The Importance of Lone Pair Electron Delocalization in the *cis–trans* Isomers of 1,2-Dibromoethenes

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The subtle experimental energy difference between isomers of 1,2-dibromoethenes (0.090 ± 0.240 kcal mol^{-1}) has been confirmed by high level MO calculations: the cis isomer is more stable by 0.04 kcal mol^{-1} than the trans isomer at the MP4(STDQ)/6-311++G(3df,3dp)//MP2/6-311++G(3df,3dp) level. It was strongly suggested that the most important origin of the cis-effect is the stabilizing hyperconjugative (charge-transfer) interaction of Br lone pairs with the $\pi_{\mathrm{C=C}}{}^*$ antibonding orbital.

It is widely accepted at the level of freshman chemistry that the structures of simple molecules, such as H_2O or SF_4 can be easily predicted by the VSEPR (valence shell electron pair repulsion) model,[1] which emphasizes that Pauli repulsion between lone pair (LP) electrons and/or bonded electron pairs should be the most important factor that dictates molecular structures. However, some phenomena out of this theory have been observed: one of the most representative ones is the cis-effect in 1,2-dihaloethenes (halogen = F, Cl, or Br).[2]

In this paper, we present theoretical evidence that delocalization of LP electrons via intramolecular charge-transfer interaction (hyperconjugative stabilization) leads to significant net thermodynamic stabilization of a molecule and that this may be the major origin of the cis-preference energies in the geometrical isomerism of 1,2-dihaloethenes. The model system we have chosen to demonstrate the importance of LP delocalization is the border-line case of cis-effect,[2] namely the isomers of 1,2-dibromoethenes.[2b] Our previous calculations performed at high ab initio and density functional theory (DFT) levels,[3] using 1,2-difluoroethenes, strongly suggested that the cis-effect should emerge from two types of electron delocalization mechanisms, which obviously override the VSEPR repulsive forces among the fluorine lone pairs and the nearby bonding electron pairs: delocalization of halogen lone pair electrons (the LP effect) and the periplanar effects. The latter include the antiperiplanar hyperconjugative (charge-transfer) interactions (the AP effect) and the synperiplanar hyperconjugative interactions (the SP effect), with the former generally being much more predominant than the latter.

The experimental evidence for the cis-effect in 1,2-dibromothenes[2b] has remained uncertain. The cis isomer was reported to be more stable than the trans isomer only by 0.090 kcal mol^{-1}. Unfortunately the experimental error exceeds the thermodynamic energy difference (0.240 kcal mol^{-1}). Moreover, no theoretical works were performed on the energy differences of the *cis*- and *trans*-1,2-dibromoethenes. Herein, we made the first theoretical consideration on this subtle cis-effect and concluded that LP electron delocalization should be the major origin of the cis-effect as demonstrated previously for 1,2-difluoroethenes.[3] Additionally, the orbital phase continuity-discontinuity theory was applied to explain these cis-preferable delocalizations.

The results of geometrical optimizations[5] at MP2 levels and the subsequent single-point calculations are shown in Tables 1 and 2, respectively. The C=C bond length (1.334 Å) and the CCBr angle (125.3°) for the cis isomer, obtained at the MP2 level, agree well with the corresponding experimental values (1.36(3) Å, 124(2)°).[6] The CCBr angle (α_{CCBr}) of the cis isomer (125.3°) is larger than that of the trans isomer (121.3°).

Table 1. Structural parameters for 1,2-dibromoethenes optimized at the MP2/6-311++G(3df,3pd) levels

cis

	d_{CC}/Å	d_{CBr}/Å	d_{CH}/Å	θ_{CCH}/°	θ_{CCBr}/°
Calcd	1.334	1.865	1.080	120.0	125.3
Expt[6]	1.36(3)	1.87(2)			124(2)

trans

	d_{CC}/Å	d_{CBr}/Å	d_{CH}/Å	θ_{CCH}/°	θ_{CCBr}/°
Calcd	1.331	1.875	1.079	123.7	121.3

The results of single point calculations collected in Table 2 shows that the HF level calculation could not reproduce the experimental trend of relative energy even though very large basis sets were employed (−0.91 kcal mol^{-1}). However, when the effects of electron correlation were taken into account through the MP2 method using a very large basis set (6-311++G(3df,3dp)), the cis isomer was found to be more stable by 0.28 kcal mol^{-1} than the trans isomer. Finally the MP4(SDTQ) level of calculation using same basis set nicely reproduced a value (0.04 kcal mol^{-1}) very close to the experimental one (0.090 kcal mol^{-1}).

In analogy to our previous results[3] and the subsequent report by Novak,[4] the cis-preference can be successfully explained by two major electron delocalization mechanisms: the LP effect and the periplanar (AP&SP) effects. In order to estimate the magnitude of these delocalization mechanisms in 1,2-dibromoethenes, we performed NBO 2nd order perturbation analysis[7a] at the MP2 level (Table 3).

According to the result, the magnitudes of SP effects are uniformly less than 1 kcal mol^{-1} and are much smaller than

Table 2. Relative energy differences (including the ZPE) between *cis*- and *trans*-1,2-dibromoethenes

Methods	kcal mol^{-1}
HF/6-311++G(3df,3pd)//MP2/6-311++G(3df,3dp)	−0.91
MP2/6-311++G(3df,3pd)//MP2/6-311++G(3df,3dp)	0.28
MP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3dp)	0.04
Expt[2b]	0.090 ± 0.240

Table 3. NBO 2nd order perturbation analysis of *cis*- and *trans*-1,2-dibromoethenes at MP2/6-311++G(3df,3dp)//MP2/6-311++G(3df,3dp) level (kcal mol^{-1})

Isomers	Periplanar effects					LP effects		
	AP effects		SP Effects		Total	$n_\sigma \rightarrow \sigma_{CC}{}^*$	$n_\pi \rightarrow \pi_{CC}{}^*$	Total
cis	10.55 ($\sigma_{CH} \rightarrow \sigma_{C'Br'}{}^*$)	4.02 ($\sigma_{CBr} \rightarrow \sigma_{C'H'}{}^*$)	0.94 ($\sigma_{CH} \rightarrow \sigma_{C'H'}{}^*$)	0.06 ($\sigma_{CBr} \rightarrow \sigma_{C'Br'}{}^*$)	31.14	5.97	20.73	53.40
trans	5.85 ($\sigma_{CH} \rightarrow \sigma_{C'H'}{}^*$)	8.09 ($\sigma_{CBr} \rightarrow \sigma_{C'Br'}{}^*$)	0.44 ($\sigma_{CH} \rightarrow \sigma_{C'Br'}{}^*$)	0.37 ($\sigma_{CBr} \rightarrow \sigma_{C'H'}{}^*$)	29.50	5.18	18.22	46.80
					$\Delta_{AP\&SP} = 1.64$	1.58	5.02	$\Delta_{LP} = 6.60$

The total values ($\Delta_{AP\&SP}$ and Δ_{LP}) are doubled because two sets of same interactions exist.

those of AP effects (4–11 kcal mol^{-1}). The periplanar effects (31.14 kcal mol^{-1} for cis and 29.50 kcal mol^{-1} for trans) are less effective than the LP effects (53.40 kcal mol^{-1}for cis and 46.80 kcal mol^{-1} for trans) to stabilize the molecule, although they both stabilize more effectively the cis isomer (84.54 kcal mol^{-1}) than the trans isomer (76.30 kcal mol^{-1}).

Secondly, the lone pair delocalization mechanisms (the LP effects) stabilize the cis isomer more effectively by 1.58 kcal mol^{-1} (two ways of $n_\sigma \rightarrow \sigma_{CC}{}^*$ in-plane NBO interactions; σ-LP effect) and by 5.02 kcal mol^{-1} (two ways of $n_\pi \rightarrow \pi_{CC}{}^*$ out-of-plane NBO interactions; π-LP effect) than they do the trans isomer. It is noted that the latter (π-LP effect) is far more effective than the former (σ-LP effect) to stabilize the cis isomer. The π-LP effect is much greater than any other delocalization mechanisms. It should be noted that the large stabilizing interactions of the LP effect (53.40 kcal mol^{-1} for cis and 46.80 kcal mol^{-1} for trans) are far greater than the total values of periplanar effects (31.14 kcal mol^{-1} for cis and 29.50 kcal mol^{-1} for trans).

The origin of the LP effects could be explained by the orbital phase continuity-discontinuity theory.[8] The through-bond interactions between two Br lone pairs, which occurs only in the cis isomer, give rise to the cyclic orbital interactions among the antibonding orbitals of the C=C bond and two Br lone pairs. Consequently, the continuous orbital phases for the cyclic orbital interaction enhance the LP effects in the cis isomer, which is 6.60 kcal mol^{-1} more effective than that in the trans isomer. Furthermore, The LP effects seem to cause elongation of the C=C bond and shortening of the C–Br bond in the cis isomer owing to some electron shift into the bonding region of the C–Br bonds and the antibonding regions of the C=C bond, relative to those of the trans isomer. Whether or not the repulsive forces between closely located bromine lone pairs and those between the C–Br dipoles in the cis isomer, which should cause widening of the CCBr angles, may be responsible for the enhancement of both $n_\sigma \rightarrow \sigma_{CC}{}^*$ (σ-LP effect) and $n_\pi \rightarrow \pi_{CC}{}^*$ (π-LP effect) interactions is presently impeded and must await further investigation.

The total value of antiperiplanar interactions (AP effect) in the cis isomer ($\sigma_{CH} \rightarrow \sigma_{C'Br'}{}^*$ and $\sigma_{CBr} \rightarrow \sigma_{C'H'}{}^*$) is 1.26 kcal mol^{-1} greater than in the trans isomer ($\sigma_{CBr} \rightarrow \sigma_{C'Br'}{}^*$ and $\sigma_{CH} \rightarrow \sigma_{C'H'}{}^*$). The AP effects may be one of the important factors of the cis-effect. The synperiplanar interactions (the SP effect) have small cis-preferable effects. The combined value of cis-stabilizing energies of the periplanar (AP&SP) effects ($\Delta_{AP\&SP}$) is 1.64 kcal mol^{-1}. On the other hand, the total cis-preference through the LP effects (Δ_{LP}) is 6.60 kcal mol^{-1}. Clearly the LP effects are far more effective than the periplanar effects. Among the three interaction mechanisms that contribute to cis-preference (two LP effects and the AP effect), the most important one is the bromine π lone pair delocalization (π-LP effect) and the second most important is the antiperiplanar effect (AP effect). The two major origins of the cis-effect found here are consistent with the mechanisms identified previously in 1,2-difluoroethenes.[3]

In Conclusion, we have confirmed the previous experimental report by high-level MO calculations. The cis-effect may most probably come from two major electron delocalizations: the π-LP effect and the AP effects, with the former being much greater than the latter. The greater LP effects in the cis isomer were clearly explained by the orbital phase continuity-discontinuity theory. The combined stabilizing energies counteract Pauli repulsions (VSEPR) or electrostatic dipole repulsions between two bulky Br atoms and between two adjacent C–Br bond dipoles in the cis isomer. An important corollary from the present work is that lone pairs tend to interact with nearby antibonding orbitals to stabilize themselves in molecules, as previously suggested by Weinhold.[7] They hate to remain lonely uninteracted in molecules, as seen typically in hydrogen bonds. Full discussion on the nature of cis-effect will be reported in due course.

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