The average values of the dihedral angles from the second calculation (DG 2, Table I) are almost identical to those found from the calculation employing all of the chiral restraints. The rms differences are larger, to be expected with the looser distance restraints, but the correct relative configuration was obtained. This indicates that DG is indeed useful in the calculation of not only conformation but also the relative configuration of a questionable center. However, it must be stressed that the bridgehead protons of 1 have many favorable properties in this respect; they are in the middle of a rigid moiety with known geometry and involved in a large number of NOEs.

Conclusions

It has been demonstrated that DG is a useful and efficient method for the determination of the conformation of small synthetic or naturally occurring molecules. Most members of this class of molecules have properties favorable for the examination by DG: NOEs are large and easily measured and the geometry (a minimum of bond lengths and angles) is usually well-defined. The determination of unknown relative configurations from DG has also been investigated. Although the correct stereo configurations were developed, compound 1 may be a special case. It is clear that more example compounds will have to be calculated before DG can be proposed as a general method for the calculation of relative configurations from NOE derived distances.

Acknowledgment. The authors wish to thank Dr. Holger Hoffmann (Schering, Berlin) and Matthias Köck (Technical University München) for their help with this project and Dr. Ruud Scheek (University of Groningen) for the DG and associated programs and help in the use of them. D.E.M. acknowledges the support and useful comments of Prof. Horst Kessler (Technical University München). The Deutsche Forschungsgemeinschaft is gratefully acknowledged for financial support.

Origin of the Unusual Infrared Absorption Band at ~1600 cm^{-1} in 1,4-Dioxaspiro[2.2]pentanes

B. Andes Hess, Jr.,*[†] Jin K. Cha,*[‡] L. J. Schaad,*[†] and Prasad L. Polavarapu*[†]

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Department of Chemistry, University of Alabama, Tuscaloosa, Alabama 35487

Received August 11, 1992

Crandall and co-workers have recently reported the synthesis of a large number of derivatives of 1,4-dioxaspiro[2.2]pentane (1, see Figure 1).[1] All of these spiro dioxides exhibited a band of medium intensity between 1600 and 1650 cm^{-1} in their infrared absorption spectra. Crandall has noted, "Although the vibrational origin of this band remains a mystery, it appears to be a dependable characteristic of this spiro-fused heterocyclic system." This prompted us to carry out an ab initio study of the vibrational spectrum of 1 to determine the vibrational mode responsible for this unusual band as well as to provide a theoretical spectrum to aid in the eventual identification of parent 1.

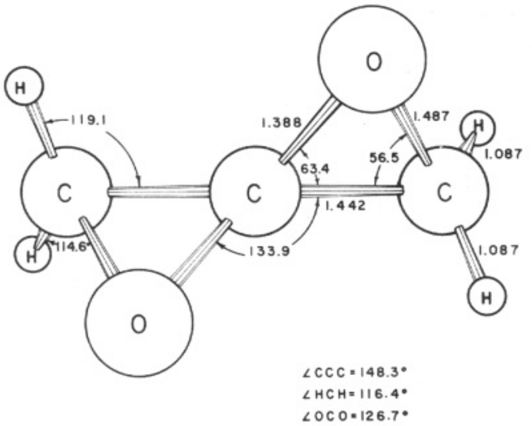


Figure 1. The calculated MP2/6-31G* structure of 1,4-dioxaspiro[2.2]pentane (1). Lengths are in angstroms and angles in degrees. The structure has C_2 symmetry with the C_2 axis through the central carbon atom and perpendicular to the page.

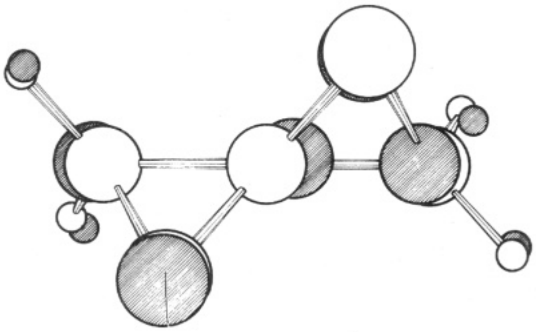


Figure 2. The B vibration at 1721 cm^{-1} calculated to give rise to the "mystery band" in 1,4-dioxaspiro[2.2]pentanes. Unshaded circles represent the equilibrium atomic positions of Figure 1. Shaded circles show displacements in this B normal mode. Bonds are drawn between equilibrium atoms (ref 5).

Table I. MP2/6-31G* Vibrational Frequencies and Absorption Intensities of 1[a]

symmetry	frequency (cm^{-1})	intensity (km/mol)	description[a]
A	320	4.69	mixture of external angle bends at C*
B	399	10.21	mixture of external angle bends at C*
A	461	2.25	mixture of external angle bends at C*
A	632	4.10	C–O stretch and C*–O stretch
B	832	72.53	C–O stretch and C*–O stretch
B	869	44.68	H–C bend and C*–O stretch
A	905	18.72	C*–O stretch and H–C bend
A	1039	5.49	C–O stretch and C–C* stretch
B	1099	22.87	H–C bend
A	1110	21.94	H–C bend
B	1114	27.49	H–C bend
A	1136	14.95	H–C bend
B	1196	12.12	H–C bend and C*–O stretch
A	1232	2.91	C–C* stretch and H–C bend
B	1514	12.20	H–C bend
A	1150	0.51	H–C bend
B	1721	97.01	C–C* stretch
A	3185	7.06	C–H stretch
B	3186	9.38	C–H stretch
B	3288	6.91	C–H stretch
A	3289	9.79	C–H stretch

[a] C* is the central carbon atom.

MP2/6-31G* calculations were carried out using the program CADPAC 4.0.[2] The geometry was first fully optimized with a C_2 symmetry constraint (see Figure 1). Of note are the relatively short (1.388 Å) bonds between the spiro carbon and oxygen. The total MP2/6-31G* en-

---

[†] Vanderbilt University.

[‡] University of Alabama.

(1) Crandall, J. K.; Batal, D. J.; Sebesta, D. P.; Lin, F. *J. Org. Chem.* **1991**, *56*, 1153 and references cited therein.

(2) Amos, R. D.; Rice, J. E. *CADPAC: The Cambridge Analytic Derivatives Package*; issue 4.0, Cambridge, 1987.

0022-3263/92/1957-6367$03.00/0

ergy is −266.30544 au, and the dipole moment is 2.664 Debyes. The MP2 analytic second derivative of the energy with respect to nuclear displacements confirmed the C_2 structure to be a minimum. Infrared vibrational frequencies and absorption intensities are given in Table I.

The most intense band of the spectrum is computed to be at 1721 cm^{-1}. MP2 frequencies are typically calculated to be ~3–5% higher than actually observed.[3] Hence we predict that this band should actually appear near 1650 cm^{-1}. While the parent system is unknown, this computed frequency is in good agreement with the observed unusual band in several simple derivatives. Crandall and coworkers have reported that tetramethyl-1 has an absorption band at 1629 cm^{-1} and mono-*tert*-butyl-1 an absorption band at 1615 cm^{-1}. Examination of the normal mode and potential energy distribution of the 1721-cm^{-1} band reveals this is primarily due to the antisymmetric stretch of the two C*–C bonds (C* is the central carbon). Isotopic substitution with tri-^{13}C shifts the computed band to 1663 cm^{-1}, with di-^{18}O to 1717 cm^{-1} and with d_4 to 1687 cm^{-1}. Smaller contributions from the C*–O stretching motions and hydrogen bending motions are also present in this mode. For methyloxirane and *trans*-dimethyloxirane which have a single oxirane ring, MP2/6-31G* calculations[4] predict modes at 1588 and 1577 cm^{-1}, respectively, with dominant C*–C stretching contributions along with hydrogen bending. The corresponding experimental bands in these two cases were found to be at ~1500 cm^{-1}. The presence of two C*–C bonds in the present case causes the antisymmetric C*–C stretch to appear at a higher frequency than the C*–C stretching frequency of a single oxirane group.

Acknowledgment. We thank the National Science Foundation for support through an instrument grant (CHE 8808018) and Intergraph Corp. of Huntsville, AL, for the provision of computing systems and software.

---

[3] Hess, B. A., Jr.; Schaad, L. J.; Čársky, P.; Zahradník, R. *Chem. Rev.* **1986**, *86*, 709.

[4] Polavarapu, P. L.; Barron, L. D.; Hecht, L. submitted for publication in *J. Phys. Chem.*

[5] Polavarapu, P. L.; Pickard, S. T.; Smith, H. E.; Black, T. M.; Rauk, A.; Yang, D. *J. Am. Chem. Soc.* **1991**, *113*, 9747.

Medium-Sized Cyclophanes. 16.[1] Bromination of 8,16-Dihydroxy[2.2]metacyclophanes

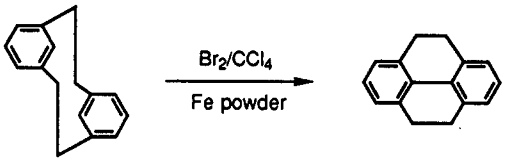
Takehiko Yamato,*,† Jun-ichi Matsumoto,†
Kiwamu Tokuhisa,† Kazuaki Suehiro,† Seiji Horie,‡ and
Masashi Tashiro‡

Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan, and Institute of Advanced Material Study, Kyushu University, 6-1, Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

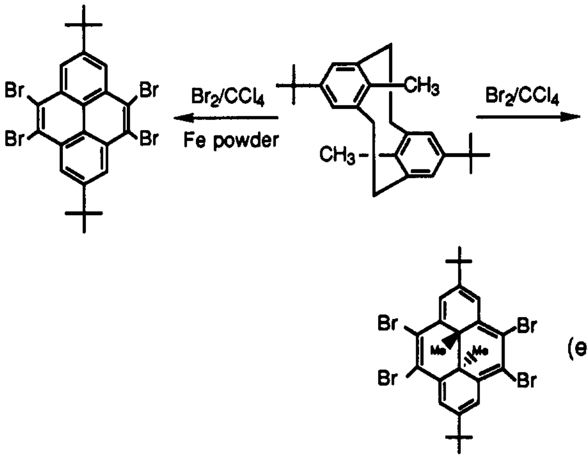
Received June 1, 1992

Introduction

Due to electronic interaction between the two benzene rings, the proximity of 8,16-positions, and considerable strain energy, [2.2]metacyclophane (MCP = metacyclophane) is prone to undergo transannular reactions.[2-6] These have usually been rationalized as involving initial dehydrogenation to 4,5,9,10-tetrahydropyrene. Sato and his co-workers[7] have reported that the reaction of 8,16-unsubstituted [2.2]MCP with bromine in the presence of iron powder affords the corresponding tetrahydropyrene via the addition–elimination mechanism (eq 1). Subsequently, we reported[8] that bromination of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP in the presence or absence of iron powder as a catalyst afforded 2,7-di-*tert*-butyl-4,5,9,10-tetrabromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene and 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene, respectively (eq 2). The results suggested a useful route to *trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes.



(eq. 1)



(eq. 2)

Although *trans*-10b,10c-dihydropyrenes where the substituents at the 10b and 10c positions are hydrogen or alkyl groups have been prepared by Boekelheide and his coworkers,[9,10] attempts at introducing other functional groups into the internal positions were unsuccessful. Thus, we undertook the present work in order to evaluate the possibility of the novel reaction mentioned above for the preparation of *trans*-10b,10c-dihydroxy-10b,10c-dihydropyrenes.

Results and Discussion

When 5,13-di-*tert*-butyl-8,16-dihydroxy[2.2]MCP (**1b**)[11] was treated with excess bromine in carbon tetrachloride at room temperature for 1 h, none of the expected product 2 was detected (Scheme I). However, a novel product 3 was obtained as colorless prisms in quantitative yield. The

---

† Saga University.

‡ Kyushu University.

[1] Medium-Sized Cyclophanes. Part 15: Yamato, T.; Matsumoto, J.; Tokuhisa, K.; Shigekuni, M.; Suehiro, K.; Tashiro, M. *J. Org. Chem.* **1992**, *57*, 396.

[2] Griffin, R. W., Jr. *Chem. Rev.* **1963**, *63*, 45.

[3] Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: New York, 1964.

[4] Boekelheide, V. *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1983; Vol. 113, p 87.

[5] Allinger, N. L.; DaRooge, M. A.; Hermann, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 1974.

[6] Allinger, N. L.; Gordon, B. J.; Hu, H.-E.; Ford, R. A. *J. Org. Chem.* **1967**, *32*, 2272.

[7] Sato, T.; Wakabayashi, M.; Okamura, T.; Amada, T.; Hata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2363.

[8] Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.

[9] Boekelheide, V.; Miyasaka, T. *J. Am. Chem. Soc.* **1967**, *89*, 1709.

[10] Boekelheide, V.; Sturm, E. *J. Am. Chem. Soc.* **1969**, *91*, 902.

[11] Tashiro, M.; Koya, K.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104*, 3707.