reduction it was necessary to assume the presence of three species. By systematically varying the mole fractions it is possible to first obtain the ORD curve of the monoanion and then the di- and trianion. The electronic absorption spectra of the anions of hexahelicene show very broad bands in the visible range that are insensitive to the change in relative concentrations. Consequently, they were of little use in following the progress in reduction or correlating with the rotations in the ORD curves.

In the visible region the spectrum of only the monoanion is given (Figure 2). The spectra of the dianion and trianion in the visible were so lacking in structure that we were unable to disentangle them from each other.

Both mono- and trianion are paramagnetic; their esr spectra are shown in Figure 3. The analysis of the esr spectrum of the monoanion has recently been reported.[5] The trianion spectrum has not yet been analyzed; however, it is obvious that the spin density distributions in the two ions are drastically different.

The intensity of the esr spectrum of the monoanion first increases as reduction proceeds and then decreases; in the final stages of reduction the intensity of the trianion spectrum reaches a maximum. The integrated intensity of a completely reduced solution is equal to the intensity of the monoanion spectrum at the stage of reduction at which it is maximum (Figure 4). Attempts to find triplet spectra in rigid media or broad spectra in fluid solution of the dianion failed, presumably because it is diamagnetic.

Acknowledgments. We wish to thank Professor M. S. Newman for generous samples of the racemic and optically active hexahelicene used in these experiments. The work has been supported by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund of the American Chemical Society.

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(5) R. D. Allendoerfer and R. Chang, *J. Magn. Resonance*, 5, 273 (1971).

Ring Opening of Cyclopropanone

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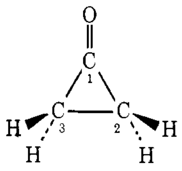
Abstract: We report the results of INDO and *ab initio* SCF calculations on cyclopropanone, oxyallyl, and allene oxide, and the con- and disrotatory openings of the closed ketone. The *ab initio* results indicate that singlet oxyallyl is 83 kcal/mol less stable than cyclopropanone, while allene oxide is 21 kcal/mol less stable. The internal $C_3C_1C_2$ angle in singlet oxyallyl is predicted to be near 105°. Although the conrotatory opening of cyclopropanone passes through a true transition state, the disrotatory opening is the lower energy pathway, and oxyallyl appears to be at, or near, the disrotatory energy maximum.

Cyclopropanone is one of the more interesting molecules in organic chemistry and much effort has gone into studying its behavior and that of its derivatives.[1-4] The parent molecule has recently been prepared[5,6] and its microwave spectrum studied.[7,8] While there is little doubt that the molecule exists, much of its chemistry is difficult to explain in terms of the conventional structure **1**, and it has been postulated that it may isomerize to oxyallyl (**2**) or allene oxide (**3**).[1,2,9] This appears to be a problem that molecular quantum chemistry can handle, and several semiempirical theoretical calculations have been reported.

Extended Hückel calculations by Hoffmann indicate that **2** is the most stable, being 23 kcal/mol more stable than **1**, and 21 kcal/mol more stable than **3**.[10] The disrotatory opening of **1** is preferred, and **2**, once formed, is reported to have an internal angle α equal to 121°.



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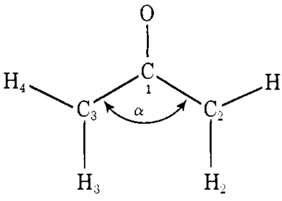

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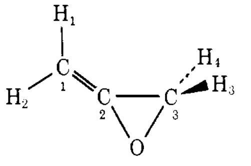

3

More recently, Bodor, Dewar, Harget, and Haselbach[11] have performed MINDO/2 calculations. Their

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(1) N. J. Turro, *Accounts Chem. Res.*, 2, 25 (1969).

(2) N. J. Turro, R. B. Gagosian, S. E. Edelson, T. R. Darling, J. R. Williams, and W. B. Hammond, *Trans. N. Y. Acad. Sci.*, 33, 396 (1971).

(3) D. G. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *J. Amer. Chem. Soc.*, 92, 7488 (1970).

(4) A. S. Kende, *Org. React.*, 11, 261 (1960).

(5) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, 88, 3672 (1966).

(6) S. E. Schaafsma, H. Steinberg, and T. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, 85, 1170 (1966).

(7) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, 91, 1896 (1969).

(8) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *ibid.*, 90, 1072 (1968).

(9) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

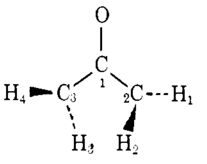
(10) R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968).

(11) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, 92, 3854 (1970).

results indicate that **1** is more stable than **2** by 78 kcal/mol; they do not mention the internal angle.

The most extensive investigation has been made by Olsen, Kang, and Burnelle[12] who, using the INDO method,[13,14] studied singlet and triplet states and points on the disrotatory energy surface.[15] They found that singlet **2** is approximately 220 kcal/mol less stable than **1**. They also searched for the best value of α and report a minimum at $\alpha = 90°$.

Our investigation calculates the energies of **1**, **2**, and **3**, as well as con- and disrotatory geometries, **4** and **5**, respectively, along the reaction coordinates.



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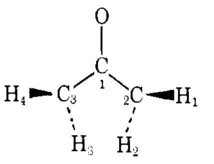

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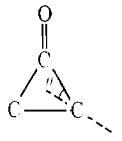
Geometries

The experimental geometry of Pochan, Baldwin, and Flygare[7] was used for cyclopropanone. The data are reported in Table I; values are in ångströms.

Table I. Bond Distances and Bond Angles in Cyclopropanone[7]

Bond distances, Å		Bond angles, deg	
C_1–O	1.200	H–C–H	114.13
C_1–C_2, C_1–C_3	1.475	C_3–C_1–C_2	64.60
C_2–C_3	1.575	C_1–C_2–C_3	57.70
C–H	1.086	C_1–C_2–H	118.43

One point that is seen to be important later in the paper is also worth mentioning at this time. In cyclopropanone, the local C_2 axis of a methylene group makes an angle θ of 28.58° with the C_1–C_2 or C_1–C_3 bond; see **6**. However, in oxyallyl, this local C_2 axis is colinear with these bonds; see **7**. Thus, the methylene group must also "tilt" as it rotates into the molecular plane. Previous calculations have not considered this tilt as the molecule passes along the reaction coordinate.



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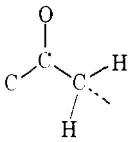

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The bond lengths and bond angles assigned to oxyallyl (**2**) are given in Table II. Since the extended Hückel and INDO treatments do not afford the same value for the internal angle α, we varied this parameter in both our INDO and *ab initio* calculations. The length of the carbon–oxygen bond is also uncertain, and we studied the energy change resulting from its stretch in our INDO calculations.

Table II. Bond Distances and Bond Angles in Oxyallyl

Bond distance, Å		Bond angle, deg	
C_1–O	Varied	O–C_1–C_2	Varies with α
C_1–C_2	1.466[a]	C_3–C_1–C_1	α
C–H	1.080	C_1–C_2–H	120.00
		H_1–C_2–H_2	120.00

[a] M. G. Brown, *Trans. Faraday Soc.*, **55**, 694 (1959).

The geometry of allene oxide (**3**) was chosen after examining the experimental values for methylenecyclopropane[16] and ethylene oxide.[17] The values used in the calculations are presented in Table III. The molecular plane bisects the H_3–C_3–H_4 angle.

Table III.[16,17] Bond Distances and Bond Angles in Allene Oxide

Bond distance, Å		Bond angle, deg	
All C–H	1.080	H_1–C_1–H_2	117.00
C_1–C_2	1.332	H_1–C_1–C_2	121.50
C_2–C_3	1.403	C_1–C_2–C_3	148.38
C_2–O	1.368	C_3–C_2–O	63.25
C_3–O	1.453	C_2–C_3–O	57.20
		C_2–C_3–H_3	118.80
		H_3–C_3–H_4	114.00

The con- and disrotatory states **4** and **5** are on reaction coordinates leading to oxyallyl. Since the previous INDO calculation[12] found an energy maximum when the plane containing a methylene group was at an angle of 30° to the molecular plane, we also decided to use this angle for **4** and **5**. This corresponds to a point approximately two-thirds of the way along a reaction coordinate, and all independent parameters were adjusted accordingly. All bond lengths and angles not varied in the calculations were assigned values corresponding to two-thirds of their difference between **1** and **2**.

The methylene groups were given the appropriate tilt in our calculations. This tilt changes the interactions and, in our calculations, lowers the energy of the disrotatory geometry below that of oxyallyl.

The bond distances and bond angles used for **4** and **5** are given in Table IV. The carbonyl length was chosen after it was determined that the energy of oxyallyl was insensitive to this distance.

Table IV. Bond Distances and Bond Angles for the Con- and Disrotatory Geometries

Bond distance, Å		Bond angle, deg	
C_1–O	1.200	O–C_1–C_2	Varies with α
C_1–C_2	1.469	C_3–C_1–C_2	α
C_2–H	1.082	C_1–C_2–H	119.44
		H–C_2–H	118.04

INDO Results

We present in Table V the results of our INDO investigation, together with those of Olsen, Kang, and Burnelle.[12] The energies are in hartrees.

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[12] J. F. Olsen, S. Kang, and L. Burnelle, *J. Mol. Struct.*, **9**, 305 (1971).

[13] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[14] J. A. Pople and D. L. Beveridge, "Approximate Molecular Theory," McGraw-Hill, New York, N. Y., 1970.

[15] We wish to thank Drs. Kang and Olsen for making their results available to us and for helpful discussions.

[16] V. W. Laurie and W. M. Stigliani, *J. Amer. Chem. Soc.*, **92**, 1485 (1970).

[17] "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11 (1958).

Table V. INDO Calculations

	α, deg	CO, Å	E, hartrees: Present work	E, hartrees: OKB[a]
1			−41.0275	−40.9958
2	120	1.20	−40.6180	−40.6004
	100	1.20	−40.6477	−40.6298
	100	1.26	−40.6486	
	90	1.20	−40.6570	−40.6400
	90	1.26	−40.6579	
3			−41.0168	
4	101.53	1.20	−40.6066	
	88.20	1.20	−40.6114	
5	101.53	1.20	−40.6756	
	88.20	1.20	−40.7315	−40.5922[b]

[a] Reference 12. [b] This is an approximate value calculated from ref 12; α is equal to 90°.

There are a number of conclusions to be drawn from Table V. Perhaps the most important is that singlet oxyallyl is calculated to be 232 kcal/mol less stable than cyclopropanone. This agrees with the previously published ΔE. It appears that the INDO method overestimates the energy change required to pass to oxyallyl, for 232 kcal/mol must be far too high. Allene oxide, on the other hand, is only 6 kcal/mol less stable than cyclopropanone.

Another conclusion to be drawn is that the energy of oxyallyl depends very little upon the length of the carbon–oxygen bond. While this calculation underestimates the energy change associated with this stretch, we felt that the parameter could be ignored in the *ab initio* calculations. Consequently the carbonyl distance was fixed at 1.20 Å.

Oxyallyl is found to be most stable with an internal angle of 90°, and this also agrees with the previous INDO calculation. However, unlike the previous study, our disrotatory 30° geometry lies below oxyallyl in energy.

This difference results from the tilt of the methylene groups, which lowers the energy of **5**. In the *ab initio* calculations, the energy difference between **2** and **5** is much less, indicating that a very late transition state may well be present. The conrotatory reaction coordinate definitely passes through a transition state.

One further point that requires comment is the angles chosen for α in **4** and **5**. During the ring opening, α changes from its initial value of 64.60° in cyclopropanone to its final value in oxyallyl. If the internal angle in the latter is 120°, then 101.53° represents about two-thirds of the total change. The other value, 88.20° assumes that the internal angle in **2** is 100°.

These were initial guesses. However, we did not continue the search for the optimum value of α in **5** for that would only further decrease its energy. Since the energy of **5** is already below that of **2**, optimization at this rotatory angle serves no purpose. A disrotatory transition state, if it is present, must occur further on the reaction coordinate.

Ab Initio Results

The *ab initio* calculations were run using the POLYATOM program of Moskowitz.[18] The 5s,3p Gaussian basis of Whitman and Hornbach[19] was placed at each heavy nucleus and two s-type Gaussians, contracted into a single basis function, at each hydrogen.

The atomic energies in hartrees for this basis set are[19] C −37.5791, O −74.5514, and H −0.4828, and this leads to a separated-atoms limit for our systems equal to −189.2199 hartrees.

This basis set has been used to calculate the methyl rotational barriers in ethane, propane, propene, and acetaldehyde and, as Table VI indicates, affords extremeley good results.[20]

Table VI. Methyl-Rotational Barriers

	Ethane	Propane	Propene	Acetaldehyde
ΔE(calcd)	+0.0052	+0.0057	+0.0027	+0.0021
ΔE(exptl)	+0.0048[a]	+0.0052[b]	+0.0032[c]	+0.0018[d]

[a] D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958). [b] The barrier to single methyl rotation was calculated by J. R. Hoyland, *J. Chem. Phys.*, **49**, 1908 (1968), after analyzing the microwave spectrum. [c] D. R. Lide, Jr., and D. E. Mann, *ibid.*, **27**, 868 (1957). [d] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957).

The geometries used in the *ab initio* calculations were the same as those employed in our semiempirical investigation. Results are presented in Table VII. The calculations pick up a reasonable fraction of the binding energy of the various species.

Table VII. *Ab Initio* Calculations

	α, deg	E, hartrees
1		−189.8850
2	120	−189.7314
	100	−189.7533
	90	−189.7350
3		−189.8516
4	88.20	−189.6872
5	88.20	−189.7651

The *ab initio* calculations indicate a much smaller energy difference between **1** and **2**. The value is about 83 kcal/mol, which agreed reasonably well with the MINDO/2 result but does not conform to either INDO or extended Hückel calculations. Allene oxide is now found to be 21 kcal/mol less stable than cyclopropanone.

According to the Table VII, the internal angle in **2** is approximately 100°. Since we have calculated the energy of **2** for three different values of α, it becomes possible to pass a parabola through these points and obtain a better value for the internal angle. The predicted minimum now occurs at 105° and corresponds to an energy lowering of about 1 kcal/mol.

Another point of interest is that the energy of **2** is about 8 kcal/mol greater than that of **5**. Thus, it becomes possible that a late transition state can be found on the disrotatory reaction coordinate.

Finally, it is worthwhile to mention the symmetries of the highest occupied and lowest unoccupied π

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(18) We wish to thank Dr. Moskowitz for making his POLYATOM program available to us.

(19) C. J. Hornbach, Thesis, Case Institute of Technology; see also, D. R. Whitman and C. J. Hornbach, *J. Chem. Phys.*, **51**, 398 (1969).

(20) A. Liberles, B. O'Leary, J. E. Eilers, and D. R. Whitman, *J. Amer. Chem. Soc.*, **94**, 6894 (1972).

molecular orbitals of **2**. The four π molecular orbitals are ψ_{12}, ψ_{15}, ψ_{16}, and ψ_{17}. We find that ψ_{15} has b_2 symmetry while ψ_{16} has a_2 symmetry. Interestingly enough, the latter has a negative orbital energy ($\epsilon_{16} = -0.0498$).

Conclusion

The results of our *ab initio* calculations indicate that singlet oxyallyl is considerably less stable than cyclopropanone and appears to be at, or near, the disrotatory energy maximum. The internal angle is found to be approximately 105°. Our calculated energy difference of 83 kcal/mol is probably too high, and there are several factors that will alter ΔE for the conversion of **1** to **2**. Most important is the low-lying virtual orbital ψ_{16} in oxyallyl. A CI calculation, taking advantage of this orbital, would certainly reduce ΔE.

Our small basis set probably overestimates the strain in cyclopropanone. Hehre, Ditchfield, Radom, and Pople[21] report that their *ab initio* calculations appear to over-estimate the strain in similar ring systems.

Finally, optimizing bond distances and bond angles will influence the energies of the various species.

The calculated energy difference between cyclopropanone and allene oxide is 21 kcal/mol; since calculations that improve the energy of one would have a similar effect upon the other, this value would appear to be reasonably accurate. Therefore, even allowing for some change in the 83 kcal/mol for the opening to oxyallyl, SCF calculations predict correctly that cyclopropanone is stable with little tendency to isomerize.

Acknowledgments. The authors wish to thank Drl David Hankins for helpful discussions and the Nationa. Science Foundation is gratefully acknowledged for its support.

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[21] W. G. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem Soc.*, **92**, 4796 (1970).

An Elementary Molecular Orbital Calculation on $U(C_8H_8)_2$ and Its Application to the Electronic Structures of $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$[1a]

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Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, and Lawrence Berkeley Laboratory, Berkeley, California 94720. Received May 13, 1972

Abstract: Molecular orbital calculations have been performed on $U(C_8H_8)_2$ using the Wolfsberg-Helmholz approximation. The results of these calculations have been used to analyze the information available on $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$, with some success. The most striking prediction of the model is that the ground state of $U(C_8H_8)_2$ should have $|J_z| = 3$, which seems to be correct.

Since the first preparation of the cyclooctatetraene compounds of actinide elements,[2a] their electronic structure has been the object of considerable interest. Thus far, cyclooctatetraene compounds of Th,[2a] U,[2a] Np,[2b] and Pu[2b] have been reported, as have compounds with some substituted cyclooctatetraenes.[3] These compounds have been given the trivial names of -cene,[2a] by supposed analogy with the iron series cyclopentadienes, so one speaks of uranocene, neptunocene, and so on.

In the original report on these compounds, a qualitative discussion of their electronic structure was given, in which they were supposed to be similar to the iron series bis(cyclopentadienyl) compounds, except that the orbitals of the rings and of the metal which were involved in bonding had one more node in going around the figure axis of the molecule. These were the e_2 orbitals of the cyclooctatetraene rings and the $f_{\pm 2}$ orbitals of the metal. Increased hydrolytic stability of $U(C_8H_8)_2$, over ionic cyclooctatetraenides, was offered as evidence for the proposed covalency of the compounds.

A number of physical measurements on cyclooctatetraene compounds have subsequently appeared, which provide information about the electronic structure of the compounds. Firstly, crystallographic work has shown the compounds to be sandwich compounds, and $U(C_8H_8)_2$ has D_{8h} symmetry.[4] The magnetic susceptibilities of $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$ have been reported.[2b] Mössbauer absorption of $Np(C_8H_8)_2$ has been reported.[2]

Finally, the ^1H nmr of uranocene and of 1,3,5,7,1′,3′,5′,7′-octamethyluranocene has been studied[3,5] and the chemical shifts have been resolved into contact and pseudocontact contributions.

The integration of these data into a model of the electronic structure of the compounds has been only moderately successful. The Mössbauer isomer shift is most easily interpreted and suggest that the charge on Np in neptunocene is about +3.5.[2b] The susceptibility data from $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$ between 4.2 and 45°K have been fit to the Curie-Weiss law.

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) University of Notre Dame; (c) Lawrence Berkeley Laboratory.

[2] (a) A. Streitwieser, Jr., and U. Muller-Westerhoff, *J Amer Chem. Soc.*, **90**, 7364 (968); (b) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *ibid.*, **92**, 4841 (1970).

[3] A. Streitwieser, Jr., D. Dempf, G. N. LaMar, D. G. Karraker, and N. Edelstein, *ibid.*, **93**, 7343 (971).

[4] A. Zalkin and K. M. Raymond, *ibid.*, **91**, 5667 (1969).

[5] N. Edelstein, G. N. LaMar, F. Mares, and A. Streitwieser, Jr., *Chem. Phys. Lett.*, **8**, 399 (1971).