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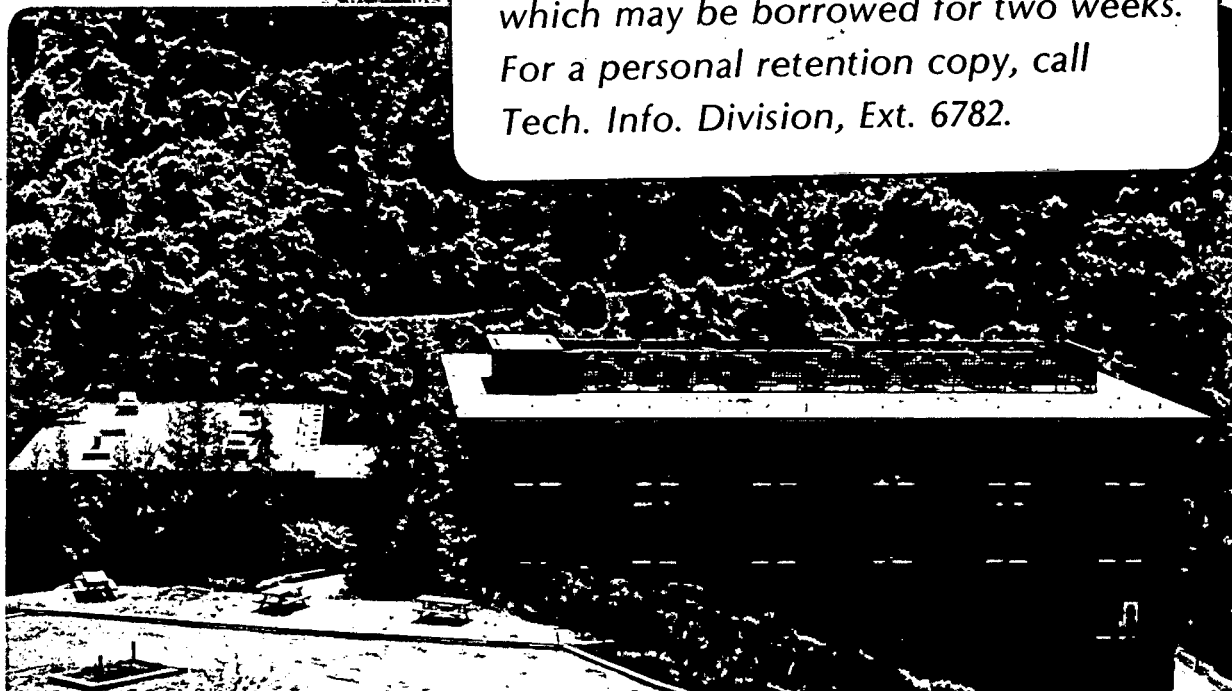
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Electronic Symmetry Breaking in Polyatomic Molecules.
Multiconfiguration Self-Consistent-Field Study
of the Cyclopropenyl Radical, C_3H_3 .

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Abstract

For equilateral triangle geometries (point group D_{3h}), the C_3H_3 radical has a degenerate ${}^2E''$ electronic ground state. Although the 2A_2 and 2B_1 components separate in energy for C_{2v} geometries, these two components should have identical energies for equilateral triangle structures. In fact, when approximate wave functions are used and the orbitals not required to transform according to the D_{3h} irreducible representations, an energy separation between the 2A_2 and 2B_1 components is observed. At the single configuration self-consistent-field (SCF) level of theory this separation is 2.8 kcal with a double zeta basis set and 2.4 kcal with double zeta plus polarization.

It has been demonstrated that this spurious separation may be greatly reduced using multiconfiguration self-consistent-field (up to 7474 variationally optimum configurations) and configuration

interaction (up to 60,685 space and spin adapted configurations) techniques. Configurations differing by three and four electrons from the Hartree-Fock reference function are found necessary to reduce the ${}^2A_2-{}^2B_1$ separation to below 0.5 kcal.

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Introduction

The cyclopropenyl radical C_3H_3 has received much attention because it is a simple example of a molecule that is expected to undergo a Jahn-Teller distortion.¹⁻⁸ If an electron is added to the lowest unoccupied molecular orbital (LUMO) of the D_{3h} ground state of the cyclopropenyl cation it will enter a degenerate e'' orbital to form the lowest ${}^2E''$ state of the radical. According to the Jahn-Teller Theorem¹⁰ a non-linear molecule of E symmetry will spontaneously distort in such a way as to lift the degeneracy. In the case of the C_3H_3 radical this distortion will lower the symmetry to C_{2v} or possibly C_s or C_2 . If the true wavefunction within the Born-Oppenheimer approximation were known at the D_{3h} and surrounding geometries it would be easy to find out what the "real" equilibrium structure looks like. However, when this exact wavefunction is not known, certain complications arise. If a full configuration interaction (CI) within a given basis set could be computed at any D_{3h} geometry it would lead to a wavefunction having D_{3h} symmetry whether Ψ was forced to be of this symmetry or not. However, for theoretical treatments carried out below the full CI level, the wavefunction symmetry may break (i.e., belong to a point group of lower symmetry) unless the correct symmetry is forced by the method. Just such a situation arises for the C_3H_3 radical.¹⁻⁸

In the case of the cyclopropenyl radical, if self-consistent-field (SCF) or truncated CI or multiconfiguration (MC) SCF theory is applied at a D_{3h} geometry, the resulting wavefunctions will be

at best of C_{2v} symmetry unless otherwise constrained.¹¹ The $^2E''$ state corresponds to a pair of states in the lower C_{2v} point group: 2A_2 and 2B_1 , which should physically be degenerate in energy at the D_{3h} geometry. However, if the calculations are carried out in C_{2v} symmetry (i.e., the wavefunctions not constrained to transform according to the irreducible representation E''), the energies of the two states will be different. The purpose of this research is to study the effects of using different CI expansions and orbital basis sets on the 2B_1 - 2A_2 energy splitting. Since Nature requires this splitting to be identically zero, the values obtained at various levels of theory provide a practical lower limit to the sort of errors one should expect in energy differences (i.e., electronic excitation energies) for moderate-sized organic systems such as C_3H_3 .

Theoretical Approach

In the present study of the cyclopropenyl radical we employed the standard Huzinaga-Dunning^{12,13} contracted Gaussian double-zeta (DZ) basis set, the precise designation of which is C(9s5p/4s2p) and H(4s/2s). All calculations were performed at a single D_{3h} geometry with the three C-C bond distances fixed at 1.40 Å and the C-H bond lengths set at 1.08 Å, as seen in the Figure. The exact cartesian geometry used was (0.0, 0.0, 0.0), (0.0, ±1.322826, -2.291202) for the three carbon atoms and (0.0, 0.0, 2.040932), (0.0, ±3.090325, -3.311668) for the three hydrogen atoms. Since the geometry was not optimized in this

study and our primary purpose was to determine the 2B_1 - 2A_2 energy splitting at a representative D_{3h} geometry, we deemed a DZ basis set to be adequate. Subsequent studies (see below) with a larger basis set confirmed our intuition that the double zeta basis set is indeed large enough to avoid misleading results with respect to the C_3H_3 symmetry breaking problem. Note in this vein that the geometry selected does not correspond to the minimum on the D_{3h} surface for this basis set, but was picked because it is in the range of previous theoretical work.¹⁻⁸

To determine how the spurious electronic splitting (at the chosen D_{3h} geometry) varies as the level of theory is changed, a series of variational wavefunctions were determined for the lowest 2B_1 and 2A_2 states of C_3H_3 . All of these calculations were done in C_{2v} symmetry (i.e., the molecular orbitals were constrained to transform according to the C_{2v} irreducible representations, and the total wavefunctions constrained to transform according to B_1 or A_2 symmetry species) at the D_{3h} geometry. Initially single configuration self-consistent-field (SCF) calculations were performed on these two states with the 2B_1 and 2A_2 reference configurations being

$$\Phi_1({}^2B_1) = \dots 5a_1^2 3b_2^2 1b_1^2 6a_1^2 2b_1 \quad (1)$$

$$\Phi_1({}^2A_2) = \dots 5a_1^2 3b_2^2 1b_1^2 6a_1^2 1a_2 \quad (2)$$

Beyond the SCF level a number of CI and MCSCF treatments were

pursued. First a set of three single and double excitation CI wavefunctions were computed for each state. In the largest, involving 11,829 and 11,800 configurations for the 2B_1 and 2A_2 states respectively, all orbitals were included in the CI. In the second the 18 orbitals with the highest orbital energies were forced to have zero occupancy in the CI (in other words, one half of the orbitals of each symmetry type were frozen) reducing the number of configurations to 1069 for either state. In the third CI the three lowest occupied SCF orbitals (in an energetic sense) were frozen in addition, resulting in 549 configurations in both the 2B_1 and 2A_2 cases. These three calculations will be abbreviated as CIALL, CIMIN and CI549. In this last CI the orbitals are partitioned such that there are 18 of the virtual, 3 of the core and 15 of the active varieties. Such a small CI limits excitations to within the valence space. The concept of the valence space is easy to visualize if one envisions the C-C and C-H bond lengths being stretched to infinity. When this happens the set of 15 active orbitals reduces to the 2s and 2p shells on the carbon atoms and the 1s orbitals on the hydrogens.

In addition to these three types of configuration interaction, a number of further calculations were performed within the valence space on both the 2A_2 and 2B_1 states. The first of these involves an MCSCF optimization within the same 549 configuration space defined above and is called MC549. To investigate the effect of higher than double excitations in this subspace on the 2B_1 - 2A_2 splitting, four further sets of calculations were carried out.

Initially standard CIs (using the canonical SCF orbitals) with configuration set composed of the reference plus all single, double and triple excitations within the valence space were performed. This increased the number of configurations to 7470 or 7474 for the 2A_2 or 2B_1 states, respectively. These were followed by MCSCF calculations employing the same configuration list to ascertain the effect of optimizing the orbitals. These two theoretical procedures will be labeled CISDT and MCSDT. Single, double, triple and quadruple excitation (SDTQ) CI using the SCF orbitals were next performed and will be identified as CISDTQ. To estimate the energetic effect of optimizing the orbitals for the SDTQ configuration set, CIs employing the MC549 (instead of single configuration SCF) orbitals were carried out. Henceforth the latter level of theory will be designated MCSD+TQ. The SDTQ CIs were relatively large, containing 60645 and 60685 configurations for the 2A_2 and 2B_1 states, respectively.

Thus far this investigation has concerned itself only with changes in the 2B_1 - 2A_2 splitting as a function of the orbital type or the configuration set employed in CI calculations. Another important factor to consider is the effect of basis set size on the energy difference. To investigate this aspect of the problem, polarization functions were added to both the carbon and hydrogen basis sets. For carbon a set of gaussian d functions was added with exponents $\alpha = 0.75$. For hydrogen a set of gaussian p functions was added with exponents $\alpha = 1.0$. This more complete basis set will be designated DZ+P and was employed only at the SCF level of theory.

All the research described above was carried out using the system of unitary group CI and MCSCF programs described in references 14-19 and was performed on a Harris Series 800 minicomputer.

Results and Discussion

In Table I the total energies for the levels of theory specified in the preceding section are presented. First, the DZ SCF results are examined. For the 2A_2 state a total energy of -115.104667 hartrees was obtained and for the corresponding 2B_1 state a lower energy of -115.109144 hartrees was found. This leads to a splitting of 0.004477 hartrees or 2.81 kcal/mole. This difference is of the same order as the minimum basis SCF results of Davidson and Borden⁷ in which a value of around 5 kcal/mole was reported. Poppinger, Radom and Vincent⁸ (PRV) also published SCF 2B_1 - 2A_2 splittings for both the minimum and the split valence 4-31G basis sets, for which they obtained 4.79 and 3.23 kcal/mole respectively.

The spurious separation between 2A_2 and 2B_1 electronic states was next considered with the larger DZ+P basis set. For the 2A_2 and 2B_1 states DZ+PSCF energies of -115.174127 and -115.178000 hartrees were obtained respectively. The 2B_1 - 2A_2 splitting is thus 0.003873 hartrees or 2.43 kcal/mole, or approximately 0.4 kcal below the corresponding DZ value. This leads to the following basis set trend, $\Delta E_{MB} > \Delta E_{4-31G} > \Delta E_{DZ} > \Delta E_{DZ+P}$ where ΔE is the 2B_1 - 2A_2 energy splitting and MB stands for minimum basis set. Since the MB results of Davidson and Borden⁷

and the MB and 4-31G results of Poppinger, Radom and Vincent were carried out at geometries different from ours, their values for ΔE will be slightly different from values calculated at our geometry. However, the geometry differences are very small and it seems likely that qualitative trend will remain the same. Thus, while improvement of the basis set does reduce the artificial energy difference between the two degenerate components of the ${}^2E''$ state of C_3H_3 , the effect nevertheless persists.

Moving on to the straight CI results, the energies of the 2B_1 and 2A_2 states are found to be -115.389963 and -115.387954 hartrees, respectively, in the all orbital single and double excitation CI treatment. These calculations which involve nearly 12,000 configurations reduce the splitting to 0.002009 hartrees or 1.26 kcal/mole. This energy difference is less than half the comparable SCF value. If the 18 highest reference unoccupied orbitals are now frozen in the single and doubles CI the corresponding 2B_1 and 2A_2 energies are -115.165587 and -115.167098 hartrees. This leads to a splitting of -0.001512 hartrees or -0.95 kcal/mole, where the minus sign indicates that the ordering of the two states has changed. This state reversal is most likely due to the choice of the frozen orbitals in the CI. If all the molecular orbitals unoccupied in the reference configuration (1) or (2) are kept in the CI, the energy is invariant to unitary transformations within this orbital subset. However, if any of these orbitals are frozen, the energy is no longer invariant in this respect. From the SCF point of view, however, the unoccupied orbitals are only required to be orthogonal to the occupied space

and amongst themselves and are thus rather arbitrary, particularly so when compared to MCSCF or natural orbitals.²⁰ A likely explanation of this sign reversal is that by chance the set of 2A_2 unoccupied orbitals retained in the CI were energetically more favorable (with respect to the correlation energy) than the corresponding 2B_2 orbitals. If, in addition to the 18 virtual orbitals, 3 core orbitals are frozen the single and doubles CI energies are found to be -115.165484 and -115.166984 hartrees for the 2B_1 and 2A_1 states. Here one notices that the ordering of the states is again reversed, with the splitting being -0.001510 hartrees or -0.94 kcal/mole. This result confirms the view that core electron correlation effects are of little importance in the theoretical prediction of valence properties, such as the energy difference between a pair of low-lying electronic states.

Continuing to the first of the MCSCF results the 2B_1 - 2A_2 energy gap is found to be +0.001336 hartrees for the valence space singles and doubles MCSCF (MC549). This 0.84 kcal/mole difference is roughly 2/3 of the analogous CIALL splitting (1.26 kcal/mole), but the CI contains only about 1/20 of the number of configurations. This result is encouraging since MCSCF calculations of this variety can be performed on nearly all systems that can be handled using SCF theory alone.¹⁷ In terms of absolute energies, -115.290106 and -115.288770 hartrees were obtained for the 2B_1 and 2A_2 states respectively. These results are perhaps surprising in that the small 549 configuration MCSCF calculations recovered around 65% of the full CI singles

plus doubles correlation energy while the CIs using SCF orbitals in the same formal valence space recovered about 20%. Optimizing the orbitals then leads to roughly 3 times as much correlation energy and the "correct" (by comparison with more complete levels of theory) prediction of the state ordering.

Four additional sets of calculations were carried out within the valence space to test the effect of inclusion of higher than double excitations. The first two of these employed a configuration set consisting of all valence single, double and triple excitations. The total energies for the straight CISDT computations are -115.166563 and -115.168311 hartrees for the 2B_1 and 2A_1 states, respectively, which leads to a splitting of -0.001748 hartrees or -1.10 kcal/mole. The ordering of the two states is again inverted as in the CIMIN and CI549 cases with the gap now larger by roughly 0.15 kcal. This result is at first glance surprising since the CISDT calculation is much more extensive than either of the CIMIN or CI549 calculations. On closer examination, however, since the 2A_2 state is above the 2B_1 state in the SCF approximation, one would expect that as the size of the CI increases so will the ratio of the 2A_2 and 2B_1 correlation energies.

The second level of theory attained using the all valence single, double and triple configuration set was MCSDT. Since the orbitals used in these MCSCF wavefunctions are optimal and the configuration lists increased, it is not surprising that the results represent an improvement with respect to the earlier

discussed MCSD (or MC549) treatment. As with the CIALL and MCSD levels of theory, MCSDT predicts the 2B_1 electronic state to lie slightly below the 2A_2 . This separation is reduced from 0.84 kcal in MCSD to 0.70 kcal in MCSDT. An error of this magnitude is now compatible with the elusive goal of "chemical accuracy", typically designated as one kcal/mole.

Straight configuration interaction employing all valence single, double, triple and quadruple excitations for both the two states of cyclopropenyl radical were next carried out. As in the other three CIs with 18 frozen SCF virtual orbitals, CISDTQ predicts the 2A_2 state to lie below the 2B_1 state. This time an energy splitting of -0.002207 hartrees or -1.38 kcal/mole is found. What these four theoretical treatments (CIMIN, CI549, CISDT and CISDTQ) demonstrate is that when the CI expansion is restricted to the minimum basis or valence space, it is necessary to optimize the orbitals if properties such as the 2A_2 2B_1 energy ordering are to be correctly predicted. Inclusion of a very large number of configurations does not in such cases compensate for the poor choice of a small virtual orbital space.

Lastly the MCSD+TQ calculations were carried out. For the 2A_1 and 2B_2 states energies of -115.309306 and -115.309002 hartrees were computed, respectively. This leads to a 2B_1 2A_2 energy splitting of just 0.000304 hartrees or -0.19 kcal/mole. This difference is by far the smallest obtained, being less than one-third of the MCSDT result of 0.70 kcal/mole. The magnitude of the splitting suggests (but by no means proves) that the MC549

orbitals employed in this calculation were nearly optimal. Comparing the 2A_2 and 2B_1 MCSD+TQ and MC549 energies energy lowerings of 0.0205 and 0.0189 hartrees are found respectively. The same differences between the MCSDT and MC549 calculations are 0.0026 and 0.0024 hartrees for the 2A_2 and 2B_1 states respectively, or almost an order of magnitude less. This suggests that triple excitations are considerably less important than quadruple excitations in valence subspace CIs employing optimized or nearly optimized orbitals. This finding tends to differ from previous results on the importance of triple and quadruple excitations in MCSCF calculations in the water molecule.¹⁹ In that study triple excitations could be made more important (via the MCSCF procedure) than quadruple excitations. Such a contrast may be due to the restriction of the CI to only the valence orbital space in this investigation or it may be related to the fact that the SCF reference is a poorer zeroth order wavefunction for cyclopropenyl radical than for water. (This can be seen by comparing the first few CI coefficients in a CI singles and doubles calculation).

In addition to the variational results, if CIALL is corrected for the effects of unlinked clusters using the Davidson's correction²¹ a splitting of 0.55 kcal/mole is obtained. This result is less than one-half of the straight CIALL difference and maintains the "correct" ordering of the two states. This seems to suggest the validity of employing this correction to all singles and doubles CI energies.

Before closing this section certain features of the CI and MCSCF wave functions should be discussed. In the course of this study it was discovered that even though cyclopropenyl radical is adequately described by one reference, two additional configurations for each of the 2A_2 and 2B_1 states are moderately important also. For the 2A_2 state these configurations are

$$\phi_2({}^2A_2) = \dots 5a_1^2 3b_2^2 1b_1 6a_1^2 2b_1 1a_2 \quad (1b_1 + 2b_1) \quad (3)$$

$$\phi_3({}^2A_2) = \dots 5a_1^2 3b_2^2 1b_1^0 6a_1^2 2b_1^2 1a_2 \quad (1b_1^2 + 2b_1^2) \quad (4)$$

while for the 2B_1 state the other two important configurations are

$$\phi_2({}^2B_1) = \dots 5a_1^2 3b_2^2 1b_1^0 6a_1^2 2b_1 1a_2^2 \quad (1b_1^2 + 1a_2^2) \quad (5)$$

$$\phi_3({}^2B_1) = \dots 5a_1^2 3b_2^2 1b_1 6a_1^2 1a_2^2 \quad (1b_1 2b_1 + 1a_2^2) \quad (6)$$

The values of the coefficients of these configurations plus those of the SCF references are compiled in Table II.

In all the CI and MCSCF wavefunctions except MCSD+TQ the principal coefficients were roughly 0.95, while the absolute values of the other two coefficients are between 0.06 and 0.17 in every case. In the four calculations involving frozen SCF virtual orbitals and in MCSD+TQ, the values of C_2 are somewhat higher (~ 0.15 for 2A_2 and ~ 0.12 for 2B_1)

than in the remaining wave functions. Also C_3 for the 2B_1 state is larger (roughly 0.10) compared to the MCSCF values of around 0.08. The two MCSCFs (MC549 and MCSDT) are quite similar in this regard, though the importance of single excitations in the former is far greater. The MCSCF results differ somewhat, however, from MCSD+TQ, which is very similar to the CIs involving the SCF virtual orbitals except that C_1 for MCSD+TQ is much smaller, being 0.932 and 0.939 in the 2A_2 and 2B_1 cases. The magnitude of C_1 for MCSD+TQ implies that the MC549 orbitals are a reasonable choice for use in the SDTQ CI expansion and also that the quadruple excitations are relatively important. This can be seen by comparing C_1 for the MC549, MCSDT and MCSD + TQ theoretical treatments.

Concluding Remarks

For the cyclopropenyl radical it was found at a representative D_{3h} geometry an artificial energy splitting of nearly 3 kcal/mole exists for the truly degenerate 2A_2 and 2B_1 states at the SCF level of theory. This energy gap can be substantially lessened if subsequent CI calculations are performed. In the case of all single and double excitation CIs the splitting is reduced by over 50%. If these two energies are corrected for unlinked cluster effects²¹ the 2A_2 - 2B_1 difference is only 0.55 kcal/mole.

Significantly improved results are also obtained for valence space MCSCF calculations. In the MCSCF employing all valence single and double excitations, the spurious splitting is roughly

two thirds of the CISD result and only about 1/20 of the number of configurations are needed. If triple excitations are added the gap is reduced still more to around 0.70 kcal/mole. The best results were obtained if the MCSCF orbitals obtained in the valence space singles and doubles procedure are used in a valence space singles, doubles, triples, and quadruples CI. In this case the 2A_2 - 2B_1 splitting is found to be only 0.19 kcal/mole which is nearly 4 times smaller than the MCSDT value.

The value of this research lies in the provision of guidelines for the prediction of electronic energy differences. The errors found here at various levels of theory refer to, in essence, a model problem for which the exact answer is known. Of course one should not take these results too literally, assuming for example that all Davidson corrected CISD excitation energies will lie within 0.55 kcal of the full CI result for the chosen basis set. But it probably is fair to conclude that when relative energy predictions to within less than 0.5 kcal are required, an explicit treatment of triple and quadruple excitations will be necessary.

The present study may be considered preliminary to a definitive theoretical examination of the equilibrium geometries (not D_{3h} , of course) and actual energy separation between the 2A_2 and 2B_1 electronic states of C_3H_3 . As long as an inherent error of 2-5 kcal in the D_{3h} energy difference persists (as is found at the SCF level of theory), then one is deprived of real

confidence in the predicted adiabatic separation: the energy difference between the 2A_2 state at its C_{2v} equilibrium geometry and the 2B_1 state at its equilibrium geometry. The same uncertainty clouds the prediction of the barrier in the three-fold degenerate C_3H_3 potential surface, an important question recently explored experimentally by Closs and co-workers.⁹ However, the MCSCF and CI techniques explored here for the model C_3H_3 problem should provide quite reasonable predictions for both of these important problems.

Acknowledgments

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Figure Caption

Assumed geometrical structure of the cyclopropenyl radical,

C_3H_3 . Bond distances are in Å.

Table I. Summary of energetic results for the cyclopropenyl radical, C_3H_3

Theoretical Method	A_2 Symmetry		B_1 Symmetry		Energy Difference $E(A_2)-E(B_1)$	
	No. of Configurations	Total Energy (hartrees)	No. of Configurations	Total Energy (hartrees)	hartrees	kcal/mole
SCF-DZ	1	-115.104667	1	-115.109144	+0.004477	2.81
SCF-DZ+P	1	-115.174127	1	-115.178000	+0.003873	2.43
CI-all orbitals-SD ^a	11800	-115.387954	11829	-115.389963	+0.002009	1.26
CI-all orbitals-SD plus Davidson's Correction	11800	-115.417994	11829	-115.418878	+0.000884	0.55
CI-18 virtual-SD	1069	-115.167098	1069	-115.165587	-0.001512	-0.95
CI-18 virtual-SD 3 core frozen	549	-115.166984	549	-115.165484	-0.001510	-0.94
MCSCF-18 virtual-SD 3 core frozen	549	-115.288770	549	-115.290106	+0.001336	0.84
CI-18 virtual-SDT	7470	-115.168311	7474	-115.166563	-0.001748	-1.10
MCSCF-18 virtual-SDT	7470	-115.2914	7474	-115.29252	+0.0011	-0.70
CI-18 virtual-SDTQ SCF orbitals	60645	-115.170483	60685	-115.168276	-0.002207	-1.38
CI-18 virtual-SDTQ MC549 orbitals	60645	-115.309306	60685	-115.309002	-0.000304	-0.19

-20-

^aSymbols S, D, T, and Q represent all single, double, triple and quadruple configurations, respectively.

Table II. Tabulated coefficients for the three most important 2B_1 and 2A_2 configurations appearing in the 549 configuration MCSCF wave functions.

	<u>SCF</u>	<u>CIALL</u>	<u>CIMIN</u>	<u>CI549</u>	<u>MC549</u>	<u>CISDT</u>	<u>MCSDT</u>	<u>CISDTQ</u>	<u>MCSD+TQ</u>
2A_2 C ₁	1.0000	0.945	0.967	0.967	0.950	0.965	0.947	0.962	0.932
C ₂		0.087	-0.152	-0.152	-0.124	-0.156	-0.128	-0.164	-0.158
C ₃		-0.070	-0.105	-0.105	-0.099	-0.106	-0.100	-0.109	-0.115
2B_1 C ₁	1.0000	0.947	0.973	0.973	0.953	0.972	0.951	0.969	0.939
C ₂		0.080	-0.120	-0.120	-0.111	-0.121	-0.112	-0.125	-0.129
C ₃		0.058	-0.101	-0.101	0.078	0.104	0.083	0.110	0.099

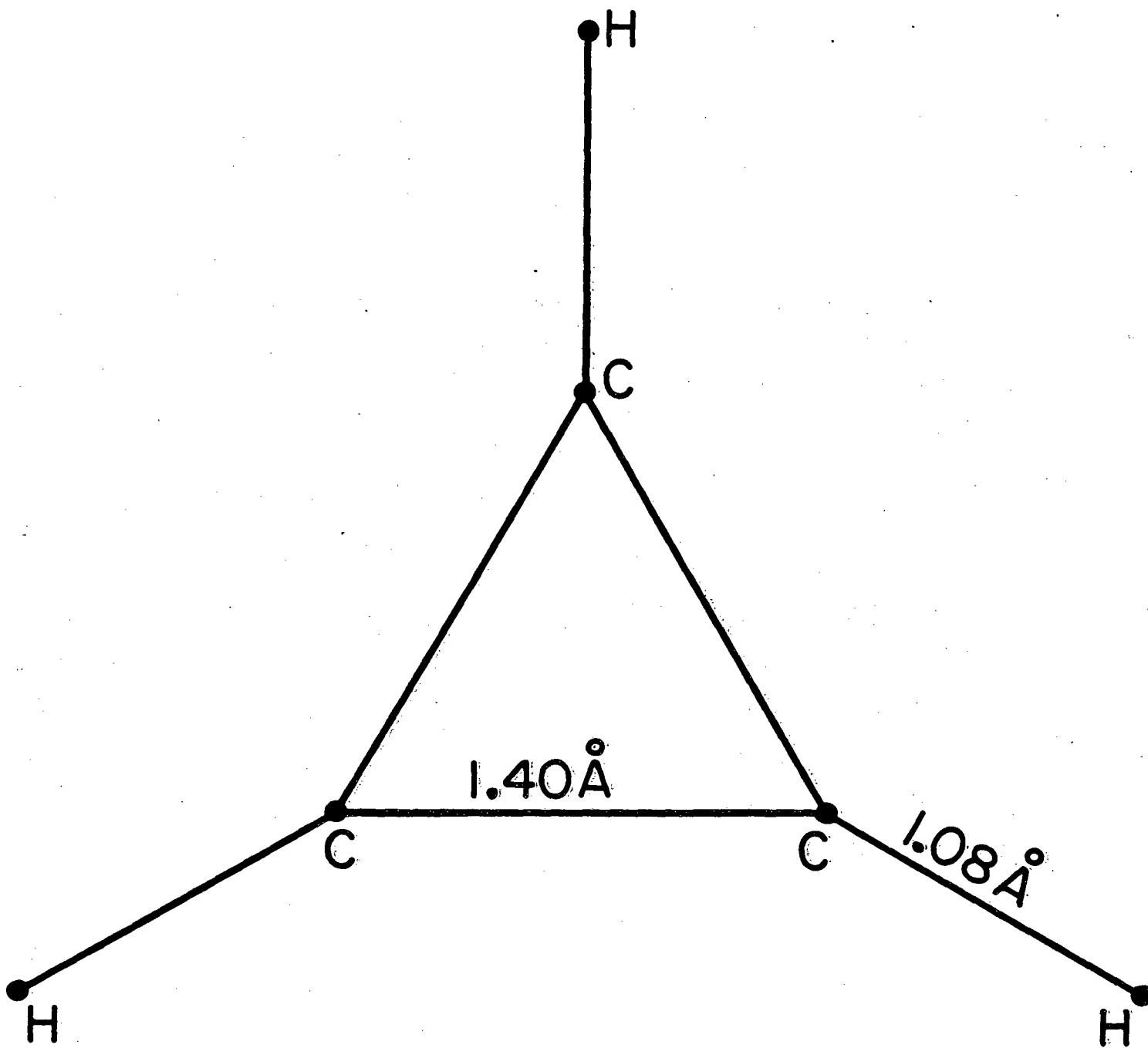


Figure 1

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