Relative Stabilities of Dihaloethylenes and Dihaloethanes. A Theoretical Study [1]

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CNDO/2-type calculations have been carried out on 1,1-dihaloethylenes, 1,2-dihaloethylenes and 1,2-dihaloethanes treating all four halogens. The energy was minimized with respect to the coordinates by use of the FORCE method. The results are consistent with experimental isomer and conformer stabilities and it is shown, by means of a cis-trans correlation diagram and calculated intramolecular atomic interaction energies, that previous explanations of the apparent halogen-halogen attraction are inconsistent with our results.

I. Introduction

Two extremely useful and generally accepted "laws" of chemistry, i) steric hindrance, and ii) coulombic repulsions between atoms of like charges, are apparently contradicted by the experimental facts that a) cis-1,2-difluoroethylene is more stable [2] than the trans isomer, this trend diminishing [3] (and apparently reversing) down the periodic table; and b) the gauche conformer of 1,2-difluoroethane is as stable [4] as the anti-conformer. These results, when considered along with the facts that a) the symmetric stretching frequency in OF_2 (in which the F–F distance changes) is greater [5] than its antisymmetric frequency (in which the F–F distance is constant), in contract to the normal YX_2 bent molecule (for example, H_2O); and b) the XCX bond angle in 1,1-difluoroethylene is smaller [6] than the HCH angle in ethylene [7] suggest an attractive interaction between halogen atoms which are not bonded to one another, i.e., a "non-bonded interaction" (really attraction).

Various explanations have been given for these phenomena, including 1) increased C–F π bonding [5, 8] in the cis-isomer relative to the trans-isomer due to the high electronegativity of the fluorine. This is considered to be of less importance as one progesses down the halogen family. This argument was presented on the context of the valence bond theory as increased stability due to a structure of the type "no bond-double bond" which is only effective for the cis-isomer, and within the context of molecular orbital theory in terms of calculations [9] which show the first excited state of 1,3-butadiene to be preferentially in the cis-configuration, the argument being that 1,3-butadiene and 1,2-dihaloethylene have the same π molecular orbitals, the difference being that 1,2-dihaloethylene has two extra π electrons, thus filling the third molecular orbital in its ground state; 2) increased stability [10] for cis isomers relative to the corresponding trans isomers because: (a) the dihaloethylene fill both a π and a π^* molecular orbital (considered as a pseudo 1,3-butadiene), (b) the trans isomers fill both of these molecular orbitals "fuller", i.e., these are delocalized orbitals and trans geometry is more favorable to electron delocalization because "electrons don't like to go around corners", and (c) the π^* molecular orbital is more destabilizing than the π molecular orbital is stabilizing; and 3) attraction between n-orbital electrons [11] on the two fluorines in 1,1-difluoroethylene through interaction between selected intramolecular localized molecular orbitals.

Explanations **1** and **2** are predicated upon the difference in the π systems of the cis and trans isomers being responsible for their relative stabilities. These arguments assume, without the slightest basis, that the σ systems are equivalent in energy. Explanation **3** has been refuted [12] by Kollman who showed that the effect is calculated to hold even in "pseudo-ethylenes" without n electrons. Kollman returned to the valence bond explanation, originally proposed by Mellish and Linnett [13], that the large difference in electronegativity in the

F–C bond causes a rehybridization of the carbon hybrid orbitals. Thus the sp^2 hybrid orbital on the carbon involved in the C–F bond increases in p-character, i.e., goes to $s^i p^j$ ($i < 1$, $j > 2$), with a corresponding increase in the s-character of the C–C bond. This would be expected to decrease the C–C distance, in comparison with ethylene, which is found [6, 7] experimentally. (The molecular orbital theory equivalent of this idea has been applied [14] to other systems.) However, Kollman's discussion was aimed at explaning the decreased bond angles FCF in 1,1-difluoroethylene and FCC in cis-1,2-difluoroethylene, relative to the corresponding HCH and HCC angles in ethylene, therefore it does not directly answer the question of relative stabilities of cis and trans isomers.

CNDO/2 results of CHF=CHF and CHCl=CHCl have been reported [15] previously. These calculations predict the cis isomer to be more stable than the trans isomer in both cases, however incorrectly predict the energy difference to be greater in the case of 1,2-dichloroethylene. This is undoubtedly due to the fact that CNDO/2 tends to overemphasize the importance of d orbitals, as the authors [15] pointed out. Ab initio results have also been reported for 1,1-difluoroethylene [12] and both cis and trans 1,2-difluoroethylene [12, 16, 17]. Epiotis et al. [16] found that the STO-3G basis set calculated the cis and trans isomers to have the same energy and the 4-31G set calculated the trans isomer to be more stable. Kollman [12] calculated the cis form to be more stable using both an STO-3G and "Double zeta" basis set. The apparent contradiction in their STO-3G results is probably due to different geometry optimization criteria, which would lead to different final coordinates. Binkley and Pople [17] used several basis sets and found that the relative stabilities were a function of the basis set chosen. However, they concluded that neither the F···F interaction nor correlation effects can fully explain the relative stabilities.

This article presents the results of CNDO/2-type calculations on the cis and trans isomers of 1,2-$C_2H_2X_2$ (X being halogen), the 1,1-$C_2H_2X_2$, and the gauche and anti conformers of 1,2-$C_2H_4X_2$, considering all four halogens as second row atoms. Relative isomer and conformer stabilities, both calculated and experimental, are compared and based upon a) a general cis-trans correlation diagram, and b) calculated intramolecular atomic interaction energies, we argue that explanations **1** and **2** above are not acceptable.

II. Method

All calculations ware done on the Burroughs B-6700 at the Universidade Federal do Rio de Janeiro. The method of calculation was basically CNDO/2, with the orbital exponent modified for carbon [18] and all of the halogen parameters modified [19]. It is important to point out that in no case were d orbitals considered. The FORCE method [20] was employed to minimize the energy with respect to the atomic coordinates. Initial coordinates were taken as standard geometries [21] with the exception of the carbon-halogen bond lengths [22]. The standard SCF calculation was then made, the force matrix calculated, and each atom then moved in the direction of the force a distance given by $\Delta X_A = -0.017 F_{X,A}$, ($\Delta X =$ displacement in Å, $F =$ force in millidynes), the only limitation being that the maximum displacement allowed in any given direction was 0.01 Å. Self-consistent coordinates were considered to obtain when both no single force element was greater than 0.10 millidynes and the average of the absolute values of the forces was no greater than 0.05 millidynes.

The cis trans correlation diagram was constructed in the following way: the two point groups, C_{2v}(cis) and C_{2h}(trans) are broken down into their four representations, in both cases two of which can be associated with π orbitals, the other two being associated with σ orbitals. Of the representations giving σ orbitals, the totally symmetric representations in each group are chosen to correlate with one another. Of the two π representations in each group, correlation is determined by parity, i.e., either an odd or even number of nodes. Thus our equivalent representations are

C_{2v}(cis)		C_{2h}(trans)
$a_1(\sigma)$	—	$a_g(\sigma)$
$b_2(\sigma)$	—	$b_u(\sigma)$
$a_2(\pi)$	—	$b_g(\pi)$
$b_1(\pi)$	—	$a_u(\pi)$.

These orbitals are connected such as to avoid crossings between orbitals of equivalent representations. (However, this restriction is not necessary for different point groups, and our transformations are not uniquely correct.)

The intramolecular atomic interaction energy matrix was calculated from Pople's equations [23] for total energy, the diagonal elements being

$$E_{\mathrm{A}} = \sum_{\mu}^{\mathrm{A}} P_{\mu\mu} U_{\mu\mu} + \tfrac{1}{2} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{A}} (P_{\mu\mu} P_{\nu\nu} - \tfrac{1}{2} P_{\mu\nu}^{2}) \gamma_{\mathrm{AA}} \quad (1)$$

and the off-diagonal elements being

$$E_{\mathrm{AB}} = \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} (2 P_{\mu\nu} H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}^{2} \gamma_{\mathrm{AB}}) + (Z_{\mathrm{A}} Z_{\mathrm{B}}/R_{\mathrm{AB}} - P_{\mathrm{AA}} Z_{\mathrm{B}} \gamma_{\mathrm{AB}} - P_{\mathrm{BB}} Z_{\mathrm{A}} \gamma_{\mathrm{AB}} + P_{\mathrm{AA}} P_{\mathrm{BB}} \gamma_{\mathrm{AB}}) \quad (2)$$

following Pople's notation.

III. Results

Tables 1 and 2 show our calculated results and some experimental data for the dipole moments, geometries (bond distances and angles), and relative energies for the various dihaloethylenes and the four 1,2-dihaloethanes considered. Table 3 shows the π overlap populations [24] for the C–X and C–C bonds as well as for the X···X interaction and the entire π system, and the intramolecular atomic interaction energies for the 1,2-dihaloethylenes. Figure 1 is the correlation diagram for the molecular orbitals of cis and trans 1,2-difluoroethylene, although it is representative of all of the 1,2-dihaloethylenes.

Table 1. Dipole moments, geometries and relative energies of $C_2H_2X_2$.

X	Isomer		μ(D)	r (Å)			Angles (degrees)		E_{rel}
				C–H	C–X	C–C	CCX	CCH	(Kcal/mole)
F	1,1	calc	0.88	1.090	1.312	1.278	120.30	119.83	−19.16
		exp	1.37[a]	1.079[b]	1.323[b]	1.315[b]	125.5[b]	119.1[b]	
	Cis 1,2	calc	2.74	1.094	1.313	1.273	121.80	120.89	− 6.85
		exp	2.42[c]	1.089[b]	1.335[b]	1.324[b]	122.1[b]	124.0[b]	− 1.08[d]
	Trans 1,2	calc	(0)	1.100	1.310	1.276	125.30	117.37	(0)
		exp	0	1.088[e]	1.338[e]	1.320[e]	119.8[e]	125[e]	(0)
Cl	1,1	calc	1.29	1.094	1.655	1.278	120.12	119.97	6.13
		exp	1.25[f]		1.710[g]	1.324[g]	122.8[g]		
	Cis 1,2	calc	3.33	1.102	1 650	1 280	121.98	119.85	1.01
		exp	2.95[h]	1.075[i]	1.718[i]	1.354[i]	123.8[i]	132[i]	− 0.71[d]
	Trans 1,2	calc	(0)	1.107	1.642	1.278	127.45	114.66	(0)
		exp	0[f]	1.084[j]	1.721[k]	1.343[k]	123.0[k]		(0)
Br	1,1	calc	1.38	1.094	1.797	1.274	120.22	120.09	7.70
	Cis 1,2	calc	3.42	1.100	1.793	1.276	122.47	119.65	2.51
		exp	1.35[l]	1.10[m]	1.871[m]	1.36[m]	124.1[m]	117.5[m]	− 0.25[d]
	Trans 1,2	calc	(0)	1.106	1.784	1.276	128.45	113.61	(0)
		exp	0[l]		1.85[n]		121[n]		(0)
I	1,1	calc	1.97	1.097	2.057	1.266	120.28	120.36	8.35
	Cis 1,2	calc	4.09	1.097	2.049	1.265	125.11	119.27	3.04
		exp	0.76[l]	1.06[o]	2.05[o]	1.34[o]	125.65[o]		0[d]
	Trans 1,2	calc	(0)	1.102	2.050	1.266	126.30	116.34	(0)
		exp	0[l]	1.06[p]	2.05[p]	1.34[p]	121.25[p]		(0)

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Table 2. Geometries, relative energies and dipole moments of 1,2-$C_2H_4X_2$.

X	Con-former		r (Å)			angles (degrees)			E_{rel}	μ(D)	
			C–C	C–X	$\overline{\text{C–H}}$	CCX	$\overline{\text{CCH}}$	X–CC–X	(Kcal/mole)	μ_{gauche}	$\overline{\mu}$[a]
F	gauche	calc	1.411	1.331	1.108	112.96	112.14	53.38	– 3.37	2.62	
		exp	1.535[b]	1.394[b]	1.13[b]	108.3[b]	108.3[b]	74.5[b]	– 1.71[b]	2.67[c]	
	anti	calc	1.416	1.329	1.110	114.69	111.31	(180)	(0)		
Cl	gauche	calc	1.415	1.671	1.113	113.13	111.37	58.68	0.41	3.28	
		exp						64[d]	1.08[e]		
	anti	calc	1.418	1.671	1.115	115.76	110.12	(180)	(0)		1.28
		exp	1.49[f]	1.78[f]	1.12[f]	110.4[f]		(180)	(0)		1.15[f]
Br	gauche	calc	1.413	1.819	1.113	113.34	111.27	58.53	2.10	3.32	
		exp						74[d]	1.45[e]		
	anti	calc	1.413	1.817	1.114	116.50	109.76	(180)	(0)		0.95
		exp						(180)	(0)		1.01[g]
I	gauche	calc	1.405	2.093	1.109	112.69	112.00	59.46	6.27	3.98	
		exp							2.60[h]		
	anti	calc	1.402	2.092	1.109	113.74	111.48	(180)	(0)		0.45
		exp						(180)	(0)		0.44[i]

[a] Calculated from an equilibrium conformer distribution ($T = 300$ °K) using experimental energies and calculated dipole moments.

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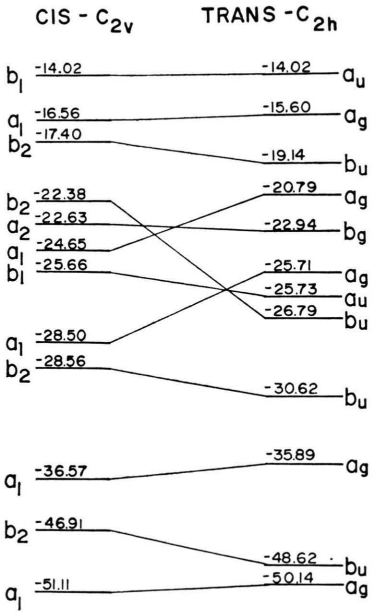

Fig. 1. Correlation diagram of 1,2-difluoroethylene. Molecular orbital energies in eV.

IV. Discussion

Our results for the calculated energy differences between the cis and trans isomers in the 1,2-dihaloethylenes (Table 1) clearly reflect the experimental trend, although "crossover" too soon. These results are an obvious improvement over the limited (only F and Cl) CNDO/2 treatment of Epiotis [15] in which consideration of the d orbitals reverses the trend. (The inversion of the calculated energy differences as one goes down the halogen group was revealed as a steric effect by increasing the Slater orbital exponents of the halogen atoms by 5%, 10%, 15%, and 20%, thereby lessening the effective radius of the electron cloud, which caused the cross-over to occur "later" in the group.) The variation of the energies of the 1,1-dihaloethylenes relative to the corresponding trans 1,2-dihaloethylene is also monotonic, goes in the same direction as the relative cis isomer energies, and is consistent with calculated [12] ab initio results, as are the relative energies of the conformers of the

1,2-dihaloethanes (Table 2). We would point out that in all cases the energy differences are exaggerated by CNDO/2, which is to be expected as it is commonly known that the method gives absolute energies much too large.

The dipole moments of the haloethylenes are reasonable, especially for the fluoro and chloro compounds. In the bromo and iodo compounds one would expect a larger contribution from the d orbitals, which were not considered in our calculations, thus increasing the expected error in electron distribution. The dipole moments of the dihaloethanes are exceptionally close to the experimental values when one uses the experimental energy differences to calculate the equilibrium conformer distribution. The experimental dipole moment values for $C_2H_4Cl_2$, $C_2H_4Br_2$, and $C_2H_4I_2$ almost certainly refer to mixtures of conformers.

The calculated bond distances are consistent, i.e., the C–H distances are all quite reasonable, the C–C distances all much too short and the C–X distances a bit too short. This is undoubtedly due to the value of the Slater orbital exponent which we use ($\xi_C = 1.72$), considerably larger than the standard 1.625. If one compares the experimental C–C bond lengths in the haloethylenes as a function of the halogen one notes that instead of the monotonic behaviour expected that this value becomes a maximum in the middle of the group, which is reflected in the calculated results. In comparing C–C bond lengths for cis-trans isomers one notes that in all cases the trans isomer has either a shorter bond or the same bond length. Our calculations reflect this for the chloro, bromo and iodo (almost) ethylenes, but predict the contrary for the fluoro case. The cis trans relative bond lengths for the C–X bond show the trans isomers to have the longer bond in the fluoro and chloro ethylenes, but not the bromo nor iodo ethylenes. Our calculations predict the cis isomers to have the longer bond in all cases, except iodo. The experimental values for the C–H bonds also are not monotonic as one scans the halogens, but have a maximum value in the middle of the group. This is reflected in our calculated results. The relative cis-trans C–H bond lengths are apparently the same except for chloro where the trans isomer is considerably longer. Our calculations do get this correct, however incorrectly predict the trans isomer to have the longer C–H bond length in all four cases.

The calculated bond angles, almost without exception, reflect the experimental trends in the haloethylenes. We would point out that our results correctly predict the separation of the halogen atoms in the cis isomers by an increase in the CCX angle to more than 120°; this angle monotonically increasing as one goes down the halogen group. In the trans isomers our calculations correctly predict the CCX angle to have a maximum value in the middle of the group, though erring on the CCF angle. The calculated bond angles in the haloethanes are much poorer, on the basis of a much more limited set of experimental values. Another striking feature of the calculated angles is the solid angle FCCF (53°) in gauche 1,2-difluoroethane being considerably smaller than the other gauche conformers (59°). These values are not consistent with experiment.

The intramolecular atomic interaction energies shown in Table 3 represent an attempt to explain the observed energy trend in terms of specific atom-atom interactions. The energy matrix elements can be considered to be weighted bond orders, and although these elements are not as simply defined as bond orders, and possibly therefore not as intuitively satisfying, one avoids totally the problem of rotational variance associated with bond orders. The simplest result would have been to find most of these elements either constant as one goes down the halogen group, or, at least the cis-trans difference constant upon variation of the halogen. Unfortunately, quite the contrary is found, and just about every element varies by at least 50% of the total cis-trans energy difference. However, we can differentiate between those matrix elements which change substantially in a manner consistent with the overall energy change and those which do not. Falling into the first group are the elements C–C, C–H and X–X. However, the element X–X cited by previous work [5, 8, 9, 11] to be responsible for the observed trend is actually calculated to be repulsive for all cis isomers. Element C–X runs in exactly the opposite direction, favoring the trans isomer in $C_2H_2F_2$ and the cis isomer in $C_2H_2I_2$. One notes that these results cannot be interpreted within the non-bonded attraction theory because not only is the X–X interaction repulsive in all of the cis isomers, but it is actually slightly more repulsive in difluoroethylene than in diiodoethylene.

Table 3. Calculated Pi overlap populations and intramolecular atomic interaction energies — 1,2-Dihaloethylenes.

		F		Cl		Br		I	
		Cis	Trans	Cis	Trans	Cis	Trans	Cis	Trans
BO	C–C	0.2529	0.2515	0.2506	0.2513	0.2543	0.2545	0.2638	0.2636
	C–X	0.0343	0.0345	0.0361	0.0364	0.0305	0.0307	0.0203	0.0196
	X–X	0.0001	0.0000	0.0009	0.0001	0.0011	0.0001	0.0008	0.0001
	Total	0.3147	0.3143	0.3114	0.3133	0.3044	0.3054	0.2953	0.2936
E_{AB}	C–C	– 44.651	– 44.224	– 44.725	– 44.694	– 45.160	– 45.106	– 46.193	– 46.167
	C_1–X_1	– 32.469	– 32.839	– 26.771	– 27.035	– 23.748	– 23.999	– 19.600	– 19.467
	C_1–H_1	– 20.648	– 20.436	– 20.451	– 20.279	– 20.400	– 20.252	– 20.311	– 20.433
	X–X	0.150	0.063	0.175	–0.138	0.151	–0.210	0.113	–0.383
	C_1–H_2	0.267	0.284	0.190	0.167	0.164	0.137	0.147	0.124
	C_1–X_2	0.166	0.197	0.362	0.337	0.427	0.353	0.435	0.325
	H_1–X_1	0.158	0.138	0.357	0.369	0.363	0.381	0.383	0.410
	H_1–X_2	–0.196	–0.007	–0.153	0.146	–0.176	0.173	–0.223	0.224
(eV)	H–H	0.073	–0.120	0.099	–0.136	0.108	–0.145	0.122	–0.137
	C	–148.864	–148.928	–149.414	–149.369	–149.608	–149.548	–149.689	–149.675
	H	– 12.115	– 12.088	– 12.253	– 12.292	– 12.264	– 12.318	– 12.236	– 12.223
	X	–697.467	–697.413	–435.913	–435.853	–388.480	–388.424	–331.991	–332.072

One can attempt to separate σ and π contributions to relative stabilities by the use of bond orders. [Energy matrix elements are not completely separable into σ and π contributions because mixed terms arise in the second summation in Eq. (1) and the first term in Equation (2).] Actually bond orders have no exact physical interpretation, although they are roughly related to bond strength. However, they clearly need to be corrected for overlap in order to compare values for different bonds. We have chosen Mulliken's definition [24] of overlap populations, $P'_{ij} = S_{ij} P_{ij}$.

We note (Table 3) that the C–X π overlap population is slightly greater for the trans isomer in all cases except $C_2H_2I_2$, in direct contrast to experimental and calculated stabilities. Therefore, the C–X π overlap population variation cannot be invoked to explain the experimental relative stabilities, contrary to previous suggestion [8].

As further evidence that the π system is not primarily responsible for the relative stabilities of the 1,2-dihaloethylenes, we refer to our cis-trans correlation diagram, Figure 1. One notes that the π system is almost unperturbed by the isomerization process; the greatest change in orbital energies being 0.31 eV. In contrast, we find major changes in orbital energies due to isomerization in the σ [25] system; the smallest difference being 0.66 eV, and varying up to 4.41 eV. It is reasonable to assume that these orbital energies reflect the differences in total energies. To attribute [8] the relative stabilities of the dihaloethylenes to their respective π systems is to neglect the large differences and concentrate on the smaller ones. Granted that this is a very attempting approach (the π system is much simpler — having fewer atomic orbitals), however we believe that it is totally without justification.

V. Conclusions

This work originally set out to answer the question: "Why are cis isomers more stable than trans isomers in 1,2-dihaloethylenes?" We have *not* succeeded in answering this question. Certainly a great deal of the difficulty stems from the manner in which the question is formulated, i.e., it assumes a certain type of answer is possible; that cis and trans isomers are basically equivalent except for one (or a few) small differences in structure and electron distribution and that these are then responsible for the differences in energy. Clearly our results are not in agreement with this picture for the compounds considered here.

We believe that in spite of the crude approximations involved in the CNDO/2 system, it has proven to be a very durable and successful method to calculate a large number of physical and chemical properties of medium size molecules, especially in the comparison of a series of similar molecules. In the case of good agreement between calculated and experimental results, which we believe is the case here, it is reasonable to accept the qualitative picture given by the calculated wavefunction. We further believe that more refined methods of calculation, such as ab initio, would yield the same qualitative picture, if their results were interpreted, as here, on the basis of a cis-trans correlation diagram and intramolecular atomic interaction energies. In conclusion, we believe that our results allow an improved, albeit incomplete interpretation of the interactions responsible for the relative stabilities of haloethylenes. Our calculations suggest that these dihalogen compound stabilities are not due to either an attraction between non-bonded atoms nor do they have their origin in the π electron system, but rather are due to various subtle differences in bonding between nearest neighbors in the σ system [26].

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[25] We find that all a_1(cis) orbitals become less stable when transforming to a_g(trans) and all b_2(cis) become more stable upon transformation to b_u(trans).

[26] *Note added in proof:* after sending out this manuscript we received a copy of STO-3G results of cis and trans 1,2-difluoroethylene from Prof. P. Kollmann, which we gratefully acknowledge. The STO-3G cis-trans correlation diagram is qualitatively very similar to Figure 1. There are two inversions for each isomer, being in both cases the molecular orbitals 4↔5 and 6↔7, 1 being the HOMO. The differences in orbital energies vary between 0-0.13 eV in the π system and 0.06-2.54 eV in the σ system, thus leading to the same argument presented here.