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GEOMETRY RELAXATION IN ACYCLICS, MOLECULAR MECHANICS CALCULATIONS OF HALOPROPANES.

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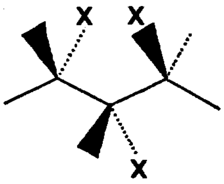
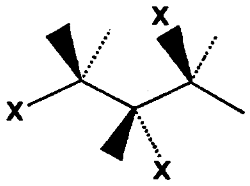
The importance of geometry optimisation for both quantum mechanical[1] and molecular mechanics[2] calculations of molecular energies is only now becoming generally acknowledged. This has led to the use of standardised but non-tetrahedral bond angles in calculations of haloethanes[3] and the development of force-field techniques in which both the bending force constants and the unstrained angles are parameterised for cyclic hydrocarbons[4].

We wish to note here further important consequences of geometry optimisation in simple halo-propanes in which considerable distortion of the C.C.C. angle occurs which is very dependent on the rotamer considered. Optimisation of this angle alone produces calculated rotamer energies and geometries in excellent agreement with observed.

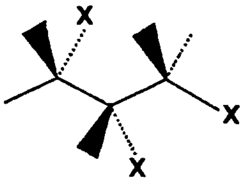
We show (figure and table) the six possible rotamers for 1,2,3 trihalopropanes (X=Cl,Br). Of these, two (E and F) both have 1,3 eclipsed X..X interactions and as predicted[5] very high energies. They may be disregarded. The four populated rotamers (A..D) provide a severe test of the molecular mechanics treatment. Use of the programme MODELS 2[6] together with a standardised geometry gives calculated energies (5th column, table) in poor agreement with observation, and this is perhaps not surprising when one considers the experimental geometries. Introduction of a single angle bending term $k_\theta.(\theta-\theta_0)^2$ for the C.C.C. angle with k equal 0.02 kcals $mole^{-1}$ $degrees^{-2}$ and θ_0 112.5° leads to rotamer energies in excellent agreement with the observed data[8,9] (Columns 6 and 7, table). Furthermore, the calculated C.C.C. angles for the most populated rotamers (see table) are within experimental error of the



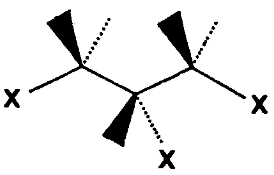
A(GGga)



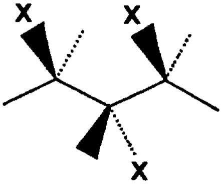
B(AGga)



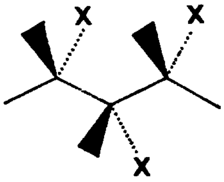
C(GAgg)



D(AAgg)



E(GGaa)



F(GGgg)

Table. Calculated and Observed Rotamer Energies in 1,2,3-trichloro (1) and tribromo (2) propanes.

Rotamer[d]	Minimum Energy Geometry			Relative Energy (kcals/mole)		
	$C_1C_2C_3$	W_{12}[c]	W_{23}[c]	Calculated		observed
				a)	b)	
1A (GGga)	116.5	-56	58	0.0	0.0	0.0
1B (AGga)	113.5	168	66	0.2	0.8	0.7
1C (GAgg)	114.5	-56	164	0.8	1.5	1.8
1D (AAgg)	112.5	168	168	1.4	2.1	>2
2A (GGga)	117.5	-56	58	0.0	0.0	0.0
2B (AGga)	114.5	164	66	0.0	1.2	1.5
2C (GAgg)	113.5	-54	162	0.6	1.6	1.5
2D (AAgg)	112.5	164	166	1.2	2.3	-

a) Standardised geometry $C_1C_2C_3$ equals 112.5°

b) Minimum Energy geometry $C_1C_2C_3$ as tabulated

c) $W_{12} = XC_1C_2C_3$ dihedral angle

$W_{23} = C_1C_2C_3X$ " "

d) The nomenclature given is that of reference 8.

observed values (115.2 (±2.6°) and 117.4 (±1.4°) for X=Cl, Br respectively).[8,9]

Of particular note are the large differences in the relative energies of the different rotamers due to changing the C.C.C. angle, which can be rationalised as follows. In rotamer A the repulsive eclipsed 1,3 H..X interactions may be relieved by opening the C.C.C. angle without any compensating interaction, thus in this rotamer the equilibrium C.C.C. angle is very large. However, in rotamers B and C and particularly D enlarging the C.C.C. angles introduces additional repulsive 1,2 X..X interactions thus the equilibrium value is only ca. 114° in B and C and remains at the standard value (112.5°) in D. Thus rotamer A gains in relative energy ca. 0.6 kcals/mole in the trichloro and ca. 1 kcal/mole in the tribromo compound from the molecular distortion.

These results serve to show that even in simple "unstrained" molecules such as 1,2,3 trihalopropanes any calculation which does not minimise at least the central C.C.C. angle for each rotamer may be seriously in error. Finally, it is pertinent to note that the observed values of the remaining bond angles do not differ significantly from the standardised values used in the calculations (e.g. all C.C.X. angles 111°), which further supports this treatment.

We thank Dr. R. Stolevik for communicating his results prior to publication which originally inspired this treatment.

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