47.2	–	–	–
CCSD (T)	−78.3219	−78.2154	66.8	−474.3789	−474.3003	49.3	–	–	–

can be only approximately represented as D_{2d} symmetry. Its dipole moment is equal 0.18 D and is less than that for the S ground state.

The total energies of molecules **1**—**3** in the S and T states are given in Table 3. Here the transition energy δE(S—T) from S to T is given.

From Table 3 one can notice the trend in the change in transition energy for molecules **1**—**3**. The energy decreases in the series **1** > **2** > **3**.

Unfortunately no calculations of the molecule **3** were made at the higher levels of theory (MP2, MP3, MP4, CCSD).

As was noted[3] the molecule **2** in the biradical state is an intermediate of the reaction of [2+2]-cycloaddition

$$2\ C_2F_4 = cyclo\text{-}C_4F_8.$$

The activation energy of formation of the biradical C_2F_4, was found to be equal to 25.1 kcal mol^{-1}. On the basis of our calculations we consider that the role of biradical states for molecule **3** in [2+2]-cycloaddition reaction is greater than that for **2**.

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