*Tetrahedron.* Vol 28, pp. 2157 to 2161. Pergamon Press 1972. Printed in Great Britain

# ACETONE, *AB INITIO* CALCULATIONS[1, 2]

N. L. ALLINGER and SISTER M. J. HICKEY, O.P.
Department of Chemistry, University of Georgia, Athens, Georgia 30601

(*Received in USA* 8 *August* 1971; *Received in the UK for publication* 6 *December* 1971)

**Abstract**—*Ab initio* calculations on acetone using a 5,2,2 (contracted to 3,1,1:1 for carbon and oxygen, and 1 for hydrogen) Gaussian basis set gives a molecular energy of − 190·68162 Hartrees. The methyls have hydrogen eclipsing oxygen in the ground state. The rotational barrier is 0·99 kcal/mole.

IT HAS been known for more than 30 years that rotation about single bonds is in general not completely "free", but rather there are rotational barriers, generally of the order of a few kcal/mole, which hinder such a rotational motion.[2] These barriers have in general been measured experimentally by one of two methods; either by a measurement of the calorimetric and spectroscopic entropies and assigning the difference to a hindered torsional motion, or from a study of the microwave spectrum. More recently, other methods have proven to be of value in many cases, especially in more complicated situations.[3]

During the last few years it has been shown that *ab initio* calculations of rotational barriers in simple molecules using modest size basis sets are capable of giving results comparable in accuracy with the best experimental measurements. In some cases where the experiments are difficult. a theoretical calculation is the method of choice for determining the rotational barrier.[4]

While rotational barriers of specific very simple small molecules are of limited interest, a knowledge of the numerical values of such barriers can often be put to use on a study of more complicated molecules. Thus a knowledge of the rotational barrier in acetone has long been of interest, because extrapolations can yield information about more substituted ketones, which are of wide occurrence and practical importance. The numerical value for the rotational barrier in acetone has been available for many years,[5] but the orientation of the rotating methyl group in the ground state and at the maximum of torsional energy has not been well defined. In 1954, Brown, from a study of thermochemical data on acetone, propane, cyclohexanone, and cyclohexane concluded[6] that the methyl group has two hydrogens staggered about oxygen in the ground state. This is in contrast to acetaldehyde, which has the oxygen eclipsed by a methyl of hydrogen in the ground state.[7] The problem was discussed at some length in 1964,[8] and it was concluded that Brown's orientation seemed the most likely, although a clear-cut decision was not possible at that time. Subsequently, on the basis of some experiments in more complicated systems,[9] it was decided that the barrier in fact must be that in which hydrogen eclipsed hydrogen in the ground state. No simple experiment or calculation on acetone or any simple small ketone has been forthcoming.

---

* This work was supported by Grant Number GP-15263 from the National Science Foundation.

In the present work, it was decided that in view of the experimental difficulty involved in determining the orientation of the methyl group in the ground state of acetone, a theoretical calculation would be well suited to giving both the barrier height and desired orientation. The former could be directly compared with the experimental value, as a check on the accuracy of the calculation.

Since *ab initio* calculations for a molecule as large as acetone are rather time consuming, two relatively small basis sets were used in the present work. While small basis sets lacking polarization functions are known to give total energies which are relatively far from the Hartree–Fock limit, computed rotational barriers, being the difference between two such quantities, turn out to be reasonably accurate.[4] The errors for the most part cancel out.

As a kind of calibration, we first calculated the total energy of formaldehyde with two relatively small basis sets, which however are believed to be very good for their size. The total energy of formaldehyde is well known experimentally,[10, 17] and the Hartree–Fock limit[11] and the geometry are also known.[12] We were therefore able to use this molecule as a simple test case to see how well our basis sets would do.

A basis set which has recently been used pretty widely for all sorts of calculations is a linear combination of three Gaussians (STO-3G), which has been studied by Pople.[13] Pople has reproduced a Slater orbital with an optimum (least squares fitted) combination of three Gaussians, and used this as a crude but well defined and reasonable small basis set. We have used this small set in the present work. In addition, we have used a second set, which consists of five $s$ and two $p_x$, two $p_y$, and two $p_z$ type Gaussian functions for each carbon and oxygen, together with two $s$-type functions for each hydrogen. This (5,2,2) set is contracted (that is, a certain group from among these orbitals have the coefficients held in constant ratio to one another rather than all being optimized individually) to give a 3,1,1;1 contracted Gaussian basis set for carbon and oxygen, and 1 for hydrogen.*

The data on orbital exponents and contraction are summarized in Table 1.

All calculations were carried out with the aid of an IBM 360/65 computer, using a modified version of IBMOL 4. In Table 2 a summary is presented of the results of this work. From Table 2 it can be seen that the (5, 2, 2) basis set gives lower total energies and requires less computer time than does Pople's small basis set. For formaldehyde, the total energy is lower by 0·7 Hartrees, and the calculation time is only 2·7 min, as opposed to 6 min for Pople's set.

TABLE 1. ORBITAL EXPONENTS, CONTRACTION COEFFICIENTS AND METHOD OF CONTRACTION OF THE (5, 2, 2) GAUSSIAN BASIS SET

| Atom | Orbital Exponents and Contraction Coefficients | Method of Contraction |
|---|---|---|
| Carbon | Ref. 14 | (3,1,1:1) |
| Oxygen | Ref. 15 | (3,1,1:1) |
| Hydrogen | Ref. 14 | (1) |

---

* The notation a, b, . . . ; e, f, . . . denotes the first a$s$-type basis functions are contracted to a single $s$-type combination, the next b$s$ functions to another combination, and so on. The numbers e, f, . . . give similar information for the construction of $p$-type functions. The basis functions are arranged in order of decreasing orbital exponents.

TABLE 2. CALCULATED TOTAL ENERGIES, CALCULATED AND EXPERIMENTAL ROTATIONAL BARRIERS, AND COMPUTER TIME FOR EACH CALCULATION

| Molecule | STO-3G basis set | | | (5,2,2) basis set | | | Exp. rotational barrier kcal/mole | |
|---|---|---|---|---|---|---|---|---|
| | Total energy Hartrees | Calc. rotational barrier kcal/mole | Time, min | Total energy Hartrees | Calc. rotational barrier kcal/mole | Time, min | Microwave | Thermodynamic |
| Formaldehyde* | −112·35282 | — | 6·0 | −113·03940 | — | 2·7 | — | — |
| Acetaldehyde: | | | | | | | | |
| eclipsed | −150·94457 | 1·37 | 36·7 | −151·87075 | 1·19 | 20·7 | 1·15 | 1·0 |
| staggered | −150·94239 | | 36·6 | −151·86886 | | 21·0 | | |
| Acetone: | | | | | | | | |
| eclipsed-eclipsed | −189·53159 | 1·14 | 122·3 | −190·68162 | 0·99 | 67·1 | 0·8 | 0·56–1·24 |
| eclipsed-staggered | −189·52977 | | 121·8 | −190·68005 | | 74·6 | | |

* Hollister and Sinanoglu[11] have predicted the total Hartree–Fock energy of formaldehyde to be −114·0309 a.u. Neumann[17] *et al.* have calculated a value for the total energy of −113·8917 a.u. Shimanouchi[10] gives an experimental value of −114·562 a.u.

We then made a cursory study of acetaldehyde, where both the rotational barrier and the geometries are known.[7,16] The geometries used were those calculated earlier;[18] the energy of the molecule was not optimized during the calculation. Again, the energy was lower with the (5, 2, 2) basis set by almost 0·9 Hartrees than it was with Pople's basis set, and the calculation time was 21 min, as opposed to 37 min. The rotational barrier was also a little better, 1·2 kcal/mol as opposed to 1·4 kcal/mol, compared with the experimental value of 1·2 kcal/mol.

Since the results obtained by these calculations seemed to be adequate, the calculation was carried out for acetone using the geometry reported by Iijima,[19] first with both methyls having hydrogens eclipsing oxygen, and then with one methyl unchanged and the other one staggered with respect to the oxygen. It was found that the former had a lower energy, −190·68182 Hartrees with the (5, 2, 2) basis set, and more than one Hartree higher with Pople's small basis set. The rotational barrier was calculated to be 1·0 kcal/mol with the (5. 2. 2) basis, and 1·1 kcal/mol with Pople's basis, compared to a microwave value of 0·8 kcal/mol.* Thus there seems no doubt that the conformation where both methyls have hydrogens eclipsing oxygen corresponds to the ground state, and the other form corresponds to a torsionally excited molecule. Actually, it is anticipated that torsional motions of the two methyls were coupled together, and this should lead to a lowering of the observed torsional barrier, compared to what has been calculated in the present case. (For an analogous situation, see the study of propane.[14])

Recently Allen[20] has offered an explanation for the rotational barrier of acetaldehyde in terms of small changes in chemical bonding. A charge density analysis indicates that an interaction which corresponds to a weak covalent bond is formed between the oxygen and the eclipsing methyl hydrogen, which is lost upon rotation to the less-stable conformer. It is no doubt true that a similar situation exists in acetone. Similarly, it has been found that in ethane the interaction between vicinal hydrogens corresponds to repulsion, and that is presumably why the staggered conformation is stable, while hydrogen eclipsing hydrogen would not yield any such stability.

There still remains the problem of the heat of formation data cited by Brown[6] and his conclusion, which is certainly incorrect, that a staggered arrangement about the carbonyl is preferable. From the data given in his paper (which rests heavily on an unpublished heat of formation by Prosen), it may be calculated that insertion of the carbonyl group into cyclohexane to give cyclohexanone introduces 0·8 kcal of strain into the molecule, compared to what happens when the carbonyl group is introduced into propane to give acetone. The earlier interpretation was that the eclipsing of the $\alpha$ hydrogens in cyclohexanone are responsible for this 0·8 kcal of strain. This value was arrived at by a comparison of the heats of formation of four compounds, however, and is not outside of the probable experimental error involved. Using a more modern published value for the heat of formation of cyclohexanone,[21] one would find by the same procedure that cyclohexanone is strained by 2·4 kcal relative to cyclohexane. This value appears large enough to be real, and the basic problem remains as before.

---

* The methyl was treated as a rigid rotor, and the geometry corresponding to the torsional maximum was determined by a rotation about the symmetry axis of the methyl (not about the bond). This motion is believed to better represent the normal coordinate which is studied by the microwave method.

There is no real reason to think that heats of formation can be calculated by such simple manipulations, however. When the heats of formation of cyclohexane and cyclohexanone are calculated in a more proper (and considerably more elaborate) way,[18] the theoretical values indicate that cyclohexanone is more strained than cyclohexane by 1·04 kcal/mole.* This number mostly comes from the inability of cyclohexanone to attain a conformation in which a methylene eclipses oxygen. Except for that, cyclohexanone contains only the amount of strain present in cyclohexane.

*Acknowledgement*—The authors wish to thank Professor I. G. Csizmadia and Saul Wolfe, and Dr. A. Veillard for making their IBMOL programs available. We are very much indebted to Dr. L. Tel for his advice and assistance with the program. We are also indebted to Dr. M. A. Miller for the calculation of some of the geometric data used in the present work.

## REFERENCES

[1] LXXXII in the series *Conformational Analysis* LXXI, N. L. Allinger and S. P. Jindal, *J. Org. Chem.* **37**, *in press* (1972) and paper XXVI in the series *Organic Quantum Chemistry* paper XXV, L. W. Chow and N. L. Allinger, *Tetrahedron*, **26**, 3717 (1970)

[2] J. Lowe, *Prog. Phys. Org. Chem.* **6**, 1 (1968)

[3] F. A. L. Anet and R. Anet, *Configuration and Conformation by NMR*, in *Determination of Organic Structure by Physical Methods*, Academic Press, New York (1971); E. Wyn-Jones and R. A. Pethrick in E. L. Eliel and N. L. Allinger, Eds., *Topics in Stereochemistry*, p. 205. Vol. 5, Wiley-Interscience, New York (1970)

[4] J. M. Lehn, *Conformational Analysis* p. 129 (papers presented at the Brussels Symposium, 1969), Academic Press, New York (1971)

[5] J. D. Swalen and C. C. Costain, *J. Chem. Phys.* **31**, 1562 (1959); R. Nelson and L. Pierce, *J. Mol. Spectrosc.* **18**, 344 (1965)

[6] H. C. Brown, J. H. Brewster and H. Shechter, *J. Am. Chem. Soc.* **76**, 467 (1954)

[7] R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *J. Chem. Phys.* **26**, 1695 (1957)

[8] N. L. Allinger, J. Allinger and M. A. DaRooge, *J. Am. Chem. Soc.* **86**, 4061 (1964)

[9] N. L. Allinger and F. M. Karkowski, *Tetrahedron Letters* 2171 (1965); N. L. Allinger, H. M. Blatter, L. A. Freiberg and F. M. Karkowski, *J. Am. Chem. Soc.* **88**, 2999 (1966)

[10] T. Shimanouchi and I. Suzuki, *J. Chem. Phys.* **42**, 296 (1965)

[11] C. Hollister and O. Sinanoglu, *J. Am. Chem. Soc.* **88**, 13 (1966)

[12] C. Kato, S. Konaka, T. Iijima and M. Kimura, *Bull. Chem. Soc. Japan* **42**, 2148 (1969)

[13] W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969)

[14] J. R. Hoyland, *Ibid.* **49**, 1908 (1968)

[15] D. R. Whitman and C. J. Hornback, *Ibid.* **51**, 398 (1969)

[16] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis*, p. 140. Interscience Division, John Wiley and Sons, New York, 1967

[17] D. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.* **50**, 2216 (1969)

[18] N. L. Allinger, M. T. Tribble and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972)

[19] T. Iijima, *Bull. Chem. Soc. Japan* **43**, 1049 (1970)

[20] W. L. Jorgensen and L. C. Allen, *J. Am. Chem. Soc.* **93**, 567 (1971)

[21] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, p. 208. Academic Press, New York (1970)

---

* If the experimental values for heats of formation are used rather than the calculated ones, the large experimental errors (0·3–0·5 kcal/mole for each compound) render conclusions along these lines very uncertain.