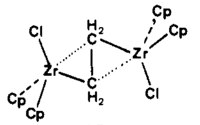
dimerization energy, 101 kcal/mol. This value may be overestimated by MNDO,[29] but aggregates of dilithioethane are certainly expected to be much more stable than the monomer.

### Triplet States of 1,2-Dilithioethane

All bonding orbitals in electron-deficient lithium compounds are not occupied. Thus triplet states are often readily accessible.[10] Geometry optimization of the triplet state of the partly bridged structure **1** leads to the symmetrical bridged **2**. Triplet **3′** was found to be lowest in energy. The well-known[10] overestimation of triplet relative to singlet stabilities at the Hartree–Fock level is partly corrected using second-order Møller–Plesset theory. At UMP2/4-31G//4-31G, triplet **3** is 17 kcal/mol less stable than singlet **1**. We thus believe 1,2-dilithioethane to be a ground-state singlet. The MNDO results[17] agree with this conclusion.

### Transition Metal Analogues

The vast majority of elements in the periodic table are metals. Lithium, the first such element, can be expected to exhibit structural features which should be common to other metals. A remarkable analogy is found between the zirconio-ethylene complex **10**,[6] with ZrCC angles of 75.9° (X-ray), and **1**, with LiCC angles of 73.3° (4-31G).



**10**

Following the analysis of Hofmann and Stauffert[30] for complexes involving $Cp_2MCl$ fragments, we can consider **10** to result from the interaction of two $Cp_2MCl{\cdot}AlR_3$ fragments with ethylene. The orbital interaction diagram (Figure 6) shows how the relevant $a_g$ and $b_u$ orbitals of the two metal fragments (Figure 6, middle) are derived from the $1a_1$ and $b_2$ $Cp_2Zr$ fragment orbitals after interaction with chlorine (Figure 6, left side). The $1b_{2u}$ and $1b_{3g}$ orbitals of ethylene (Figure 6, right side) interact with the $1b_u$ and $1a_g$ orbitals of the metal fragment combination to produce two new stabilized orbitals ($b_u$ and $a_g$) which are occupied by four electrons (the two $\pi$ electrons of ethylene and the one extra electron from each of the two zirconium fragments).

In **10**, the distortion from the symmetrical bridged structures results from a gain in energy due to interaction of the ethylene $1b_{3g}$ ($1b_{2u}$) orbitals with the $2a_g$ ($1b_u$) fragment orbital. This interaction is not possible in the symmetrical bridged structure. The distortion in **1** has similar causes. Thus, both 1,2-dilithioethylene and **10** are electron-deficient compounds whose unusual bent geometries result from additional interactions of formally unoccupied lithium and metal fragment orbital with the occupied orbitals of $C_2H_4$.

**Acknowledgment.** We thank P. Hofmann and V. Routenstroud for discussions and J. Chandrasekhar for assistance. Support was provided by the Fonds der Chemischen Industrie, BASF Ludwigshafen, the National Science Foundation under Grant CHE-79-01061-01, and a NATO grant.

---

(30) P. Hofmann and P. Stauffert, submitted for publication. See J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).

---

# A Theoretical Study of the Core Binding Energies of Ozone and Oxygen Difluoride

**C. S. Ewig, R. D. Mathews, and M. S. Banna***

*Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.* *Received February 23, 1981*

**Abstract:** The core binding energies of $O_3$ and $OF_2$ have been calculated as the difference between the total Hartree–Fock energies of the hole states (core electron missing) and the neutral ground states. The results are compared with experimental values. The agreement is very good except for the central oxygen of ozone. The trends in binding energies, as they reflect the bonding in the two molecules, are discussed in terms of the $\sigma$ and $\pi$ contributions.

The recent experimental study of core ionization in ozone[1] has produced two interesting results: a large splitting between the terminal and central oxygens of 4.7 eV and the highest $O_{1s}$ binding energy ever reported in the gas phase, 546.2 eV, which is 1 eV higher than that of $OF_2$.[2] This would imply that the central oxygen atom of $O_3$ is more positively charged than that of $OF_2$, despite the more electronegative nature of F. In an attempt to reproduce these results theoretically and hence obtain a better understanding of bonding in ozone, Noodleman (Banna et al.[1]) performed X$\alpha$ scattered wave calculations on the ground states, core-hole states, and "transition states" (obtained by removing half a core electron from the neutral molecule) for both $O_3$ and $OF_2$. The X$\alpha$ method proved satisfactory in predicting the splitting, giving 5.1 eV when the binding energies were calculated as the difference between the total energy of the ion with a core hole and the total energy of the neutral molecule ("$\Delta$SCF" method). However, the absolute binding energy was some 6 eV too high for both the $OF_2$ and the $O_3$ oxygen atoms.

Table I. Computed Total Energies (hartrees)

| | |
|---|---|
| $O_3$ | |
| neutral | −224.2177 |
| central $O_{1s}$ hole state | −204.0835 |
| terminal $O_{1s}$ hole state | −204.3165 |
| $OF_2$ | |
| neutral | −273.4763 |
| $O_{1s}$ hole state | −253.4321 |
| $F_{1s}$ hole state | −247.9557 |

We report here the first ab initio SCF calculations of these properties. The molecular orbitals obtained are used to perform separate population analyses for $\sigma$ and $\pi$ orbitals, thus providing a more detailed picture of bonding than is possible on the basis of the total populations reported previously for $O_3$[3] and $OF_2$.[4]

---

(1) M. S. Banna, D. C. Frost, C. A. McDowell, L. Noodleman, and B. Wallbank, *Chem. Phys. Lett.* **49**, 213 (1977).

(2) J. W. Koepke and W. L. Jolly, *J. Electron Spectrosc.*, **9**, 413 (1976).

(3) S. Rothenberg and H. F. Schaefer III, *Mol. Phys.*, **21**, 317 (1971).

0002-7863/81/1503-5002$01.25/0

Table II. Comparison of Ionization Potentials (eV)[a] [Relaxation Energies in Parentheses]

| | calcd | exptl |
|---|---|---|
| | $O_3$ | |
| terminal O | 541.54 (22.45) | 541.5[b] |
| central O | 547.88 (21.46) | 546.2[b] |
| central-terminal | 6.34 (−0.99) | 4.7 |
| | $OF_2$ | |
| O | 545.43 (21.54) | 545.2[c] |
| F | 694.46 (24.33) | 694.9[c] |

[a] Based on 1 Ry = 13.605804 eV as recommended by E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data*, 2, 663 (1973). [b] From ref 1. [c] From ref 2.

## Computational Details

For both $O_3$ and $OF_2$, a 4s3p contracted Gaussian basis set, proposed by Dunning,[5] was used. All the results reported here were obtained by employing our version of BISONMC, the multiconfiguration SCF program originally written Das and Wahl.[6] Both ground-state and hole-state calculations were performed, and the core binding energies were obtained as the difference between the total energies. Highly localized holes were obtained in each case. Hole states involving terminal atoms thus possessed $C_s$ rather than $C_{2v}$ symmetry.

The geometries used were $R_{\mathrm{O-O}} = 2.415$ a.u. and $\theta = 116.8°$ for $O_3$[7] and $R_{\mathrm{O-F}} = 2.681$ and $\theta = 103.2°$ for $OF_2$.[8] Multiconfiguration calculations would have been desirable, especially for $O_3$ in light of what is known about the extent of configuration mixing in the ground state of this molecule.[9] Unfortunately, hole states in this case are not readily obtainable with presently available methods due to the difficulty of formulating an appropriate variation condition.[10]

## Results and Discussion

The total energies obtained are shown in Table I. These appear to be close to the minimum values obtainable with s and p symmetry basis functions in a single-configuration calculation.[9] Lower total energies for the neutral species have of course been obtained with the addition of d functions. Thus, for example, Rothenberg and Schaefer report −224.3093 hartrees for $O_3$[3] and −273.5294 hartrees for $OF_2$.[4] The lowest energies to date derived from single configuration calculations appear to be −224.324 hartrees for $O_3$ found by Cederbaum et al.[11] and −273.5507 hartrees for $OF_2$ by von Niessen.[12] These suggest that d functions may be more important in determining the total energy of neutral $O_3$ than of $OF_2$. However, since we are concerned here only with binding energies of core electrons, it is not clear a priori what basis would give the most accurate results.

In Table II, we compare our ΔSCF results with experiment. Except for the central oxygen of $O_3$, the agreement is very good. It is interesting that the splitting between the central and terminal oxygens in ozone is better predicted by the difference of the Koopmans' theorem energies (5.35 eV) than the difference between the ΔSCF (6.34 eV). The good agreement of the former value with experiment (4.7 eV) suggests that the splitting is primarily due to ground-state effects. We note that our Koopmans' theorem splitting lies between the two splittings obtained by Rothenberg and Shaefer[3] with and without d functions in the basis set (5.63 and 4.88 eV, respectively). The increased separation between the binding energies of the central and terminal oxygens upon addition of d functions is in line with the change in gross populations on the oxygens when d functions are included (the central oxygen population decreases from 7.779 to 7.697 while the terminal oxygen population increases from 8.110 to 8.151). On the assumption that the best Koopmans' theorem energies are those obtained from the calculation of Rothenberg and Schaefer since d functions are included, it would appear that there should be more relaxation energy (defined as the difference between the orbital energy and the ΔSCF energy) associated with ionization of the central oxygen than with ionization of one of the terminal oxygens in order to reduce the splitting to the experimentally observed value. This is contrary to the results of our calculation, which predicts ~1 eV more relaxation for the terminal oxygens. Perhaps this is caused by the absence of d functions in our basis set since Rothenberg and Schaefer[3] determined that the d function population is three times as high on the central oxygen compared to the terminal oxygens (0.15 vs. 0.05). On the other hand, in $OF_2$ where d oribitals are not as important[4] the relaxation energy is predicted very well as evidenced by the excellent agreement with experiment. It is not unreasonable to expect more relaxation for the central oxygen despite its positive charge since it is connected to two other atoms thus allowing for more charge flow. In drawing this conclusion based on the Koopmans' theorem energies we are of course assuming that the correlation energy contribution is the same for both oxygens.

Table III. Population Analysis of Neutral $O_3$ and $OF_2$[a]

| | gross charge | | overlap |
|---|---|---|---|
| | *A* | *B* | *A–B* |
| | | $O_3$ | |
| σ | 6.1602 | 5.9199 | 0.1151 |
| π | 1.6185 | 2.1908 | −0.0322 |
| total | 7.7787<br>(+0.2213) | 8.1107<br>(−0.1107) | 0.0829 |
| | | $OF_2$ | |
| σ | 5.7663 | 7.1168 | 0.1556 |
| π | 2.0042 | 1.9979 | −0.0924 |
| total | 7.7705<br>(+0.2295) | 9.1147<br>(−0.1147) | 0.0632 |

[a] A and B represent the central and terminal atoms respectively of both molecules.

Chong, Herring, and McWilliams[13] have also calculated the core ionization energies of $OF_2$, using perturbation corrections to Koopmans' theorem. Using a basis set slightly smaller than ours, they obtained 542.74 and 693.60 eV for the O and F ionization, respectively. From analysis of their results it seems likely their somewhat larger error was due more to the choice of basis set than to their computational technique.

The results of the population analysis are given in Table III. The total atomic populations are partitioned into σ and π contributions in order to assess the relative importance of the two types of orbitals. The total atomic populations for the oxygen of $OF_2$ and the central oxygen of $O_3$ are almost identical, suggesting that the core binding energies should be similar, as seen experimentally.

Comparing the σ vs. π contributions, note that although the fluorines in $OF_2$ do indeed withdraw a large amount of charge from the oxygen (~0.12 each), they do so almost completely via σ orbitals. In contrast, the π orbitals in $O_3$ are very effective in withdrawing charge from the central to the terminal oxygens thus causing the large positive charge on the central oxygen (as expected from drawing resonance structures). On the other hand, the electrons in σ orbitals flow from the terminal to the central oxygen.

Our calculation also shows that in both $O_3$ and $OF_2$, the three π orbitals are composed of one bonding, one nonbonding, and one

---

(4) S. Rothenberg and H. F. Schaefer III, *J. Am. Chem. Soc.*, **95**, 2095 (1973).

(5) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

(6) G. Das and A. C. Wahl, BISON-MC: A FORTRAN computing system for multiconfiguration self-consistent-field (MCSCF) calculations on atoms, diatoms, and polyatoms, Argonne National Laboratoy REP. ANL-7955, July 1972.

(7) T. Tanaka and Y. Morino, *J. Mol. Spectrosc.*, **33**, 538 (1970).

(8) J. A. Ibers and V. Schomaker, *J. Phys. Chem.*, **57**, 699 (1953).

(9) An overview of previous calculations on ozone, especially those employing configuration mixing, is given by C. W. Wilson, Jr., and D. G. Hopper, *J. Chem. Phys.*, **74**, 595 (1981). See in particular W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).

(10) G. Das, private communication.

(11) L. S. Cederbaum, W. Domcke, W. von Niessen, and W. P. Kraemer, *Mol. Phys.*, **34**, 381 (1977).

(12) W. von Niessen, *J. Electron Spectrosc.*, **17**, 197 (1979).

(13) D. P. Chong, F. G. Herring, and D. McWilliams, *J. Chem. Phys.*, **61**, 958 (1974).

antibonding orbital, with the last having the largest overlap of the three. The overall effect is antibonding for $\pi$ and bonding of course for $\sigma$ plus $\pi$. Surprisingly, although the $\pi$ overlap population is much larger in $OF_2$ than in $O_3$, in the former this bonding leads to virtually no charge redistribution in these orbitals, in contrast to $O_3$.

Our results therefore confirm the qualitative conclusion of the X$\alpha$ calculation[1] that the high binding energy of the central oxygen 1s level is mainly due to charge migration into the bond; in particular, we have shown that $\pi$ orbitals play a crucial role. The higher binding energy in ozone compared to oxygen difluoride appears to be due to ground-state effects, as reflected in the Koopmans' theorem energies. This is despite the fact that the calculated total charges are almost equal. Conflicts of this type have been observed previously and are usually resolved in favor of the Koopmans' theorem energies.[4] Comparison of our computed orbital energies with experimental binding energies for ozone suggests that the relaxation energy should be slightly greater for the central oxygen ionization; this conclusion, however, may have to be altered if it is shown that correlation energies contribute differently to the two binding energies. In this connection, it would be very interesting to carry out accurate configuration interaction calculations to determine the correlation energies for core ionization.

**Acknowledgment.** This work was supported in part by the Air Force Office of Scientific Research under Grant No. AFOSR-77-3145 and in part by the National Science Foundation (Grant No. CHE-7918390). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Vanderbilt University Research Council for partial support of this research.

---

# Optical Rotatory Dispersion Studies. 134.[1] Absolute Configuration and Circular Dichroism Spectrum of (*R*)-[2-$^2H_1$]Cyclopentanone. Demonstration of a Conformational Isotope Effect

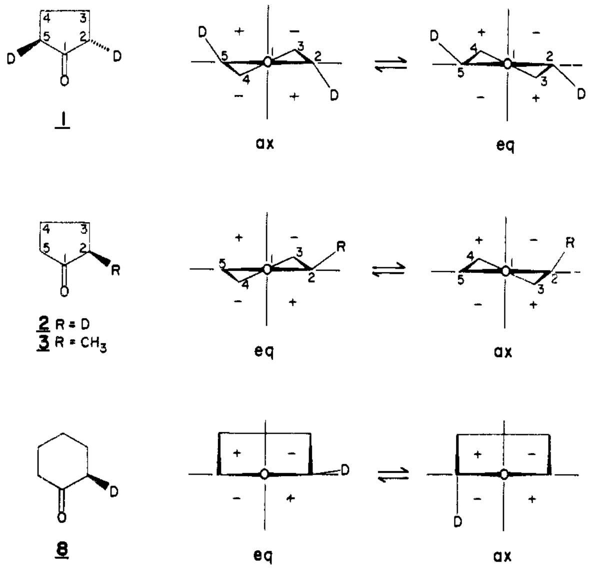
**P. Sundararaman, Günter Barth, and Carl Djerassi***

*Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305.* *Received March 19, 1981*

**Abstract:** The absolute configuration of (*R*)-[2-$^2H_1$]cyclopentanone is established through synthesis using as the key step chiral epoxidation with the Sharpless reagent. Its circular dichroism (CD) spectrum is unusual in that it exhibits a bisignate Cotton effect being negative at 310 and positive at 275 nm. From the interpretation on the variable-temperature CD measurements, the unexpected conclusion is reached that the twist conformation with the deuterium in the quasi-equatorial position is energetically preferred by ca. 10 ± 2 cal/mol. Evidently, even at room temperature, the contribution toward the spectrum resulting from the conformational isotope effect is of the same or larger amplitude but opposite sign compared to the difference between the partial octant contributions of an $\alpha$-quasi-equatorial and $\alpha$-quasi-axial deuterium substituent.

## Introduction

Scheme I



Several recent publications[2] have been concerned with the determination of the octant contribution of a deuterium substituent toward the Cotton effect associated with the n → $\pi^*$ transition of ketones. This work resulted in a consistent picture in cyclohexanones; i.e., deuterium was found to make a dissignate contribution in the $\alpha$-axial and $\beta$-equatorial position and a much smaller consignate contribution in the $\alpha$-equatorial and $\beta$-axial positions. Similar results were obtained for $\beta$-deuterium substitued cyclopentanones.[3] Therefore, it was surprising to note that $\alpha$-deuterium substituted cyclopentanones apparently behave anomalously. Hine et al.[4] have reported that the chiral base-catalyzed $\alpha$-deuterium exchange of [2,2,5,5-$^2H_4$]cyclopentanone yields optically active [2,5-$^2H_2$]cyclopentanone (**1**, Scheme I) which exhibits a positive Cotton effect. From considerations of the reaction mechanism the 2*S*, 5*S* configuration was assigned to this molecule. Dauphin et al.[5] obtained [2-$^2H_1$]cyclopentanone (**2**, Scheme I)

---

[1] For preceding paper, see: Sundararam, P.; Barth, G.; Djerassi, C. *J. Org. Chem.* **1980**, *45*, 5231-5236.

(2) (a) Numan, H.; Wynberg, H. *J. Org. Chem.* **1978**, *43*, 2232-2236. (b) Lightner, D. A.; Chang, T. C.; Horwitz, J. *Tetrahedron Lett.* **1977**, 3019-3023; errata, *ibid.* **1978**, 696. (c) Sundararaman, P.; Djerassi, C. *Ibid.* **1978**, 2457-2460; errata, *ibid.* **1979**, 4120. (d) Levine, S. G.; Gopalakrishnan, B. *Ibid.* **1979**, 699-702.

(3) (a) Simek, J. W.; Mattern, D. L.; Djerassi, C. *Tetrahedron Lett.* **1975**, 3671-3674. (b) Sing, L. Y.; Lindley, M.; Sundararaman, P.; Barth, G.; Djerassi, C. *Tetrahedron* **1981**, *37*, 181-189. (c) Lightner, D. A.; Gavronski, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 1983-1990.

(4) (a) Hine, J.; Li, W.-S. *J. Am. Chem. Soc.* **1975**, *97*, 3550-3551. (b) Hine, J.; Li, W.-S.; Zeigler, J. P. *Ibid.* **1980**, *102*, 4403-4409.

0002-7863/81/1503-5004$01.25/0