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Halogenotropy in the CNC Triad of Trihalomethyl Isocyanates and Conformational Lability of Their Iminocarbonyl Isomers

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Abstract—According to the MNDO calculations, halotropic transformation of trihalomethyl isocyanates X_3CNCO (X = F, Cl, Br) follows sigmatropic mechanism with formation of a contact ion pair. In keeping with the experimental data, the isocyanate structure of the fluorine derivative and carbamoyl structure of the chlorine and bromine analogs are determined by the relative stabilities of isomeric forms. Specific solvation gives rise to a weak tendency to reduction of the activation energy of chlorotropy and leveling of the stability of chlorotropic isomers.

As was shown previously [1, 2], 1,3-chlorine shift in chloromethyl isocyanates follows an intramolecular sigmatropic mechanism and displacement of the equilibrium toward one or another isomeric form is governed by their relative thermodynamic stabilities. It seemed reasonable to extend the series of the simplest anionotropic systems by including trihalomethyl isocyanates. These compounds are expected to undergo halotropic isomerization by alternative dissociation–recombination mechanism with regard to specific solvation which plays an important role in the chlorotropy of *P*-chloro ylides [3]. The main contribution to the energy of specific solvation is that of only two solvate shell molecules which directly interact with chloride ion in the transition state (with subsequent saturation of the solvate shell up to a solvation number of 8 [4]). Therefore, when estimating the effect of specific solvation on halotropic transformations of CNC systems a limited number of solvate shell molecules can be taken into account.

The present communication reports on the results of semiempirical MNDO study [5] (in the supermolecular approximation) of the effects of halogen nature and specific solvation on the structure and mechanism of halogenotropy in the CNC triad of trihalomethyl isocyanates X_3CNCO (X = F, Cl, Br) and their solvates with chloroform (1:2, X = Cl), as well as of conformations of their halotropic isomers, dihalomethylenecarbamoyl halides $X_2C=NC(O)X$ (X = F, Cl, Br). The calculations of $M \cdot nCHCl_3$ structures were performed with full geometry optimization;

$n = 0, 2$; M is a halotropic isomer of trihalomethyl isocyanate **Ia–IIIa** or **Ic–IIIc** or transition state **Ib–IIIb** or **Id**–IIId corresponding to sigmatropic (*a*) and dissociation–recombination path (*b*) of 1,3-halogen shift or conformational transformation of dihalomethylenecarbamoyl halides **Ic–IIIc** (path *c*) (Scheme 1). As previously [1–4], transition states **Ib–IIIb** were localized by the differential vector technique [6], and the subsequent refinement of the geometry and energy parameters was performed using the eigenvector-following procedure [7]. The kind of stationary points was determined from the Hessian by solving vibrational problem. Electronic correlation of transition states was not additionally taken into account, for it was indirectly included in the MNDO parametrization.

The results of calculations are given in Tables 1–5. Mutual arrangement of the substrate and chloroform molecules in the solvates $M \cdot 2CHCl_3$ of chlorine derivative **II** is depicted in Scheme 2 in the form of optimized Z-matrices (for the sake of simplicity, only a part of atoms is denoted), and the corresponding geometric parameters are collected in Table 1.

According to the calculations, isocyanates **Ia** and **IIa** and their carbamoyl halide isomers **Ic–IIIc** are thermodynamically stable compounds. The nature of the halogen only slightly affects the bond lengths in the C^1NC^2 triad and the C^1NC^2 angle in both isomers; one exception is an appreciable weakening of the C^1-N bond in trifluoromethyl isocyanate **Ia**, as compared to its chlorine- and bromine-containing

Scheme 1.
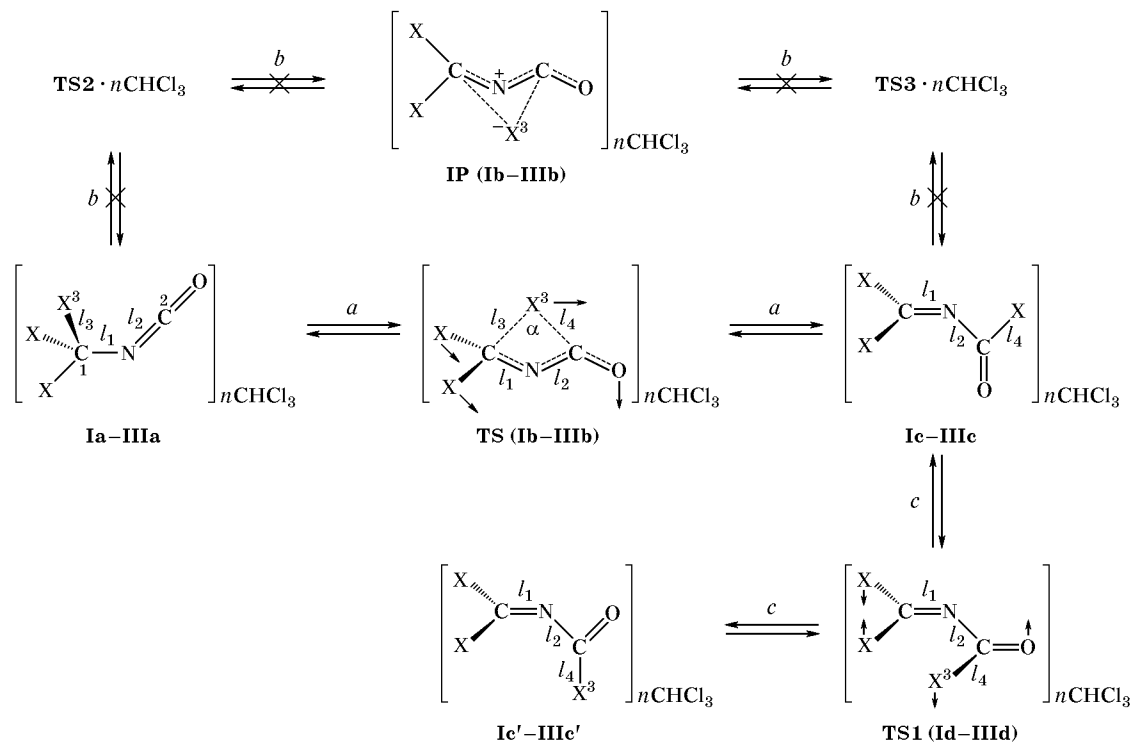
Ia–Id, $n = 0$, X = F; **IIa–IId**, $n = 0$, X = Cl; **IIIa–IIId**, $n = 0$, X = Br; **IIa$_2$–IId$_2$**, $n = 2$, X = Cl.

analogs **IIa** and **IIIa** (Table 1). Dihalomethylene-carbamoyl halides **Ic–IIIc** have a *gauche* structure in which the haloformyl group is nearly orthogonal to the X$_2$C=N– fragment: the torsion angle τ(OCNC) is 60–95° (Table 1). The relative stability (or the heat of transformation ΔH) of halotropic forms was calculated as the difference of their gas-phase enthalpies of formation. The results were qualitatively different for different halogen derivatives **I–III** (Table 2) and were valid both for the gas phase and the other aggregate states. The isocyanate isomer was found to be more stable for fluorine compound **Ia**, whereas the more stable form of chlorine derivative is carbamoyl chloride **IIc**. This is consistent with the experimental data, according to which the above compounds

were isolated as CF$_3$NCO [8] and Cl$_2$C=NCOCl [2, 9, 10]. A weak effect of the aggregate state on the relative stabilities of trihalomethyl isocyanate isomers is consistent with a fairly good agreement between the dipole moment and stretching vibration frequencies of dichloromethylenecarbamoyl chloride **IIc**, calculated for the gas phase (Table 3), on the one hand, and experimental dipole moment of **IIc** measured for neat liquid [9] and IR frequencies of a solution of **IIc** [10], on the other hand. The ^{35}Cl frequencies in the NQR spectrum of crystalline compound **IIc** change in the opposite direction to the total charges on the chlorine atoms Cl^1–Cl^3 [1, 2]. In this respect, energy parameters of the 1,3-bromine shift in compound **IIIa** are very interesting. According
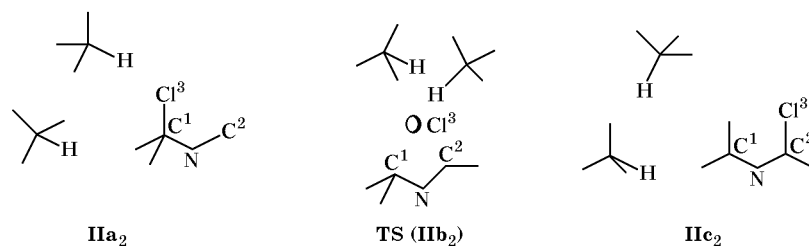
Scheme 2.

Table 1. Principal energy and geometry parameters of trihalomethyl isocyanates **Ia–IIIa**, dihalomethylenecarbamoyl halides **Ic–IIIc**, transition states **TS(Ib–IIIb)** for 1,3-halogen shift and **TS1(Id–IIId)** for conformational *gauche–gauche* transformation of dichloromethylenecarbamoyl chlorides **Ic–IIIc** and **Ic′–IIIc′**, and their solvates with chloroform $M \cdot 2CHCl_3{}^a$

Structure	ΔH_f^{298}, kJ/mol	l_1, Å	l_2, Å	l_3, Å	l_4, Å	α, deg	$\tau,^b$ deg	$\nu_{im},^c$ cm^{-1}
				$n = 0$				
Ia	–700.3	1.456	1.254	1.361	–	112.5^d	55.6	–
TS(Ib)	–412.3	1.413	1.385	1.797	1.443	80.7	1.9	567
Ic	–690.9	1.269	1.412	–	1.317	126.2^e	59.4	–
TS1(Id)	–681.0	1.299	1.422	–	1.325	117.8^e	159.7	40
IIa	–130.7	1.408	1.256	1.788	–	107.0^e	0.0	–
TS(IIb)	35.9	1.357	1.339	2.181	2.070	63.9	23.1	626^f
IIc	–157.8	1.269	1.412	–	1.771	112.2^e	93.1	–
TS1(IId)	–139.1	1.267	1.411	–	1.780	118.9^e	180.0	47
IIIa	2.3	1.406	1.256	1.890	–	113.0^d	61.1	–
TS(IIIb)	166.4	1.344	1.350	2.247	2.109	62.1	25.6	677
IIIc	–28.1	1.266	1.415	–	1.860	112.1^e	94.9	–
TS1(IIId)	–7.2	1.264	1.418	–	1.869	119.5^e	180.0	36
				$n = 2$				
IIa$_2$	–371.8	1.408	1.257	1.805	–	107.2^d	1.0	–
TS(IIb$_2$)	–212.9	1.350	1.334	2.233	2.057	64.2	14.6	599
IIc$_2$	–396.0	1.269	1.416	–	1.770	112.3^e	91.2	–

^{a} In the solvates $M \cdot 2CHCl_3$, the shortest contacts $Cl \cdots HCCl_3$ between the substrate and two chloroform molecules are as follows: 3.46 and 3.88 Å (**IIa$_2$**), 3.54 and 3.79 Å (**IIb$_2$**), 3.42 and 3.89 Å (**IIc$_2$**); the $H-CCl_3$ bond length does not change to the second decimal place upon solvation.
^{b} Dihedral angle $X^3C^1NC^2$; for transition state **TS1(Id–IIId)**, torsion angle OC^2NC^1.
^{c} The imaginary vibration mode ν_{im} of transition states **TS(Ib–IIIb, Id–IIId)** is shown in Scheme 1.
^{d} Bond angle XC^1N.
^{e} Bond angle XC^2N.
^{f} Refined value [1].

to the calculations (Table 1), the isocyanate form of **III** is thermodynamically unstable; the energy gain upon formation of more stable carbamoyl isomer **IIIc** is quite small (–28 kJ/mol). These data are consistent with those obtained experimentally for a solution and neat liquid [11]. Careful analysis of the reaction mixture showed [11] that the primary product had structure **IIIa**; in methylene chloride at 213 K isomer **IIIa** occurs in equilibrium with **IIIc**; and at 295 K isomer **IIIa** is rapidly converted into **IIIc** with subsequent decomposition during 24 h. By contrast, dichloromethylenecarbamoyl chloride (**IIc**) is stable [2], though its enthalpy of formation is appreciably greater, –157.8 kJ/mol (Table 1).

Sigmatropic transition states **Ib–IIIb** (Scheme 1, path *a*) have similar structures: the angle α at the migrating halogen atom decreases in the range from 60 to 80°, and the C–X bond length in the C^1XC^2 triad increases (Table 1). An appreciable leveling of

bond lengths in the C^1NC^2 triad and decrease of the C^1NC^2 angle to 98° (**Ib**) and 113° (**IIb** and **IIIb**) are observed. The shapes of the transition vectors for transition states **TS(Ib–IIIb)** become similar; they correspond to shift of the X^3 halogen atom along the line connecting the C^1 and C^2 atom. The imaginary eigenfrequency monotonically increases. The electrophilicity of C^1 and C^2 increases (except for C^1 in the fluorine derivative), and the charge on X^3 does not exceed –0.5 a.u. (Table 4). The highest occupied molecular orbital of the transition state is destabilized, while the lowest unoccupied orbital is considerably stabilized; the orbital coefficients of C^1 and C^2 in the latter remain significant. These findings, together with positive charges on C^1 and C^2, indicate an important role of both orbital and charge factors.

From the purely theoretical viewpoint, 1,3(P,C)-chlorine migration in the PNC triad of 2-chloro-2-pentachloroethylimino-1,3,2λ^5-benzodioxaphosphole

Table 2. Activation energies E_a (kJ/mol) for 1,3-halogen shift in trihalomethyl isocyanates **Ia–IIIa** and conformational (+)-*gauche*–(–)-*gauche* transformations of dihalomethylenecarbamoyl halides **Ic–IIIc** and **Ic′–IIIc′** and heats of transformation of halotropic isomers ΔH (kJ/mol) and their solvates with chloroform $M \cdot 2CHCl_3$

Reaction	Mechanism	Ia–Id	IIa–IId		IIIa–IIId
		$n = 0$	$n = 0$	$n = 2$	$n = 0$
Direct $C^1 \rightarrow C^2$	Sigmatropic	288	167	159	164
Reverse $C^2 \rightarrow C^1$	Sigmatropic	279	194	183	194
(+)-*gauche* $\rightarrow$ (–)-*gauche*	Reorientational	10	19	–	21
ΔH^a	Sigmatropic	–39	27	24	30

^{a} Calculated by the formula $\Delta H = \Delta H_f^{298}(\mathbf{a}) - \Delta H_f^{298}(\mathbf{c})$.

$Cl_5C_2NP(Cl)O_2C_6H_4$ is possible to occur by the dissociation–recombination mechanism (path *b*) through formation of loose ion pair as stable intermediate [12]. By contrast, there is no such possibility in isocyanate systems **I–III**. Attempts to localize loose ion pair **IP (Ib–IIIb)** in the halotropic isomerization along path *b* (Scheme 1) were unsuccessful, for it is converted into the energy-rich structure X–X–C(X)NCO (cf. structure $H_2C–Cl–H$ which was obtained by calculations of higher level of complexity [13]).

Transition states **TS1 (Id–IIId)** in the conformational transfromation of (±)-*gauche* isomers of dihalomethylenecarbamoyl halides **Ic–IIIc** (Scheme 1, path *c*) have planar structure with *trans* arrangement of the double C=O and C=N bonds. As compared to alternative mechanisms of conformational transformations of isomers **Ic–IIIc** involving inversion at the nitrogen atom and rotation about the C=N double bond, reorientation of the haloformyl group about the single C–N bond seems to be the lowest-energy process in the series of dihalomethylenecarbamoyl halides **Ic–IIIc**. The calculated energies of activation for conformational transformation increase from 10 to 30 kJ/mol (cf. $\Delta G_{244}^{\neq} = 52.9$ kJ/mol for rotation about the double C=N bond in *N*-alkylidenethioureas [14]) in the series F < Cl < Br (Table 2), in parallel with the size of the halogen atom; the torsion angle OCNC increases in the same series: 59.4 (**Ic**) < 93.1 (**IIc**) < 94.9° (**IIIc**) (Table 1). The low activation barrier for conformational transformation of the (±)-*gauche* isomers is likely to be responsible for polymorphic phase transition in dichloromethylenecarbamoyl chloride (**IIc**) whose structure was recently studied in detail by ^{35}Cl NQR spectroscopy [2].

By analyzing delocalized MOs of sigmatropic transition states **TS (Ib–IIIb)** (Table 4) it is quite difficult to distinguish between 1,3-migration of the halogen atom (its charge remains appreciably lower than unity) and 1,3-migration of halide ion with formation of a contact ion pair and fairly strong dative $X^- \rightarrow C$ bonds (which considerably reduce the charge of halide ion to the same value). In terms of the localized bond formalism (Perkins–Stewart localization [15]) applied to transition states **Ib–IIIb**, the latter process seems to be preferred (Table 5). In fact, sigmatropic transition state **TS (Ib–IIIb, IIb$_2$)** is characterized by three localized low-energy orbitals which include unshared electron pairs of the migrating halide ion. Two of these form dative bonds with carbon atoms of the CNC triad, and the third one is involved in interaction with chloroform molecules in the solvate as shown in Scheme 3.

Table 3. Total energy E_{tot}, enthalpy of formation ΔH_f^{298}, dipole moment μ, stretching vibration frequencies $\nu(C=O)$ and $\nu(C=N)$, and charges q on the chlorine atoms, calculated by the MNDO method, and experimental ^{35}Cl NQR frequencies (77 K, β-phase) [2], dipole moment [9], and IR frequencies [10] of dichloromethylenecarbamoyl chloride (**IIc**)

Parameter	(±)-*gauche*-Isomers **IIc** and **IIc′**	
	calculation	experiment
E_{tot}, a.u.	–67.911	–
ΔH_f^{298}, kJ/mol	–157.870	–
μ, D	1.84	1.75
$\nu(C=O)$, cm^{-1}	1807^a	1780
$\nu(C=N)$, cm^{-1}	1643^a	1660
$q(Cl^1)$, a.u.	–0.010	38.277 MHz
$q(Cl^2)$, a.u.	–0.067	37.091 MHz
$q(Cl^3)$, a.u.	–0.117	33.392 MHz

^{a} The C=O and C=N stretching vibration frequencies were scaled by a factor of 0.84, for MNDO procedure is known to overestimate these quantities.

Table 4. Charges on atoms q_i (a.u.), orbital coefficients c_{ij}, and energies ε_i (eV) of frontier orbitals of trihalomethyl isocyanates **Ia–IIIa**, dihalomethylenecarbamoyl halides **Ic–IIIc**, and transition states **TS(Ib–IIIb)** for 1,3-halogen shift and **TS1(Id–IIId)** for conformational (+)-*gauche* → (–)-*gauche* transformation of dichloromethylenecarbamoyl chlorides **Ic–IIIc** and **Ic′–IIIc′** and their solvates with chloroform $M \cdot 2CHCl_3$[a]

| Atom, parameter	q_i	c_{ij} HOMO	c_{ij} LUMO	q_i	c_{ij} HOMO	c_{ij} LUMO	q_i	c_{ij} HOMO	c_{ij} LUMO	q_i	c_{ij} HOMO	c_{ij} LUMO
	Ia			**TS(Ib)**			**Ic**			**TS1(Id)**		
C^1	0.77	0.00	0.28	0.74	0.02	0.11	0.56	0.06	–0.02	0.56	0.04	–0.04
C^2	0.46	–0.06	0.48	0.48	0.02	–0.10	0.52	0.11	–0.18	0.50	0.05	–0.12
F	–0.22	0.08	–0.09	–0.45	0.01	0.24	–0.16	0.14	0.08	–0.20	–0.04	0.02
ε_i		–12.36	–0.77		–11.44	–2.07		–12.66	–1.40		–12.67	–1.65
	IIa/IIa$_2$			**TS(IIb)/TS(IIb$_2$)**			**IIc/IIc$_2$**			**TS1(IId)**		
C^1	0.42 (0.43)	–0.05	–0.50	0.48 (0.51)	–0.08	0.07	0.28 (0.28)	0.06	0.61	0.31	0.05	0.00
C^2	0.46 (0.46)	0.17	–0.30	0.52 (0.53)	0.07	0.15	0.42 (0.41)	–0.12	–0.25	0.42	–0.12	0.00
Cl	–0.14 (–0.14)	0.20	0.38	–0.41 (–0.46)	0.01	0.25	–0.12 (–0.11)	0.18	0.20	–0.16	–0.24	0.00
ε_i		–12.07 (–12.17)	–1.28 (–1.42)		–11.59 (–11.91)	–2.54 (–2.88)		–12.07 (–12.24)	–1.28 (–1.47)		–11.94	–1.65
	IIIa			**TS(IIIb)**			**IIIc**			**TS1(IIId)**		
C^1	0.20	0.10	–0.41	0.29	–0.08	–0.14	0.14	0.10	–0.51	0.17	0.08	0.00
C^2	0.45	–0.12	–0.25	0.49	–0.08	0.15	0.35	–0.14	0.30	0.35	–0.15	0.00
Br	–0.06	–0.30	–0.39	–0.31	–0.16	–0.40	–0.04	0.30	0.35	–0.08	–0.21	0.00
ε_i		–11.53	–1.10		–10.97	–2.47		–11.56	–1.24		–11.35	–1.52

[a] Parameters of solvated structures are given in parentheses; the corresponding c_{ij} values are not given, for they are similar to those found for nonsolvated analogs.

Table 5. Structure and energy of localized orbitals including unshared electron pairs of the migrating halide ion in transition states **TS(Ib–IIIb)** for halotropic transformation of trihalomethyl isocyanates and their solvates with chloroform $M \cdot 2CHCl_3$[a]

Structure	Number of centers	Orbital composition, % X	C^1	C^2	Energy, eV	Bond type
Ib	1.00	100	–	–	–33.31	UEP1
	1.68	73	–	25	–27.39	$C^2 \leftarrow F$
	1.21	90	8	–	–22.58	$C^1 \leftarrow F$
	1.03	98	–	1	–17.77	UEP4
IIb	1.00 (1.00)	100 (100)	–	–	–24.15 (–24.27)	UEP1
	1.34 (1.39)	86 (84)	–	12 (13)	–14.61 (–15.31)	$C^2 \leftarrow Cl$
	1.37 (1.27)	84 (88)	13 (10)	–	–14.61 (–14.59)	$C^1 \leftarrow Cl$
	1.00 (1.01)	100 (100)	–	–	–13.25 (–13.43)	UEP4
IIIb	1.00	100	–	–	–25.02	UEP1
	1.52	79	–	17	–14.57	$C^2 \leftarrow Br$
	1.35	85	13	–	–13.79	$C^1 \leftarrow Br$
	1.01	100	–	–	–12.42	UEP4

[a] In parentheses are given the values corresponding to solvated structures $M \cdot 2CHCl_3$.

Scheme 3.

TS (**Ib₂–IIIb₂**)
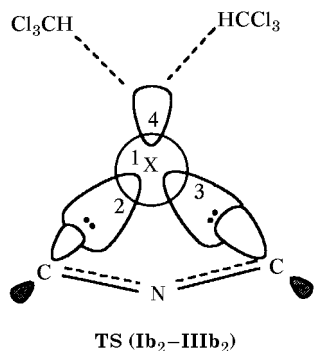
In the three systems the dative $C \leftarrow X^-$ bonds, apart from unshared electron pairs of the halide ion, include a small but a definite contribution of the other atoms attached to carbon. Specific solvation destabilizes the $C^1 \leftarrow Cl^-$ bond (**IIb₂**) while the other, $C^2 \leftarrow Cl^-$ (**IIb₂**), is stabilized. The difference between orbital components of dative bonds increases by 1–7% for $C^1 \leftarrow Cl^-$ bonds and decreases for $C^2 \leftarrow Cl^-$ (**IIb₂**); however, the UEP interacting with chloroform molecules is stabilized. The negative charge on the chloride ion increases (Table 4), leading to reduction of the activation barrier to C,C-chlorotropic isomerization in system **II** (Table 2) and probably in the other related systems. The magnitude of this reduction is minimal (more reasonably, it should be regarded as a tendency), as compared to appreciable shift of the halotropic equilibrium, resulting in formation (see above) of isocyanate or carbamoyl halide structures as isolable products.

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