Structure and isomerization of arenonium ions of dichlorobenzenes in the gas phase. A theoretical study

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Ab initio MP2 calculations of all isomeric arenonium ions (AI) of *ortho*-, *meta*-, and *para*-dichlorobenzenes in the gas phase were carried out with full optimization of geometry with the 6-31G* basis set. The calculated proton affinities depend substantially on the position of geminal center in the corresponding dichlorobenzenonium ion and decrease in the series 1,2-dichloro-4*H*-benzenonium > 1,2-dichloro-3*H*-benzenonium > 1,2-dichloro-2*H*-benzenonium; 1,3-dichloro-4*H*-benzenonium > 1,3-dichloro-2*H*-benzenonium > 1,3-dichloro-5*H*-benzenonium > 1,3-dichloro-3*H*-benzenonium; 1,4-dichloro-2*H*-benzenonium > 1,4-dichloro-4*H*-benzenonium. The structures of transition states and activation energies (E_a) of almost all 1,2-shifts of H and Cl atoms in AI were determined. The activation energies of migrations of H atoms are about 6 kcal mol^{-1} less than those of migrations of Cl atoms in similar structures. The isomerization routes and relations between the rate constants for isomerization of dichlorobenzenes through AI were established.

Key words: *ab initio* calculations, MP2 method; dichlorobenzenes, arenonium ions, proton affinity; 1,2-shifts of H and Cl atoms, activation energy.

Individual isomers of dichlorobenzenes (DCB) are important initial compounds for production of various chemicals such as drugs, pesticides, dyes, thermostable polymers, *etc*. It is of interest to study isomerization of DCB since some isomers cannot be obtained directly. Isomerization of DCB can occur at the strongly acidic centers of the catalyst surface[1,2] and in superacidic solutions.[3] It is assumed that isomerization occurs through intermediate formation of arenonium ions (AI) of DCB.

Recently,[4,5] one of the authors of this work has performed quantum-chemical studies of the electronic structure and reactivity of DCB arenonium ions by the semiempirical AM1 method. The proton affinities for different positions of isomeric DCB molecules and activation energies of migration of H atoms in AI were determined.

The aim of this work was to carry out a more in-depth study of DCB arenonium ions and their isomeric transformations by the *ab initio* MP2/6-31G* method.

Procedure for Calculations

The calculations of DCB and their AI were carried out at the second-order level of Møller—Plesset perturbation theory (MP2)[6] with the 6-31G* basis set. The geometries of all systems were optimized using analytical gradients without considering the symmetry point group. The quasi-Newton method of synchronous transition[7] was used for the calculation of transition states. The calculations were carried out using the GAUSSIAN-92, GAUSSIAN-94,[8,9] and GAMESS [10] programs on CRAY C-90 (Livermore, California, USA), CRAY J-90 (Berkeley, California, USA), and DEC AXP 3000-400 (Moscow, Russian Federation) computers.

Results and Discussion

Calculations of the geometry and electronic structure of DCB arenonium ions

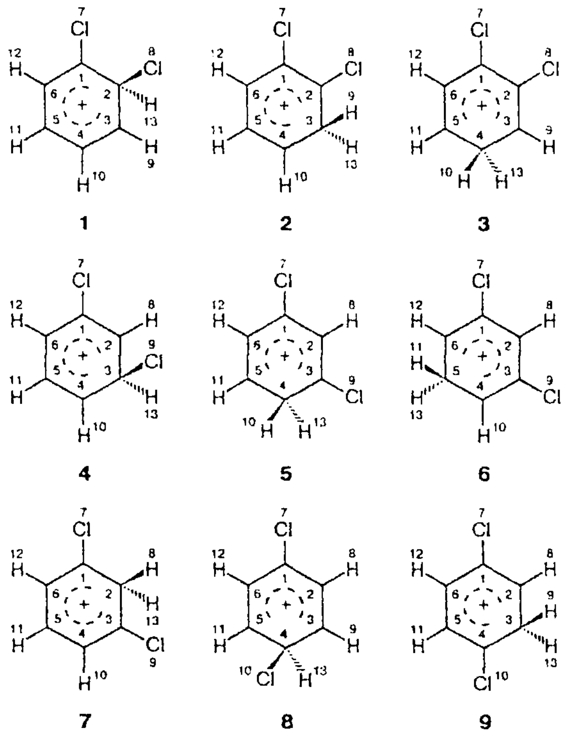
The numbering of the atoms in isomeric DCB arenonium ions used in this study is given below. Structures **1—3** correspond to arenonium ions of 1,2-DCB, structures **4—7** correspond to arenonium ions of 1,3-DCB, and structures **8**, **9** correspond to arenonium ions of 1,4-DCB (Scheme 1).

The results of calculations of the geometry of neutral DCB molecules are given in Table 1, in which the nearest interatomic distances and bond angles in *ortho*-, *meta*-, and *para*-isomers of DCB obtained from the *ab initio* MP2/6-31G* calculations are listed. The calculated values of total energies and quantum corrections for zero-point energy are also given in Table 1.

The calculated interatomic distances and angles in *meta*-isomer of dichlorobenzene can be compared with the available experimental data for the 1,3-DCB mol-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1726—1731, September, 1998.

Scheme 1



ecule in the gas phase obtained by the combined analysis of electron diffraction, microwave spectroscopy, and NMR (in a liquid-crystal solvent) data.[11] The interatomic distances and bond angles we calculated deviate from experimental data by ~0.5%. This is a rather good agreement between theoretical and experimental geometric parameters of 1,3-$Cl_2C_6H_4$ molecule in the gas phase. The calculated series of relative stabilities of isomeric DCB is in qualitative agreement with the experimental data.[12] If the energy of formation of *ortho*-isomer is taken as 0, then the relative stabilities (kcal mol^{-1}) can be ordered as follows (the experimental values of relative energies of formation are given in parentheses): 1,2-DCB, 0 (0); 1,3-DCB, −1.85 (−1.08±0.50); and 1,4-DCB, −1.87 (−1.84±0.5). The zero-point energy corrections $\Delta E(ZPC)$ are nearly the same for all three isomers of neutral DCB molecules.

The optimized values of geometric parameters of analyzed structures **1**—**9** of arenonium DCB ions and the zero-point energy corrections $\Delta E(ZPC)$ are listed in Table 2.

The proton affinities can be calculated as differences between the total energies of neutral molecules of *ortho*-, *meta*-, and *para*-isomers of DCB (see Table 1) and those of AI in the gas phase. These results are listed in Table 3. Along with the data obtained by the MP2/6-31G* method, this table summarizes the results of HF/6-31G* calculations (with optimization of the geometry of corresponding molecules and arenonium ions by the HF/6-31G* method).

Table 1. Results of calculations of the structure of DCB molecules in the gas phase: nearest interatomic distances (*i*—*j*), bond angles (*i*—*j*—*k*), total energies (*E*), and zero-point energy corrections ($\Delta E(ZPC)$)

Parameter	1,2-DCB	1,3-DCB*	1,4-DCB
i—*j*/Å			
1—2	1.401	1.394 (1.3906)	1.395
2—3	1.397	1.394 (1.3906)	1.394
3—4	1.393	1.395 (1.3944)	1.395
4—5	1.396	1.395 (1.4069)	1.395
5—6	1.393	1.395 (1.4069)	1.394
1—6	1.397	1.395 (1.3944)	1.395
1—7	1.732	1.739 (1.7390)	1.739
2—8	1.732	1.085 (1.1071)	1.086
3—9	1.086	1.739 (1.7390)	1.086
4—10	1.087	1.086 (1.0973)	1.739
5—11	1.087	1.087 (1.1050)	1.086
6—12	1.086	1.086 (1.0973)	1.086
i—*j*—*k*/deg			
1—2—3	119.8	118.3 (118.09)	119.6
2—3—4	120.3	121.6 (122.27)	119.6
3—4—5	120.0	118.8 (118.13)	120.9
4—5—6	120.0	121.0 (121.10)	119.6
5—6—1	120.3	118.8 (118.13)	119.6
6—1—2	119.8	121.6 (122.27)	120.9
7—1—2	121.4	118.9 (118.91)	119.6
8—2—3	118.8	120.9 (121.19)	120.4
9—3—4	120.9	119.5 (118.82)	120.1
10—4—5	120.5	121.1 (120.68)	119.6
11—5—6	119.6	119.5 (119.45)	120.4
12—6—1	118.8	120.1 (121.19)	120.1
E/au	−1149.5191	−1149.5220	−1149.5220
$\Delta E(ZPC)$/au	0.0815	0.0814	0.0814

* Corresponding experimental values[11] are given in parentheses.

Calculations of activation energies of isomerization of DCB arenonium ions

Arenonium DCB ions undergo isomeric transformations followed by migration of H or Cl atoms. These processes are of importance for the synthesis of those DCB isomers which cannot be obtained directly. We determined the structures of transition states of migration of H and Cl atoms for all AI considered by the quasi-Newton method of synchronous transition.[7]

The calculated structures of eight transition states (structures **10**—**17**) describe almost all transformations of isomeric DCB arenonium ions and are shown in Scheme 2.

The geometric parameters, total energies, and zero-point energy corrections for transition states **10**—**17** are listed in Table 4.

When discussing the geometry of DCB arenonium ions it should be noted that in all structures the proton is bonded to one of C atoms to form a local structure close to the tetrahedral structure. Attachment of the proton to a carbon atom not bonded to the Cl atom (structures **2**, **3**, **5**, **6**, **7**, and **9**) does not lead to violation of planarity

Table 2. Geometric parameters of arenonium ions of DCBs in the gas phase: interatomic distances (*i*—*j*), bond angles (*i*—*j*—*k*), dihedral angles (*i*—*j*—*k*—*l*), and $\Delta E(ZPC)$ values

Parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
i—*j*/Å									
1—2	1.492	1.397	1.431	1.382	1.408	1.410	1.483	1.422	1.372
2—3	1.482	1.476	1.374	1.470	1.378	1.410	1.483	1.366	1.472
3—4	1.367	1.470	1.467	1.468	1.479	1.382	1.379	1.479	1.473
4—5	1.417	1.370	1.465	1.377	1.476	1.460	1.404	1.479	1.389
5—6	1.397	1.412	1.369	1.406	1.363	1.460	1.404	1.366	1.395
1—6	1.387	1.404	1.419	1.414	1.425	1.382	1.380	1.421	1.420
1—7	1.677	1.707	1.678	1.710	1.685	1.711	1.689	1.678	1.712
2—8	1.772	1.682	1.709	1.087	1.086	1.090	1.105	1.085	1.088
3—9	1.088	1.108	1.089	1.767	1.691	1.711	1.689	1.088	1.107
4—10	1.085	1.088	1.109	1.088	1.106	1.088	1.085	1.782	1.684
5—11	1.088	1.085	1.088	1.086	1.088	1.112	1.089	1.088	1.086
6—12	1.087	1.089	1.085	1.089	1.085	1.088	1.086	1.086	1.089
*a**	1.114	1.106	1.109	1.126	1.106	1.112	1.104	1.111	1.107
i—*j*—*k*/deg									
1—2—3	115.9	120.4	118.3	120.0	118.7	123.0	116.1	118.9	121.0
2—3—4	121.3	117.5	122.1	117.5	121.8	119.2	121.3	121.6	117.1
3—4—5	119.0	120.8	116.7	119.8	115.7	120.1	118.6	115.8	120.6
4—5—6	123.2	119.1	121.1	119.7	122.1	118.5	124.2	121.6	119.1
5—6—1	119.6	123.9	119.9	122.8	118.7	120.1	118.6	118.9	123.3
6—1—2	120.07	118.4	122.0	119.0	123.1	119.2	121.3	122.6	118.9
7—1—2	119.1	122.2	120.1	121.1	118.5	119.4	117.3	118.7	121.8
8—2—3	111.8	117.8	120.7	118.4	121.2	118.5	109.1	121.6	118.2
9—3—4	121.9	109.2	118.6	114.6	117.9	121.4	121.5	117.5	109.0
10—4—5	120.0	121.4	109.6	122.0	109.6	119.2	120.6	111.6	120.9
11—5—6	118.1	119.4	120.2	119.5	120.3	109.2	117.9	120.9	120.2
12—6—1	119.8	117.3	118.6	118.1	119.4	120.7	120.7	119.5	118.1
*b**	103.7	109.2	109.6	100.1	109.6	109.2	109.2	105.6	109.0
i—*j*—*k*—*l*/deg									
1—2—3—4	−10.2	0.0	0.0	12.4	0.0	0.0	−0.1	5.1	0.0
2—3—4—5	5.7	−0.1	0.0	−12.1	0.1	0.0	0.1	−8.5	0.0
3—4—5—6	−1.7	0.1	0.0	7.4	0.0	0.0	−0.1	8.5	0.0
4—5—6—1	2.8	−0.0	0.0	−2.8	0.0	0.0	0.0	−5.1	0.0
5—6—1—2	11.2	0.0	0.1	3.1	0.1	0.0	0.0	1.3	0.0
7—1—2—3	−173.9	−180.0	−180.0	176.0	−180.0	180.0	180.0	178.4	−180.0
8—2—3—4	−143.6	−180.0	−180.0	−173.5	180.0	−180.0	−123.9	−177.9	−179.9
9—3—4—5	−179.0	−124.6	−180.0	−150.4	180.0	180.0	180.0	174.9	124.6
10—4—5—6	−178.6	−180.0	−124.8	−178.8	124.0	180.0	−180.0	137.5	180.0
11—5—6—1	−177.3	−180.0	−180.0	−179.0	180.0	125.7	180.0	178.4	−180.0
12—6—1—2	−176.5	−180.0	180.0	−177.6	−180.0	−180.0	180.0	178.3	−180.0
*c**	101.9	124.6	124.7	96.1	−124.0	−125.7	123.8	−107.8	−124.7
$\Delta E(ZPC)$/au	0.0938	0.0929	0.0927	0.0929	0.0933	0.0918	0.0934	0.0938	0.0927

* Parameter "*a*" for AI **1**—**9** corresponds to the following interatomic distances: 2—13 (**1**), 3—13 (**2**), 4—13 (**3**), 3—13 (**4**), 4—13 (**5**), 5—13 (**6**), 2—13 (**7**), 4—13 (**8**), and 3—13 (**9**); parameter "*b*" corresponds to the following bond angles: 13—2—3 (**1**), 13—3—4 (**2**), 13—4—5 (**3**), 13—3—4 (**4**), 13—4—5 (**5**), 13—5—6 (**6**), 13—2—3 (**7**), 13—4—5 (**8**), and 13—3—4 (**9**); and parameter "*c*" corresponds to the following dihedral angles: 13—2—3—4 (**1**), 13—3—4—5 (**2**), 13—4—5—6 (**3**), 13—3—4—5 (**4**), 13—4—5—6 (**5**), 13—5—6—1 (**6**), 13—3—4—5 (**7**), 13—4—5—6 (**8**), and 13—2—3—4 (**9**).

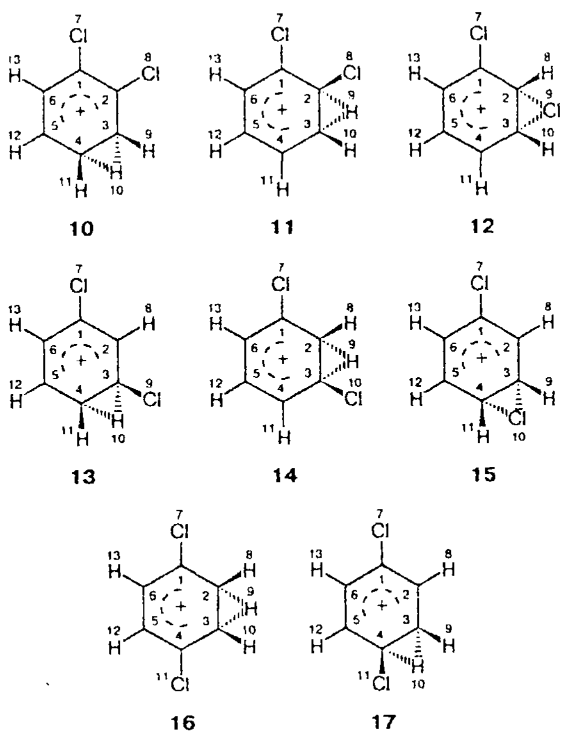
of the carbon skeleton of AI. However, if the carbon atom to which proton is attached forms a C—Cl bond (structures **1**, **4**, and **8**), the planarity of the carbon skeleton of AI is violated. For instance, the 2—3—4—5 dihedral angle in structure **4** exceeds 10°. Alternation of C—C bonds occurs in the carbon skeleton of AI, *viz.*, the lengths of the C—C bonds with the participation of the "tetrahedral" C atom are within the limits 1.46—1.49 Å, those of neighboring bonds are 1.36—1.39 Å, and those of more distant bonds are 1.40—1.42 Å. The C—H bonds at the "tetrahedral" C atom are longer than other bonds (1.10—1.13 Å).

The character of the electron density distribution in DCB arenonium ions shows that (1) "tetrahedral" C atoms have large negative charges (from −0.41 to −0.49); (2) the effective charges on Cl atoms vary over a wide range (from +0.10 to +0.24) depending on their position; and (3) an appreciable alternation of

Table 3. Total energies (*E*/au) and proton affinities (*PA*/kcal mol^{-1}) of 1,2-, 1,3- and 1,4-DCB (protonation with different localization of proton)

Molecule	Proton position	HF/6-31G* -*E*	HF/6-31G* *PA*	MP2/6-31G* -*E*	MP2/6-31G* *PA*	*PA* with inclusion of *ZPC*
1,2-DCB	C(1), C(2)	1148.7829	179.4	1149.7881	168.7	161.0
	C(3), C(6)	1148.7910	184.5	1149.8004	176.4	169.3
	C(4), C(5)	1148.7922	185.2	1149.8018	177.3	170.3
1,3-DCB	C(1), C(3)	1148.7765	172.5	1149.7781	160.6	153.4
	C(4), C(6)	1148.8033	189.3	1149.8125	182.2	174.7
	C(5)	1148.7847	177.6	1149.7903	168.3	161.8
	C(2)	1148.8011	187.9	1149.8102	180.8	173.2
1,4-DCB	C(1), C(4)	1148.7886	179.9	1149.7919	167.4	161.5
	C(2), C(3), C(5), C(6)	1148.7935	183.0	1149.8006	172.9	167.7

Scheme 2



charges along the chain of the carbon atoms in the ring occurs.

Analysis of the data in Table 4 makes it possible to draw some important conclusions. The position of carbon atom bonded to the Cl atom is the least favorable for the proton addition to the DCB molecule. In the case of *ortho*-isomer, positions C(4) and C(5) are the most favorable while positions C(3) and C(6) are less favorable for the proton addition, though the energy difference does not exceed 1 kcal mol^{-1}. This means that positions C(4), C(5), C(3), and C(6) in *ortho*-isomer are approximately equivalent. The situation differs substantially in the case of *meta*-isomer where the most stable forms of AI are those in which proton is added to C(4) or C(6) atoms. The arenonium ion with proton bonded to the C(2) atom is less favorable (approximately by 1.5 kcal mol^{-1}) while that with the proton at the C(5) atom is considerably unfavorable. The most stable AI in the case of *para*-isomer are those where proton is added to C(2), C(3), C(5), or C(6) atoms. When comparing the calculated absolute proton affinity (*PA*) of DCB isomers it should be noted that it increases on going from *ortho*- (177.3 kcal mol^{-1}) to *meta*-isomer (182.2 kcal mol^{-1}) and decreases on going from *meta*- to *para*-isomer (172.9 kcal mol^{-1}). We have no information on experimental values of the proton affinity of 1,2-, 1,3-, and 1,4-DCB; however, the regularity we obtained for DCB isomers is also characteristic of difluorobenzene (DFB) isomers. It is known from the published data[13] that the proton affinity in the series 1,2-DFB, 1,3-DFB, and 1,4-DFB changes as follows: 175.7, 180.0, and 171.5 kcal mol^{-1}, respectively.

The proton affinity of benzene molecule calculated by the MP2/6-31G* method is equal to 181.3 kcal mol^{-1} and that with inclusion of zero-point energy corrections is equal to 175.9 kcal mol^{-1}. The experimental value[13] is equal to 180.0 kcal mol^{-1}. Thus, according to our calculations, the proton affinity decreases approximately by 5—8 kcal mol^{-1} on going from benzene molecule to *ortho*- and *para*-isomers of DCB, while it changes only slightly on going from benzene molecule to *meta*-isomer of DCB (the proton affinity increases by 2 kcal mol^{-1} without inclusion of zero-point energy corrections).

Some peculiarities of the structure of transition states of 1,2-migrations of H and Cl atoms should be noted. In transition state, the migrating group (H or Cl atom) is always above or under the plane of AI ring. For instance, the 10—3—4—5 dihedral angle in structure **10** (see Table 3) corresponding to migration of H atom is 95°, while the 9—2—3—4 dihedral angle in structure **12** corresponding to migration of Cl atom is 109.6°. It is of interest that migration of a H atom in AI is accompa-

Table 4. Geometric parameters of transition states **10—17**: interatomic distances (*i*—*j*), bond angles (*i*—*j*—*k*), dihedral angles (*i*—*j*—*k*—*l*), total energies,* and zero-point energy corrections

Parameter	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
i—*j*/Å								
1—2	1.409	1.435	1.417	1.391	1.405	1.370	1.413	1.396
2—3	1.414	1.460	1.471	1.431	1.456	1.450	1.454	1.404
3—4	1.449	1.402	1.453	1.453	1.429	1.470	1.413	1.453
4—5	1.413	1.394	1.367	1.402	1.389	1.413	1.401	1.426
5—6	1.388	1.400	1.432	1.390	1.404	1.376	1.396	1.383
6—1	1.411	1.398	1.381	1.413	1.399	1.441	1.401	1.415
1—7	1.700	1.696	1.710	1.708	1.707	1.708	1.703	1.703
2—8	1.700	1.715	1.088	1.086	1.089	1.086	1.089	1.086
2—9	2.176	1.258	2.113	2.728	1.513	2.174	1.303	2.183
3—9	1.088	1.377	1.905	1.730	1.207	1.089	1.303	1.089
3—10	1.321	1.088	1.089	1.204	1.728	1.910	1.089	1.381
4—11	1.088	1.086	1.086	1.088	1.086	1.087	1.703	1.719
5—12	1.086	1.087	1.086	1.086	1.087	1.085	1.087	1.087
6—13	1.086	1.087	1.088	1.087	1.088	1.088	1.087	1.087
i—*j*—*k*/deg								
1—2—3	118.8	118.5	120.1	119.2	119.4	119.2	119.7	119.6
2—3—4	120.5	120.4	118.4	119.4	119.3	118.6	119.7	120.2
3—4—5	119.2	119.3	119.1	119.0	118.9	120.0	119.0	118.5
4—5—6	119.4	121.2	121.5	120.2	121.4	119.1	121.3	119.9
5—6—1	122.0	121.6	121.8	121.1	121.0	122.0	121.3	121.0
6—1—2	120.2	118.8	118.9	120.6	119.5	120.9	119.0	120.7
7—1—2	120.8	120.5	118.8	119.8	119.2	121.1	119.6	120.0
8—2—3	118.7	118.7	119.0	119.4	118.4	119.4	118.6	119.6
9—2—3	25.6	60.3	61.2	33.7	47.9	26.5	56.1	25.1
9—3—4	119.1	107.4	113.5	119.1	104.6	117.3	108.9	118.1
10—3—4	55.2	122.6	117.8	68.9	119.9	77.1	121.5	52.6
11—4—5	122.2	121.5	121.9	122.7	121.9	120.9	121.5	120.6
12—5—6	120.8	119.1	118.5	120.4	119.2	120.9	119.6	121.1
13—6—1	118.2	118.2	118.9	118.9	118.9	118.2	119.1	119.3
i—*j*—*k*—*l*/deg								
1—2—3—4	−0.7	−3.7	−5.3	6.7	7.1	−4.3	−0.1	3.6
2—3—4—5	0.8	3.0	3.0	−7.2	−6.1	5.4	−0.4	−3.6
3—4—5—6	−0.6	−2.5	−0.8	6.0	4.1	−4.5	0.4	3.0
4—5—6—1	0.2	2.7	0.8	−4.2	−3.0	2.6	0.1	−2.4
5—6—1—2	0.0	−3.4	−3.1	3.7	3.9	−1.6	−0.6	2.5
7—1—2—3	−180.0	−177.3	−177.0	178.2	177.3	179.8	−179.0	178.3
8—2—3—4	−179.7	−172.2	164.9	−176.2	−178.4	176.6	−175.3	−178.7
9—2—3—4	−176.4	89.3	−109.6	−162.2	95.2	149.9	93.8	−179.0
10—3—4—5	95.1	−178.3	153.0	89.0	−168.8	−104.6	−175.6	−94.1
11—4—5—6	−174.4	179.5	179.2	180.0	−178.7	166.4	−179.0	170.8
12—5—6—1	−179.4	−178.8	178.8	179.1	180.0	179.3	−179.9	178.4
13—6—1—2	−179.8	179.1	176.8	−178.7	−178.5	178.1	179.6	−179.7
ΔE/au	−0.7812	−0.7735	−0.7636	−0.7722	−0.7710	−0.7660	−0.7805	−0.7752
$\Delta E(ZPC)$/au	0.0897	0.0899	0.0931	0.0902	0.0901	0.0932	0.0896	0.0897

* Total energy $E = -1149 + \Delta E$ (au).

nied by a slight deviation of the substituents at the C—C bond involved into migration from the ring plane in the opposite direction relative to the migrating group. In the case of migration of the Cl atom the deviation of the substituents from the C—C—C plane can exceed 15°.

The effective charges on migrating H atoms in transition states differ slightly from corresponding values in AI. At the same time, the charges on migrating Cl atoms in transition states are smaller than those in AI. For instance, the charge on the Cl atom in structure **12** is +0.18 *e*, whereas it is equal to +0.25 *e* in arenonium ion **3**.

The data on transition states **10—17** make it possible to determine the activation energies and estimate the relations between the rate constants for DCB isomerization through the formation of AI. Isomerization of DCB can be described by the following scheme:

$$1,2\text{-}Cl_2C_6H_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1,3\text{-}Cl_2C_6H_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 1,4\text{-}Cl_2C_6H_4,$$

where k_1, k_{-1}, k_2, and k_{-2} are the rate constants for corresponding stages. Let us assume that only the most

Table 5. Activation energies (E_a) of 1,2-shifts of H and Cl atoms as elementary steps of DCB isomerization through arenonium ions

Reaction	E_a/kcal mol^{-1}					
	3—2	2—1	1—4	4—5	4—8	8—9
Direct	12.9 (11.0)	16.9 (15.0)	15.4 (14.9)	3.7 (2.1)	7.6 (7.8)	10.5 (7.9)
Reverse	12.0 (10.0)	9.2 (6.7)	9.1 (9.3)	25.3 (23.3)	16.2 (15.9)	15.9 (14.0)

Note. Corresponding values with inclusion of zero-point energy corrections (*ZPC*) are given in parentheses.

stable form of arenonium ion occurs upon proton addition to the DCB molecule. This is an actually justified assumption, since according to NMR spectroscopy data,[3] the fraction of the most stable 1,3-DCB AI (structure 5) is ~95%. Thus, according to our calculations, AI of 1,2-DCB, 1,3-DCB, and 1,4-DCB will have structures 3, 5, and **9**, respectively, before isomerization. Then the transformation of the most stable structure of 1,2-DCB AI into the most stable 1,3-DCB AI will occur through four successive 1,2-shifts of H and Cl atoms: $\mathbf{3} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{1} \rightleftharpoons \mathbf{4} \rightleftharpoons 5$.

Transformation of the most stable 1,3-DCB AI into the most stable 1,4-DCB AI can occur through three successive 1,2-shifts of H and Cl atoms, *viz.*, $5 \rightleftharpoons \mathbf{4} \rightleftharpoons \mathbf{8} \rightleftharpoons \mathbf{9}$. The activation energies of individual 1,2-shifts of H and Cl atoms for the reactions of isomerization of DCB through AI are listed in Table 5. It follows from the data in Table 5 that the transformation of structure **2** into structure **1** (E_a = 15.0 kcal mol^{-1}) is the limiting (with the highest activation energy of 1,2-shift) stage of isomerization of 1,2-DCB into 1,3-DCB through AI and that the transformation of structure 5 into structure **4** (E_a = 23.3 kcal mol^{-1}) is the limiting stage of the reverse reaction (1,3-DCB → 1,2-DCB). The transformation of structure 5 into structure **4** (E_a = 23.3 kcal mol^{-1}) is the limiting stage of isomerization of 1,3-DCB into 1,4-DCB through arenonium ions and the transformation of structure **8** into structure **4** (E_a = 15.9 kcal mol^{-1}) is the limiting stage of the reverse reaction (1,4-DCB → 1,3-DCB).

Taking into account the values of activation energies of individual reaction stages and the number of 1,2-shifts of H and Cl atoms in the course of isomerization, we obtained the following relations for the rate constants for reaction of DCB isomerization: $k_1 > k_{-1}$, $k_2 < k_{-2}$, and $k_{-1} < k_2$. The relations we found are in agreement with the data obtained[1a] in studies of DCB isomerization on zeolites.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest Laboratory.

References

1. (a) J. Perdillos, D. Brunel, B. Coq, P. Massiani, L. C. De Menorval, and F. Figueras, *J. Am. Chem. Soc.*, 1990, **112**, 1313; (b) J. Perdillos, B. Coq, P. Massiani, and F. Figueras, *Appl. Catal.*, 1989, **51**, 285; (c) B. Coq, J. Perdillos, and F. Figueras, *Appl. Catal.*, 1990, **62**, 281.
2. L. T. Scott and J. S. Highsmith, *Tetrahedron Lett.*, 1980, **21**, 4703.
3. V. A. Koptyug, *Arenonievye iony. Stroenie and reaktsionnaya sposobnost'* [*Arenonium Ions. The Structure and Reactivity*], Nauka, Sib. Branch, Novosibirsk, 1983 (in Russian).
4. Yu. A. Borisov, N. I. Raevskii, E. S. Mortikov, V. A. Plakhotnik, and I. I. Leshchiner, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 731 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 547 (Engl. Transl.)].
5. Yu. A. Borisov, R. M. Kurbanbaev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1213 [*Russ. Chem. Bull.*, 1993, **42**, 1156 (Engl. Transl.)].
6. C. Møller and S. Plesset, *Phys. Rev.*, 1968, **49**, 4852.
7. C. Peng and H. B. Schlegel, *Isr. J. Chem.*, 1993, **33**, 449.
8. M. J. Frisch, J. B. Foresman, and A. Frisch, *Gaussian 92*, Gaussian. Inc., Pittsburgh (PA), 1993.
9. M. J. Frisch, J. B. Foresman, and A. Frisch, *Gaussian 94. User's Reference, Copyright 1994—1996*, Gaussian Inc., Pittsburgh (PA), 1996.
10. M. Dupius, D. Spangler, and J. J. Wendolowski, *Nat. Resour. Comut. Chem. Software Cat. 1. Prog. QG01 (GAMESS)*, 1980.
11. D. G. Anderson, S. Gradock, P. B. Lieschaeski, and D. W. Rankin, *J. Mol. Struct.*, 1990, **216**, 181.
12. *Thermochemical Data of Organic Compounds*, Eds. J. B. Pedley, R. D. Neylor, and S. P. Kirby, Chapman and Hall, New York, 1986.
13. J. E. Szulejko and T. B. McMahon, *J. Am. Chem. Soc.*, 1993, **115**, 7839.

Received February 16, 1998;
in revised form March 23, 1998