CC single bond in thiete, which evolves into the CC double bond in thioacrolein, changes from 1.507 to 1.417 Å (−50%). In terms of transition-state structure and exothermicity, the thiete to thioacrolein reaction is reminiscent of the cyclobutene to butadiene case.

The scaled 6-31G* SCF vibrational frequencies for thiete in Table VII are of interest as the molecule has been made, but its vibrational spectrum is unexplored. The three most intense bands are predicted to occur at 688 cm⁻¹ (65.4 km·mol⁻¹), 819 cm⁻¹ (15.7 km·mol⁻¹), and 2939 cm⁻¹ (31.0 km·mol⁻¹). The probable reliability[43] of the frequency predictions is ±30 cm⁻¹.

Trends in the Ring-Opening Reactions. All of the transition-state structures are qualitatively similar in that a twist into a C_2 or ("C_2 like" in the case of C_1 symmetry) structure occurs as would be anticipated on orbital symmetry grounds.[1,2] As discussed previously,[17] the absence of a C_2 axis in the oxetene or thiete reactions has no important effect on the course of the ring opening. The reaction proceeds much as in the cyclobutene to butadiene case, except that in the absence of CH_2 groups the distinction between conrotatory and disrotatory processes is removed.[31]

Heteroatom substitutions for the methylene groups in cyclobutene do have significant effects upon the height of the reaction barriers and in two cases upon the reaction energies. The cyclobutene to butadiene conversion is about 10 kcal·mol⁻¹ exothermic.[5,6] Incorporation of one or two oxygens to give oxetene or dioxetene leads to much more strongly exothermic reactions. The strength of the CO double bond in the open isomer and the difficulty of incorporating strongly electronegative elements into the four-membered ring can explain this trend. With one or two sulfurs substituted for the CH_2 groups in cyclobutene, the reactions are calculated to be slightly exothermic. Sulfur can much more readily adapt to the four-membered ring environment than can oxygen. The differential energy effect between CS single and double bonds also is not as large as for these bond types involving oxygen.

With the exception of dioxetene, all the rings face barriers of ~20–25 kcal·mol⁻¹ to opening. These barriers are 8–13 kcal·mol⁻¹ less than the cyclobutene activation energy[5,6] predicted to be ~33 kcal·mol⁻¹ by comparable theoretical methods. The qualitative analyses[30] of heterosubstituted butadienes suggested a barrier lowering of ~7–11 kcal·mol⁻¹ with a single oxygen or sulfur substituted for a CH_2 group, and this prediction has been confirmed here. Such a reduced barrier will have a dramatic effect on the rates of isomerization of these rings.[14,31] Dioxetene is predicted to face a small barrier, and further high-level computations will be required to definitively establish its stability. The barrier for dithiete isomerization to dithioglyoxal is quite substantial at 20–22 kcal·mol⁻¹. The experimental isolation of the dithioglyoxals along with dithiete[23] should be possible.

Concluding Remarks

The ring openings of dioxetene, oxetene, dithiete, and thiete are of interest both individually and as orbital symmetry allowed electrocyclic isomerizations analogous to the cyclobutene to butadiene reaction. Spectroscopic and/or kinetic studies of these reactions should be assisted considerably by the theoretical predictions of this research.

NMR Studies of Bond Order in Distorted Aromatic Systems

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Sever Sternhell,[*,‖] **Charles W. Tansey,**[‖] **and Yoshito Tobe**[§]

Contribution from the Departments of Biochemistry, Chemistry, and Organic Chemistry, University of Sydney, Sydney, New South Wales, Australia 2006, and Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. Received March 5, 1990

Abstract: The $^4J_{H-C=C-Me}$ coupling constant has been previously established[1,2] as a probe of bond order. This has now been used to examine the bond orders of compounds containing severely distorted benzene nuclei. In the case of 3,4-di-*tert*-butyltoluene, no electronic distortions in the aromatic ring can be detected by this method. A series of moderately to severely distorted paracyclophanes show no perturbation of electronic structure, with the possible exception of 8-methyl[6]paracyclophane, which exhibits a barely significant deviation from unstrained values. These conclusions are supported by the results of SCF–MO calculations.

Introduction

The orthobenzylic coupling constant involving a methyl group, $^4J_{H-C=C-Me}$, henceforth referred to as J_{OB}, has been shown to correlate well with the square of the SCF bond order and the Pauling bond order.[2] This coupling constant has been used previously to probe the electronic structure of quinonoid, hydroaromatic, heterocyclic and other systems.[3] This work describes the use of this method to probe the bond orders in systems containing distorted benzene nuclei. The systems examined were

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(2) Barfield, M.; Collins, M. J.; Gready, J. E.; Sternhell, S.; Tansey, C. W. *J. Am. Chem. Soc.* **1989,** *111,* 4285.
(3) Barfield, M.; Collins, M. J.; Gready, J. E.; Hatton, P. M.; Sternhell, S.; Tansey, C. W. *Pure Appl. Chem.* **1990,** *62,* 463.

o-di-*tert*-butylbenzene and a series of paracyclophanes. The structure of 3,4-di-*tert*-butylbenzoic acid (**1**, R = COOH) has

∠ C3-C2-C1-C6 = 3.0°

∠ C2-C1-C6-C5 = 4.5°
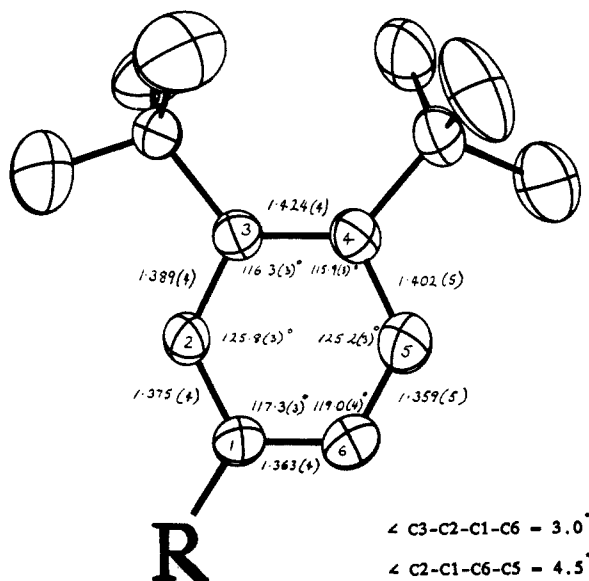
STRUCTURE 1

been reported,[4] and the distortions in this molecule are assumed to be similar to those in 3,4-di-*tert*-butyltoluene (**1**, R = CH₃). The mode of distortion of the aromatic ring is 3-fold—torsional distortions leading to a skewing of the benzene nucleus, bond stretching and compression, and angular in-plane distortions. A summary of the major distortions of the aromatic ring is shown in structure **1**.
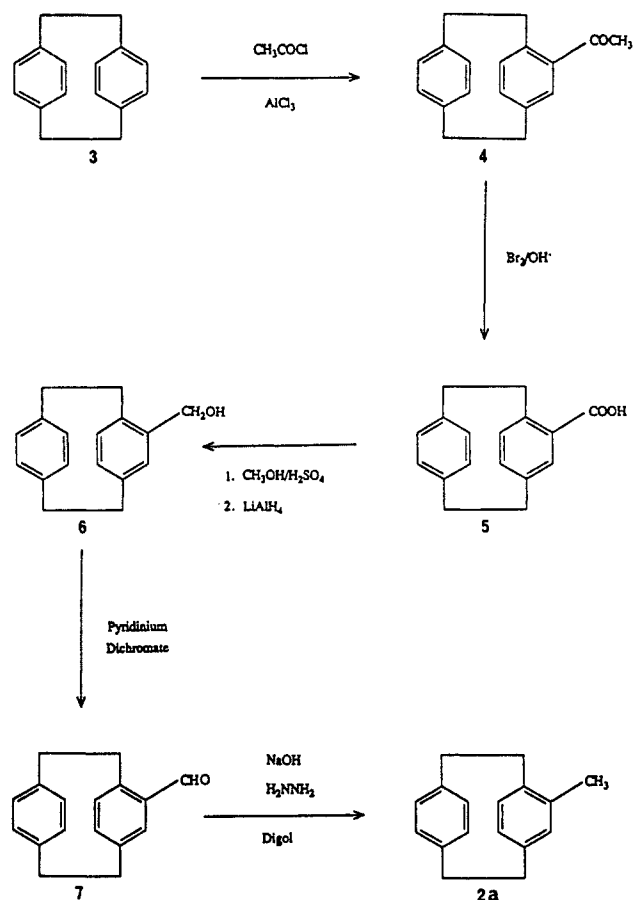
The distortion of the benzene ring in paracyclophanes **2**[5] is more severe, as the para bridge causes the two carbons in the ring to
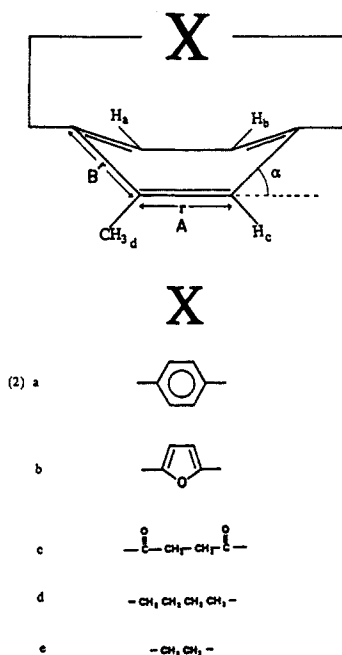
STRUCTURE 2

which the chain is fused to move out of plane in a syn fashion. The result of this is that the benzene ring takes on a "boatlike" shape (**2**), similar to the boat form of cyclohexane. As the length
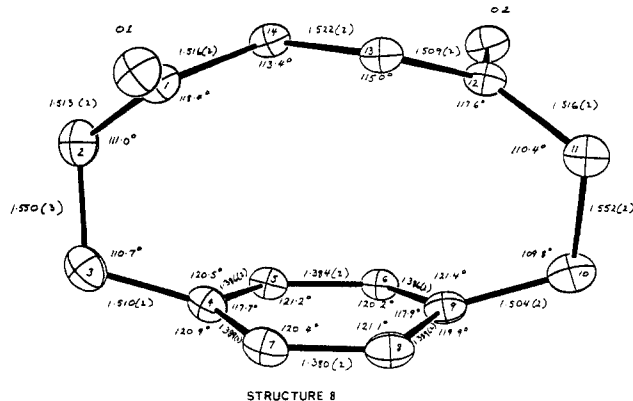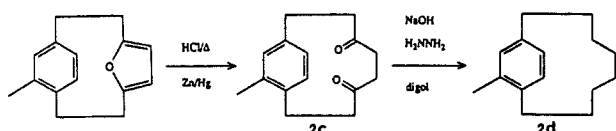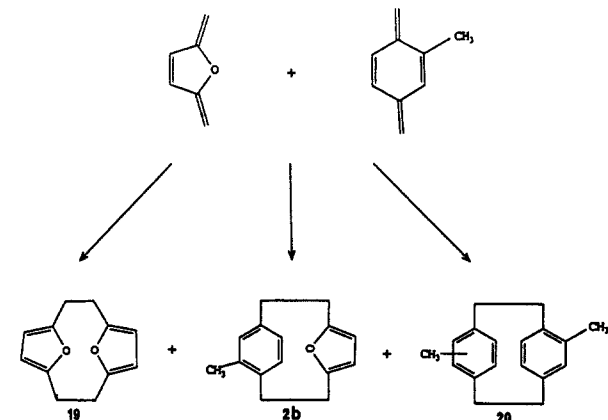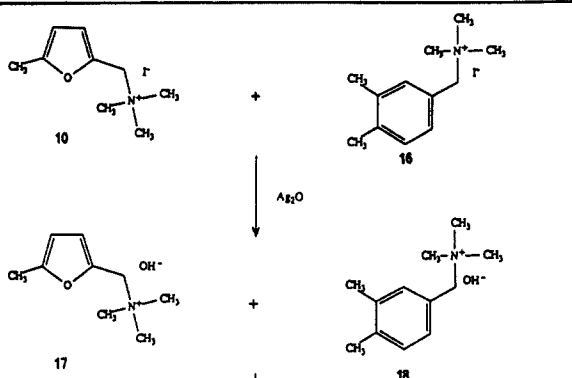
Scheme I

of the bridge decreases, the bending angle (α) as defined in structure **2** increases. Such deformation may be extreme and invites the question "how deformed can a benzene ring become before it can no longer be classed as aromatic?".

Preparation of Compounds

The preparation of 3,4-di-*tert*-butyltoluene (**1**, R = CH₃) and the corresponding carboxylic acid (**1**, R = COOH) has been described.[4] 4-Methyl[2.2]paracyclophane (**2a**) was prepared by acetylation of [2.2]paracyclophane (**3**) and conversion of the acetyl group to a methyl group by the procedure shown in Scheme I. 3,6-Diketo[8]para-cyclophane (**8**) was prepared by the method of Cram.[6] 4-Methyl[2]-

STRUCTURE 8

paracyclo[2](2,5)furanophane (**2b**), 3,6-diketo-10-methyl[8]para-cyclophane (**2c**), and 10-methyl[8]paracyclophane (**2d**) were prepared by a route analogous to that described by Cram[6] (Scheme II), using 3,4-dimethylbenzyl iodide rather than 4-methylbenzyl iodide to generate the methylated cyclophane. 8-Methyl[6]paracyclophane was prepared

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Scheme II

Scheme III

Table I. Ortho-Benzylic Coupling Constants for Paracyclophanes

J_{OB} $J_{c,d}$, Hz	$^3J_{H,H}$ $(J_{a,b})$, Hz	α, deg	bond length, Å A	B
2a	−0.66	7.81	12.6[8]	1.386–1.387[8]	1.384–1.386[8]
2b[a]	−0.65	7.70	13.8–14.2[9]	1.383–1.387[9]	1.391–1.395[9]
2c	−0.66	7.85	14.6–14.9	1.380–1.389	1.386–1.389
2d	−0.66	7.62	9.00–9.23[10]	1.380–1.384[10]	1.389–1.397[10]
2e[b]	−0.61	7.27	20.1–20.9[10]	1.376–1.399[7,c]	1.385–1.393[7,c]
			19.4–19.5[11]	1.370–1.395[11,d]	1.385–1.393[11,d]

[a] 4-Methyl[2]paracyclo[2](2,5)furanophane is a fluxional molecule with two unequally populated conformers discernible in the 400-MHz spectrum in $C_2D_2Cl_4$ at 215 K. The coupling constants refer to the major isomer (~80%). Details of the NMR experiments will be reported elsewhere. [b] 8-Methyl[6]paracyclophane is a fluxional molecule with two unequally populated conformers discernible in the 400-MHz NMR spectrum in CD_2Cl_2, acetone-d_6, and toluene-d_8 at 220 K. The coupling constants refer to the major isomer (~75%). An identical value was obtained in toluene-d_8 at 400 K for the averaged spectrum. The details of the NMR experiments will be reported elsewhere. [c] Data for the corresponding acid.[7] [d] Data for the related diesters.[11]

from the corresponding methyl ester[7] by the method shown in Scheme III.

Structure of 3,6-Diketo[8]paracyclophane

Crystallographic data (see supplementary material) gave the molecular structure of 3,6-diketo[8]paracyclophane summarized in the ORTEP diagram (8) and Table I in the supplementary material.

Results and Discussion

3,4-Di-*tert*-butyltoluene, whose distortions are assumed to be identical with those in *o*-di-*tert*-butylbenzoic acid, has J_{OB} values of 0.75 ± 0.03 Hz for the 1–2 bond and 0.73 ± 0.03 Hz for the 1–6 bond. These results show no significant difference and are identical within experimental error. This suggests that there is no appreciable electronic distortion accompanying the torsional distortions (1, R = CH_3) that are present in this part of the molecule. The coupling constants are also close to that of toluene (0.75 Hz[2]), suggesting that not only are the bonds similar, but they are normal aromatic bonds. These results are in accord with SCF bond orders of 0.554 and 0.594 for the 1–2 and 1–6 bonds, respectively, calculated by the procedure described below for paracyclophanes using the experimental bond lengths in structure 1. The calculated bond orders for the other bonds which are not accessible by this NMR experiment are 0.610 (5–6), 0.459 (4–5), 0.382 (3–4), and 0.505 (2–3).

The results for the paracyclophane series are shown in Table I.

The bending angles (α) (structure 2) and C–C bond distances (r) were obtained from related crystalline derivatives[7–11] by

(7) Tobe, Y.; Ueda, K. I.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron* **1986**, *42*, 1851.

(8) (a) Hope, H.; Bernstein J.: Trueblood, K. N. *Acta Crystallogr.* **1972**, *B28*, 1733. (b) Brown, C. J. *J. Chem. Soc.* **1953**, 3265. (c) Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 442.

(9) Hama, F.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3557.

(10) Newton, M. G.; Walter, T. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1973**, *95*, 5652.

Table II. Calculated Strain Energies, Geometries, and Bond Orders for "Boat" Benzenes[a]

α, deg	destabilization energy[b] ΔE, kJ/mol	bond A length, Å	bond A bond order	bond B length, Å	bond B bond order
0	0	1.387	0.512	1.387	0.512
5	+12.6	1.387	0.512	1.388	0.508
10	+50.2	1.386	0.515	1.391	0.498
15	+114.7	1.385	0.519	1.398	0.473
20	+208.5	1.385	0.519	1.408	0.438
25	+339.1	1.384	0.522	1.421	0.392
30	+504.5	1.384	0.522	1.441	0.322

[a] This table shows calculations for "boat" benzene, distorted in the manner of 2. All geometric parameters apart from α are optimized at the STO-3G level. Bond orders were calculated by using the bond-order/bond-length correlation described elsewhere (Figure 8 of ref 13). [b] Relative to benzene.

previous workers for compounds **2a, 2b, 2d,** and **2e** and in these laboratories for 3,8-diketo[8]paracyclophane (**8**) as a model for **2c**. The increase in the angle of out of plane bending, α, can be seen to increase as the length of the bridge decreases. The J_{OB} coupling constant can be seen to be unchanged and identical with the unstrained analogue (1,2,4-trimethylbenzene J_{OB} = –0.66 Hz[1]) in all but the most strained case, [6]paracyclophane. These results suggest that only [6]paracyclophane may have a detectable amount of π-electron distortion. The bond order/bond length and bond order/$^3J_{HH}$ relationships, although less reliable,[1,2] also support this conclusion in this series.

(11) (a) Tobe, Y.; Nakayama, A.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Org. Chem.* **1987,** *52,* 2639. (b) Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985,** *118,* 4414.

(12) (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986,** *58,* 137. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1987,** *109,* 1676.

(13) Gready, J. E. *J. Comput. Chem.* **1984,** *5,* 411.

It therefore appears that a benzene ring can undergo severe distortions of the σ-framework without disruption of the ground-state π-electron distribution. Such a conclusion is also in accord with the theoretical work of Haddon,[12] which postulates that significant rehybridization occurs in distorted systems to allow maintenance of pp overlap.

SCF–MO calculations on a series of benzenes distorted in the manner of **2** were performed and are summarized in Table II. It can be seen that, in agreement with the experimental results, no significant changes in the bond order of bond A are predicted for a boat-shaped benzene distorted up to 30°. Interestingly, the calculations predict a decrease of bond order in bond B, but measuring this is inherently outside the scope of our NMR method.

Experimental Section

All experimental NMR data in Table I were obtained on a Bruker Instruments WM-400 MHz NMR spectrometer using 5-mm sample tubes with approximately 5% w/v solutions in the solvent stated (supplementary material). The solvents were degassed and the spectra acquired at 300 K, except for compounds **2b** and **2e** (see footnotes to Table II). The spectra were acquired under conditions of high digital resolution, at least 0.03 Hz. All systems were either first order at the frequency used or were analyzed by using the PANIC (closely related to LAOCOON) program. Ortho-benzylic coupling constants are assumed to be negative.[1] Synthetic and crystallographic details are given in the supplementary material.

Supplementary Material Available: Preparation procedures and analytical data for all compounds and tables of positional parameters, crystal data, bond lengths, bond angles, thermal parameters, details of least-squares planes calculations, and torsion angles for **8** (23 pages). Ordering information is given on any current masthead page.

Theoretical Characterization of the Potential Surfaces and Properties of Weakly Bonded Acetylene

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Abstract: Acetylene is a simple molecule for probing weak hydrocarbon interactions. There exist extensive spectroscopic data for a number of acetylene complexes, which demonstrate a variety of structures. Acetylene weakly attaches at one of its hydrogens in some cases, at the molecule center, or just along the molecular axis. However, there is little characterization of the potential surface features of these complexes, features that are manifested in the structural observations, and there does not seem to be a uniform means of understanding the structures and properties. In this report, the electrically based molecular mechanics for clusters (MMC) approach has been applied to small complexes of acetylene, first to test whether it can uniformly account for the observations and second to provide a characterization of the interaction energetics and properties of the complexes. The systems considered are the acetylene dimer, trimer, and tetramer as well as mixed, binary complexes with argon, water, hydrogen fluoride, hydrogen cyanide, and ammonia. The calculations yield equilibrium structures, stabilities, dipole moments, and harmonic frequencies for the intermolecular vibrational modes. The calculational results show certain floppiness, some unexpected structural parameters, and for one complex, an isomer that has not been detected experimentally.

Introduction

Even excluding chemical bonding, the interactions of hydrocarbons with other hydrocarbons, with water, and with other kinds of molecules comprise a fundamental element in analyzing and simulating biomolecular processes of many types. These interactions are generally categorized as weak interactions, as hydrogen bonding, or as van der Waals attractions, and at the least, explicit potentials for these interactions can be used in, and are a prere-

quisite for, computational simulation studies. For these purposes, it is likely that gross characteristics suffice and that certain detailed aspects of potentials can be overlooked. Still, a fundamental basis for the interactions, with detailed aspects, affords the greatest and widest applicability in the end.

Perhaps the first step in probing weak hydrocarbon interactions is examining small, weak complexes containing the simplest possible hydrocarbons, e.g., methane, acetylene, ethylene, and