MOLAR COTTON—MOUTON CONSTANTS OF LIQUID HALOALKANES AND NONADDITIVITY OF THE CONFORMATIONAL ENERGIES OF METHYLATED CHLORO-, BROMO-, AND IODOPROPANES

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In the preceding communication [1] we substantiated and demonstrated the use of magnetic birefringence (the Cotton—Mouton effect) in conformational analysis in the example case of liquid polyhaloalkanes. In the present work we obtained molar Cotton—Mouton constants and analyzed the conformations of monohaloalkanes with the general formula $C(R^1R^2R^3)CR^4R^5Hal$, where $R^1 = CH_3$, $R^2 = R^3 = R^4 = R^5 = H$, Hal = Cl (Ia), Br (Ib), I (Ic); $R^2 = R^3 = CH_3$, $R^1 = R^4 = R^5 = H$, Hal = Cl (IIa), Br (IIb), I (IIc); $R^2 = R^3 = H$, $R^1 = R^4 = R^5 = CH_3$, Hal = Cl (IIIa), Br (IIIb), I (IIIc); $R^1 = H$, $R^2 = R^3 = R^4 = R^5 = CH_3$, Hal = Cl (IVa), Br (IVb), I (IVc). More than half of the compounds just listed were previously investigated by the methods of vibrational spectroscopy in the liquid phase: Ia and b [2], IIa and b [3], IIc [4], and IIIa-c [5]. The unequivocal nature of the interpretation of the experimental material in [5] was questioned in [6]. However, a conformational analysis of the entire set of experimental data was not carried out, and the influence of the methyl groups introduced into propyl halides on the rotational isomerism was not considered, although the nonadditivity of the $CH_3...Cl$ conformation interactions upon the transition from Ia to IIa was pointed out even in the monographic literature [7, p. 26]. All the compounds investigated may be represented in the form of energetically inequivalent rotamers, one of high (C_s) symmetry and another of low (C_1) symmetry (Fig. 1). The symmetric bisector conformer (C_s) will be called trans, and the asymmetric conformer will be called gauche. It is obvious that the probability of the formation of the gauche form is twice as high as the probability of the formation of the trans form.

The molar Cotton—Mouton constants ($_mC$) of the conformers were calculated from the relation

$$_mC = (2\pi N/45kT)\,[\Sigma (b_{ii} - b_{jj})(k_{ii} - k_{jj}) + 6b_{ij}k_{ij}] \tag{1}$$

where b_i and k_i are the components of the molecular tensors of the optical polarizability and the magnetic susceptibility. The geometry of the rotational isomers was assumed to be standard: the bond angles are tetrahedral, the torsion angles have a 120° step, and deviations from this value within 10° in the gauche forms do not noticeably alter the calculated Cotton—Mouton constants.

In the calculations we used the optical (b_i, $\mathring{A}^3$) and magnetic ($k_i \cdot 10^{29}$) anisotropic parameters of C—Hal bonds found from the model compounds with consideration of the local environment of the carbon atoms [8]: for I and II from C_2H_5Hal, for a C—Cl bond $K_L = -3.73$, $k_T = -2.63$, $b_L = 3.59$, $b_L = 3.59$, $b_T = 1.99$; for a C—Br bond $k_L = -5.56$, $k_T = -4.17$, $b_L = 5.3$, $b_T = 2.7$; for a C—I bond, $k_L = -8.12$, $K_T = -6.64$, $b_T = 7.65$, $b_L = 4.40$; for III and IV from $t\text{-}C_4H_9Hal$, for a C—Cl bond $k_L = -4.1$, $k_T = -2.43$, $b_L = 3.94$, $b_T = 1.81$, for a C—Br bond $k_L = -5.74$, $k_T = -4.0$, $b_L = 5.98$, $b_T = 2.58$, for a C—I bond: $k_L = -8.37$, $k_T = -6.36$, $b_L = 3.92$. For a C—C bond we used the following parameters: $k_L = -0.48$, $k_T = 0$, $b_L = 0.98$, $b_T = 0.27$ [8]. The C—H bonds were assumed to be isotropic in the framework of the additive scheme adopted [8]. The Cotton—Mouton constants are additive in mixtures. The mole fractions of the trans (n_t) and gauche conformers (n_g) participating in the equilibrium and the differences between their enthalpies ($\Delta H = H_{gauche} - H_{trans}$) were evaluated from relations (2a), (2b), and (3). The accuracy of the calculation of n_i was determined by the error in the experimental Cotton—Mouton constants

$$_mC_t n_t + 2\,_mC_g n_g = {}_mC_{exp} \tag{2a}$$

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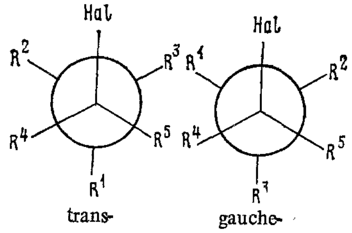

Fig. 1. Possible conformations of the halopropanes investigated.

TABLE 1. Cotton–Mouton Constants ($_mC\cdot10^{15}$), Enthalpy Differences between Rotamers (ΔH, kcal/mole), and Mole Fractions of the trans Forms (n_t) of the Compounds Studied

Compound	$_m\bar{C}_{exp}$	$_m\bar{C}_{cal}$		n_t	ΔH_{exp}	ΔH_{lit}	ΔH_{ad}
		trans	gauche				
(Ia)	0,075	0,135	0,049	0,30±0,08	–0,1	–0,30 [2]	–
(Ib)	0,136	0,231	0,106	0,24±0,06	–0,3	–0,44 [2]	–
(Ic)	0,184	0,317	0,160	0,16±0,04	–0,6	–	–
(IIa)	0,119	0,019	0,140	0,18±0,07	–0,5	–0,30 [3]	0,1
(IIb)	0,170	0,065	0,201	0,22±0,06	–0,3	–0,26 [3]	0,3
(IIc)	0,239	0,114	0,279	0,24±0,05	–0,3	–0,36 [4]	0,6
(IIIa)	0,082	0,145	0,063	0,23±0,10	–0,3	–0,36 [5]	–0,9
(IIIb)	0,160	0,240	0,129	0,25±0,07	–0,2	–0,38 [5]	–1,1
(IIIc)	0,230	0,357	0,184	0,26±0,05	–0,2	–0,69 [5]	–1,5
(IVa)	0,100	0,133	0,073	0,45±0,16	0,3	–	0,9
(IVb)	0,149	0,224	0,100	0,40±0,08	0,2	–	1,1
(IVc)	0,222	0,322	0,162	0,36±0,06	0,1	–	1,4

$$n_t + 2n_g = 1 \tag{2b}$$

$$n_g/n_t = 2\exp(\Delta H/RT) \tag{3}$$

Table 1 presents the molar Cotton–Mouton constants of compounds I-IV, which were obtained experimentally and calculated for the trans and gauche conformers, the mole fractions of the trans forms, and the values of ΔH_{exp} found in our work, as well as the literature values (ΔH_{lit}) of the enthalpy differences between the rotamers.

As can be seen from Table 1, the enthalpy differences between the gauche and trans conformers which we obtained and which were previously determined by the methods of vibrational spectroscopy are in good agreement with one another, confirming the conclusion drawn in [1] regarding the additivity and transferrability of the anisotropies of the diamagnetic susceptibilities.

Proceeding to an analysis of the conformations of the compounds studied, we note that in the case of I-III, the equilibrium is displaced in favor of the asymmetric form and that ΔH_{exp} is positive only for IV. The nature of the halogen has practically no influence on the ratio between the gauche and trans rotamers in each isologous group of compounds, with the exception of the propane series (I), in which the percentage of the sterically hindered gauche form increases with increasing size of the halogen. The influence of gem-dimethyl groups introduced into propyl halides on the composition of the equilibrium mixture is more ambiguous. It was, therefore, of interest to calculate the enthalpy difference between the rotamers under the condition of complete additivity of the CH_3...Hal and CH_3...CH_3 conformational interactions on the basis of the data for Ia-c and butane (ΔH = 0.8 kcal/mole [9]). The values obtained for ΔH_{ad} are also presented in Table 1. A comparison of these values with ΔH_{exp} (or ΔH_{lit}) shows that the agreement between them is extremely unsatisfactory. The differences exceed 1 kcal/mole in a number of cases, and they do not agree even in sign in the case of II. A similar situation is also observed in the series consisting of 1,2-di-, 1,1,2-tri-, and 1,1,2,2-tetrachloroethanes [9], and the experiment for the corresponding methyl derivatives'is unequivocal. The early spectroscopic investigations pointed out that while ΔH = 0.8 kcal/mole for butane, ΔH = ∞ or 0 for 2-methylbutane, and ΔH = 0 for 2,3-dimethylbutane [9]. However, in contrast to these findings, the results of the acoustical

TABLE 2. Energies of $CH_3...Hal$ Conformational Interactions (kcal/mole) in the Compounds Studied

Hal	Compound			
	(I)	(II)	(III)	(IV)
Cl	−0,1	0,5	0,5	0,5
Br	−0,3	0,3	0,6	0,6
I	−0,6	0,3	0,6	0,7

measurements give practically identical values for ΔH: 0.9 kcal/mole for 2-methylbutane and 1.0 kcal/mole for the 2,3-dimethyl derivative [10], i.e., the additivity of the $CH_3...CH_3$ interaction is maintained. In the framework of this theory we calculated the values of the $CH_3...Hal$ conformational energies in I-IV (Table 2). It is seen that the energy of the $CH_3...Hal$ conformational interaction changes sign upon the transition from I to more sterically stressed molecules.

The disparity between the observed and expected spatial structure of the monohaloalkanes was first pointed out in [11], in which not only the composition of the equilibrium mixture in the gaseous phase (80% gauche isomer) was established as a result of an electron diffraction investigation of IIa, but it was also found that the dihedral angle between the $C-CH_3$ and the C–Cl bond in the asymmetric form is equal to 66°. This led Pauli, Momany, and Bonham [11] to the ideal that the realization of the most favorable interaction between the methyl group and the chlorine atom in the gauche form requires a slight increase in the normal angle, which is equal to 60°. In the trans conformation, of course, the $CH_3...Cl$ dihedral angle cannot increase on the one hand without a simultaneous decrease on the other [7]. The same explanation was given in support of the nonadditivity of ΔH for the conformations of chloroethanes in [9], although it should be noted that in the cases of 1,2-dibromoethane and 1,1,2-tribromoethane, the values of ΔH for the rotamers in the gaseous and liquid phases are close to one another.

The laws governing the deviations of the calculated conformational energies from the experimental values as a function of the local environment of the C–Hal bonds can be established only after the nature of the forces responsible for the stabilization of the gauche structures in I will be understood. The attempts to ascribe the attractive $CH_3...Hal$ effect to electrostatic interactions between the $C-CH_3$ and C–Hal groups [9] cannot account for the entire set of experimental data. The quantitative calculation of ΔH for Ia and b carried out in the framework of the classical model (the van der Waals and electrostatic forces were considered) describes the conformational composition only of propyl chloride, and the theory predicts stabilization of the trans form for Ib [12]. The differences are so significant that even an hypothesis concerning the possible erroneousness of the experiment for Ib was advanced in [7]. Our results support the data from vibrational spectroscopy for Ib. We note that even more striking disparity between the calculation and the experiment should be observed for Ic. In fact, the role of the attractive dipole–dipole and dipole–induction interactions should decrease along the series consisting of Ia, Ib, and Ic, since not only the distance between the interaction centers increases, but also the dipole moment (m) of the C–Hal bonds decreases: m(C–Cl) > m(C–Br) > m(C–I) [13].

Besides the steric and electrostatic interactions, which are, by the way, additive, it is necessary to take into account the donor–acceptor orbital effects. In light of the theory of frontier orbitals [14], the strength of the interactions is determined: 1) by the width of the energy gap between the highest occupied molecular orbital (HOMO) of the donor fragment and the lowest unoccupied molecular orbital (LUMO) of the acceptor fragment; 2) by the values of the interaction matrix elements, which are proportional to the overlap integrals; 3) by the symmetry of the orbitals.

In the compounds studied here we can single out the interactions with the participation of group orbitals of the CH_2 and $C(CH_3)_2$ fragments of the $\pi(CH_2)$ or $\pi[C(CH_3)_2]$– $\sigma^*(C-Hal)$ types. Despite the fact that the $\pi[C(CH_3)_2]$ orbital has a somewhat higher energy than the $\pi(CH_2)$ orbital, it is more delocalized (this lowers the coefficients of the matrix elements), and, therefore, in the final analysis the $\pi C(CH_3)_2$– σ^*(C—Hal) and $\pi(CH_2)$—σ^*C—Hal interactions should be energetically similar. Interactions of the π type are absent in the symmetric "bisector" conformation due to the zero values for the overlap integrals, but they should exist in the asymmetric gauche form, since they are maximal when φ = 90° (we have taken the trans form as a reference point). Thus, consideration of the $\pi(CH_2)$—σ^*C—Hal interaction, which is attractive in nature, makes it possible to explain not only the conformational composition of the individual propyl halides, but also the increase in the percentage of the gauche structure upon the transition from Ia to Ic, since the level of the LUMO of the C—Hal bonds and thus the width of the energy gap decrease along the series Cl > Br > I [14, pp. 12, 154].

It must be noted that an alternative model, which explains the preferability of the gauche form in propyl fluoride and is based on the postulation of the existence of a hydrogen bond between the fluorine atom and a hydrogen atom of the methyl group, was proposed in [14, pp. 59-61). Such an H bond, which appears as a result of the overlapping of the $2p_x$ orbital of the lone pair of the fluorine atom and the s orbital of the C—H bond in the methyl group in space, should stabilize the eclipsed syn form and be absent in the anti conformation. However, the opposing ethane-like torsion barrier results in a gauche structure, and the F...CH_3 steric repulsion also promotes the appearance of the trans rotamer. This conception, like the classical theory, is not capable of describing the conformational structure of compounds II-IV, although it is capable of predicting an increase in the percentage of the gauche isomers along the series Ia—Ib—Ic.

A contribution from the πCR_2—σ^*(CHal) orbital interactions to the conformational energies which is comparable to the classical is indicated by the data from the microwave investigations of propyl fluoride in [15]. The barrier to internal rotation around the C—C bond found for it was expanded in a Fourier series (φ= 0 in the trans form):

$$V = {}^1/_2[V_1\,(1 - \cos\varphi) + V_2(1 - \cos 2\varphi) + V_3\,(1 - \cos 3\varphi) + \ldots] \qquad (4)$$

In accordance the miltiplicity of the barrier, the V_i may be identified with interactions of concrete types. For example, V_1 should be defined as the energy of the steric and electrostatic interactions, V_3 is the ethane-like torsional barrier, and V_2, which reaches a maximum when φ = 90°, may be assigned a hyperconjugation character, such as πCH_2—σ^*C-Cl. According to [15], V_1 = 3.92, V_2 = −3.05, and V_3 = 6.48 kcal/mole, and the remaining terms are small. As we can see, the hyperconjugation contribution is, in fact, attractive and comparable in absolute value to the overall effect of the van der Waals and electrostatic interactions of the C—CH_3 group and the C—F bond.

The observed disparity between ΔH_{exp} and ΔH_{ad} (see Table 1) can be explained on the basis of a molecular-orbital analysis. The CH_3...Hal conformational energies lose their additive character, since they become dependent on the symmetry of the interacting fragments, i.e., on the symmetry of the conformation as a whole (the stabilization of the gauche form). However, a concrete discussion of each isologous series is impossible without utilizing the conception of the nonideality of the torsion angles [7, 9]. The increase in the dihedral angle between C—CH_3 and C—Hal in compounds I to 70° (φ= 110°) [16, 17] is favorable from the point of view of both the steric and π-orbital interactions. In series II the effects indicated act in opposite directions. Under the action of the steric forces in IIa, the angle φ increases to 126° [11]; therefore, the angle between the CH_2 orbital and the C—Cl bond decreases to 54°, thereby weakening the strength of the πCH_2—σ^*_{CCl} attractive interaction. The mutual compensation of the two effects eliminates the role of the nature of the halogen: the values of ΔH_{exp} for IIa-c are close to one another.

The conformational analysis of III and IV is more difficult, since there are no data on the geometry of the molecules from diffraction or microwave methods. Being sterically overstressed, the molecules of compounds III and IV can hardly undergo distortion of the torsion angles, i.e., the $\pi C(CH_3)_2$—σ^*C-Hal effect should be somewhat smaller than in I and should be dependent to a smaller degree on the nature of the halogen.

EXPERIMENTAL

The compounds studied were obtained by reacting the corresponding alcohols with halogenating agents: the chlorides, with PCl_5; the bromides, with PBr_3; the iodides, with KI, H_3PO_4, and P_2O_5. The products were purified by distillation until the constants coincides with the literature values [18].

TABLE 3. Physical Characteristics of I-IV in the Liquid State

Compound	n_λ^{20}	d_{20}^4	$-C\cdot 10^{12}$	$-{}_mC\cdot 10^{15}$
(Ia)	1,3834	0,891	0,025	0,075±0,007
(Ib)	1,4300	1,353	0,045	0,136±0,007
(Ic)	1,5009	1,743	0,060	0,184±0,007
(IIa)	1,4107	0,8829	0,036	0,119±0,008
(IIb)	1,4346	1,272	0,046	0,170±0,008
(IIc)	1,4714	1,605	0,065	0,239±0,009
(IIIa)	1,4126	0,871	0,020	0,082±0,009
(IIIb)	1,4393	1,2159	0,040	0,160±0,009
(IIIc)	1,4916	1,500	0,060	0,230±0,009
(IVa)	1,4109	0,8784	0,022	0,100±0,010
(IVb)	1,4517	1,1772	0,033	0,149±0,010
(IVc)	1,4907	1,4455	0,048	0,222±0,010

The birefringence in a magnetic field was measured in analogy to [8] at λ = 632.8 nm and 20°C. The Cotton–Mouton constants were calculated with the use of the equation

$$ {}_mC = \frac{6\lambda n_\lambda C}{(n_\lambda^2+2)^2 d} \qquad (5)$$

where n is the index of refraction, d is the density, and C is the Cotton–Mouton constant of the individual liquids (Table 3).

CONCLUSIONS

1. The molar Cotton–Mouton constants of chloro-, bromo-, and iodopropanes and their methylated derivatives have been determined by a method involving measurement of the magnetic birefringence, and the conformational composition of the molecules investigated has been established.

2. The nonadditivity of the potential interactions of vicinal C–CH_3 and C–Hal substituents has been analyzed. The dominant role of the orbital effects in the stabilization of asymmetric gauche conformations of the molecules of the halopropane series has been revealed.

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