Lawrence Berkeley National Laboratory

Title
INTERNAL ROTATION IN THE GROUND ELECTRONIC STATE OF ALLENE

Permalink
https://escholarship.org/uc/item/9d33w0bm

Author
Dykstra, Clifford E.

Publication Date
1976-09-01

INTERNAL ROTATION IN THE GROUND
ELECTRONIC STATE OF ALLENE

Clifford E. Dykstra

September 1976

DISCLAIMER

INTERNAL ROTATION IN THE GROUND ELECTRONIC

STATE OF ALLENE*

Clifford E. Dykstra
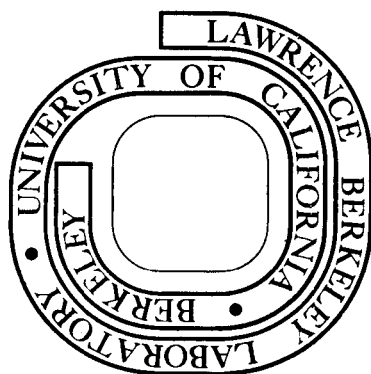
Department of Chemistry and Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

-1-

ABSTRACT

The internal rotation potential of allene has been studied with ab intio self-consistent field (SCF) methods using a double-zeta basis set of 38 contracted Gaussian functions and an extended set of 65 functions including polarization functions, and with the method self-consistent electron pairs (SCEP) using the double-zeta set. The ground state of allene is a closed shell $^1A_1$ state in D_{2d} symmetry. In the D_2 symmetry of the twisted form, this closed shell state mixes with a $2b_3 \to 3b_3$ open shell $^1A_1$ state which correlates with a ^1A_u state in the D_{2h} symmetry of the planar form of the molecule. The planar closed shell state, ^1A_g, is higher in energy than the ^1A_u state. Examination of pair correlation energies indicates that correlation effects will not reverse this order. The internal rotation barrier is predicted to be about 49 kcal, after geometry optimization, and there is little effect on relative energies from including polarization functions.

INTRODUCTION

Allene is the simplest molecule containing two carbon-carbon double bonds and like ethylene, the effects of internal rotation on electronic structure have been of theoretical interest. The lowest energy structure of the ground state of allene is with the two CH_2 groups in perpendicular planes. A detailed molecular orbital comparison of the planar ground state (D_{2h}) structure of ethylene and the out of plane (D_{2d}) structure of allene has been given by Buenker[1]. Experimental studies of allene include the UV spectrum taken by Sutcliffe and Walsh[2] who identified several Rydberg series at short wavelengths. Maki and Toth[3] used high resoltuion infrared spectra to determine the structure of allene: $R_{C=C} = 1.308$ Å, $R_{C-H} = 1.087$ Å and $\angle_{HCH} = 118.2°$.

There have been several ab initio theoretical studies of allene. The largest basis set allene calculation appears to be that of Hariharan and Pople[4] who showed that polarization functions were important in comparing energetics of C_3H_4 isomers. FSGO calculations include those of Talaty, Schwartz and Simons[5] who found a C=C length 0.03 Å longer than experiment and a rather large H-C-H angle of 126° in the non-planar structure. Weimann and Christoffersen[6] used FSGO to predict a barrier to rotation (to the planar ^1A_g state) of 75.1 kcal. Earlier calculations on a large number of molecules by Preuss and Janoschek[7] gave a 65 kcal difference between planar and non-planar closed shell states. A partial geometry optimization determined the C=C bond length to be 1.310 Å in the D_{2d} form, quite close to experiment, and 1.323 in the planar form. A geometry optimization of the D_{2d} form by Radom, Lathan, Hehre and Pople[8]

used a minimum STO-3G basis and gave the C=C length as 1.288 $\overset{o}{A}$ and the

bond angle as 116.2°. In another STO-3G study, by Radom and Pople,[9] a

separation of 92 kcal for the closed shell states was given from

calculations performed without optimization of the geometry.

Schaad, Burnelle and Dressler[10] studied the excited states of allene

in the D_{2d} and D_{2h} structures and confirmed Buenker's[1] result that the

lowest planar allene electronic state is a ^3A_u state ($1b_{2g} \to 2b_{2u}$) and

that the lowest singlet is a ^1A_u state arising from the same occupancy.

(The convention for distinguishing b_2 and b_3 symmetry species of the D_{2h}

point group used by Buenker and Schaad et al. is opposite that used here.)

Buenker[1] determined that the open shell singlet was about 6 kcal lower than

the closed shell singlet and estimated that the real difference could be

five times that. The separation between the ^3A_u and ^1A_u states was

estimated to be less than 0.1 ev (2.3 kcal). Furthermore, it was suggested

that the singlet might have a relative minimum in the planar form. The

SCF calculations of Schaad and coworkers[10] yield a smaller value for the

energy difference of the closed shell states, 3.15 ev (73 kcal), a

$^3A_u - ^1A_u$ separation of 0.09 ev and a very small separation for the ^1A_u

and ^1A_g states of 0.03 ev (0.7 kcal). The open shell energies were

calculated using the virtual orbitals from a closed shell calculation.

Correlated wavefunctions were not used in any of the studies.

The closeness of the two lowest planar singlet states of allene

determined in these two SCF calculations suggests that even small

correlation effects or the inclusion of polarization functions could

reverse the relative ordering of these states and change the nature of

the correspondence of the electronic states upon internal rotation (see

figure). Another potentially important effect not taken into account is

geometry optimization of the various states. This is especially
important since the likely planar ground state is an open shell state.
In recent SCF calculations on small carbonyl systems, including glyoxal,[11]
ketene[12] and acrolein,[13] we have found large energy changes upon geometry
optimization of certain low-lying open shell states and thus, this effect
should not be overlooked in studying allene.

THEORETICAL APPROACH

A double zeta (DZ) basis set of Dunning-contracted functions,[14,15] carbon (9s 5p / 4s 2p) and hydrogen (4s / 2s), was used in the (SCF) geometry optimization calculations and the SCEP calculations. In addition, SCF calculations were performed at the optimized geometries with a double-zeta plus polarization (DZ+P) basis of 115 primitives contracted to 65 functions. In this set, hydrogen p functions with an exponent of 1.0 and carbon d functions with an exponent of 0.75 were added as in a previous study of ketene.[12] The ground state occupancy was confirmed to be $1a_1^2 \, 1b_2^2 \, 2a_1^2 \, 3a_1^2 \, 2b_2^2 \, 4a_1^2 \, 3b_2^2 \, 1e^4 \, 2e^4$ in D_{2d} symmetry. In the D_{2h} planar form, the lowest closed shell occupancy is $1a_g^2 \, 1b_{1u}^2 \, 2a_g^2 \, 3a_g^2 \, 2b_{1u}^2 \, 4a_g^2 \, 3b_{1u}^2 \, 1b_{3u}^2 \, 1b_{2g}^2 \, 1b_{2u}^2 \, 1b_{3g}^2$ and in the intermediate D_2 structures is $1a_1^2 \, 2b_1^2 \, 2a_1^2 \, 3a_1^2 \, 2b_1^2 \, 4a_1^2 \, 3b_1^2 \, 1b_3^2 \, 1b_2^2 \, 2b_2^2 \, 2b_3^2$.

A complete geometry optimization was performed for the closed shell SCF wavefunctions at several internal rotation angles and for the two open shell planar states. The three structural parameters were optimized cyclically with simple parabolic fits used to determine the minimum for a given parameter and a few cycles through the three parameters were used.

Some consideration of correlation effects has been achieved using the recently introduced method of self-consistent electron pairs (SCEP)[16-17] due to Meyer. SCEP is an efficient method for obtaining correlated wavefunctions which include singly and doubly substituted configurations from a closed shell reference determinant. The calculations reported here are all variational fixed-ψ_o calculations[17] where the singly substituted configurations are included explicitly in the wavefunction after convergence

of the iterative treatment of the doubly substituted configurations. This neglects the very small effect of the singles on the doubles which is typically less than 0.1% of the correlation energy.[17] Conveniently obtained from an SCEP calculation are variationally additive pair correlation energies for each pair of electrons in the closed shell reference determinant. For each such pair, there is a doubly susbtituted function given directly in terms of basis functions which implicitly includes all double substitutions of the pair by virtual or external orbitals. Explicit manipulation of a configuration list and an explicit integrals transformation are avoided.

RESULTS AND DISCUSSION

The results of the geometry optimization of the closed shell states are given in Table I and it is seen that the calculated structure of the lowest energy D_{2d} form is quite close to the experimental structure.[3] Most of the changes in structure upon internal rotation are minor, though the carbon-carbon distance increases by 0.02 Å. The structures and energies for the D_2 intermediate forms may be somewhat different than those determined since a proper description of the wavefunction in this region should include at least two configurations. The energy difference between the closed shell $^1A_1$ (D_{2d}) and ^1A_g (D_{2h}) is about 70 kcal with the DZ basis which is close to the 73 kcal value obtained by Schaad et al.[10] Orbital energies obtained from the closed shell calculations at the optimized geometries are given in Table II. As Buenker[1] has explained, the removal of the 2e and 3e orbital degeneracy upon rotation produces a very low-lying virtual orbital, $2b_{3u}$, and an occupied orbital, $1b_{3g}$, higher in energy than in the out of plane form. Promotion of an electron from this highest filled occupied orbital to the low-lying virtual yields the ^1A_u and ^3A_u states.

As shown in Table III, the addition of polarization functions (DZ+P) changed the relative closed shell state energies very slightly. As seen in Table IV, the DZ and DZ+P sets yielded about the same relative energies for the planar open shell states as well. Some understanding of correlation effects can be obtained from the SCEP results in Table III. Including only single and double substitutions from the 2e orbital (D_{2d}) and the two D_{2h} orbitals which correlate with the 2e (see Table II), raises the energy of the ^1A_g relative to the $^1A_1$ by about 8 kcal. Comparison of pair correlation energies suggests that the two electrons in the planar $1b_{2u}$ orbital show less correlation than

electrons in the D_{2d} 2e orbital. The diagonal pair energies (i.e., pair energies with both electrons of the pair in the same internal orbital) for planar allene with 9 frozen orbitals are -0.0223 for $1b_{3g}^2$ and -0.0133 for $1b_{2u}^2$. A calculation with 10 frozen orbitals gave essentially the same pair energy for the $1b_{3g}$ electrons. The diagonal pair energies for orbitals which correlate with the D_{2d} 1e orbital, however, do not show as much difference. With 7 frozen orbitals, the additional correlation energy from these electrons is 0.0510 in D_{2d} and 0.0514 in D_{2h}. The effect of unfreezing additional orbitals on the relative energies of the closed shell states is likely to be small since contributions to the total energy from lower lying electrons will tend to be the same for both structures. For example, with 6 frozen orbitals, the D_{2d} $3b_2^2$ diagonal pair energy is -0.0045 while the D_{2h} $3b_{1u}^2$ diagonal pair energy is -0.0048 and the overall effect on relative energies is only 0.0014 au. It seems clear that correlation effects will raise the separation between the ^1A_g and $^1A_1$ by about 10% relative to the SCF determined difference and this results primarily from the unexpectedly small correlation contribution of the $1b_{2u}$ electrons.

The geometries of the open shell ^1A_u and ^3A_u states were optimized and the results are given in Table IV. Geometry optimization had only a small effect, less than 2 kcal, on the energy relative to the ^1A_g state; however, the bond length of the carbon-carbon bond was determined to be 0.03 Å longer than for the ^1A_g state. The energy difference between the D_{2d} ground state and the planar ^1A_u state is 0.0785 au or 49.3 kcal. Interestingly, the ^3A_u and ^1A_u are very close in energy, 0.0021 au with DZ basis and 0.0031 au with DZ+P basis. The fact that these energies are so close suggests little correlation energy for the $1b_{3g}$ $2b_{3u}$ pair. Thus, we can take as an estimate of the upper limit on the lowering of the $^1A_g - ^1A_u$ separation from correlation effects to be the

$1b_{3g}^2$ electrons' pair energy, -0.0223 au. But this energy is still less than the SCF determined separation energy of 0.0350 au (DZ) or 0.0276 au (DZ+P). Thus, it's clear that the planar open shell singlet, and not the closed shell state, correlates with the D_{2d} $^1A_1$ ground state. The SCF predicted internal rotation barrier ($^1A_u - {}^1A_1$ energy difference) is 49.3 kcal which is substantially lower than previous reported values. The maximum effect of correlation energy should be the change in the closed shell state energies from correlation plus the $1b_{3g}^2$ pair energy, which is used as the maximum $^1A_u - {}^1A_g$ correlation energy difference. From this analysis, we conclude that 1) the value for the barrier is about 49 kcal, though possibly as much as 70 kcal due to correlation, 2) the $^1A_u - {}^3A_u$ separation is, in fact, small, about 2 kcal, and 3) the ^1A_g is higher than both open shell states.

ACKNOWLEDGMENTS

-11-

REFERENCES

1. R. J. Buenker, J. Chem. Phys. <u>48</u>, 1368 (1968).

2. L. H. Sutcliffe and A. D. Walsh, J. Chem. Soc. (London) <u>1952</u>, 899.

3. A. G. Maki and R. A. Toth, J. Molec. Spectroscopy <u>17</u>, 136 (1965).

4. P. C. Hariharan and J. A. Pople, Chem. Phys. Letts. <u>16</u>, 217 (1972).

5. E. R. Talaty, A. K. Schwartz and G. Simons, J. Amer. Chem. Soc. <u>97</u>, 972 (1975).

6. L. J. Weimann and R. E. Christoffersen, J. Amer. Chem. Soc. <u>95</u>, 2074 (1973).

7. H. Preuss and R. Janoschek, J. Molec. Struct. <u>3</u>, 423 (1969).

8. L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, J. Amer. Chem. Soc. <u>93</u>, 5339 (1971).

9. L. Radom and J. A. Pople, J. Amer. Chem. Soc. <u>92</u>, 4786 (1970).

10. L. J. Schaad, L. A. Burnelle and K. P. Dressler, Theoret. Chim. Acta (Berlin) <u>15</u>, 91 (1969).

11. C. E. Dykstra and H. F. Schaefer, J. Amer. Chem. Soc. <u>98</u>, 401 (1976).

12. C. E. Dykstra and H. F. Schaefer, J. Amer. Chem. Soc. <u>98</u>, 2689 (1976).

13. C. E. Dykstra, J. Amer. Chem. Soc. <u>98</u>, 0000 (1976).

14. T. H. Dunning, J. Chem. Phys. <u>53</u>, 2823 (1970).

15. T. H. Dunning and P. J. Hay, in "Modern Theoretical Chemistry," ed. H. F. Schaefer (Plenum, New York, 1976).

16. W. Meyer, J. Chem. Phys. <u>64</u>, 2901 (1976).

17. C. E. Dykstra, H. F. Schaefer and W. Meyer, J. Chem. Phys. <u>65</u>, 0000 (1976).

Table I. Allene closed shell state optimized structures and energies.[a]

	$R_{C=C}$	R_{C-H}	$\angle^o_{HCH}$	Energy
90°	1.310	1.074	117.6	-115.8303
	(1.308)	(1.087)	(118.2)	
75°	1.310	1.075	117.6	-115.8267
55°	1.314	1.075	117.3	-115.8110
35°	1.319	1.076	117.0	-115.7836
15°	1.327	1.076	117.1	-115.7465
0° - planar	1.330	1.074	119.6	-115.7195

[a] Bond lengths are in angstroms and energies are in atomic units.
The basis set used in these calculations was the DZ set. Experimental
results[3] are in parentheses.

Table II. Allene SCF orbital energies (in a.u.) at optimum geometries.

	D_{2d} Symmetry		D_2 Symmetry					D_{2h} Symmetry	
		$90°$		$75°$	$55°$	$35°$	$15°$		$0°$ – planar
Improved virtuals (IVO's)	$5a_1$	0.2946	$5a_1$	0.2945	0.2940	0.2932	0.2919	$5a_g$	0.2854
	$4b_2$	0.2619	$4b_1$	0.2618	0.2618	0.2619	0.2627	$4b_{1u}$	0.2665
	$3e$	0.1596	$3b_2$	0.1758	0.1931	0.2036	0.2036	$2b_{2u}$	0.1842
			$3b_3$	0.1413	0.1145	0.0861	0.0569	$2b_{3u}$	0.0327
Occupied	$2e$	-0.3776	$2b_3$	-0.3588	-0.3328	-0.3063	-0.2797	$1b_{3g}$	-0.2567
			$2b_2$	-0.3955	-0.4178	-0.4384	-0.4603	$1b_{2u}$	-0.4979
	$1e$	-0.6141	$1b_2$	-0.6085	-0.6002	-0.5917	-0.5841	$1b_{2g}$	-0.5795
			$1b_3$	-0.6189	-0.6237	-0.6265	-0.6274	$1b_{3u}$	-0.6301
	$3b_2$	-0.6317	$3b_1$	-0.6319	-0.6326	-0.6338	-0.6352	$3b_{1u}$	-0.6353
	$4a_1$	-0.7193	$4a_1$	-0.7195	-0.7203	-0.7214	-0.7218	$4a_g$	-0.7161
	$2b_2$	-0.9667	$2b_1$	-0.9697	-0.9675	-0.9669	-0.9667	$2b_{1u}$	-0.9804
	$3a_1$	-1.0821	$3a_1$	-1.0872	-1.0832	-1.0822	-1.0821	$3a_g$	-1.1058

Table III. Correlation and basis set effects in allene closed shell states.

Calculation	$^1A_1$ Energy (au) 90°	^1A_g Energy (au) Planar	Difference (kcal)
SCF – DZ	-115.8303	-115.7195	69.5
SCF – DZ+P	-115.8834	-115.7750	68.0
SCEP – DZ; 9 frozen orbitals[a]	-115.8884	-115.7651	77.4
Pair energies[b] $2e_x^2$ -0.0243	$1b_{3g}^2$ -0.0223		
$2e_y^2$ -0.0243	$1b_{2u}^2$ -0.0133		
Sum of pair energies	-0.0573	-0.0450	7.7
SCEP – DZ; 7 frozen orbitals	-115.9394	-115.8165	77.1
SCEP – DZ; 6 frozen orbitals	-115.9739	-115.8524	76.2

[a] Orbitals were frozen with respect to substitution in the SCEP wavefunction on the basis of orbital energies. In the D_{2d} structure, the degenerate e orbitals have been counted as two orbitals for comparison with the D_{2h} wavefunction where no orbital is occupied by more than two electrons.

[b] The pair energies given are for pairs with both electrons in the same orbital. However, with 9 frozen orbitals there are a total of four electron pairs (see ref. 17).
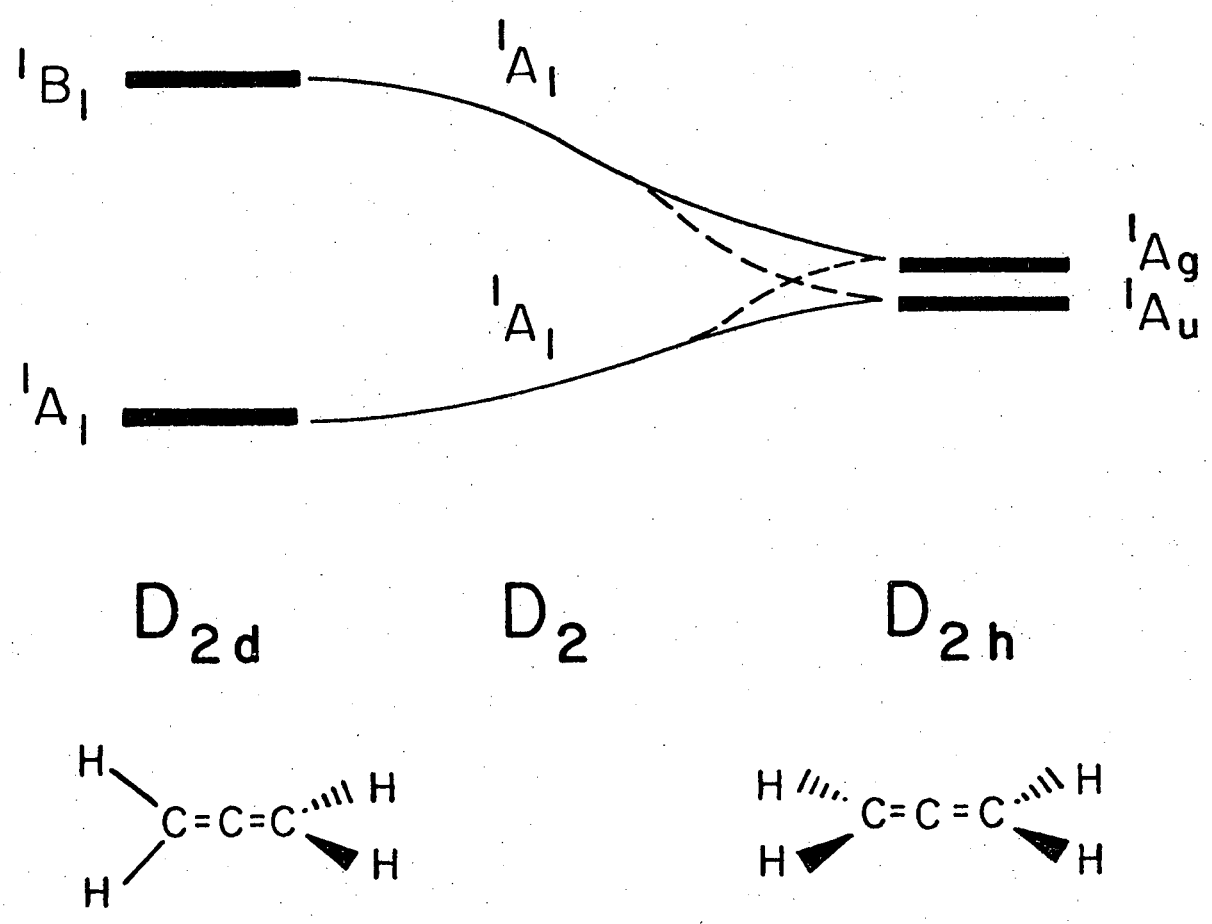
Table IV. Allene planar open shell states.[a]

	^3A_u $(1b_{3g} \rightarrow 2b_{3u})$	^1A_u $(1b_{3g} \rightarrow 2b_{3u})$
Energy at ^1A_g optimum geometry: DZ	-115.7539	-115.7518
DZ+P	-115.8057	-115.8026
Optimized structures:		
$R_{C=C}$	1.360	1.361
R_{C-H}	1.078	1.077
$\angle_{HCH}^{o}$	116.6	116.6
Energy (DZ)	-115.7566	-115.7545

[a] Results from SCF calculations with energies in atomic units and bond lengths in angstroms. The DZ basis was used for the optimization.

FIGURE CAPTION

Qualitative potential curves for the D_2 symmetry $^1A_1$ states which could correlate with the non-planar D_{2d} $^1A_1$ ground state. The avoided crossing is indicated by the broken lines.

$^1B_1$ ▬▬▬ $^1A_1$

$^1A_1$

^1A_g
^1A_u

$^1A_1$ ▬▬▬

D_{2d} D_2 D_{2h}

$$\begin{array}{c} H \\ \diagdown \\ C=C=C \\ \diagup \\ H \end{array} \begin{array}{c} H \\ \diagup \\ \diagdown \\ H \end{array}$$

$$\begin{array}{c} H \\ \diagdown \\ C=C=C \\ \diagup \\ H \end{array} \begin{array}{c} H \\ \diagup \\ \diagdown \\ H \end{array}$$

XBL767-3191

Fig. 1