A Calculation of the Rotamer Energies of Halogenoethanes

By R. J. ABRAHAM* and K. PARRY

(*Department of Organic Chemistry, The University, Liverpool* L69 3BX)

Summary A calculation is given, based on a classical model of nonbonded interactions, which successfully predicts the vapour-phase rotamer energy differences of 1,2-dihalogeno, 1,1,2-trihalogeno-, and 1,1,2,2-tetrahalogeno-ethanes.

ONE of the most long-standing problems in rotational isomerism is the rotamer energy differences in 1,2-dihalogeno-, 1,1,2-trihalogeno- and 1,1,2,2-tetrahalogeno-ethanes (I, II, III; X = Cl, Br).[1]

These well documented vapour-phase energy differences ($E_g - E_t$) are for (I) 1·20 and 1·66; for (II) *ca.* 2·6 and >1·5; and for (III) 0·0 and 0·0 kcal./mole for X = Cl and Br, respectively.[1,2] On any additive scheme of the interactions present, the energy differences in (I), (II), and (III) would all be equal.[1] Clearly this is far from the case. The suggestion has been made that these energy differences are due to nontetrahedral X–C–X angles,[3] but previous attempts at quantitative calculations did not reproduce even the general trends of the observed data.[3,4]

Since this early work, more accurate data on intramolecular forces and on molecular geometries has lead to an increasing interest in such calculations, but although a number of successful schemes for hydrocarbons have been put forward,[5] none has yet been reported for the more complex halogeno-compounds. We report the results of a model we have devised which successfully predicts the observed energies in (I), (II), and (III) and a variety of other halogenated compounds.

Calculated and observed rotational energies[a] *in halogenoethanes*

				Calculated contributions				Energy differences[1,2]	
					X···X	H···X			
Molecule			ω	Steric	dipolar	dipolar	torsional	Calc.	Obs.
(I)	X = Cl	g	70	1·54	2·32	−3·25	0·20	1·50	1·20
		t		1·05	1·81	−3·57	0·00		
	X = Br	g	70	0·84	1·84	−2·87	0·20	1·57	1·66
		t		0·15	1·42	−3·15	0·00		
(II)	X = Cl	g		2·89	4·79	−3·91	0·01	1·93	2·3, 3·0
		t	68	1·90	4·15	−4·33	0·13		
	X = Br	g		2·01	3·82	−3·45	0·01	2·11	>1·5, 2·0[9]
		t	70	0·65	3·27	−3·82	0·20		
(III)	X = Cl	g	66	3·64	8·96	−3·24	0·07	0·29	0·0 (±0·2)
		t		4·16	8·52	−3·55	0·00		
	X = Br	g	66	2·47	7·12	−2·86	0·07	0·59	0·00
		t		2·58	6·76	−3·13	0·00		

[a] All energies are in kcal./mole.

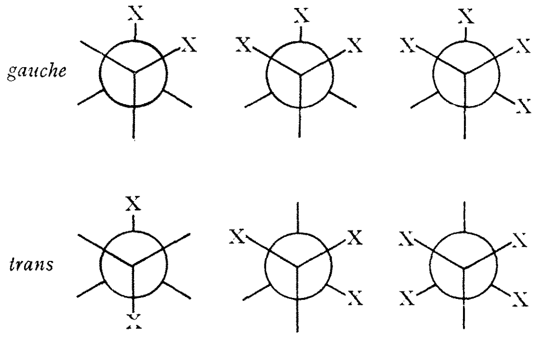
On this model, the total energy of any rotamer is given by the torsional strain plus the sum of the nonbonded interactions, which must include both the steric and dipolar interactions in these molecules.

This gives, for any given dihedral angle ω

$$U(\omega) = (V_0/2)(1 + \cos 3\omega) + \sum_{ij}[a_{ij}\exp(-b_{ij}r_{ij}) - (c_{ij}/r_{ij}^6) + (d_{ij}/r_{ij})]$$

where the coefficients *a*, *b*, *c*, and *d* are characteristic of the interacting atoms.

This treatment is well known.[6] The novel features of our model are: (i) The coefficients a_{ij} are obtained as those values which make the steric term zero at the van der Waals distance, *not* the values which minimise the steric term at this distance. (ii) The coefficients d_{ij} are related to the charge on X *via* the dipole moment of the C–X bond, *not* the electronegativity of X. The charges are taken to be the same in both CH_2X and CHX_2 groups, and the dipole moments are related to those of the ethyl halides.[7,8] (iii) The attractive electrostatic interaction between H and X is included. Also a consistent scheme of bond lengths and angles is maintained, *e.g.*, all C–C–X and X–C–X angles are taken as 111·0° and all H–C–H and C–C–H angles are tetrahedral. This then defines the H–C–X angles in any molecule. Full details of the model will be given elsewhere.



(I) (II) (III)

The results using this model for (I), (II), and (III) are shown in the Table. The dihedral angles of the unsymmetric isomers were varied and the Table gives the values of ω and E corresponding to the minimum energy.

The Table shows that the observed energy differences are well reproduced. In most cases the calculated values are within the experimental error of the observed values.

In particular the "anomalous" results for the tetrahalogeno-compounds are now explained. The model demonstrates that the observed energy difference in (I) is almost equally divided into steric and polar effects (*ca.* 0·5 kcal./mole for each). Whereas the electrostatic term in (I), (II), and (III) is virtually constant (*ca.* 0·5 kcal./mole for XX) the steric term changes considerably, increasing in (II) (1·0 X = Cl; 1·4 X = Br) and reversing sign in (III) (−0·5 X = Cl; −0·1 X = Br). This is undoubtedly due to the nontetrahedral X–C–X angles, thus giving quantitative confirmation to Miyagawa's original suggestion.[3]

(*Received, June* 16*th*, 1969; *Com.* 855.)

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[1] N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 288.

[2] J. P. Lowe, *Progr. Phys. Org. Chem.*, 1969, **6**, 1.

[3] I. Miyagawa, *J. Chem. Soc. Japan*, 1954, **75**, 1162 and 1173.

[4] M. M. Kreevoy and E. A. Mason, *J. Amer. Chem. Soc.*, 1957, **79**, 4851.

[5] J. E. Williams, P. J. Stang, and P. von R. Schleyer, *Ann. Rev. Phys. Chem.*, 1968, **19**, 531.

[6] R. A. Scott and H. A. Sheraga, *J. Chem. Phys.*, 1965, **42**, 2209.

[7] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[8] A. L. McLellan, "Table of Experimental Dipole Moments," Freeman, San Francisco, 1963.

[9] F. Heatley and G. Allen, *Mol. Phys.*, 1969, **16**, 77.