J. Am. Chem. Soc. **1982**, *104*, 4592–4593

The Importance of van der Waals' Attractions in Determining the Equilibrium between 1,4- and 1,6-Dialkylcyclooctatetraenes

N. L. Allinger,*[1a] M. Frierson,[1a] and F. A. Van-Catledge*[1b]

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602, and the Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898. *Received October 26, 1981*

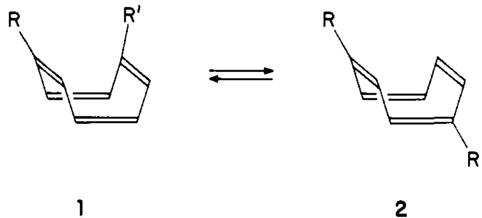
Abstract: The position of equilibrium between the title compounds, which are valence-bond isomers, is governed by the magnitude of the van der Waals' attraction between the two alkyl groups. This is calculated (MMP2) to favor the 1,6 isomer by less than 0.02 kcal/mol in the case where the two groups are methyl and more than 1.07 kcal/mol in the case where the two groups are *tert*-butyl.

Nonbonded or van der Waals' forces between two atoms or molecules containing filled shells of electrons are attractive at relatively long distances and repulsive at short distances. Organic chemistry is awash with examples in which these repulsive forces are very important (steric hindrance),[2] but examples of van der Waals' attractions leading to observable chemical consequences are quite rare. Such attractions are sometimes referred to as "hydrophobic bonding" in the biochemical literature, and examples involving two large molecules (or a large molecule and a small molecule) are well documented.[3] The only intramolecular example of which we are aware in which an observable effect has been convincingly attributed to van der Waals' attraction in a small molecule is in the equilibrium between the conformations of 1,3,5-trineopentylbenzene.[4] In this molecule, the three groups can either all fold over on the same side of the benzene ring or two can be on one side with the third opposite. The former conformation is found to predominate, and this has been attributed to the mutual van der Waals' attractions among the neopentyl groups.

Recently, Streitwieser has published some results on the equilibrium between **1** and **2** (Scheme I, R, R′ = *tert*-butyl).[5] These are valence-bond isomers, but the double-bond shift in cyclooctatetraene (COT) is known to occur rather easily at room temperature,[6] and it does also in these compounds. The interesting observation[5] was that **1** is more stable than **2** by 0.67 kcal/mol. Streitwieser suggested that this might be due to van der Waals' attraction between the two *tert*-butyl groups.

This is a problem that is ideally suited to attack by the molecular mechanics method.[7] The MMP2 force field was used in the present work.[8] The van der Waals' parameters used in this force field stem mainly from studies involving the interplanar spacing in graphite[9] and the crystal spacing and heat of sublimation of the hexane crystal.[10] While there has been a good deal of discussion about the repulsive part of the van der Waals' curve for hydrogen and carbon over the past several years,[7] the attractive portion of the curve has been less thoroughly studied. Detailed studies showing how the attractive part of the van der Waals' curve was evaluated have been presented for only a few of the force fields in the literature.[7-10]

Scheme I



1
1,6 – ISOMER

2
1,4 – ISOMER

Results and Discussion

In the present study, COT itself was first examined, and the geometry and inversion barrier are reasonably well reproduced. The basic computational procedure involves a π-electron self-consistent-field calculation on the planar COT molecule with alternating bond lengths. From this treatment, the necessary force constants for stretching and torsion involving the bonds connecting the π-system atoms are evaluated. Once the force constants are available, a straightforward molecular mechanics calculation is carried out, which causes the molecule to pucker into its well-known tub form. The basic calculation follows that described earlier,[11] but the details differ somewhat. While it would be desirable to calculate the inversion barrier that separates **1** from **2** (R, R′ = *t*-Bu), there is a limitation in the self-consistent-field calculation that prevents this.[12] We can calculate the barrier to mechanical inversion (without the double-bond shift) through a planar conformation, and for **1** (R, R′ = *t*-Bu), the value is 25.81 kcal/mol. The experimental enthalpy of activation for the conversion **1** → **2** is 15.5 kcal/mol. The calculated inversion barrier for COT itself is 13.7 kcal/mol, essentially identical with the experimental value.[11] The only conclusion we can draw is that the transformation pathway for **1** → **2** involves a transition state that is of substantially lower energy than the planar structure. Examinations of models suggest that the molecule need not become planar, but rather undergoes a pseudorotational motion for the

---

[1] (a) University of Georgia. (b) Du Pont: Contribution No. 2974.

[2] Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.

[3] (a) Lehninger, A. L. "Biochemistry"; Worth: New York, 1970; p 43. (b) Mahler, H. R.; Cordes, E. H. "Biological Chemistry", 2nd ed.; Harper and Row: New York, 1971; p 165. (c) Gabler, R. "Electrical Interactions in Molecular Biophysics"; Academic Press: New York, 1978; (d) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membranes"; Wiley-Interscience: New York, 1973.

[4] (a) Aurivillius, B.; Carter, R. E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1033. (b) Carter, R. E.; Stilbs, P. *J. Am. Chem. Soc.* **1976**, *98*, 7515. (c) Carter, R. E.; Nilsson, B.; and Olsson, K. *Ibid.* **1975**, *97*, 6155.

[5] Lyttle, M. H.; Streitwieser, A., Jr.; Kluttz, R. Q. *J. Am. Chem. Soc.* **1981**, *103*, 3232.

[6] Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 671.

[7] This topic has been widely reviewed in recent years. Some recent reviews are: Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D.C., 1982. Warshel, A. In Modern Theor. Chem. **1977**, *7*, 133ff.

[8] This program is available from Molecular Design, Ltd. It is an updated version of MMP1: *QCPE* **1977**, *10*, 318.

[9] Allinger, N. L.; Sprague, J. T. *J. Comput. Chem.* **1980**, *1*, 257.

[10] Allinger, N. L.; Miller, M. A.; Van-Catledge, F. A.; Hirsch, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.

[11] Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

[12] Allinger, N. L.; Sprague, J. T.; Finder, C. J. *Tetrahedron* **1973**, *29*, 2519.

0002-7863/82/1504-4592$01.25/0

J. Am. Chem. Soc. 1982, 104, 4593-4598

Table I. van der Waals' and Total Energy Changes: 1 → 2 kcal/mol

R	R′	E_{vdw}	E_{total}
Me	Me	0.07	0.02
Me	*t*-Bu	0.29	0.33
t-Bu	*t*-Bu	0.86	1.07

transformation **1** → **2**. Unfortunately, we are unable to carry out calculations that would model this pathway.

Next, we considered placing methyl groups and *tert*-butyl groups at atoms 1 and 4 or at atoms 1 and 6. If one examines a Dreiding model of the 1,6-di-*tert*-butyl compound, the alkyl groups appear to be much too close together, with the nearest hydrogens being separated by about 1.5 Å. Since the van der Waals' H–H minimum is around 3 Å, this implies large repulsions between the *tert*-butyl groups. This implication is erroneous, however, due to the well-known inaccuracy of Dreiding molecular models. The C–C–C bond angles in COT are 126.1° (experimental[13] and 124.6° (MMP2), while the models show an idealized value of 120°. The difference is quite significant. With the correct bond angle, the *tert*-butyl groups are moved away from one another to the point where there is no repulsion between them but rather attractions between even the nearest hydrogen atoms. The interaction between any pair of atoms is not very large (for two hydrogens at their van der Waals' minumum the interaction energy with the MMP2 force field is −0.06 kcal/mol). Most of the atoms are somewhat further apart than the van der Waals' minimum; thus, most of the interactions are of the order −0.01 kcal/mol per atom pair. But the *tert*-butyl group contains 13 atoms; therefore, for 2 interacting *tert*-butyl groups, there are 169 interactions! Clearly, though the numbers are individually small, their total is significant. In the 1,4-di-*tert*-butyl case, the groups are much farther apart; hence, the total interaction is correspondingly less.

Table I summarizes our calculations for the dimethyl, di-*tert*-butyl, and methyl-*tert*-butyl cases. The van der Waals' attraction is always greater for the 1,6 isomer, and the steric energy correspondingly lower. The trend in van der Waals' attraction energy parallels the total number of interactions between the alkyl groups: 169 for di-*tert*-butyl, 52 for methyl-*tert*-butyl, and 16 for dimethyl. The conclusion is interesting: large groups such as *tert*-butyl, which are quite polarizable, will show large van der Waals' attractions; small groups like methyl, which are not very polarizable, will show extremely small interactions. Of course, the total energy difference between **1** and **2** depends upon other contributions besides the van der Waals' attractions. But these other factors appear to be quite small, and the nonbonded attractions dominate the situation.

Conclusions

Thus, the MMP2 force field clearly indicates **1** to be more stable than **2** in the gas phase. We emphasize that ther are no adjustable parameters in the calculation; this is a necessary result of this force field. The measurements by Streitwieser are in solution, and some change in the equilibrium constant may attend a change to the gas phase. In particular, a difference in molecular volume for the two isomers might alter the experimental value. Since there are no overlapping van der Waals' radii that differ significantly in the two isomers, one might expect this effect to be negligible. Also, the enthalpy difference may be sensitive to differences in the polarizability of the solvent molecules. We believe that experiment and theory are in good agreement. The proposal by Streitwieser that this equilibrium is determined primarily by van der Waals' attraction between the *tert*-butyl groups is borne out by the molecular mechanics calculations.[14]

Acknowledgment. Thanks are due to Professor Streitwieser for informing us of the experimental results prior to publication. Also, discussions of possible modes of solvent effects with Dr. L. L. Shipman have been helpful.

Registry No. 1 (R, R′ = Me), 29554-56-1; **1** (R = Me; R′ = *t*-Bu), 82209-38-9; **1** (R, R′ = *t*-Bu), 76794-05-3.

---

(13) Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724.

(14) One of the referees has suggested that the structural parameters for the molecules in this study should be made available. The atomic coordinates for all of these structures are available from the authors upon request.

Electron-Transfer Rates in Mixed-Valence Europium Sulfide by Time Domain Reflectometry

Bruce C. Bunker, Russell S. Drago,* and Michael K. Kroeger

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801.
Received September 25, 1981

Abstract: Intervalence electron transfer in a mixed-valence sample of europium sulfide is shown to give rise to dielectric relaxation which can be studied by using the technique of time domain reflectometry (TDR). It is demonstrated that the dielectric relaxation times measured by using these techniques can be directly related to the rates of intervalence electron transfer. Rates obtained via time domain reflectometry are compared with Mössbauer results obtained on the same sample and with other published Mössbauer and conductivity studies. The significance of these results relative to Hush theory is also examined.

Electron-transfer processes are dominant phenomena in a number of important areas in both chemistry and physics such as redox reactions, electrochemistry, and semiconductor science. Understanding the rate at which these processes occur and the energetics which govern both the rate and extent of electron transfer should help scientists to understand and manipulate electron-transfer processes to optimize desired chemical and/or physical properties for many systems. Unfortunately, the actual electron-transfer process is often difficult to study directly, especially in those oxidation reduction reactions where the electron transfer is one in a series of rapidly occurring steps. Electron transfer in mixed-valence compounds is a simpler process whose understanding can provide fundamental information which relates to a wide range of electron-transfer phenomena.

Experiments aimed at determining electron-transfer rates in a variety of mixed-valence compounds have been undertaken by using physical methods which include electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), magnetic

0002-7863/82/1504-4593$01.25/0