Theory of Structural Isomerism. Vicinal vs. Geminal Homodisubstituted Molecules

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Abstract: The linear combination of fragment configurations (LCFC) method is utilized to predict the most stable structural isomer of disubstituted alkanes and alkenes. It is argued that the 1,1 isomer (X_2A-A or $X_2B{=}B$) will be more stable than the 1,2 (cis or trans) isomer (XA-AX or XB=BX) when the two substituents are identical or electronically similar. Furthermore, a connection is made between the relative stability of the 1,1 and 1,2 isomers and A-A or B=B bond strengths in these two isomers. The predictions agree with known thermochemical data, microwave data, and quantum mechanical calculations.

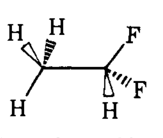
A great deal of work dealing with structural problems in organic chemistry has been aimed at developing an understanding of the electronic factors which determine the relative stability of isomers. However, while great attention has been paid to conformational and, more recently, to geometric isomerism,[2] structural isomerism has strangely remained out of the focus of interest. This work advances the viewpoint that structural isomerism is the type of isomerism which is easiest to understand. Predictive rules which can be utilized without the aid of any explicit computations are formulated.

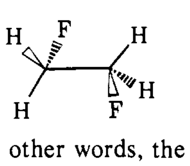
Theory

The key ideas pertinent to the discussion of structural isomerism have been described in a work dealing with an entirely different problem: chemical reactivity.[3] In problems of chemical reactivity, one focuses on the stabilization of a reaction complex of two molecules (e.g., an intermolecular reaction) or two submolecular fragments (e.g., an intramolecular rearrangement). Similarly, in problems of molecular structure, one focuses on the stabilization of a geometric arrangement of two submolecular fragments. In short, reactivity and structural problems can be viewed through the same lens. Concepts developed in one area are also applicable to the other.

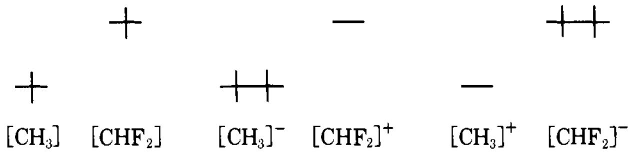
Experimental results suggest that reactions which are "allowed" in the Woodward-Hoffmann sense, as well as reactions "forbidden" in the Woodward-Hoffmann sense, are accelerated as the donor ability of one reactant (or fragment) increases.[3,4] In other words, the reaction between two electronically identical or similar molecules (or molecular fragments) will be slower than the reaction of two molecules (or molecular fragments) of opposite polarity. A donor-donor (D-D) combination will be stabilized less than a donor-acceptor (D-A) combination and, as the donor-acceptor properties are enhanced, the stabilization of the D-A combination will increase. The correlation of the donor-acceptor properties of reactants with reaction rates has been emphasized by several authors.[5]

We can now transplant these ideas to the area of molecular structure. Consider the model systems 1,1- and 1,2-difluoroethane shown below. The 1,1 isomer can be thought to arise from the union of $HF_2C\cdot$ and $\cdot CH_3$, while the 1,2 isomer from the union of two $H_2FC\cdot$ fragments. In other words, the 1,1 isomer is a D-A (or A-D) combination and the 1,2 isomer is a D-D or A-A combination. Accordingly, we can formulate the following rules:

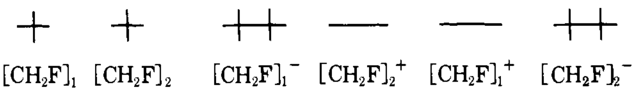




Scheme I



Scheme II



(a) A 1,1-disubstituted molecule will be more stable than its 1,2 isomer, if the two substituents are identical. Furthermore, the difference in their stability will increase as the donor-acceptor properties of the two fragments in the 1,1 isomer are enhanced relative to those in the 1,2 isomer.

(b) A 1,1-disubstituted molecule may be more or less stable than its 1,2 isomer, if the two substituents are different. The 1,1 isomer will be more stable if it corresponds to a better D-A combination, and vice versa.

We shall now illustrate how the linear combination of fragment configurations (LCFC) approach can be applied to the problem at hand. The fundamentals of this approach can be found in a previous article as well as references therein.[3]

The basis set configurations, which contain only the singly occupied (SO) MO's of the two radical fragments, are shown in Scheme I (F_2HC-CH_3) and Scheme II (FH_2C-CH_2F). Only the two charge transfer configurations of lowest energy which can mix with the no-bond configuration have been included, since we are only interested in the ground electronic states of the two isomers.[6] The energies of the various basis set configurations can be calculated empirically on the basis of the equations shown below:

$$E(CH_3,CF_2H) \approx E(\dot{C}H_2F,\dot{C}H_2F) = K$$

$$E(CH_3^-,CHF_2^+) = [I(\dot{C}HF_2) - A(\dot{C}H_3) + C] + K$$

$$E(CH_3^+,CHF_2^-) = [I(\dot{C}H_3) - A(\dot{C}HF_2) + C'] + K$$

$$E(CH_2F^-,CH_2F^+) = [I(\dot{C}H_2F) - A(\dot{C}H_2F) + C''] + K$$

In the above equations, I symbolizes the ionization potential, A the electron affinity, and C, C', and C'' the coulomb attraction resulting from the interaction of the "excess electron" of one fragment with the "positive hole" of the other. The assumption is made that the no-bond configurations of the 1,1

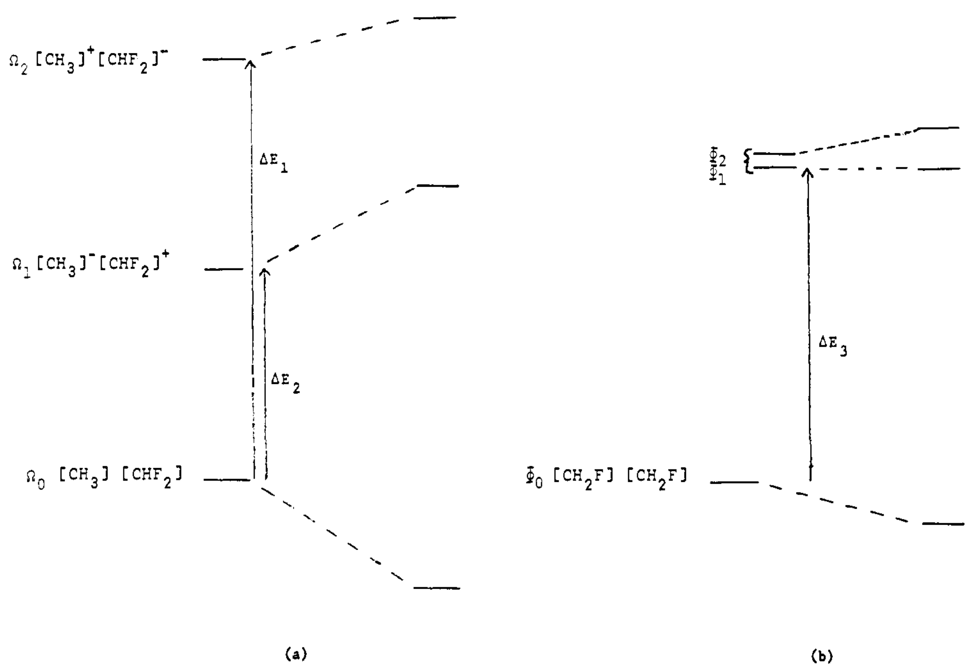


Figure 1. Configuration interaction diagram for (a) 1,1-difluoroethane and (b) 1,2-difluoroethane. Φ_1 and Φ_2 are charge resonance configurations, i.e., $\Phi_1 = 1/\sqrt{2}\,([CH_2F]^-[CH_2F]^+ + [CH_2F]^+[CH_2F]^-)$; $\Phi_2 = 1/\sqrt{2}\,([CH_2F]^-[CH_2F]^+ - [CH_2F]^+[CH_2F]^-)$.

and 1,2 isomers have identical energies. The ranking of the various configurations is shown in Figure 1.[7] Clearly, the D^+A^- configuration of a D-A pair will lie lower in energy than the D^+D^- configuration of a D-D pair. Also, the D^-A^+ configuration of a D-A pair will lie higher in energy than the D^+D^- configuration of a D-D pair. These predictions are valid assuming that the electrostatic terms do not vary significantly in the problem at hand. The ranking can also be confirmed by explicit calculations of the various configurations by a suitable computational method. Finally, the interaction matrix element between two configurations μ and ν, $P_{\mu\nu}$, is evaluated with respect to an effective one-electron Hamiltonian and is approximated by the overlap integral, S_{ij},[8] of the i and j MO's which differ by one electron in occupancy in the two configurations, μ and ν.[9]

We are now prepared to examine how configurations interact to produce the final electronic states in $F_2CH\text{-}CH_3$ and $FCH_2\text{-}CH_2F$, recalling that the energy change of a configuration μ due to interaction with a configuration ν is given by the expression shown below.

$$\Delta E_\mu \propto \frac{S_{ij}^2}{E_\mu - E_\nu}$$

First, we compare the Ω_0-Ω_1 and Φ_0-Φ_1 interactions. Both the I-A and the C terms (see Table I) vary so that the energy gap factor favors the former. On the other hand, the relative size of the interaction matrix elements depends on two conflicting factors. First, MO overlap favors a greater Ω_0-Ω_1 matrix element (see Table II) while the intrinsic difference between Ω_1 and Φ_1, the former being a single determinant and the latter the symmetry adapted linear combination of two determinants, works in an opposite sense. Hence, one may say that the two effects tend to cancel and the matrix element remains relatively constant. In such an event, there will be greater Ω_0-Ω_1 interaction. At worst, the matrix element may favor a greater Φ_0-Φ_1 interaction thus canceling the opposite effect of the energy gap. However, the additional Ω_0-Ω_2 interaction still tilts the balance in favor of greater configuration interaction in the 1,1 isomer. A convenient way of summarizing the above arguments is embodied in the statement that the energetic depressions of Ω_1 relative to Φ_1 coupled with a greater MO overlap in the case of the 1,1 isomer ensures that the interactions of the no bond and charge transfer configurations is greater in CH_3CHF_2 than in $CH_2F\text{-}CH_2F$ giving rise to greater stabilization of the former. Furthermore, shortening of the C-C bond will increase spatial overlap and the electronic stabilization due to configuration interaction will also increase. The rate of change of the stabilization will be greater in the case of the 1,1 isomer which, as a result, is expected to have a shorter C-C bond length than the 1,2 isomer. These conclusions can be generalized to any pair of 1,1 and 1,2 structural isomers involving identical groups.

Table I. Coulombic Attraction Term (C)

Fragments	C, eV	Fragments	C, eV
$[CH_3]^-[CHF_2]^+$	−4.05	$[CH_3]^-[CH(SH)_2]^+$	−3.39
$[CH_2F]^-[CH_2F]^+$	−3.85	$[CH_2SH]^-[CH_2SH]^+$	−2.15
$[CH_3]^-[CHCl_2]^+$	−3.18	$[CH_3]^-[CH(NH_2)_2]^+$	−4.20
$[CH_2Cl]^-[CH_2Cl]^+$	−1.93	$[CH_2NH_2]^-$ $[CH_2NH_2]^+$	−3.22
$[CH_3]^-[CH(OH_2)]^+$	−4.13		
$[CH_2OH]^-[CH_2OH]^+$	−3.61		

Table II. MO Overlap Integrals (S_{ij}) for Configuration Interaction

Interaction	S_{ij}
$[CH_3][CHF_2]$-$[CH_3]^-[CHF_2]^+$	0.4672
$[CH_2F][CH_2F]$-$[CH_2F]^-[CH_2F]^+$	0.4460
$[CH_3][CHCl_2]$-$[CH_3][CHCl_2]^+$	0.3822
$[CH_2Cl][CH_2Cl]$-$[CH_2Cl]^-[CH_2Cl]^+$	0.3096
$[CH_3][CH(OH)_2]$-$[CH_3]^-[CH(OH)_2]^+$	0.4382
$[CH_2OH][CH_2OH]$-$[CH_2OH]^-[CH_2OH]^+$	0.3970
$[CH_3][CH(SH)_2]$-$[CH_3]^-[CH(SH)_2]^+$	0.3588
$[CH_2SH][CH_2SH]$-$[CH_2SH]^-[CH_2SH]^+$	0.2694
$[CH_3][CH(NH_2)_2]$-$[CH_3]^-[CH(NH_2)_2]^+$	0.4195
$[CH_2NH_2][CH_2NH_2]$-$[CH_2NH_2]^-[CH_2NH_2]^+$	0.3514
$[CH_3][CH(CN)_2]$-$[CH_3]^+[CH(CN)_2]^-$	0.4190
$[CH_2CN][CH_2CN]$-$[CH_2CN]^+[CH_2CN]^-$	0.3536

Computations

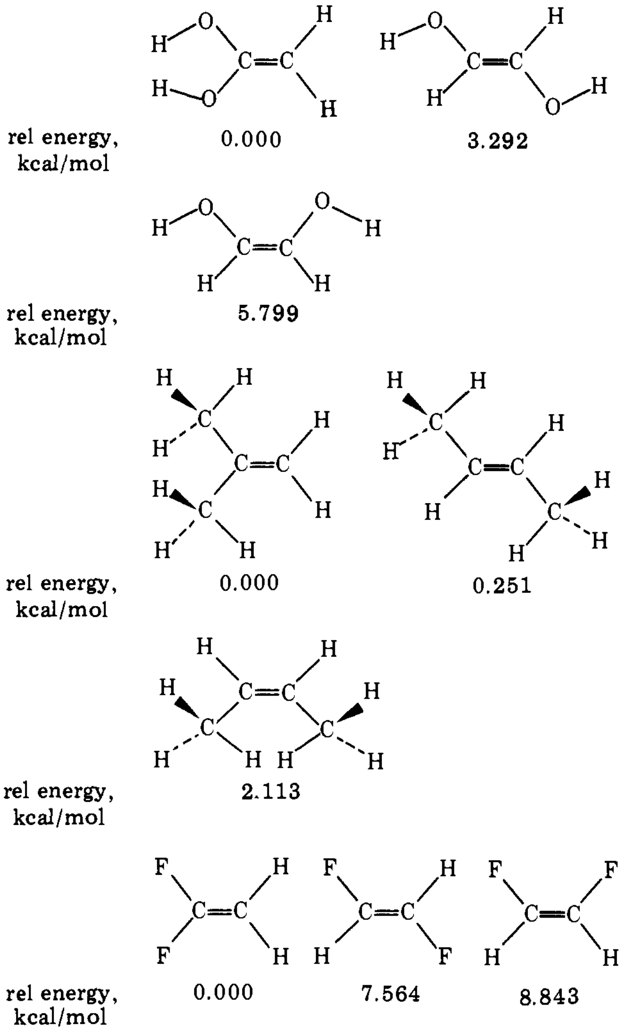
Since the ground electronic wave function of a molecule developed on the basis of the LCFC method approximates that

Table III. CNDO/2 Computed Relative Energies of 1,1- and Trans 1,2-Homodisubstituted Ethenes[a]

X	Rel energy, kcal/mol	
	CX_2CH_2	*t*-CHXCHX
F	0.000	9.786
Cl	0.000	4.809
OH	0.000	16.778
SH	0.000	10.085
NH_2	0.000	4.603

[a] Standard bond angles and bond lengths employed in all cases.

Scheme III



generated by single determinant MO theory, we have undertaken to test the model presented in the previous section by ab initio[10] and semiempirical (CNDO/2) SCF-MO computations.

Ab initio calculations of isomeric olefins were carried out employing limited geometry optimization. The results of the computations are shown in Scheme III. In all cases, and regardless of the nature of X, $CX_2{=}CH_2$ is found to be more stable than either cis or trans CHX=CHX.

CNDO/2 calculations of isomeric olefins were carried out employing standard bond angles and bond lengths.[11] The results are shown in Table III. Once again, the 1,1 isomer is found to be more stable than either the cis or trans isomers of 1,2-substituted $X_2C_2H_2$ molecules.

Additional computational data pertinent to this work can be extracted from the work of Pople and his co-workers.[12] These data are summarized in Table IV. Once again, the 1,1 isomer is found to be more stable than the 1,2 isomer in $X_2C_2H_2$, $X_2C_2H_4$, and XYC_2H_4 molecules, where X and Y are electronically similar.

Table IV. 4-31G Computed Relative Energies of 1,1- and 1,2-Disubstituted Isomers

Molecule	Rel energy, kcal/mol	Ref
2-Methylpropane	0.00	*a*
n-Butane		
Gauche	1.55	*a*
Trans	0.46	*a*
Isobutene	0.00	*a*
2-Butene		
Cis	1.99	*a*
Trans	0.31	*a*
1,1-Diaminoethane	0.00	*b*
1,2-Diaminoethane	5.67	*c*
1-Aminoethanol	0.00	*b*
2-Aminoethanol	8.45	*c*
1-Fluoroethylamine	0.00	*b*
2-Fluoroethylamine	11.40	*c*
Ethane-1,1-diol	0.00	*b*
Ethane-1,2-diol	10.50	*c*
1-Fluoroethanol	0.00	*b*
2-Fluoroethanol	11.41	*c*
1,1-Difluoroethane	0.00	*b*
1,2-Difluoroethane		
Gauche	13.56	*c*
Trans	12.10	*c*

[a] See ref 12a. [b] See ref 12b. [c] See ref 12c.

Experimental Evidence

The type of evidence available to test the proposed rules is the following: (a) Experimental heats of formation and π-bond dissociation energies. Pertinent data are shown in Tables V and VI. (b) Spectroscopic data. Pertinent data are presented in Table VII.

An examination of Tables V–VII leads to the following generalizations:

(a) In most cases where experimental heats of formation are available, *and irrespective of the nature of the substituent*, the 1,1 isomer is more stable (Table V). Furthermore, an examination of π-bond dissociation energies (Table VI) reveals that the replacement of a (CH_2) fragment in ethene with the more electronegative fragment (CF_2) leads to an increase in the strength of the C–C π bond. However, the replacement of a (CH_2) fragment in 1,1-difluoroethene by a (CF_2) fragment has exactly the opposite effect.

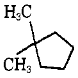
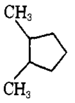
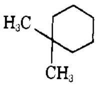
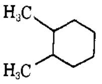
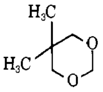
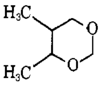
(b) The variation in the C–C or C=C bond length as a function of the type of substitution is such that it is shorter in the 1,1 isomer than in the 1,2 isomer, irrespective of the nature of the substituent (Table VII).

The ideas described in this work can be extended to reaction thermodynamics. For example, the reaction of two molecules A_2 and B_2 to form two AB molecules will become increasingly exothermic as A and B become a better donor-acceptor pair. A similar idea, based on VB theory, was originally advanced by Pauling.[13] However, as the donor-acceptor properties of the fragments decrease the difference in energy gap may be counterbalanced by an opposite change in the interaction matrix element. Typical examples are given in Table VIII. The reactions are always exothermic when the difference in the electronic nature of the reactants is large (a good donor-acceptor pair, e.g., $H_2 + F_2$); when this difference is small (e.g., $CH_3CH_3 + I_2$), the reaction may be endothermic.

Discussion

The major conclusion of this work is that, in $X_2A{-}A$ or $X_2B{=}B$ molecules, the A–A or B=B bond ionicity and, hence,

Table V. Standard Heats of Formation of 1,1- and 1,2-Homodisubstituted Isomers

Compd		$\Delta H_f°$, kcal/mol	Ref
MeHC=CHMe			
	Cis	−1.67	*a*
	Trans	−2.67	*a*
$Me_2C=CH_2$		−4.04	*a*
EtHC=CHMe			
	Cis	−6.71	*a*
	Trans	−7.59	*a*
$EtMeC=CH_2$		−8.68	*a*
EtHC=CHEt			
	Cis	−11.38	*a*
	Trans	−13.01	*a*
$Et_2C=CH_2$		−13.38	*a*
$CH_3CH_2CH_2CH_3$		−30.15	*a*
$(CH_3)_2CHCH_3$		−32.15	*a*
		−33.05	*a*
	Cis	−30.96	*a*
	Trans	−32.67	*a*
		−43.26	*a*
	Cis	−41.15	*a*
	Trans	−43.02	*a*
		−100.6	*a*
		−98.1	*a*
MeHNNHMe		+21.6	*a*
Me_2NNH_2		+20.4	*a*
$CH_3CH(OH)_2$		−103.1	*a*
$HOCH_2CH_2OH$		−92.4	*a*
CF_3CH_3		−178.0	*a*
CH_2FCF_2H		−167.0	*a*
$CHCl_2CH_3$		−30.6	*b*
CH_2ClCH_2Cl		−29.7	*b*

[a] S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Show, and R. Walsh, *Chem. Rev.*, 69, 279 (1969). [b] J.D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970.

Table VI. π-Dissociation Energies of Selected Olefins

Molecule	π-Dissociation energy, kcal/mol[a]	Ref
1,1-Difluoroethene	62.1 ± 1.0	*b*
Tetrafluoroethene	52.3 ± 2.0	*c*
Ethene	59.1 ± 2.0	*d*

[a] The π-dissociation energy is defined as the difference between the first and second bond dissociation energies in converting a saturated system into an unsaturated one. For ethene: H_π (C=C) = DH°(CH_3CH_2-H) − DH°(·CH_2CH_2-H). For further explanation, see ref 18. [b] J. M. Pickard and A. S. Rodgers, *J. Am. Chem. Soc.*, **98**, 6115 (1976). [c] E. Wu and A. S. Rodgers, *ibid.*, **98**, 6112 (1976). [d] See ref 18.

Table VII. Carbon-Carbon Double Bond Lengths of 1,1- and 1,2-Homodisubstituted Ethenes

Olefin	r(C=C),[a] Å	Ref
CH_2CH_2	1.337	*a*
cis-CHFCHF	1.324	*b*
CF_2CH_2	1.315	*b*
cis-CHClCHCl	1.354	*c*
trans-CHClCHCl	1.343	*d*
CCl_2CH_2	1.324	*e*
trans-$CH_3CHCHCH_3$	1.347	*f*
$(CH_3)_2CCH_2$	1.331	*g*

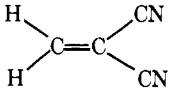
[a] L. S. Bartell, E. A. Roth, C. P. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965). [b] W. Laurie and P. T. Pence, *ibid.*, **38**, 2693 (1963). [c] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69**, 4091 (1965). [d] "Table of Interatomic Distances and Configuration in Molecules and Ions", Supplement 1956-1959, *Chem. Soc., Spec. Publ.*, No. **18** (1965). [e] R. L. Livingston, C. N. R. Roo, L. M. Kaplan, and L. Rocks, *J. Am. Chem. Soc.*, **80**, 5368 (1958). [f] A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970). [g] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **32**, 824 (1960).

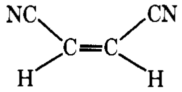
the A-A and B=B bond strength, is greater than in the structurally isomeric molecules XA-XA or XB=BX. Thus, there is a relationship among bond strength, bond length, and stability in structural isomers. The theoretical analysis is strictly comparative and rests on two assumptions:

(a) The energy of e.g., X_2A and A is comparable to that of XA and XA.

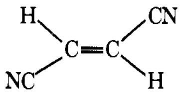
(b) The exchange stabilization of DD(XA,XA) is comparable to that of the DA(X_2A,A) configuration. In fact, it may very well be that exchange, being a function of the overlap integral between the two singly occupied MO's, favors the 1,1 isomer.

While the theoretical prediction that a 1,1-homodisubstituted molecule is more stable than the corresponding 1,2 isomer holds irrespective of the type of substituent, exceptions to this rule are anticipated with certain classes of substituents. For example, when R is an alkynyl or cyano substituent overlap repulsion of the two substituents in the 1,1 isomer can become dominant and responsible for a reversal of the stability order. This is indicated by the calculations shown below.





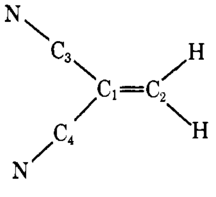
E_T(STO-3G) −258.17095 au −258.17390 au



E_T(STO-3G) −258.17484 au

A characteristic feature of the 1,1 isomer is a very large repulsive interaction of the two cyano groups which is manifested in the following ways:

(a) The C_3-C_4 overlap population becomes increasingly antibonding as the $C_3C_1C_4$ angle becomes smaller and attains a large and negative value at the equilibrium geometry.



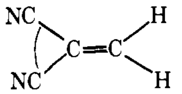
C_3–C_4	120°	116.26°	116°	112°	108°
overlap population	−0.0269	−0.0307	−0.0310	−0.0354	−0.0403

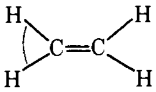
Table VIII. Heats of Metathesis Reactions for Diatomic and Polyatomic Molecules, $A_2 + B_2 \rightarrow 2AB$

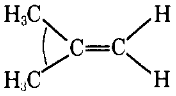
A_2	B_2	AB	Heats of metathesis reactions,[a,b] kcal/mol
H_2	F_2	HF	−130
H_2	Cl_2	HCl	−44
H_2	Br_2	HBr	−25
H_2	I_2	HI	−3
CH_3CH_3	F_2	CH_3F	−80
CH_3CH_3	Cl_2	CH_3Cl	−20
CH_3CH_3	I_2	CH_3I	+12
CH_3CH_3	H_2	CH_4	−16
F_2	Cl_2	FCl	−26
F_2	Br_2	FBr	−36
F_2	I_2	FI	−42
N_2	P_2	NP	+7

[a] A negative value corresponds to an exothermic reaction. [b] Values calculated from bond energies found in ref 18.

(b) The optimum $C_3C_1C_4$ angle $(CN)_2C{=}CH_2$ is comparable to the HCH angle of ethylene and the $C_3C_1C_4$ angle of isobutene.


116.3° (computed STO-3G)

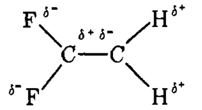

116.2° (exptl)

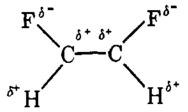

112.0° (exptl)

This suggests the presence of a repulsive interaction because both the stabilization component of nonbonded attractive and the substituent inductive effect favor a small $C_3C_1C_4$ angle in $(CN)_2C{=}CH_2$.

Other exceptions to our general rule can be anticipated when there is steric inhibition to conjugation in the 1,1 isomer, but not the 1,2 isomer, due to the bulk of the substituents. Thus, for example, $Ph_2C{=}CH_2$ is less stable than trans $PhCH{=}CHPh$ because the phenyl rings deviate from planarity to a larger extent in the case of the 1,1 isomer.[14]

Interpretations of the relative stability of structural isomers has been virtually nonexistent. Benson[15] mentioned in passing that the unusual stability of CF_3CH_3 could be due to dipolar effects. Kollman[16] proposed that 1,1-difluoroethene is more stable than *cis*-1,2-difluoroethene because there is better charge dispersal in the former isomer as the following illustrations seem to imply. This "charge" model would not work for substituents which are not highly electronegative; in such an event, "charge" effects would be small. Furthermore, one might suspect that, even in the case of electronegative substituents, such as F, the model is actually wrong, i.e., 1,1-difluoroethene is destabilized relative to *cis*-1,2-difluoroethene because of the proximity of the negatively charged fluorines.


I


II

electrostatic energy (kcal/mol) +26.454 −6.671

To test our suspicions, we used a point charge model and CNDO/2 calculated atomic charges in order to evaluate the electrostatic energy of I and II.[17] The results above invalidate the "charge" model of isomer stability. We conclude that the relative stability of structural isomers is due to a bond ionicity effect.

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