J. Am. Chem. Soc. **1987**, *109*, 2902-2909

[5]Paracyclophane: An Important Example of Ring Strain and Aromaticity in Hydrocarbon Compounds

Julia E. Rice, Timothy J. Lee, Richard B. Remington, Wesley D. Allen,[†] D. Allen Clabo, Jr., and Henry F. Schaefer III*

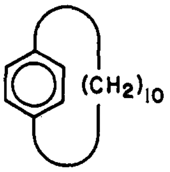
Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received October 7, 1986*

Abstract: Ab initio molecular quantum mechanical methods have been applied to the [5]paracyclophane molecule ($C_{11}H_{14}$), which has recently been prepared by Bickelhaupt and nine co-workers. The complete molecular structure has been predicted via the self-consistent-field (SCF) method, by using both minimum (STO-3G) and double-ζ (DZ) basis sets. The critical geometrical parameter is the deviation ϕ of the benzene ring from planarity, and ϕ is predicted to be 22.4° and 23.7°, respectively, with the STO-3G and DZ basis sets. Both angles are significantly less than those predicted with empirical and semiempirical computational methods. DZ SCF harmonic vibrational frequencies and infrared intensities are presented and compared with similar results for benzene. The lowest triplet and first excited singlet states of [5]paracyclophane are also considered at the ground-state equilibrium geometry. Finally the resonance energy is estimated from a suitable homodesmotic reaction and compared to the analogous prediction for benzene.

The family of [*n*]paracyclophanes range from the highly unstable butalene (or [0]paracyclophane, a C_6H_4 isomer closely related to the lower energy diradical *p*-benzyne) to compounds such as [10]paracyclophane for which more subtle differences with benzene are observed in the matter of aromaticity. The [*n*]paracyclophanes with $n < 7$ have been difficult to prepare in the laboratory, and these are the systems for which theoretical chemistry is most likely to lead to new insights. We intend ultimately to predict the molecular structures, vibrational frequencies, infrared and Raman intensities, and energetics of the [*n*]paracyclophanes $n = 0, 1, 2, 3, 4, 5, 6, 7$, and 8. The present paper reports the first results of this long-range study.

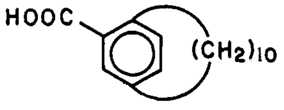
1

The [*n*]paracyclophane family of molecules has been of continuing interest to organic chemists for more than 35 years.[1,2] [10]Paracyclophane (**2**) was first synthesized in 1950 by Wiesner, MacDonald, Ingraham, and Kelley.[3] Two years later the same research group in New Brunswick reported the synthesis of [9]paracyclophane[4] but were unsuccessful in their attempts to prepare the analogous compound with eight bridging methylene groups. At this point Cram's group at UCLA became very active in the area, reporting many novel discoveries[1] during the 1950s.



2

A number of important physical measurements on [*n*]paracyclophanes were made rather early. Perhaps one should note first[2] the work of Waugh and Fessenden[5] on the NMR spectra of [10]- and [12]paracyclophane. They showed that the CH_2 peaks were shifted to higher field the closer they were to the middle of the chain, confirming that the degree of aromaticity may be interrogated via the NMR spectrum. Waugh and Fessenden's work thus supported Pople's free electron model[6] to account for chemical shifts in the NMR of protons attached to aromatic rings. A second matter of some interest is the intuition[7] that for substituted [*n*]paracyclophanes resolution into optically active forms should be possible if *n* is sufficiently small. As early as 1961, restricted rotation of the benzene ring through the $(CH_2)_n$ chain was demonstrated[8] for *n* as large as 10, specifically for the simple –COOH substituted [10]paracyclophane.



3

It is apparent that ring strain increases rapidly as the *n* in [*n*]paracyclophane is reduced. Nine years elapsed between the Canadian synthesis[4] of [9]paracyclophane and the preparation, in 1961, of [8]paracyclophane, a camphoraceous smelling liquid, by Cram and Knox.[9] The ultraviolet spectrum of [8]paracyclophane suggested to Cram and Knox that "the benzene ring is seriously bent from its normal planar configuration". Eleven more years elapsed before the synthesis of the first substituted [7]paracyclophane was reported by Allinger and Walter.[10] And the following year, 1973, the parent [7]paracyclophane was made at Princeton by the group of M. Jones.[11]

The step from [7]paracyclophane to [6]paracyclophane required just short of 1 year's time and was accomplished by Jones and co-workers[12] by using a carbene route analogous to that devised for the $n = 7$ compound.[11] Perhaps surprisingly, the UV spectrum of [6]paracyclophane is only moderately shifted from that of [7]paracyclophane. Kane, Wolf, and Jones conclude their paper stating that "The question of aromaticity of [6]- and [7]paracyclophanes requires most careful scrutiny, but the PMR spectrum clearly reveals a ring current and thus within the limits of this single criterion, these paracyclophanes are still aromatic".

The very interesting report of the interconversion of [6]paracyclophane with its isomer 1,4-hexamethylene (Dewar benzene) was given in 1977 by Kammula, Iroff, Jones, van Straten, de Wolf,

---

[†] NSF Predoctoral Fellow.

(1) Cram, D. J.; Daeniker, H. U. *J. Am. Chem. Soc.* **1954**, *76*, 2743. Cram, D. J.; Allinger, N. L.; Steinberg, H. *J. Am. Chem. Soc.* **1954**, *76*, 6132. Cram, D. J. *Rec. Chem. Prog.* **1959**, *20*, 70.

(2) March, J. *Advanced Organic Chemistry*, 3rd ed., Wiley: New York, 1985; see especially pp 38, 92, and 1113.

(3) Wiesner, K.; MacDonald, D. M.; Ingraham, R. B.; Kelley, R. B. *Can. J. Res.* **1950**, *B28*, 561.

(4) Bartlett, M. F.; Figdor, S. K.; Wiesner, K. *Can. J. Chem.* **1952**, *30*, 291.

(5) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846.

(6) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.

(7) Lüttringhaus, A.; Gralheer, H. *Liebigs Ann. Chem.* **1947**, *557*, 112. Prelog, V. *J. Chem. Soc. London* **1950**, 420.

(8) Blomquist, A. T.; Stahl, R. E.; Meinwald, Y. C.; Smith, B. H. *J. Org. Chem.* **1961**, *26*, 1687.

(9) Cram, D. J.; Knox, G. R. *J. Am. Chem. Soc.* **1961**, *83*, 2204.

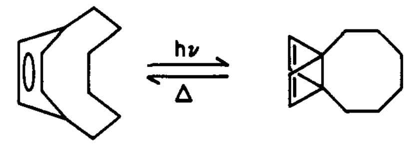
(10) Allinger, N. L.; Walter, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 9267.

(11) Wolf, A. D.; Kane, V. V.; Levin, R. H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1680.

(12) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643.

0002-7863/87/1509-2902$01.50/0

4

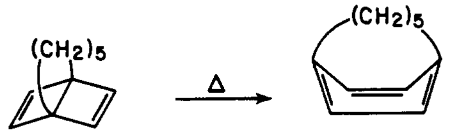


5

and Bickelhaupt (KIJSWB).[13] The work of KIJSWB apparently establishes the "breakpoint" in the series of [n]paracyclophanes and their Dewar isomers. For $n \geq 6$, the paracyclophane structure is the lower lying energetically, while for $n = 5$ (and presumably smaller values of n as well) the Dewar form appears to be favored energetically.[14]

During the middle 1970s there were two reports[14,15] of the intermediacy of [5]paracyclophane in the thermal rearrangement of 1,4-pentamethylene Dewar benzene.[16] However, the first direct spectroscopic and chemical evidence for [5]paracyclophane did not appear until mid-1985, a dozen years after the Princeton synthesis of [6]paracyclophane. No less than ten authors, hereafter designated Jenneskens and co-workers,[17] appeared on the masthead of this important publication. A qualitative sketch of the structure of [5]paracyclophane is given in Figure 1. If one were a statistician (rather than a chemist) the period between 1950 ($n = 10$) and 1985 ($n = 5$) could be used to predict that [4]paracyclophane will be synthesized in 1992. In the meantime there is ample opportunity for theoretical chemistry to play a role in the continuing story of the [n]paracyclophanes.

6



7

Aromaticity in [n]Paracyclophanes

The fundamental question in [n]paracyclophane chemistry is, as simply stated by Cram and Cram,[18] "How bent can a benzene be?". The critical geometrical parameter in this regard would be, for [5]paracyclophane, the angle ϕ in Figure 2. This question is in turn obviously related to the issue of whether the [n]paracyclophanes with n values smaller than seven are truly aromatic. Because the aliphatic chain causes the benzene ring to bend into a boatlike conformation, the effect on the aromatic nature of the benzene ring is an important question. The major difficulty in this regard, of course, is defining precisely what is meant by aromaticity or aromatic character.

Researchers in different branches of chemistry picture aromaticity from vastly dissimilar viewpoints. For example, synthetic organic chemists often define an aromatic compound as one which is exceptionally stable and which participates more readily in electrophilic substitution reactions than addition reactions. In contrast, UV spectroscopists frequently note an aromatic compound by the bathochromic shift from conjugated dienes. NMR spectroscopists typically view an aromatic compound as one in which the aromatic proton signals are shifted to low field due to the ring current, and, as in the case of many cyclophanes,[17] protons inside the cone of the ring are shifted to high field. It is also clear from recent articles on aromaticity and aromatic compounds that even today a universal definition of aromaticity does not exist.

An example of this divergence of aromaticity perspectives is seen in a news brief in the July 1, 1985 issue of Chemical & Engineering News. This writeup is sufficiently interesting to quote in its entirety, with the most inflammatory statement highlighted (by us).

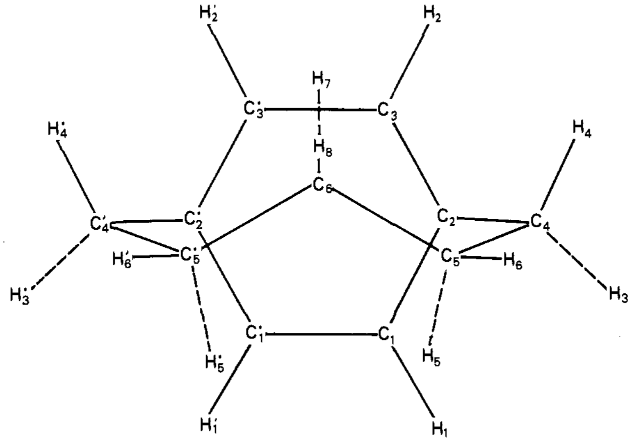


Figure 1. A qualitative sketch of the molecular structure of [5]paracyclophane.

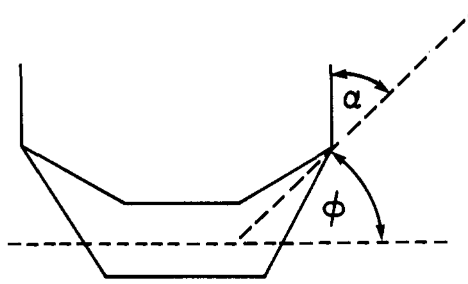


Figure 2. Definition of the two most important angles showing the distortion of the benzene ring from planarity in [n]paracyclophanes.

> Researchers in the Netherlands and Japan have produced [5]paracyclophane, a benzene ring in which the para positions are linked by a five-carbon alkyl chain. The alkyl bridge, as expected, strains the benzene ring by bending it, they find. However, "the benzene ring retains its aromatic character with remarkable tenacity," they note, although it does "pay a toll" by giving up its stability. *The degree to which the molecule retains its aromaticity flies in the face of predictions based on theoretical calculations, the researchers say.* Friedrich Bickelhaupt and his collaborators at Vrije Universiteit, Amsterdam, and Osaka University made the strained paracyclophane at −60 °C by irradiating its Dewar benzene precursor, a tricyclic molecule dubbed propelladiene. NMR spectroscopy reveals that the [5]paracyclophane has much lower thermodynamic and kinetic stability than the related molecule having a six-carbon bridge. [5]Paracyclophane decomposes at room temperature, but its decay products haven't yet been fully identified.

The Netherlands–Japan collaboration (Jenneskens and coworkers, ref 17) concluded that [5]paracyclophane retains its aromaticity, based on the observed UV and NMR spectra. In striking contrast the two pilloried theoretical studies concluded that [5]paracyclophane was not aromatic due to its excessive predicted strain energy. The first theoretical study,[19] by Schmidt, Schweig, Thiel, and Jones, used the semiempirical MNDO method[20] and stated explicitly that the aromatic character of the benzene moiety in [5]paracyclophane is completely lost. The second theoretical study,[21] by Carballeira, Casado, Gonzalez, and Rios, used the molecular mechanics method of Boyd[22] and concluded that for [5]paracyclophane the loss of aromaticity is "total".

---

(13) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1977**, *99*, 5815.

(14) van Straten, J. W.; Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 4499.

(15) Weinges, K.; Klessing, K. *Chem. Ber.* **1976**, *109*, 793.

(16) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

(17) Jenneskens, L. W.; de Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; de Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716.

(18) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204.

(19) Schmidt, H.; Schweig, A.; Thiel, W.; Jones, M., Jr. *Chem. Ber.* **1978**, *111*, 1958.

(20) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(21) Carballeira, L.; Casado, J.; González, E.; Ríos, M. A. *J. Chem. Phys.* **1982**, *77*, 5655 and references therein.

(22) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574.

Table I. Comparison of Benzene Ring Structural Parameters for [5]Paracyclophane[a]

method	ab initio min basis SCF	ab initio double-ζ SCF	molecular mechanics	molecular mechanics[b]	MNDO[c]
authors	Remington[25]	this work	Carballeira[21]	Allinger[24]	Schmidt[19]
dihedral angle ϕ					
($C_1'C_1C_3C_2$)	22.4°	23.7°	35.9°	29.6°	31.4°
bond lengths					
C_2-C_3	1.382	1.392	1.382	1.402	1.423
C_1-C_2	1.412	1.409	1.383	1.401	1.428
C_3-C_3'	1.396	1.401	1.384	1.392	1.403
C_1-C_1'	1.365	1.384	1.383	1.392	1.398

[a] Bond lengths in Å. The carbon atoms are numbered in Figure 1. The angel ϕ describes the bending of the benzene ring from planarity and is defined in Figure 2. [b] The molecular mechanics results presented here are from the more recent, unpublished MM2 study by Allinger. [c] The results actually presented in this column are from a more precise unpublished MNDO study by W. Thiel, one of the authors of ref 19.

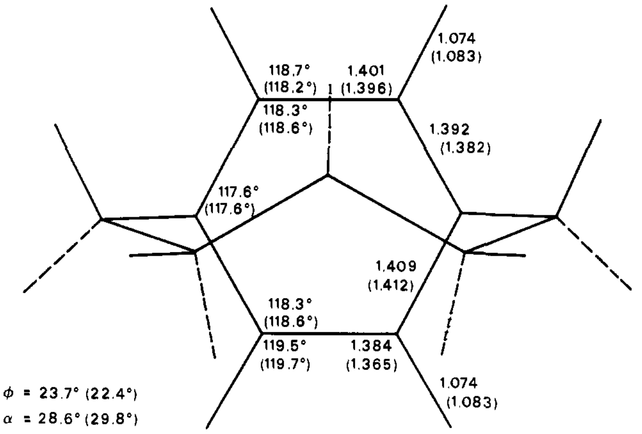


Figure 3. The theoretical molecular structure of [5]paracyclophane based on the double-ζ (DZ) self-consistent-field (SCF) method. This sketch shows only the geometrical parameters for the benzene ring portion of the molecule. Refer to the supplementary material (Table Is) for a complete set of geometrical parameters. In parentheses is given the minimum basis structure of ref 25.

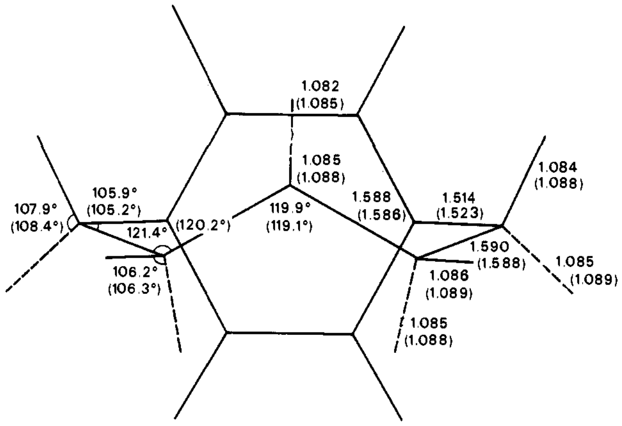


Figure 4. The theoretical molecular structure of [5]paracyclophane based on the double-ζ (DZ) self-consistent-field (SCF) method. Shown here are geometrical parameters for the five methylene groups [i.e., $(CH_2)_5$] bridging the para positions of the benzene ring. Refer to the supplementary material (Table Is) for a complete set of geometrical parameters. In parentheses is given the minimum basis set structure of ref 25.

Vigorous controversy in chemistry is often constructive, and the dispute over the aromatic character of [5]paracyclophane is certainly robust. However, without wanting to affirm the reliability of the previous theoretical predictions of the strain energy of [5]paracyclophane, we are not entirely convinced that there is more than a semantic difference here. NMR and UV spectra may simply be painting a different part of the picture than are the semiempirical strain energy calculations. Streitwieser's recent comment[23] in this regard is quite apt: "There is no operational definition of aromaticity".

Structural Predictions for [5]Paracyclophane

Given the ambiguities discussed above, it is of interest to optimize the structure of [5]paracyclophane by using ab initio theoretical methods. The ab initio structure could then be compared with previous theoretical structures[19,21,24] and also used to confirm (or deny) that the C_s symmetry structure of [5]paracyclophane is a minimum on the potential energy surface. As reported in a recent communication,[25] we previously optimized all of the structural parameters (36 independent internal coordinates) of the C_s symmetry conformer of [5]paracyclophane by using the STO-3G minimum basis SCF method (virtually the simplest ab initio method imaginable). Here, beginning with the earlier structure,[25] a second complete geometrical optimization has been carried out with a much larger double-ζ (DZ) basis set, specifically, the standard Huzinaga–Dunning C(9s5p/4s2p), H(4s/2s) set.[26,27] The usual hydrogen s function scale factor of 1.2 was employed, i.e., all Gaussian exponents α were multiplied by $(1.2)^2 = 1.44$.

With 138 contracted Gaussian functions and 25 atoms, the present DZ treatment of [5]paracyclophane is one of the more demanding structural optimizations reported in the literature. All final internal coordinate energy gradients were less than 1×10^{-5} hartree/bohr for the DZ SCF structure shown in Figures 3 and 4, and it is found to be a genuine minimum. The most important internal coordinate values for the optimized structure are listed in Table I along with previous results given by Allinger, Sprague, and Liljefors,[24] Schmidt,[19] and Carballeira.[21] Note that the results of Allinger and Carballeira were obtained via different molecular mechanics modeling techniques, and Schmidt's results were obtained from MNDO calculations.

The dihedral angle ϕ as defined pictorially by Allinger[24] gives a measure of the degree to which the benzene ring is bent and is illustrated in our Figure 2. This angle appears to be well-defined in Figure 2, but there exists some ambiguity concerning the plane of the four central or nonbridgehead carbon atoms of benzene. For [*n*]paracyclophanes with C_s symmetry, these central four benzene carbons do indeed lie in a common plane; however, for structures with C_2 symmetry (notably in [*n*]paracyclophanes where *n* is even-numbered) these carbons do not necessarily lie in the same plane. However, for the present work on [5]paracyclophane this ambiguity is not a problem. The angle ϕ is identically zero for the unsubstituted benzene molecule. The two most important differences between the DZ SCF structure reported here and the molecular mechanics (MM) structure due to Carballeira[22] are the benzene ring carbon–carbon bond lengths and the dihedral angle ϕ. The ab initio structure is much less bent than the MM structure with ϕ taking on the values 23.7° (DZ SCF) and 35.9° (MM), respectively. It is also important to note that ϕ has the

---

(23) Streitwieser, A., personal communication.

(24) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100. A more recent unpublished MM2 study by Allinger was received in a personal communication. We thank Professor Allinger for permission to include these results in Table I.

(25) Remington, R. B.; Lee, T. J.; Schaefer, H. F. *Chem. Phys. Lett.* **1986**, *124*, 199.

(26) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

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

value 29.6° for the MM2 model used by Allinger,[24] in closer agreement with the DZ SCF value. The MNDO value of 31.4° is intermediate between the two MM models. Thus we see that SCF theory, using a DZ basis, predicts a more nearly planar benzene ring than those previously reported by using empirical and semiempirical methods for [5]paracyclophane. This result tends to empathize with the experimental conclusions of Jenneskens and co-workers.[17]

Note also in Table I the good agreement with the earlier minimum basis SCF prediction $\phi = 22.4°$. This comparison provides further evidence[28] for the qualitative reliability of hydrocarbon geometrical predictions from the minimum basis SCF level of theory. In fact, minimum basis SCF theory seems to do a better job for [5]paracyclophane than for the experimentally characterized bicyclo[1.1.0]butane.[29] In the latter compound (structure V in ref 29) the STO-3G dihedral angle between the two three-membered-ring planes is 2.8° less than that predicted with a basis set of roughly DZ quality.[30] This deviation in angle may be compared to (23.7° - 22.4° = 1.3°) for benzene-bending in [5]paracyclophane. It should be emphasized, however, that the minimum basis set SCF treatment of the structure of bicyclo[1.1.0]butane provides unusually poor agreement with experiment,[31] as such comparisons go.[28]

The benzene ring carbon–carbon bond lengths of [5]paracyclophane vary noticeably (0.047 Å) for the ab initio minimum basis SCF structure, with the shortest and longest being 1.365 and 1.412 Å, respectively. The more reliable DZ SCF level reported here shows significantly less variation, namely 0.025 Å, with ring carbon–carbon distances ranging from 1.384 to 1.409 Å. This observation is consistent with those of many others[32-35] concerning polyenes. Specifically, the STO-3G basis generally underestimates C–C double bond lengths (compared with experiment), which leads to a larger bond length alternation in polyenes. It is, however, encouraging that the *order* of the four independent ring C–C distances is correctly predicted with the minimum basis set. Also, it is fascinating that the minimum basis predicts [5]paracyclophane to be "more aromatic" as measured by deviation from planarity but "less aromatic" in terms of having a greater degree of bond length alternation. In comparison, Carballeira's MM structure[21] shows little variation, from 1.382 to 1.384 Å, and the MNDO structure[19] displays bond distances from 1.398 to 1.428 Å.

When one considers that at the DZ SCF level benzene has a C–C bond length[36] of 1.396 Å, then it is clear that the differences between benzene and [5]paracyclophane are quite small compared to the difference between conventional single (1.54 Å) and double (1.35 Å) carbon–carbon bonds. We conclude that while some bond alternation is predicted, it is modest in magnitude.

Comparison with Experimental Structures

The controversy concerning the degree of aromaticity possessed by the [*n*]paracyclophanes might fade away entirely if accurate crystal structures existed for the molecules with $n = 4$–6. In fact, it may surprise the reader that there are no crystal structures or other experimental structural data for any of the unsubstituted [*n*]paracyclophanes. The only crystallographic information available[37,38] prior to 1983 was for 4-carboxy[8]paracyclophane and 3-carboxy[7]paracyclophane. The prefixes 3- and 4- in these compounds indicate the positions of the COOH substituent along the $(CH_2)_n$ chain connecting the para carbons of the benzene ring, the first carbon in this chain being labeled 1. While providing valuable geometrical information, the experiments on 3-carboxy[7]paracyclophane were limited in accuracy due to disorder in the crystal.[38] However, Allinger and co-workers did determine that the angle ϕ of benzene ring deformation is approximately 17° for this [7]paracyclophane. The earlier study by Newton, Walter, and Allinger[37] found that the para carbon atoms of the benzene lie 9° out of the plane of the other four ring carbons for 4-carboxy[8]paracyclophane.

In 1983 two crystal structures of [6]paracyclophanes were reported.[39,40] The group of Tobe[39] in Osaka characterized the 8-carboxy[6]paracyclophane, where the prefix 8- (in the sense defined above) implies that the COOH substituent is attached to one of the benzene ring carbons adjacent to one of the two para carbons. That is, their molecule is just like **3** except that it includes two fewer methylenes in the $(CH_2)_n$ chain. Tobe and co-workers found the average value of the ring distortion angle ϕ to be 20.7°.

The second 1983 crystal structure, of 8,9-dimethoxycarbonyl[6]paracyclophane, was reported by Krieger, Liebe, and Tochtermann.[40] The two methoxycarbonyl groups are attached to adjacent positions on the benzene ring and are expected to result in a molecular structure somewhat further from the unsubstituted [6]paracyclophane than the just discussed 8-carboxy[6]paracyclophane. In any case the para carbons of Tochtermann's compound are lifted 19.4° and 19.5°, respectively, out of the plane of the other four benzene carbon atoms. Thus Tochtermann's disubstituted [6]paracyclophane is 1.3° or 1.2° closer to benzene planarity than is Tobe's monosubstituted compound.

How do the above experimental structures compare with the ab initio DZ SCF geometrical prediction? This comparison is inevitably a bit indirect, since there is no experimental structure for a [5]paracyclophane. Nevertheless, the progression of benzene-bending angles ϕ from 9° ([8]paracyclophane) to 17° ([7]paracyclophane) to 20.7° ([6]paracyclophane) does seem broadly consistent with the theoretical prediction of 23.7° for the unsubstituted [5]paracyclophane.

Tochtermann and co-workers[40] report the following carbon–carbon distances within the benzene ring of their disubstituted [6]paracyclophane: 1.370, 1.385, 1.386, 1.393, 1.401, and 1.406 Å. The range of C–C distances is 0.036 Å, which is actually a bit greater than the 0.025 Å predicted from theory for [5]paracyclophane. In principle, of course, the [6]paracyclophane should be *more* benzenelike than the [5]paracyclophane and display *less* bond variation. However, the presence of the two methoxycarbonyl substituents clouds the comparison. It will be interesting to see comparable DZ SCF predictions for [6]paracyclophane.

In Tochtermann's [6]paracyclophane crystal structure,[40] the two shortest C–C single bond distances are those from the para benzene carbons to the first members of the chain. These distances are 1.495 and 1.506 Å, consistent with the general notion that C–C single bonds adjacent to carbon–carbon multiple bonds are shorter than the standard value, namely 1.54 Å. The longest bond in the $(CH_2)_n$ chain is just adjacent to the second shortest C–C bond (described above) and has r(C–C) = 1.564 Å in Tochtermann's [6]paracyclophane. The remaining experimental C–C single bond distances are fairly normal, falling in the range 1.55 ± 0.01 Å.

The theoretical predictions for the $(CH_2)_n$ chain distances (seen in Figure 4) of [5]paracyclophane are generally consistent with the experimental [6]paracyclophane structure. The variation in C–C single bond distances is greater than for [6]paracyclophane, as expected. This variation is in fact greater (0.076 Å) at the DZ SCF level of theory than with the minimum basis set (0.065 Å).

---

[28] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[29] Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

[30] Skancke, P. N. *J. Mol. Struct.* **1982**, *86*, 255.

[31] Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976; **1970**, *53*, 858.

[32] Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5339.

[33] Mains, G. J.; George, P.; Bock, C. W.; Trachtman, M.; Brett, A. M. *J. Mol. Struct.* **1977**, *41*, 87.

[34] Banks, A.; Mains, G. J.; Bock, C. W.; Trachtman, M.; George, P. *J. Mol. Struct.* **1979**, *56*, 267.

[35] Haddon, R. C. *Pure Appl. Chem.* **1982**, *54*, 1129.

[36] Clabo, D. A., Jr.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 1664.

[37] Newton, M. G.; Walter, T. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1973**, *95*, 5652.

[38] Allinger, N. L.; Walter, T. J.; Newton, M. G. *J. Am. Chem. Soc.* **1974**, *96*, 4588.

[39] Tobe, Y.; Kakiuchi, K.; Odaira, Y.; Hosaki, T.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 1376.

[40] Krieger, C.; Liebe, J.; Tochtermann, W. *Tetrahedron Lett.* **1983**, *24*, 707.

Table II. A Comparison between the Benzene Ring C–H Stretching Frequencies (in cm^{-1}) of [5]Paracyclophane, Paradideuteriobenzene, and Benzene[a]

	[5]paracyclophane			paradideuteriobenzene			benzene		
	symmetry	DZ SCF theory	intensity (km/mol)	symmetry[b]	DZ SCF theory	intensity (km/mol)	symmetry	DZ SCF theory	intensity (km/mol)
$(C_1-H_1) + (C_1'-H_1') + (C_3-H_2) + (C_3'-H_2')$	ω_1 a′	3391	1.3	a_g	3410 (3067)	0	a_{1g}	3422 (3074)	0
$(C_1-H_1) + (C_1'-H_1') - (C_3-H_2) - (C_3'-H_2')$	ω_2 a′	3386	48.6	b_{3u}	3406 (3089)	73.9	e_{1u}	3406 (3048)	74.2
$(C_3-H_2) - (C_3'-H_2')$	ω_{37} a″	3365	15.5	b_{1u}	3384.19 (3084)	25.7	e_{1u}	3406 (3048)	74.2
$(C_1-H_1) - (C_1'-H_1')$	ω_{38} a″	3362	14.1	b_{2g}	3384.24 (NG)	0	e_{2g}	3384 (3057)	0
				a_g	2516 (2285)	0	e_{2g}	3384 (3057)	0
				b_{1u}	2513 (2279)	27.5	b_{1u}	3373 (NG)	0

[a] Note that the last two frequencies have no counterpart in [5]paracyclophane. The numbering of atoms is from Figure 1. Experimental fundamentals (given in parentheses) are from the recent paper by Thakur, Goodman, and Ozkabak (ref 41). NG means that there is no observed gas-phase fundamental frequency for a particular mode. [b] The chosen coordinate system places the y axis out of the plane of the molecule, while the z axis (twofold) passes through the deuterium atoms. The appropriate D_{2h} character table appears in Cotton, F. A. *Chemical Applications of Group Theory*; 2nd ed.; Wiley Interscience: New York, 1971.

All four C–C distances interior to the $(CH_2)_n$ chain (1.590, 1.588, 1.588, and 1.590 Å as one moves along the chain) are notably longer than the standard carbon–carbon single bond distance of 1.54 Å. Comparable theoretical predictions for the unsubstituted [6]paracyclophane would allow closer comparison with experiment.

The Infrared Spectrum of [5]Paracyclophane

At the DZ SCF level of theory, analytic energy second derivative methods were used to evaluate the harmonic vibrational frequencies of [5]paracyclophane. The assignment of these vibrational frequencies is a challenging task, as is any attempt to relate these frequencies to those of benzene, the prototypical aromatic molecule. In the Supplementary Material provided with this article the details of the vibrational analysis are given. In Tables Is and IIs (s denotes Supplementary Material) a complete, nonredundant set of A′ and A″ internal coordinates is defined, and the DZ SCF equilibrium values of the A′ coordinates are listed to unambiguously establish the molecular structure. These symmetry internal coordinates were carefully chosen in order to (a) maximize correspondence with appropriate D_{6h} coordinates for benzene, (b) reduce the values of the off-diagonal quadratic force constants as much as possible, and (c) describe the benzene ring modes and the $(CH_2)_5$ bridging modes separately. Figures Is and IIs consist of pictorial representations of the internal coordinates. In Table IIIs all 69 DZ SCF harmonic frequencies appear, and with each frequency the symmetry, intensity, and dominant components of the potential energy distribution (PED) are tabulated. Finally, Tables IVs and Vs are comprised of the entire A′ and A″ force constant matrices relative to the symmetry internal coordinates. For the sake of brevity, only the most salient features of the infrared spectrum are presented here.

The DZ SCF infrared spectrum of [5]paracyclophane consists of two distinct parts, the C–H stretching modes from 3183 to 3391 cm^{-1} and all other stretching and bending modes from 179 to 1765 cm^{-1}. Among the 14 C–H stretches, there is a clear separation between those associated with the benzene ring and those associated with the $(CH_2)_5$ chain. The former frequencies are higher, separated by a gap of 3362 - 3287 = 75 cm^{-1}. This separation is consistent with the penchant for C–H bonds adjacent to multiple bonds (C$\doteq$C in the case of the benzene ring) to be shorter than those adjacent to C–C single bonds. Note in this regard that the benzene ring C–H distances of [5]paracyclophane are 1.074 Å, while those for the $(CH_2)_5$ chain lie in the range 1.082–1.086 Å.

Table II gives the benzene ring C–H stretching frequencies of [5]paracyclophane. These are compared with analogous DZ SCF predictions for benzene and more importantly for *p*-dideuteriobenzene. The dideuteriation removes the two (benzene ring) hydrogen atoms which are not present in [5]paracyclophane. The very recently tabulated gas-phase fundamentals of Thakur, Goodman, and Ozkabak[41] are also given in Table II.

The correlation between the DZ SCF harmonic C–H stretching frequencies of [5]paracyclophane and *p*-dideuteriobenzene is quite good. Note first that for both [5]paracyclophane and *p*-dideuteriobenzene the totally symmetric C–H stretch lies highest with low IR intensity. The second predicted frequency lies 5 cm^{-1} lower for [5]paracyclophane and 4 cm^{-1} lower for *p*-dideuteriobenzene, both frequencies having a large infrared intensity. Accordingly, a good opportunity for observing the IR spectrum of [5]paracyclophane may lie with the fundamental ν_2. Given the present prediction that this mode lies 20 cm^{-1} below the analogous result for *p*-dideuteriobenzene, one may estimate the fundamental to lie at 3089 - 20 = 3069 cm^{-1}, assuming the correctness of the recent experimental assignment of Thakur et al.[41]

The third and fourth highest C–H stretching frequencies of [5]paracyclophane (ω_{37} and ω_{38}) correspond to the b_{1u} and b_{2g} modes of *p*-dideuteriobenzene. Since the b_{1u} and b_{2g} harmonic frequencies of *p*-dideuteriobenzene are separated by a minuscule 0.05 cm^{-1} (at the DZ SCF level of theory), it is hardly surprising that a pair of closely spaced, strongly mixed modes are present in [5]paracyclophane. Specifically, ω_{37} and ω_{38} lie 3 cm^{-1} apart, contain almost exactly 50% of each of the b_{1u} and b_{2g} stretching coordinates, and share nearly equally the intensity of the b_{1u} mode of *p*-dideuteriobenzene.

The reader should keep in mind while evaluating these predictions that the analogous DZ SCF harmonic C–H stretching frequencies for benzene (Table II) lie uniformly above the observed fundamentals.[41] In particular, the theoretical harmonic frequencies lie 300–358 cm^{-1}, or 10–12%, above the experimental anharmonic frequencies. Such errors are indeed typical at the DZ SCF level of theory.

In summary, two principal predictions are apparent from theory concerning the benzene ring C–H stretching frequencies of [5]paracyclophane. First, the close correspondence between the frequencies of [5]paracyclophane and *p*-dideuteriobenzene suggests that [5]paracyclophane might aptly be labeled "benzenelike" or "aromatic". Second, the "aromatic" C–H stretching fundamentals are *downshifted* (approximately 20 cm^{-1}) relative to those of benzene. Such shifts can be explained by noting that in the theoretical structure of [5]paracyclophane the hydrogen atoms attached to the benzene ring lie about 15° out of the plane of the three nearest carbon atoms (in the direction of the $(CH_2)_5$ bridge). Hence, the carbon hybridized atomic orbitals involved in the C–H bonds of [5]paracyclophane possess less s character than those in benzene, which results in downward shifts of the corresponding C–H stretching frequencies.

The C–H stretching fundamentals associated with the $(CH_2)_5$ chain are reported and assigned in Table III. Although the carbon–carbon bonds in the $(CH_2)_5$ chain are significantly strained and abnormally long (Figure 4), the C–H bond lengths and C–H stretching frequencies in the $(CH_2)_5$ bridge have values typical of saturated hydrocarbons. For example, the DZ SCF frequencies of [5]paracyclophane occur between 3183 and 3287 cm^{-1} while

---

[41] Thakur, S. N.; Goodman, L.; Ozkabak, A. G. *J. Chem. Phys.* **1986**, *84*, 6642.

Table III. Predicted C–H Stretching Vibrational Frequencies (in cm^{-1}) and Infrared Intensities for the $(CH_2)_5$ Chain of [5]Paracyclophane

assignment[a]	symmetry	DZ SCF theory	intensity (km/mol)
$(C_6{-}H_7) - (C_6{-}H_8)$	ω_3 a′	3287	46.9
$(C_4{-}H_3) - (C_4{-}H_4) + (C_4'{-}H_3') - (C_4'{-}H_4')$	ω_4 a′	3272	4.4
$(C_4{-}H_3) - (C_4{-}H_4) - (C_4'{-}H_3') + (C_4'{-}H_4')$	ω_{39} a″	3271	0.8
$(C_5{-}H_5) - (C_5{-}H_6) + (C_5'{-}H_5') - (C_5'{-}H_6')$	ω_5 a′	3250	43.8
$(C_5{-}H_5) - (C_5{-}H_6) - (C_5'{-}H_5') + (C_5'{-}H_6')$	ω_{40} a″	3240	25.9
$(C_6{-}H_7) + (C_6{-}H_8)$	ω_6 a′	3226	88.8
$(C_4{-}H_3) + (C_4{-}H_4) - (C_4'{-}H_3') - (C_4'{-}H_4')$	ω_{41} a″	3214	25.3
$(C_4{-}H_3) + (C_4{-}H_4) + (C_4'{-}H_3') + (C_4'{-}H_4')$	ω_7 a′	3210	7.4
$(C_5{-}H_5) + (C_5{-}H_6) - (C_5'{-}H_5') - (C_5'{-}H_6')$	ω_{42} a″	3192	1.3
$(C_5{-}H_5) + (C_5{-}H_6) + C_5'{-}H_5') + (C_5'{-}H_6')$	ω_8 a′	3183	37.3

[a] The numbering of the atoms is from Figure 1.

the analogous DZ SCF frequencies for propane range from 3184 to 3278 cm^{-1}. Of the ten frequencies in Table III, the most intense by far is ω_6 (3226 cm^{-1}, 88.8 km/mol), the symmetric C–H stretch on the central methylene unit of the chain. However, ω_3, ω_5, ω_8, ω_{40}, and ω_{41} also have sizeable infrared intensities so that any experimental spectrum in the region is likely to exhibit absorptions due to at least six bands.

In Table IV appears a correspondence between the harmonic frequencies below 2000 cm^{-1} of [5]paracyclophane and those of benzene and *p*-dideuteriobenzene. The correspondence is based on an examination of the DZ SCF potential energy distributions for each molecule. While most of the associations shown in Table IV were clear from the vibrational analysis, not all were unambiguous. Table IV presents what is in our opinion the best possible correspondence. The reader is referred to the Supplementary Material for more precise descriptions of the normal modes of [5]paracyclophane.

In general, the frequencies of [5]paracyclophane in Table IV are surprisingly close to their counterparts for *p*-dideuteriobenzene. For example, for four of the six benzene ring C–C stretches the correspondence is excellent. In particular, there are C–C stretches of *p*-dideuteriobenzene at 1768, 1764, 1555, and 1351 cm^{-1}, and the [5]paracyclophane counterparts lie at 1765, 1739, 1549, and 1394 cm^{-1}, respectively. The totally symmetric C–C stretch for *p*-dideuteriobenzene (the ring-breathing mode) occurs at 1051 cm^{-1} and that for [5]paracyclophane is significantly higher at 1291 cm^{-1}. This phenomenon can be explained by realizing that benzene ring expansion in [5]paracyclophane comes at the expense of additional strain in the $(CH_2)_5$ bridge; hence, the potential energy surface along the ring-breathing mode rises more sharply for [5]paracyclophane than for *p*-dideuteriobenzene. Thus, the lack of correspondence between the ring-breathing modes does not indicate a fundamental difference in the nature of the C–C bonds in the two molecules. With regard to the remaining benzene ring C–C stretch, the b_{1u} frequency at 1624 cm^{-1} for *p*-dideuteriobenzene is 71% C–H in-plane bend and 28% C–C stretch, and another b_{1u} frequency for $C_6H_4D_2$ lying at 1131 cm^{-1} is 61% C–C stretch and 22% C–H in-plane bend. The 1650-cm^{-1} frequency (ω_{44}) of [5]paracyclophane is 50% C–H in-plane bend and 32% C–C stretch, and the correspondence with the 1624-cm^{-1} mode of $C_6H_4D_2$ is reasonably good. The 1318-cm^{-1} frequency (ω_{53}) of [5]paracyclophane is a strong mixture of several modes, a C–H in-plane bend (23%) and a C–C stretch (10%) being the first and fourth most important components. For this mode the coupling due to the $(CH_2)_5$ chain greatly reduces the correlation with the 1131-cm^{-1} mode of *p*-dideuteriobenzene.

Three of the C–H in-plane bends of *p*-dideuteriobenzene lie at 1467, 1311, and 1219 cm^{-1}, and these frequencies exhibit an

Table IV. A Correspondence between the Harmonic Vibrational Frequencies (below 2000 cm^{-1}) and Infrared Intensities of [5]Paracyclophane and Those of Benzene[a]

	[5]paracyclophane			paradideuteriobenzene			benzene		
description[b]	symmetry	DZ SCF theory	intensity (km/mol)	symmetry[c]	DZ SCF theory	intensity (km/mol)	symmetry	DZ SCF theory	intensity (km/mol)
C–C stretch (S_2)	ω_9 a′	1765	15.2	a_g	1768	0	e_{2g}	1782 (1610)	0
C–C stretch (S_{38})	ω_{43} a″	1739	0.1	b_{2g}	1764	0	e_{2g}	1782 (1610)	0
C–H in-plane bend + C–C stretch ($S_{52} + S_{37}$)	ω_{44} a″	1650	4.9	b_{1u}	1624 (1474)	13.1	e_{1u}	1636 (1484)	14.5
C–C stretch (S_3)	ω_{13} a′	1549	5.4	b_{3u}	1555 (1414)	8.0	e_{1u}	1636 (1484)	14.5
C–H in-plane bend (S_{53})	ω_{49} a″	1470	1.2	b_{2g}	1467	0	a_{2g}	1516	0
C–C stretch (S_4)	ω_{16} a′	1394	1.2	b_{3u}	1351	0.006	b_{2u}	1380 (1310)	0
C–H in-plane bend (S_{17})	ω_{19} a′	1305	0.6	a_g	1311	0	e_{2g}	1311 (1178)	0
C–H in-plane bend (S_{18})	ω_{21} a′	1228	6.2	b_{3u}	1219 (1105)	1.5	b_{2u}	1264 (1149)	0
C–H out-of-plane bend (S_{55})	ω_{57} a″	1099	5.5	a_u	1135	0	e_{2u}	1135	0
C–C stretch + C–H in-plane bend ($S_{37} + S_{52}$)	ω_{53} a″	1318	6.9	b_{1u}	1131 (1033)	6.3	e_{1u}	1138 (1038)	7.3
C–H out-of-plane bend (S_{54})	ω_{56} a″	1115	4.5	b_{3g}	1126	0	b_{2g}	1164	0
C–C in-plane bend (S_{40})	ω_{59} a″	1067	1.2	b_{1u}	1091	1.2	b_{1u}	1113	0
C–C stretch (S_1)	ω_{20} a′	1291	0.5	a_g	1051 (979)	0	a_{1g}	1068 (993)	0
C–H out-of-plane bend (S_{19})	ω_{25} a′	936	64.1	b_{2u}	1023	29.9	e_{2u}	1135	0
[C–D in-plane bend][d]	a″			b_{2g}	1011	0	e_{2g}	1311 (1178)	0
C–H out-of-plane bend (S_{20})	ω_{28} a′	730	10.0	b_{1g}	986	0	e_{1g}	986	0
[C–D in-plane bend][d]	a′			b_{3u}	908 (822)	5.6	e_{1u}	1138 (1038)	7.3
[C–D out-of-plane bend + ring torsion (chair)][e]	ω_{62} a″	(814)	(78.0)	b_{3g}	853	0	e_{1g}	986	0
ring torsion (chair) (S_{41})	ω_{63} a″	751	20.0	b_{3g}	718	0	b_{2g}	796	0
[C–D out-of-plane bend][d]	a′			b_{2u}	691	137.5	a_{2u}	781	200.1
C–C in-plane bend (S_{39})	ω_{64} a″	681	0.3	b_{2g}	669 (602)	0	e_{2g}	675 (608)	0
C–C in-plane bend (S_5)	ω_{31} a′	557	0.7	a_g	660 (596)	0	e_{2g}	675 (608)	0
ring torsion (twist) (S_{42})	ω_{66} a″	505	1.5	a_u	458	0	e_{2u}	458	0
ring torsion (boat) (S_6)	ω_{30} a′	686	25.3	b_{2u}	411	2.0	e_{2u}	458	0

[a] All frequencies are in cm^{-1}. The experimental fundamentals (given in parentheses) are from the recent paper by Thakur, Goodman, and Ozkabak (ref 41). [b] See the Supplementary Material for a definition of the internal coordinates (given in parentheses) and more precise descriptions of the normal modes. [c] See footnote b of Table II. [d] These modes have no counterpart in [5]paracyclophane. [e] The 853-cm^{-1} mode for *p*-dideuteriobenzene is a strong mixture of C–D out-of-plane bend and C–C ring torsion (chair). The 814-cm^{-1} mode for [5]paracyclophane also involves a significant amount of ring torsion (chair), and thus a correspondence is shown in parentheses.

excellent correspondence with the 1470, 1305, and 1228 cm^{-1} bands of [5]paracyclophane. The other C–H in-plane bend is mixed with a C–C stretch as discussed in the preceding paragraph. There are several other cases in Table IV of high correlation between modes of [5]paracyclophane and *p*-dideuteriobenzene, e.g., two of the C–H out-of-plane bends and one of the C–C in-plane bends. The conclusion apparent from the low-frequency region of the IR spectrum of [5]paracyclophane is thus the same as that from the high-frequency region: the close correspondence between the frequencies of [5]paracyclophane and *p*-dideuteriobenzene suggests that [5]paracyclophane might suitably be labeled "benzenelike" or "aromatic". In particular, the carbon–carbon bonding structures in the two components are apparently very similar.

Finally, a few comments are warranted concerning the infrared intensities of the modes of [5]paracyclophane below 2000 cm^{-1}. Of the 54 frequencies in this region, there are only ten with an intensity as large as 10.0 km/mol and only five with an intensity as large as 20.0 km/mol (see Table IIIs). Six of the ten most intense theoretical absorptions involve significant amounts of chair motion or C–H out-of-plane bend associated with the benzene ring. In fact, the two frequencies (below 2000 cm^{-1}) which are the most intense by far are ω_{62} (814 cm^{-1}, 78.0 km/mol), which involves chair motion, and ω_{25} (936 cm^{-1}, 64.1 km/mol), which is a C–H out-of-plane bend.

Lowest Triplet and Excited Singlet Electronic States

At the DZ SCF ground-state equilibrium geometry, some consideration of other electronic states was made. The highest occupied molecular orbital (HOMO) of [5]paracyclophane is a π orbital (a'', $\epsilon = -0.28$ hartree) centered on the para carbon atoms. The lowest unoccupied molecular orbital (LUMO) is the corresponding π^* orbital, which is of a' symmetry with an SCF virtual orbital energy of +0.11 hartree. The HOMO is 0.05 hartree above the second highest occupied MO, and the LUMO is 0.03 hartree below the second lowest unoccupied MO, so the HOMO–LUMO pair is unambiguously defined.

The ground-state DZ SCF energy of [5]paracyclophane is −424.47317 hartrees. The lowest triplet and excited singlet states arise from the $a'' \rightarrow a'$ or HOMO → LUMO excitation and are of $^3A''$ and $^1A''$ symmetry, respectively. The vertical DZ SCF energies of these states are −424.39455 and −424.25500 hartrees, respectively. Therefore, the predicted $\tilde{X}^1A' \rightarrow \tilde{a}^3A''$ vertical excitation energy of [5]paracyclophane is 2.14 eV or 17 300 cm^{-1}, and the corresponding $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ value is 5.94 eV or 47 900 cm^{-1}. The triplet value may be compared to the recent experimental results of Hopf, Haase, Hunger, Tochtermann, and Zander.[44] These workers measured the phosphorescence spectra of several paracyclophanes, the smallest of which was a substituted [7]paracyclophane. For the [10]-, [8]-, and [7]paracyclophanes the triplet state spectral centers were observed to lie at 2.99, 2.75, and 2.48 eV, respectively. The trend, of course, is toward lower excitation energies as the benzene ring becomes more bent. In this light our prediction of 2.14 eV for [5]paracyclophane fits in nicely with the observations of Hopf et al.[44] for the larger paracyclophanes.

Table V. Total SCF Electronic Energies and Zero-Point Vibrational Energies (ZPVE)[a] of STO-3G and DZ Optimum Structures of the Molecules Used in the Homodesmotic Reactions 1 and 2

molecule	STO-3G energy	STO-3G ZPVE	DZ energy	DZ ZPVE
propane (C_3H_8)	−116.886 422	78.0	−118.228 940	69.6
ethylene (C_2H_4)	−77.073 955	37.7	−78.011 990	34.5
ethane (C_2H_6)	−78.306 180	56.3	−79.206 407	50.2
trans-1,3-butadiene (C_4H_6)	−153.020 366	62.7	−154.878 382	57.7
2-methylpropene (C_4H_8)	−154.245 893	80.7	−156.067 369	72.8
propene (C_3H_6)	−115.660 299	59.4	−117.039 686	53.8
benzene (C_6H_6)	−227.891 361		−230.641 695	68.2
[5]paracyclophane	−419.517 997	164.4	−424.473 174	149.5

[a] Total electronic energies in hartrees and ZPVE values in kcal/mol.

In order to estimate the accuracy of the DZ SCF prediction of 2.14 eV for the $\tilde{X}^1A' \rightarrow \tilde{a}^3A''$ vertical excitation energy of [5]paracyclophane, analogous results were obtained for *p*-xylene, for which the vertical triplet[45,46] and singlet[47] excitation energies are experimentally known. The DZ SCF vertical excitation energies of *p*-xylene which correspond to the $\tilde{X}^1A' \rightarrow \tilde{a}^3A''$ and $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ values of [5]paracyclophane are 38 697 and 54 784 cm^{-1}, respectively, 1.30 eV and 2.28 eV higher than the experimental values of 28 135 and 28 246 cm^{-1} for the triplet state[45,46] and 36 400 cm^{-1} for the singlet state.[47] These results suggest that the vertical excitation energies of [5]paracyclophane might be lower than predicted at the DZ SCF level. In many cases SCF theory provides a good description of the ground state and a poorer description of excited states, and thus an overestimation of the excitation energies would not be unexpected. By using the *p*-xylene results to correct the DZ SCF $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ excitation energy of [5]paracyclophane, one arrives at 5.94 − 2.28 = 3.66 eV (29 500 cm^{-1}), which is in excellent (but somewhat fortuitous) agreement with the 3.76 eV (330 nm) UV absorption ascribed to [5]paracyclophane by Jenneskens and co-workers.[17] This suggests that the analogous $\tilde{X}^1A' - \tilde{a}^3A''$ separation could be as small as 2.14 − 1.30 = 0.84 eV. Even if the $\tilde{X}^1A' \rightarrow \tilde{a}^3A''$ vertical excitation energy of [5]paracyclophane does turn out to be significantly less than 2.14 eV, the DZ SCF prediction would still be in qualitative agreement with the experimental observations for larger paracyclophanes. Obviously, DZ SCF results for larger paracyclophanes would be of interest.

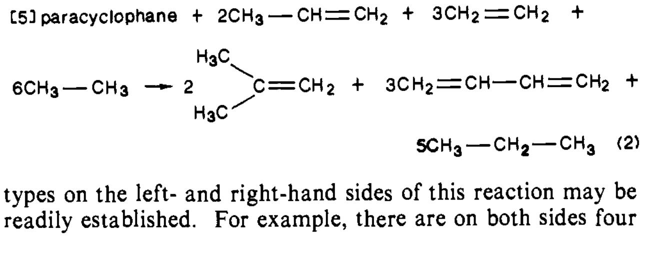
Resonance Energy of [5]Paracyclophane

Perhaps the most traditional way of quantifying aromaticity[42] is by way of the "resonance energy". For benzene, this is in essence the energy lowering relative to a hypothetical system with three carbon–carbon single bonds and three carbon–carbon double bonds. More quantitatively, a specific value for the resonance energy of benzene is given by the endothermicity of the *homodesmotic* reaction[43]

$$C_6H_6 + 3CH_2{=}CH_2 \rightarrow 3CH_2{=}CH{-}CH{=}CH_2 \quad (1)$$

The experimental value of the resonance energy defined in this manner is $\Delta H(1) = 21.2$ kcal/mol. The homodesmotic comparison is intended to relate benzene thermochemically to molecules having strictly analogous numbers of isolated single and double bonds. To quote George and co-workers[43] "The term homodesmotic denotes reactions in which: (1) there are equal numbers of each type of carbon–carbon bond ($C_{sp^3}{-}C_{sp^3}$, $C_{sp^2}{-}C_{sp^3}$, $C_{sp^2}{-}C_{sp^2}$, $C_{sp^2}{=}C_{sp^2}$, etc.) in reactants and products; and (2) there are equal numbers of each type of carbon atom (C_{sp^3}, C_{sp^2}, etc.) with zero, one, two, and three hydrogen atoms attached in reactants and products."

For [5]paracyclophane the analogous homodesmotic reaction is necessarily more complicated The equality of numbers of bond



$$[5]\text{paracyclophane} + 2CH_3{-}CH{=}CH_2 + 3CH_2{=}CH_2 + 6CH_3{-}CH_3 \rightarrow 2(H_3C)_2C{=}CH_2 + 3CH_2{=}CH{-}CH{=}CH_2 + 5CH_3{-}CH_2{-}CH_3 \quad (2)$$

types on the left- and right-hand sides of this reaction may be readily established. For example, there are on both sides four

---

(42) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

(43) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.

(44) Hopf, H.; Haase, M.; Hunger, J.; Tochtermann, W.; Zander, M. *Chem. Phys. Lett.* **1986**, *127*, 145.

(45) Kanda, Y.; Shimada, R. *Spectrochim. Acta* **1961**, *17*, 279.

(46) Blackwell, L. A.; Kanda, Y.; Sponer, H. *J. Chem. Phys.* **1960**, *32*, 1465.

(47) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, New York, Springer-Verlag: Berlin, 1964.

(48) Amos, R. D. *Chem. Phys. Lett.* **1984**, *108*, 347.

carbon–carbon single bonds connecting an sp^2 carbon with an sp^3 carbon.

Comparison of the resonance energy $\Delta H(2)$ or [5]paracyclophane with that for benzene provides an immediate measure of the former's thermodynamic stability. In table V STO-3G and DZ SCF total electronic energies and zero-point vibrational energies (ZPVE) are listed for the molecules which occur in eq 1 and 2. In the Supplementary Material (Table VIs and Figure IIIs) the optimum SCF structural parameters for these molecules are tabulated and defined. At the minimum basis set SCF level of theory $\Delta H(2) = -54.9$ kcal/mol, and from DZ SCF theory $\Delta H(2) = -55.0$ kcal/mol. The agreement between the two theoretical methods is encouraging. Taking into account the effects of ZPVE we arrive at a final DZ SCF value of $\Delta H(2) = -50.1$ kcal/mol. When one considers that the experimental value $\Delta H(1)$ for benzene is of the opposite sign, +21.2 kcal/mol, it is apparent that the thermochemical approach is unambiguous in stating that [5]paracyclophane is *not* aromatic.

How reliable is the above prediction of -50.1 kcal/mol for the resonance energy of [5]paracyclophane? For the analogous benzene reaction 1, the minimum basis and DZ SCF methods predict 32.7 and 26.7 kcal/mol,[43] respectively, for the resonance energy, and taking into account ZPVE gives a DZ SCF value of 28.1 kcal/mol. This estimate is in reasonable agreement with the experimental value $\Delta H(1) = 21.2$ kcal/mol. Thus we are confident that the thermochemical prediction of nonaromaticity will eventually be confirmed in the laboratory. In this respect our ab initio predictions are in qualitative agreement with the earlier semiempirical (MNDO) study of Schmidt, Schweig, Thiel, and Jones[19] and the earlier empirical study (molecular mechanics) of Carballeira, Casado, Gonzãlez, and Rios.[20] Arguments in favor of the aromaticity of [5]paracyclophane cannot be based on thermochemistry.

On the basis of the difference in the ΔH values of the above homodesmotic reactions, one may conclude that [5]paracyclophane is approximately 78 kcal/mol less stable than benzene. A question one may ask, then, is how much of the 78 kcal/mol is due to the nonplanarity of the benzene ring. In an attempt to gain some insight on this point we performed a DZ SCF calculation on benzene, freezing the ring in the conformation present in [5]-paracyclophane and placing the additional two hydrogen atoms at a typical C–H distance in the same direction as the first carbon atoms of the chain. The DZ SCF energy obtained was -230.545839 hartrees, 60.1 kcal/mol higher in energy than the optimum structure of benzene (see Table V). Thus, this simple approach indicates that the major reason for the lack of stability of [5]paracyclophane is, not surprisingly, the nonplanarity of the benzene ring. This conclusion was reached previously by Schmidt, Schweig, Thiel, and Jones,[19] who used the same approach in conjunction with MNDO calculations. These authors obtained a destabilization of 49.5 kcal/mol due to the nonplanarity of the benzene ring as compared to a total strain energy of 63.2 kcal/mol. While both of these values are over 10 kcal/mol smaller than our values, the fractional destabilization of 49.5/63.2 = 0.783 due to nonplanarity is in close agreement with our result of 60.1/78.2 = 0.769.

Conclusions

Is [5]paracyclophane aromatic? The answer to this question depends on the window through which one observes this molecule. The answer also depends on the observer's intuitive understanding of what it means for a molecule to be aromatic. Here we present views through several windows by using the intuition available to us. (1) On the basis of the small degree of bond alternation (0.025 Å) in the benzene ring, [5]paracyclophane may be judged to be aromatic. (2) On the basis of the substantial nonplanarity of the benzene ring (ϕ in Figure 2 is 23.7° at the highest level of theory), [5]paracyclophane may be judged not to be aromatic. (3) On the basis of the close correspondence between the predicted vibrational frequencies of [5]paracyclophane and *p*-dideuteriobenzene, [5]paracyclophane may be judged to be benzenelike or aromatic. (4) On the basis of the prediction that the resonance energy is 78 kcal/mol less than that for benzene, [5]paracyclophane may be judged not to be aromatic. Where do these deliberations leave us? The answer is obvious: in need of an unambiguous operational definition of aromaticity.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. All computations were performed at the San Diego Supercomputer Center, by using time granted by the SDSC Allocation Committee. These calculations were performed by using the Cambridge Analytic Derivatives Package supplied by Dr. R. D. Amos.[48] Parts of this paper are based upon work supported under a National Science Foundation Graduate Fellowship held by W.D.A. in 1986. We thank Roger S. Grev for constructing the homodesmotic reaction 2 and for many general insights on the subject of aromaticity. Dr. Walter Thiel is thanked for allowing us to cite his unpublished MNDO results in our Table I. We thank Professors Norman Allinger, Philip George, and Andrew Streitwieser for helpful discussions.

Registry No. Propane, 74-98-6; ethylene, 74-85-1; ethane, 74-84-0; 1,3-butadiene, 106-99-0; 2-methylpropene, 115-11-7; propene, 115-07-1; benzene, 71-43-2; [5]paracyclophane, 53600-57-0; *p*-dideuteriobenzene, 1684-46-4.

Supplementary Material Available: Internal coordinates (Tables Is and IIs), DZ SCF harmonic frequencies (Table IIIs), and force constant matrices (Tables IVs and Vs) are listed for [5]paracyclophane; Figures 1s and 2s consist of pictorial representations of the internal coordinates; SCF structural parameters (Table VIs) and sketches (Figure 3s) of the molecules in reactions 1 and 2 are given (22 pages). Ordering information is given on any current masthead page.