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DISTORTION OF THE DOUBLE BOND IN ETHYLENE

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In the preceding letter,[1] one of us has discussed reactive consequences of conjectured distortions of double bonds due to two types of torsional strain (steric repulsion between *cis* substituents or *trans* linkage). In this note we examine such distortions in ethylene as a simple model system by prescribing a non-planar HCCH arrangement for two hydrogens (either *cis* or *trans*) and determining the consequent positions of the other two. This problem can be approached quantitatively either by molecular orbital theory or (for small displacements) by using the vibrational force field for ethylene in its equilibrium form.

In the molecular orbital studies, we have used an ab initio method with the STO-3G minimal basis.[2] The results are given in Table 1. The equilibrium geometry and energy of ethylene (I) with this method have been reported previously.[3] In structure II, a pure torsional motion is considered in which each CH_2 is rotated 10° out of the original plane (angles θ,ϕ) and all remaining geometrical parameters are reoptimized. The energy is then 7.1 kcal/mol above that of I. In structure III, cis hydrogens H_A are distorted out of the original plane by 10° (θ) and the other hydrogens H_B allowed to relax to lowest energy positions. They are found to distort slightly on the same side of the plane as the H_A attached to the same carbon (angle ϕ) rather than on the opposite side as indicated by the simple torsional model II. On relaxation from II to III, the strain energy is reduced to 2.5 kcal/mol. Finally, in structure IV, trans hydrogens H_A are distorted by 10° as shown (θ) and the other trans pair H_B are allowed to relax (ϕ). Again, all displacements are on the same side of the original plane and the strain energy (3.0 kcal/mol) is reduced from its value in II.

Similar conclusions may be drawn from the out-of-plane vibrational frequencies of ethylene. We designate ν_4 as the twisting frequency (a_u) and ν_7' and ν_8' as the CH_2 wagging frequencies (b_{1u} and b_{2g} respectively) appropriate for infinite carbon mass. It can be shown in the harmonic approximation and in the limit of small displacements that, if θ is fixed and ϕ is chosen to minimize the energy, then

$$\phi/\theta \text{ (III)} = [\nu_4^2 - (\nu_8')^2]/[\nu_4^2 + (\nu_8')^2]$$

$$\phi/\theta \text{ (IV)} = [\nu_4^2 - (\nu_7')^2]/[\nu_4^2 + (\nu_7')^2]$$

Using $\nu_4 = 1023\ \text{cm}^{-1}$, $\nu_7' = 878\ \text{cm}^{-1}$ and $\nu_8' = 752\ \text{cm}^{-1}$ (derived from the experimental frequencies[4] ν_4, ν_7 and ν_8) we obtain $\phi/\theta = +0.30, +0.15$ for III and IV respectively. For pure torsion (II), ϕ/θ would be -1; $\phi/\theta = 0$ corresponds to the hydrogens H_B (in III and IV) remaining in the original ethylene plane. The positive ϕ/θ ratios calculated from the vibrational frequencies indicate displacements in the directions shown in III and IV and are quite close to the theoretical values (+0.33, +0.20) from Table I.

TABLE 1. Calculated geometries and energies of ethylene and distorted ethylenes

	θ^a	ϕ^b	C-C (Å)	$C-H_A$ (Å)	$C-H_B$ (Å)	H_ACC	H_BCC	H_ACH_B	Total energy (hartrees)	Relative energy[c] (kcal/mol)
I. Planar ethylene[d]	0	0	1.306	1.082		122.2°		(115.6°)	-77.07396	0
II. Pure torsion	10.0°	-10.0° [e]	1.309	1.083		122.3°		(115.4°)	-77.06264	7.1
III. <u>Cis</u> distortion	10.0°	3.3°	1.308	1.082	1.082	121.6°	121.8°	115.4°	-77.06995	2.5
IV. <u>Trans</u> distortion	10.0°	2.0°	1.308	1.082	1.082	121.6°	122.0°	115.4°	-77.06915	3.0

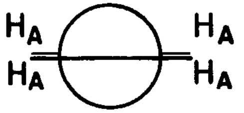
a. θ = prescribed (dihedral) angular distortion of $C-H_A$ bonds from the original ethylene plane.

b. ϕ = resultant (dihedral) angular distortion of the $C-H_B$ bonds (from the ethylene plane).

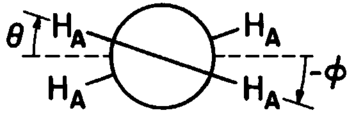
c. Energy calculated relative to planar ethylene.

d. From ref. 3

e. Constrained value because pure torsion considered.



I



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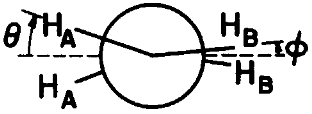
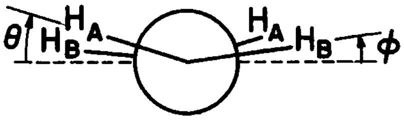


III



IV

In summary, both molecular orbital calculations and the analysis of observed vibrational frequencies indicate that *cis* or *trans* out-of-plane deformations in ethylene are not pure torsions; they are accompanied by significant bending, and hence pyramidalization, of the bonds at the carbon atoms. Such distortions are likely to have interesting stereochemical consequences.[1]

References

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