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THE INTERNAL ROTATION BARRIER IN ALLENE

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Abstract—The barrier to internal rotation in allene is computed to be 72·7 kcal/mole from an LCAO SCF computation using 41 Gaussian basis orbitals. The results are compared to predictions from a simple Hückel calculation. Attempts to interpret the rotation barrier simply in terms of the allene orbitals fail.

AN LCAO SCF calculation using the 41 simple Gaussian basis orbitals in Table 1 was carried out, with the New York University POLYATOM program, on the allene ground state (D_{2d} geometry) and on a twisted allene in which one CH_2 group was rotated to make the entire molecule planar (D_{2h} geometry). For both forms the C—H bond length was taken to be 1·087 Å = 2·054 au,* the C—C to be 1·308 Å = 2·472 au and the H—C—H angle to be 118° 10′.[2] No further approximations were made, and all integrals were evaluated exactly. The resulting orbitals are in Table 2. The energy of D_{2h} allene is calculated to be 72·7 kcal/mole higher than that of the normal D_{2d} form. This is shown in Table 3 with other energies that will be needed.

We wish to consider the question: Can the 72·7 kcal of twisting strain energy be interpreted simply in terms of changes in allene orbitals? For comparison, let us first examine the rotation using the simplest possible Hückel model. Localized bonds and the 4 $2p\pi$ AO's, each contributing one electron, are shown for the D_{2d} and D_{2h} structures in Fig 1. In the D_{2d} ground state the π AO's form what is essentially a pair of isolated double bonds whose π energy in the Hückel approximation is $4(\alpha + \beta)$. On twisting to the D_{2h} geometry, one of the double bonds is broken with one of the π AO's rotating into conjugation with the second double bond to form an allyl-like radical, the π levels of which lie at α and $\alpha \pm \sqrt{2}\,\beta$. The other π AO remains as an isolated 2p orbital of energy α. Two electrons would be expected to go into the $\alpha + \sqrt{2}\,\beta$ level and one into each of the non-bonding levels to give an energy of $4\alpha + 2\sqrt{2}\,\beta$ which is $-1{\cdot}17\beta$ above that of the D_{2d} form.

In a similar way the energy to twist one end of ethylene by 90° is computed to be -2β. This may be equated to the observed 65 kcal/mole for the activation energy of *cis-trans* isomerization of dideuteroethylene,[3] to give $\beta = -32{\cdot}5$ kcal. Thus the Hückel model would predict an allene rotational barrier of 1·17 × 32·5 = 38 kcal. This does not agree well with the 72·7 kcal from the SCF calculation. One can extrapolate Moskowitz and Harrison's[4] SCF results for ethylene from 80° to 90° to give an estimated SCF barrier of 105 ±5 kcal. Since this is high, one might expect the allene SCF barrier to be high. As far as we are aware, there is no experimental value of the allene barrier available for comparison.

Let us now return to our SCF results. The valence orbitals of allene are pictured roughly in Fig 2, together with the orbitals to which they transform on flattening the molecule. The 3 lowest orbitals of each geometry at about −11 au (Table 2) are 1s

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* Values of fundamental constants and conversion factors were taken from the recent survey.[1] 1 au of length = 0·52917 Å, 1 au of energy = 27·211 eV = 627·5 kcal/mole.

inner shells of carbon and are not shown. Correlation of D_{2d} and D_{2h} levels is made taking care not to violate the non-crossing rule in intermediate D_2 geometries. The result is that a_1 and b_1 orbitals of normal allene both go to either a_g or a_u orbitals in the flattened form. a_2 and b_2 orbitals go to b_{1g} or b_{1u} orbitals, and an e orbital gives one of either b_{2g} or b_{2u} plus one of either b_{3g} or b_{3u} symmetry.

The degenerate pair 2e corresponds to the 4 electrons in isolated double bonds in the Hückel approximation. These two orbitals together with the corresponding excited pair 3e correlate with $1b_{3u}$ (the bonding allyl orbital), $1b_{2g}$ (the non-bonding allyl orbital), $2b_{2u}$ (the non-bonding p orbital in the plane of the molecule), and $2b_{3u}$ (the antibonding allyl orbital). This is roughly in accord with the Hückel picture. The main difference is that $1b_{2g}$ and $2b_{2u}$ are not of the same energy. One might ascribe their large difference (0·29 au = 184 kcal) to destabilization of the $2b_{2u}$ level by antibonding interaction of the central p orbital in the plane of the molecule with the hydrogen orbitals.

Because of this removal of the accidental degeneracy between $1b_{2g}$ and $2b_{2u}$, the expected D_{2h} ground state would be a closed-shell ^1A_g structure with orbitals through $1b_{2g}$ doubly filled. The D_{2h} orbitals in Fig 1 were computed on this assumption. However, even with these orbitals, promotion of 1 electron from $1b_{2g}$ to $2b_{2u}$ gives rise to a ^1A_u state 0·7 kcal/mole below and a ^3A_u state 2·8 kcal/mole below the ^1A_g "ground state". If the SCF computations were done directly on these states, they would lie still lower. Thus in this indirect way the more rigorous SCF results are in agreement with the simple Hückel model.

Returning to the problem of whether or not the rotational barrier can be understood by a simple inspection of the allene orbitals, we shall consider rotation to the ^1A_g state, the state corresponding to the 72·7 kcal barrier mentioned above, since this is the state for which the orbitals in Fig 1 were computed. Similar comments would apply to the slightly lower ^1A_u and ^3A_u states.

The most striking effect of the rotation is the splitting of the degenerate 2e orbital to the $1b_{3u}$ and $1b_{2g}$. But the splitting is very nearly symmetric, and 2 electrons in $1b_{3u}$ plus 2 in $1b_{2g}$ have only 11 kcal more orbital energy than 4 in 2e. Hence, this does not account for the main part of the rotational barrier.

Looking down the list of orbitals, the clearest remaining effect of rotation is the unsymmetrical splitting of the 1e orbital into $1b_{2u}$ and $1b_{3g}$. The result of this is an increase in orbital energy of 43 kcal. Since the 1e orbital is due to hyperconjugation between the end hydrogens and $p\pi$ orbitals on the central atom, it might appear that loss of hyperconjugation is the main cause of the rotational barrier. Unfortunately, this simple picture does not hold up either. Although the largest orbital shift comes from the 1e, all others move up or down a little. Summing over all gives the total difference in orbital energies of only 0·25 kcal (Table 3).

Of course the sum of orbital energies is not the total molecular energy. In summing the orbital energies, each electron-electron repulsion has been counted twice instead of once. Further, the coulomb repulsions between nuclei have not been included. The change in nuclear-nuclear repulsion on rotating allene is particularly small since all that happens is that the hydrogen nuclei are brought slightly closer together. This gives an energy gain of only 1·9 kcal (Table 3) and accounts for only a very small part of the rotation barrier. By default one can say that the main part of this barrier is due to changes in electron-electron repulsion energy. This repulsion energy may be apportioned among the orbitals to give what Coulson and Nielson[5] call "partitioned energies" that do add to give the total molecular energy, or it may be dissected into π-π, π-σ and σ-σ contributions. We have examined the electron repulsion energy in these ways, but the results do not seem especially illuminating. Other, more elaborate, dissections of the total energy might be considered,[6] but we conclude that here, and probably in other cases, discussions based on a naive inspection of orbital shapes or energies are not sound.

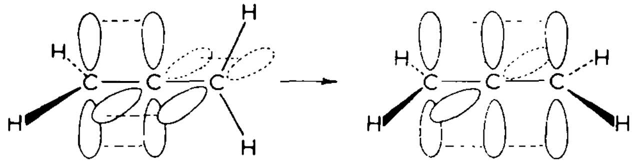

FIG 1. Hückel model of the rotation.

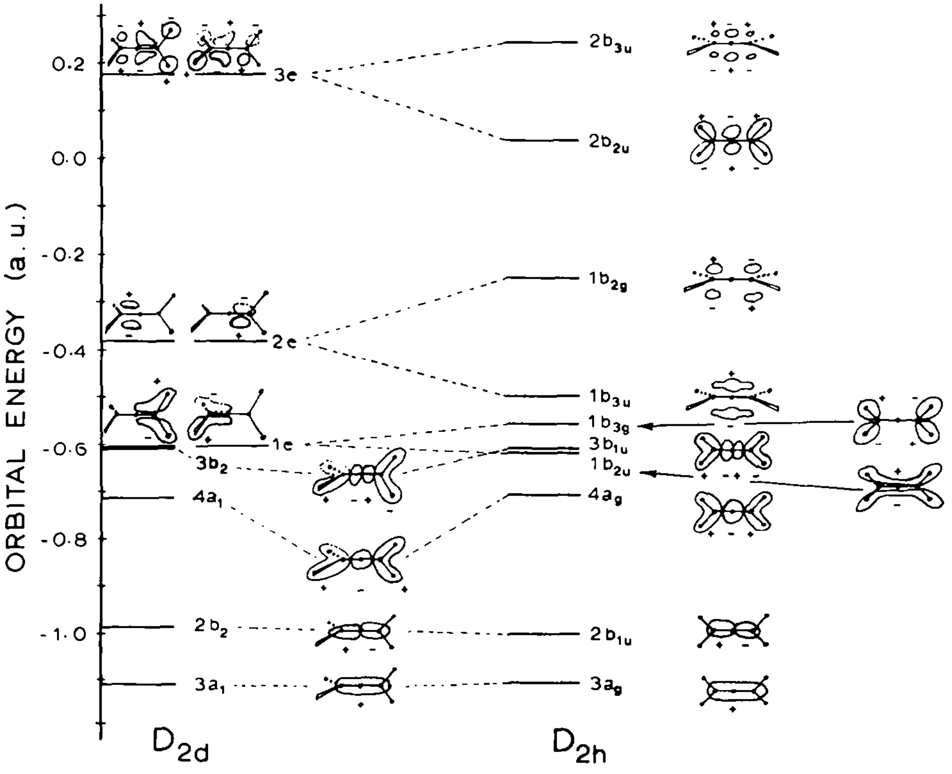

FIG 2. The valence orbitals of allene.

TABLE 1. GAUSSIAN BASIS ORBITALS USED

	Orbital exponents[a]
On each carbon atom:	
s orbitals	0·32, 1·6, 8·0, 40·0, 200
p_x, p_y, p_z orbitals	0·2469, 1·481
On each hydrogen atom:	
s orbitals	0·27, 1·8

[a] Taken from Ref 4

TABLE 2. ALLENE ORBITALS

D_{2d} (= normal) geometry		D_{2h} (= flattened) geometry	
orbital	energy (au)	orbital	energy (au)
$1a_1$	−11·3321	$1a_g$	−11·4363
$1b_2$	−11·3012	$1b_{1u}$	−11·2580
$2a_1$	−11·3003	$2a_g$	−11·2571
$3a_1$	− 1·1061	$3a_g$	− 1·1284
$3b_2$	− 0·9822	$2b_{1u}$	− 0·9912
$3a_1$	− 0·7124	$4a_g$	− 0·7045
$3b_2$	− 0·6067	$1b_{2u}$	− 0·6155
1e	− 0·6036	$3b_{1u}$	− 0·6082
2e	− 0·3728	$1b_{3g}$	− 0·5576
3e	+ 0·1863	$1b_{3u}$	− 0·4894
		$1b_{2g}$	− 0·2474
		$2b_{2u}$	+ 0·0459
		$2b_{3u}$	+ 0·2511

TABLE 3. ENERGY QUANTITIES FOR THE TWO FORMS OF ALLENE

	D_{2d} geometry (au)	D_{2h} geometry (au)	D_{2d}–D_{2h} (kcal/mole)
Electronic	−173·9599	−173·8467	71·0
Nuclear repulsion	59·1207	59·1234	1·9
Total	−114·8392	−114·7233	72·7
Orbital energy[a]	− 78·5876	− 78·5872	0·25

[a] Twice the sum over filled orbitals of the orbital energies

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