ELECTRONIC ASPECTS OF THE CHLORINATION OF 2,4-DICHLOROPENTANE AS A MODEL FOR THE STUDY OF THE CHLORINATION OF POLY(VINYL CHLORIDE)*

Miroslav BÁRTA**, Rudolf LUKÁŠ and Miloslav KOLÍNSKÝ

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

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The semiempirical quantum chemical method CNDO/2 was used in the calculation of the electronic structure of TT and GG conformers of d,l-2,4-dichloropentane and TG′ conformer of *meso*-2,4-dichloropentane. Relative stability of their model conformations was determined and compared with data of ^{1}H-NMR spectroscopy. The TT conformer of *d,l*-2,4-dichloropentane was found to possess the highest stability. The chlorination mechanism of 2,4-dichloropentane was discussed using the knowledge of the total electron densities on atoms, frontier orbital electron densities and interatomic bond indices. The INDO method was employed to calculate the spin densities of stereoisomers of 2,4-dichloropentane. Results thus obtained led to a conclusion that the reactivity of monocarbon groups in the chlorination of 2,4-dichloropentane decreased in the order $CH_3— > —CH_2— > —CHCl—$.

In our earlier papers[1-7] we investigated the selectivity of chlorination of poly(vinyl chloride) (PVC); in other words, we tried to find out if the new chlorine atom entered only the $—CH_2—$ or $—CHCl—$ groups, or both of them, and at what mutual ratio. To solve these problems, we used specifically deuterated polymer models of PVC, namely, α-deuterated PVC (α-d-PVC) (ref.[1,2]) and β,β-dideuterated (β,β-d_2-PVC) (ref.[3-6]). An attempt to obtain more data on the reactivity of the $—CH_2—$ and $—CHCl—$ groups was made by chlorinating the stereoisomeric mixture and the individual stereoisomers of a low-molecular weight model of PVC, 2,4-dichloropentane[7]. However, even samples of low-chlorinated stereiosomers of 2,4-dichloropentane gave such complicated ^{1}H-NMR and Raman spectra (overlap of signals caused by the different chemical composition and by stereoisomerism) that these spectra could not be given an unambiguous interpretation. In spite of this, however, a valuable finding was obtained about the different reactivity of *d,l*-2,4-dichloropentane (*syndio*-2,4-dichloropentane) and *meso*-2,4-dichloropentane (*iso*-2,4-dichloropentane). In this paper quantum-chemical calculations have been used to carry out a theoretical investigation of the chlorination of 2,4-dichloropentane.

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** Present address: Power Research Institute, 250 97 Prague 9, Běchovice.

RESULTS

The electronic structure of stereoisomers of 2,4-dichloropentane and their various steric conformations were determined by using theoretical approaches which with relative success respected the correlation between the total molecular energy and molecular geometry. Since 2,4-dichloropentane contains also atoms of the second row, the method chosen by us in calculating the electronic structures of a closed shell system was the CNDO/2 method (Complete Neglect of Differential Overlap)[8] including also the d-atomic orbitals. The INDO method (Intermediate Neglect of Differential Overlap) was utilized in calculating the spin densities of radical intermediates[9].

Molecular Geometry of Stereoisomers of 2,4-*Dichloropentane*

The structure of stereoisomers of 2,4-dichloropentane has been studied earlier on the basis of an analysis of the vibrational and NMR spectra[10–13]. It was proved that the *syndio*-form existed prevailingly as the TT and in a small amount as the GG′ conformer. The preference given to these three conformation forms was also confirmed by a comparison of calculated conformation energies of various conformers in the approximation of the Lennard–Jones[12] or Buckingham[10,14] type of interaction between nonbonding atoms.

We assumed in this work that the molecular geometry of stereoisomers of 2,4-dichloropentane could be expressed in a „staggered" approximation, *i.e.* dihedral angles are regarded as being 60°, even though optimalization of the geometry in the approximation of the Buckingham type of non-binding interactions[14] exhibits small departures from „staggered" conformations. Our assumption is in agreement with the conformation studies of PVC and two-unit molecules[11]. The X-ray diffraction study of PVC also indicates the presence of a predominantly planar chain in the syndiotactic order[15,16]. From these papers we took the distance between the end carbon atoms of the TT conformer of the syndiotactic form, 0·51 nm, and the valence angle $\sphericalangle$ CCC = 112°. The bond lengths were taken as follows: R(C—H) = 0·1096 nm in the —CH_3 group, r(C—H) = 0·1073 nm in the —CH_2— and —CHCl— group, and r(C—Cl) = 0·1767 nm. From this model geometry of the chain of the TT conformer of syndio-2,4-dichloropentane, the geometric structures of the GG conformer of *syndio*-2,4-dichloropentane and of the TG′ conformer of iso-2,4-dichloropentane were also derived.

Total Molecular Energy of the Conformers of 2,4-*Dichloropentane*

The total molecular energy E_{total} in the LCAO approximation is given by the sum of electron energy, E_{el}, and of the core repulsion energy, E_{nucl}:

$$E_{total} = E_{el} + E_{nucl} \,. \tag{1}$$

The electron energy E_{el} can be expressed by

$$E_{el} = 1/2 \sum_{\mu\nu} \mathbf{P}_{\mu\nu}(\mathbf{H}^{core}_{\mu\nu} + \mathbf{F}_{\mu\nu}), \tag{2}$$

where $\mathbf{P}_{\mu\nu}$ denotes elements of the electron density matrix between atomic orbitals μ and ν; $\mathbf{H}^{core}_{\mu\nu}$ and $\mathbf{F}_{\mu\nu}$ in such matrix representation are matrix elements of operators $\mathbf{H}^{core}$ and $\mathbf{F}$. The core repulsion energy E_{nucl} may be expressed in the approximation of point charges,

$$E_{nucl,p} = 1/2 \sum_{A \neq B} \frac{Z_A Z_B e^2}{r_{AB}} \tag{3}$$

or through two-centre coulomb integrals $\gamma_{AB} = (\mu_A\mu_A/\nu_B\nu_B)$

$$E_{nucl,c} = 1/2 \sum_{A \neq B} Z_A Z_B \gamma_{AB}\,; \tag{4}$$

the symbols Z_A, Z_B denote the core charges of atoms A, B respectively, e is the electronic charge, r_{AB} is the distance between these atoms. The total molecular energies of the conformes of 2,4-dichloropentane are given in Table I. Table II contains the relative energies of GG-*syndio* and TG′-iso conformers of 2,4-dichloropentane with respect to its TT-*syndio* conformation, compared with the experimentally determined energy for the *GG-syndio* form of 2,4-dichloropentane.

Bond Indices and Atomic Binding Indices of Conformers of 2,4-*Dichloropentane*

In the expression for the total energy of molecules (*1*) there are terms related to the bond energy of two atoms. This energy may be characterized as a sum of contributions

TABLE I

Total Molecular Energy of TT and GG Conformers of *syndio*-2,4-Dichloropentane and TG′ of iso-2,4-Dichloropentane

Isomer	$E_{el} + E_{nucl,p}$ eV	$E_{el} + E_{nucl,c}$ eV
syndio-Form		
TT	—2 060·09846	—2 150·389180
GG	—2 059·89073	—2 150·27615
Iso-form		
TG′	—2 060·00186	—2 150·33894

characterizing the stabilization of conformation by coulomb and exchange interactions similarly to the partition scheme of Fischer and Kollmar[17]

$$E_{AB} = E^{R}_{AB} + E^{J}_{AB} + E^{K}_{AB} + E^{V}_{AB} + E^{N}_{AB}\,, \tag{5}$$

where

$$E^{R}_{AB} = 2\sum_{\mu}^{A}\sum_{\nu}^{B}\mathbf{P}_{\mu\nu}\mathbf{H}^{core}_{\mu\nu} \tag{6}$$

$$E^{J}_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B}\mathbf{P}_{\mu\mu}\mathbf{P}_{\nu\nu}(\mu\mu/\nu\nu) \tag{7}$$

$$E^{K}_{AB} = -\,1/2\sum_{\mu}^{A}\sum_{\nu}^{B}\mathbf{P}^{2}_{\mu\nu}(\mu\mu/\nu\nu) \tag{8}$$

$$E^{V}_{AB} = -\sum_{\mu}^{A}\sum_{\nu}^{B}(\mathbf{P}_{\mu\mu}n_{\nu} + \mathbf{P}_{\nu\nu}n_{\mu})\,(\mu\mu/\nu\nu) \tag{9}$$

$$E^{N}_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B}n_{\mu}n_{\nu}(\mu\mu/\nu\nu)\,, \tag{10}$$

E^{R}_{AB} denotes the two-centre resonance energy, E^{J}_{AB} and E^{K}_{AB} are contributions of the coulomb and exchange electron interaction, E^{V}_{AB} and E^{N}_{AB} are contributions of the electron-core and core-core interaction, n_{μ} and n_{ν} are atomic orbital charges. The bond energy E_{AB} is a quantitative measure of bond stability; the more negative its value, the stronger the bond between the A–B atoms. Quite obviously, the bond index thus defined is only a very rough measure of bond stability, characterizing the bond only for small departures of atoms from the equilibrium position. A similar

TABLE II

Relative Energies of GG-*syndio* and TG′-iso Conformers of 2,4-Dichloropentane with Respect to Its TT-*syndio* Conformation

GG-*syndio* kJ	TG′-iso kJ	References
6·45	3·01	[14] (stable conformation)
7·53	—	[14] ("staggered" conformation)
12·39	6·11	[12]
20·05	9·34	this paper ($\Delta E_{el} + \Delta E_{nucl,p}$)
10·93	4·86	this paper ($\Delta E_{el} + \Delta E_{nucl,c}$)
10·47	—	[10] (ΔH_{exp})

characteristic allowing to compare bond energies can also be seen in the bond index in the form[18], based on Mulliken's population analysis

$$T_{AB} = 2 \sum_{\mu}^{A} \sum_{\nu}^{B} \mathbf{P}_{\mu\nu} \mathbf{S}_{\mu\nu} , \qquad (11)$$

where $\mathbf{S}_{\mu\nu}$ is the overlap integral between the atomic orbitals μ and ν.

The calculated values of bond indices E_{AB} and T_{AB} were in a very good correlation, obviously because the resonance contribution E^{R}_{AB}, which corresponds to the bond index T_{AB} (Eq. (*11*)), predominates in the expression for E_{AB} (Eq. 5) (other terms in the expression for E_{AB}, even though being larger by an order of magnitude, approximately compensate each other). Since in some cases the strength of the C—H bond characterized by the bond indices E_{AB} or T_{AB} was approximately the same, the nonbonding interactions had to be included in the calculation. A preliminary measure of stability of the hydrogen atom A in the molecule is then given by

$$E_A = \sum_{A \neq B}^{A} E_{AB} \quad \text{or} \quad T_A = \sum_{A \neq B}^{B} T_{AB} , \qquad (12)$$

where summation is performed over all remaining atoms in the molecule. We therefore used the atomic binding indices E_A, T_A (Table III) throughout this work in order to compare the feasibility with which hydrogen atoms are abstracted in various positions of the conformers of 2,4-dichloropentane.

TABLE III

Atomic Binding Indices of Conformers of 2,4-Dichloropentane

The values of symmetric atoms are not given.

Atom H	TT-*syndio*		GG-*syndio*		TG′-iso	
	T_A	E_A	T_A	E_A	T_A	E_A
H3	1·320	—0·802	1·329	—0·782	1·320	—0·790
H4	1·355	—0·817	1·354	—0·797	1·353	—0·804
H_5	1·344	—0·814	1·339	—0·794	1·347	—0·802
H6					1·339	—0·801
H7					1·358	—0·808
H8					1·319	—0·787
H9					1·328	—0·794
H10					1·331	—0·793

Total Charge Densities and Electron Densities of Frontier Orbitals of Conformers of 2,4-Dichloropentane

The interaction of the Cl• radicals with a closed shell system can be studied using the conception of charge- or frontier-orbital controlled reactions[19,20].

In the former case the perturbation energy of interaction is expressed predominantly through the total charge densities in the reagents; in the latter, it is given by the electron density of frontier orbitals. Table IV presents calculated total charge densities q on atoms, frontier-orbital electron densities $f^{(R)}$ (ref.[20]) and electron densities in the highest occupied molecular orbitals $C^{(HO)}$. The calculated charge densities correspond well with the value calculated in a recent paper by Ando and coworkers[21], who correlated the NMR spectra with a model stochastic distribution of vinyl chloride in PVC.

TABLE IV

Total Charge Densities q on Atoms, Frontier Orbital Electron Densities $f^{(R)}$ and Electron Densities in the Highest Occupied Molecular Orbitals $C^{(HO)}$ for TT, GG and TG′ Conformers of 2,4-Dichloropentane

Atom	TT-*syndio*			GG-*syndio*			TG′-iso		
	q	$f^{(R)}$	$C^{(HO)}$	q	$f^{(R)}$	$C^{(HO)}$	q	$f^{(R)}$	$C^{(HO)}$
C_1	—0·010	0·017	0·016	—0·010	0·004	0·003	—0·010	0·022	0·019
C_2	0·088	0·101	0·027	0·087	0·114	0·037	0·089	0·176	0·027
C_3	0·022	0·040	0·036	0·022	0·056	0·053	0·022	0·045	0·043
C_4							0·088	0·034	0·033
C_5							—0·009	0·003	0·003
H_1	0·011	0·005	0·001	0·010	0·007	0·003	0·012	0·009	0·000
H_2	0·014	0·003	0·002	0·018	0·001	0·000	0·017	0·002	0·000
H_3	0·013	0·005	0·005	0·013	0·005	0·005	0·014	0·006	0·005
H_4	0·028	0·004	0·003	0·019	0·002	0·001	0·018	0·002	0·000
H_5	0·013	0·009	0·000	0·013	0·002	0·000	0·013	0·009	0·000
H_6							0·013	0·001	0·000
H_7							0·030	0·007	0·006
H_7							0·030	0·007	0·006
H_8							0·013	0·005	0·004
H_9							0·013	0·001	0·001
H_{10}							0·012	0·001	0·001
C_{11}	—0·169	0·336	0·177	—0·162	0·337	0·173	—0·167	0·443	0·122
C_{12}							0·169	0·233	0·232

Total Energy of Radicals of the TT *Conformer* 2,4-*Dichloropentane*

For the most stable conformation of 2,4-dichloropentane, *i.e.* for TT-*syndio*-2,4-dichloropentane, the total energies of assumed radicals and the spin densities on the respective carbon atoms were calculated by means of the INDO[9] method (Table V). Since the geometries of radical species are not known, two steric arrangements were adopted, namely, for the planar ordering of bonds on $-\overset{|}{\underset{|}{C}}{}^{\bullet}$ and for the pyramidal ordering of bonds on $-\overset{|}{\underset{|}{C}}{}^{\bullet}$, which corresponds to a simple abstraction of the hydrogen atom without any subsequent geometrical rearrangement of the rest of the molecule. Both geometrical models lead to the same conclusions; we believe, therefore, that the uncertainty in the geometry of radicals is not decisive in this case. At the primary carbon atom radical we assumed the planar sp^2 hybridization[22].

DISCUSSION

Assuming a substitution reaction course, the radical chlorination proceeds by the chain mechanism, and its propagation stage may generally be described by two mechanisms[23]:

Mechanism A

$$\mathrm{R{-}H} + \mathrm{Cl}^{\bullet} \rightarrow [\mathrm{R{\ldots}H{\ldots}Cl}] \rightarrow \mathrm{R}^{\bullet} + \mathrm{H{-}Cl}\,,$$

$$\Delta H = 0 \quad \text{to} \quad -54\ \mathrm{kJ/mol}$$

$$\mathrm{R}^{\bullet} + \mathrm{Cl{-}Cl} \rightarrow [\mathrm{R{\ldots}Cl{\ldots}Cl}] \rightarrow \mathrm{R{-}Cl} + \mathrm{Cl}^{\bullet}\,,$$

$$\Delta H = -88 \quad \text{to} \quad -113\ \mathrm{kJ/mol}$$

Mechanism B

$$\mathrm{H{-}R} + \mathrm{Cl}^{\bullet} \rightarrow [\mathrm{H{\ldots}R{\ldots}Cl}] \rightarrow \mathrm{H}^{\bullet} + \mathrm{R{-}Cl}\,,$$

$$\Delta H = 46 \quad \text{to} \quad 75\ \mathrm{kJ/mol}$$

$$\mathrm{H}^{\bullet} + \mathrm{Cl{-}Cl} \rightarrow [\mathrm{H{\ldots}Cl{\ldots}Cl}] \rightarrow \mathrm{H{-}Cl} + \mathrm{Cl}^{\bullet}\,,$$

$$\Delta H = -188\ \mathrm{kJ/mol}$$

In the case of mechanism A, the selectivity of attack by the chlorine radical is affected by the different electron density of reacting hydrogen atoms, while in the case of mechanism B this influence is exerted by the different electron density of the

carbon skeleton. By comparing ΔH of the first stages of mechanism A and B one can see that the mechanism B is thermodynamically less advantageous.

Reaction of 2,4-*Dichloropentane with the Chlorine Radical*

It follows from Table I and II that the total energy of the TT conformer of 2,4-dichloropentane is lower than that of GG and TG′ of 2,4-dichloropentane, in agreement with the planar syndiotactic structure of PVC found by the X-ray diffraction[15,16]. The comparison between the conformation energies of the TT and GG forms in the approximation of core repulsion energy through coulomb integrals is in good agreement with the experiment[10] (Table II).

If one starts by assuming that chlorination proceeds by the mechanism A, it would follow from a comparison of the atomic binding indices E_A. T_A, of the TT and TG′ forms (Table III) that the easiest abstraction of the hydrogen atom may be expected for the methyl group (carbon C_1); next comes abstraction of the hydrogen atom on the carbon atom C_3, while the hydrogen atom on the carbon atom C_2 should be relatively the most reluctant to abstraction. A similar result is obtained by the comparison of electron densities q (Table IV). By respecting the reactivity order given above, one may infer from the comparison of the atomic indices E_A, T_A and of the electron densities q of TT and TG′ of 2,4-dichloropentane that TT-*syndio*-2,4-dichloropentane is somewhat more reactive than TG′-*iso*-2,4-dichloropentane, in agreement with the experiment[7].

With the chlorination mechanism B, the reactivities of carbon atoms C_1, C_2 and C_3 may be compared by comparing their electron densities q. It follows from Table IV that the order of feasibility with which the carbon atoms are attacked by the chlorine radical of the TT and TG′ form of 2,4-dichloropentane is $C_1 > C_3 > C_2$. Table IV

TABLE V

Total Energies of Radicals of TT-*syndio*-2,4-Dichloropentane in Planar and Pyramidal Ordering and Spin Densities on Carbon Atoms C_1, C_2 and C_3

Ordering	Carbon Atoms	$E_{total,c}$ eV	Spin density
Planar	C_1	—2 118·1532	0·8963
	C_2	—2 118·5998	0·7520
	C_3	—2 117·3281	0·8112
Pyramidal	C_2	—2 117·9450	0·7030
	C_3	—2 117·7669	0·7857

also shows that TT-*syndio*-2,4-dichloropentane is somewhat more reactive than TG′-iso-2,4-dichloropentane.

Frontier orbital $f^{(R)}$ values and the highest occupied orbital charges $C^{(HO)}$ (Table IV) give different results as regards the electrophilic attack of the chlorine radical compared with the order of reactivities determined by means of electron densities q, which, however, is consistent with the experimentally known fact that the TT-form of 2,4-dichloropentane undergoes chlorination somewhat more quickly than the TG′-form[7]. In the case of frontier-orbital controlled reaction, a reversed order of reactivities may rather be assumed. Hence, it may be supposed that (*a*) the reaction type under study is rather charge- than frontier-orbital controlled, or *b*) the HOMO and LUMO (Highest Occupied and Lowest Unoccupied Molecular Orbitals) conceptions of approximation are too simplifying for more complicated molecules, so that larger orbital configuration mixing should be taken into account. For simplicity's sake, the electronic structure of the chlorine radical was not considered[24], which also may become a limiting factor in the interpretation of results.

Reaction of the Radical 2,4-*Dichloropentane with Chlorine*

The comparison of total energy values E_{total} (Table V) shows that planar ordering of bonds on the carbon radical $C_2^{\bullet}$ is somewhat more advantageous than pyramidal ordering; on the other hand, pyramidal ordering seems to be more advantageous for the carbon radical $C_3^{\bullet}$ (these findings are in a good accordance with the study of α-halogenethyl radicals by ESR spectroscopy[22]). In both geometries the radical $C_2^{\bullet}$ has the lowest total energy. Attempts to identify these radicals and determine their lifetimes by means of ESR spectroscopy were unsuccessful. Hence, the magnitude of spin density seems to be the decisive factor in the course of chlorination. Table V shows that the highest density of unpaired electrons is found with the radical $C_1^{\bullet}$ and decreases in the order $C_3^{\bullet} > C_2^{\bullet}$.

If one summarizes the results just described, it can be said that with both the A and B chlorination mechanism being operative in the chlorination of 2,4-dichloropentane, the entrance of a new chlorine atom is given by the different reactivity of the monocarbon groups CH_3—, —CH_2— and —CHCl—, with the reactivity decreasing in the order CH_3— > —CH_2— > —CHCl—. The stereoisomerism of 2,4-dichloropentane has no effect on this order. TT-*syndio*-2,4-dichloropentane is somewhat more reactive than TG′-iso-2,4-dichloropentane, but no unambiguous conclusion could be made to the extent to which the methyl end groups and the internal —CH_2— and —CHCl— groups participate in the different reactivity. A more important contribution to the determination of the mechanism of chlorination of PVC can be seen either in the utilization of the trimer, 2,4,6-trichloroheptane, or in the calculation of the electron band structure of the polymer in the idealization of an infinite periodic chain.

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