The hexapeptides **1** and **2** have been synthesized from their linear precursors $\text{H-Xxx-Phe}^{7}\text{-Yyy-Phe}^{11}\text{-Thr}^{10}\text{-Lys}^{9}\text{(Z)-NHNH}_2$ (**1**, Xxx = Trp and Yyy = D-Pro; **2**, Xxx = D-Trp and Yyy = Pro) via the azide method.[77] The linear precursor were prepared by the solid-phase method as described previously.[78,79] For the deuteriated analogues the Boc-protected deuteriated amino acids were used.

Boc-(*S*,*S*)-$[\alpha\text{-}^{2}\text{H},\beta\text{-}^{2}\text{H}]$phenylalanine and Boc-(*R*,*R*)-$[\alpha\text{-}^{2}\text{H},\beta\text{-}^{2}\text{H}]$-tryptophane were prepared by deuteriation of *N*-acetyl-Z-dehydrophenylalanine[80,81] and *N*-acetyl-Z-dehydrotryptophane.[82] The N-acetylated racemic phenylalanine was asymmetrically hydrolyzed by the action of porcine kidney acylase[83] (Sigma Chemical Co., No. A-8376); the amino functionality was directly protected (Boc) under usual conditions[84] and separated by crystallization.

Deuteriated *N*-acetyl-*d*,*l*-tryptophane has been resolved by means of the *d*-α-phenylethylamine salt with the isolation of *N*-acetyl-*d*-tryptophane.[85,86] The acetyl group was removed by refluxing with 48% aqueous hydrobromic acid (5 equiv) in water/methanol (1/1), and again the amino functionality was protected (Boc).

Acknowledgment. We thank Dr. A. Müller for making available the spectra of **3** and for valuable discussions concerning its conformation. We are grateful to the Sandoz AG for a gift of **4** and to Dr. H. Oschkinat for helpful discussions. We thank Dr. W. Studer (ETH, Zürich) who did the computer simulations concerning strong coupling effects. We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. C.G. also thanks the Fonds der Chemischen Industrie for a personal grant during early stages of this work.

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π-Electron Valence Bond Calculations on Benzenoid Hydrocarbons via Graphical Unitary Group Methods

S. A. Alexander[†] and T. G. Schmalz*

Contribution from the Theoretical Chemical Physics Group, Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77553. *Received April 17, 1986*

Abstract: Graphical unitary group techniques are applied to the valence bond model of π-electron systems. These techniques, which have produced highly efficient solution methods for ab initio quantum chemical problems, are found to yield a corresponding increase in the efficiency with which valence bond (and other approximate model) calculations can be carried out. As a result, it becomes feasible to solve the valence bond model exactly for systems of up to about 24 π-centers. The exact valence bond ground state energy is presented for all benzenoid hydrocarbons of up to 20 carbon atoms plus selected 22 and 24 atom systems. Using these energies we show that the resonance energy predicted by valence bond theory correlates well with resonance energy predicted by Hückel theory, in spite of the very different assumptions underlying the two methods.

I. Introduction

The past decade has witnessed a dramatic increase in the number of ab initio quantum chemical studies of molecular electronic structure. The reason for this growth is due primarily to the development of efficient computational techniques, e.g., the graphical unitary group approach,[1-3] which significantly reduce the amount of computer time needed for such studies. Although seldom used, many of the same concepts that have been so fruitful in ab initio programs can also be applied to approximate and/or semiempirical calculations. These calculation lack the absolute predictive power of their ab initio counterparts, but for certain classes of systems semiempirical theories can provide useful insight into molecular behavior. In this paper we focus on one such theory—the valence bond (VB) model.

The valence bond model was introduced in the early years of quantum mechanics by Pauling[4] and others[5-7] as an extension of classical chemical bonding concepts. Indeed, most chemists today continue to think in terms of valence bond concepts when they "push electrons" in organic reactions. Because the complexity of valence bond calculations rises very rapidly as a function of the size of the chemical system, these ideas are frequently abandoned in favor of molecular orbital based ideas whenever even semiquantitative results are called for. Clearly if the VB model is to be usefully applied to moderate or large-size molecules, efficient computational techniques are essential.

One class of molecules where the valence bond model has had a number of qualitative successes is conjugated π-electron systems. To illustrate this point we examine the phenomenon of resonance stabilization in such molecules. Our discussion is outlined roughly as follows: In Section II we present the valence bond model Hamiltonian and discuss its adequacy in studies of conjugated π-electron systems. Section III discusses how ab initio techniques

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[†] Robert A. Welch Foundation Fellow. Current Address: Quantum Theory Project, University of Florida, Gainsville, FL 32611.

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may be applied to VB calculations. When these ideas are used, molecules with up to 24 π centers can be routinely handled. As an example of such calculations we compute the exact VB ground state of a number of benzenoid hydrocarbons. Section IV uses these ground-state energies to examine the resonance stabilization of these molecules and compares the VB results to the predictions of Hückel molecular orbital theory.

II. The Valence Bond Model

The valence bond model for neutral conjugated hydrocarbons specifies a π-electron Hamiltonian that is to operate only in the space of covalent VB structures. That is, each carbon atom has a π orbital that is to be singly occupied. The space of covalent VB structures consists of all possible ways of assigning spin-up or spin-down to these singly occupied orbitals consistent with the required overall spin of the molecular state.

For a system in which all sites and bonds are identical, the nearest neighbor VB Hamiltonian may be written in several equivalent ways.

$$\mathcal{H} = -J\sum_{i\sim j}\sum_{\sigma,\sigma'} a_{i\sigma}{}^{+}a_{j\sigma}a_{j\sigma'}{}^{+}a_{i\sigma'} \qquad (1a)$$

$$\mathcal{H} = J\sum_{i\sim j}(2\vec{s}_i\cdot\vec{s}_j - \tfrac{1}{2}) \qquad (1b)$$

$$\mathcal{H} = -J\sum_{i\sim j}\hat{E}_{ij}\cdot\hat{E}_{ji} \qquad (1c)$$

Equation 1a is the second quantized form in which $a_{i\sigma}{}^{+}$ and $a_{i\sigma}$ are fermion creation and annihilation operators for an electron of spin σ on site i, J is an (positive) exchange parameter, and i $\sim$ j denotes nearest-neighbor sites. Equation 1b rewrites the Hamiltonian in the perhaps more familiar form of an operator in spin space, with $\vec{s}_i$ being the spin operator for site i. In this form it is easily recognized that the VB Hamiltonian is equivalent to the Heisenberg model Hamiltonian used in solid-state physics.[6,8] Equation 1c expresses the Hamiltonian in terms of the generators of the unitary group,[9] a form that will prove convenient for the developments of the next section. In all forms of eq 1 the value of the integral giving the attraction of an isolated π-electron to the core (comparable to the α of Hückel theory) has been chosen as the zero of energy.

Early derivations of eq 1 have been severly criticized[10] because they imply that J should be interpreted as an exchange integral (which must be negative) rather than as an exchange parameter. However, a number of authors have now pointed out that a model Hamiltonian of the form of eq 1 can be generated as the lowest order term in several systematic schemes for deriving effective π-electron Hamiltonians such as degenerate or quasidegenerate perturbation theory,[11] cluster expansions,[12] or wave operator methods.[13] All of these methods lead to physically acceptable values of J by expressing the exchange parameter as a function of other molecular integrals. In this work we will simply take it as an empirical parameter. (A value of J in the range 1.4–1.9 eV should be appropriate for benzenoid hydrocarbons.)

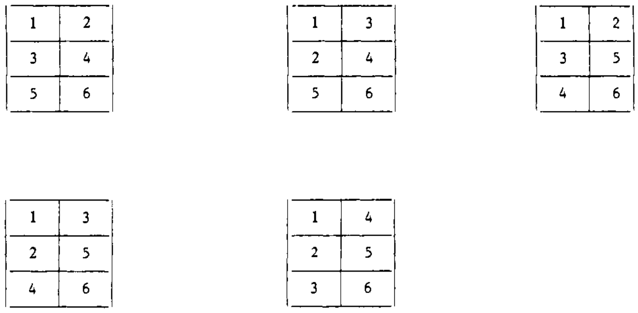

Figure 1. The Gelfand states spanning the valence bond space for benzene.

Table I. Number of Singlet Valence Bond States

$N = 6$	5	$N = 18$	4862
8	14	20	16796
10	42	22	58786
12	132	24	208012
14	429	26	742900
16	1430	28	2674440

The above methods for deriving eq 1 also lead to systematic procedures for introducing higher order corrections into the model Hamiltonian. The use of eq 1 without higher order corrections must be examined critically. For instance, the nearest-neighbor VB Hamiltonian predicts considerable stability for cyclobutadiene; comparison of cyclobutadiene, benzene, and cyclooctatraene reveals no trace of the Hückel $4n + 2$ rule. Our own investigations agree with others[14,15] in showing that the two most important corrections to eq 1 for cyclic systems are next nearest neighbor transpositions and cyclic permutations which permute the electrons around the circumference of the ring. For benzene these two corrections for the ground state are of comparable magnitude but opposite sign, so that the uncorrected eq 1 gives a value for the energy in good agreement with the exact result. For example, the exact Pariser–Parr–Pople ground-state energy for benzene with use of the parameters of Schulten, Ohmine, and Karplus[16] (β = 2.60 eV) and the Ohno formula for two-center electron-repulsion integrals is −15.679 eV. The nearest-neighbor VB Hamiltonian derived from the PPP model via a 2-site cluster expansion[12] (J = 1.857 eV) gives a ground-state energy of −15.978 eV, and error of only −0.3 eV. The next-nearest-neighbor and ring-permutation terms can be estimated from higher order cluster expansions to give corrections of +1.5 and −0.9 eV, respectively.

By contrast, for other than six-membered rings the correction terms to eq 1 do not usually cancel. In cyclobutadiene they are both positive and so tend to raise the ground-state energy of cyclobutadiene relative to that of benzene, as is required to recover the Hückel $4n + 2$ rule. We therefore conclude that the VB Hamiltonian of eq 1 can be used to make reliable comparisons among the ground-state energies of benzenoid hydrocarbons (i.e., those in which every carbon atom is a member of six-membered rings only) but should not be used without corrections to compare systems with rings of different sizes.

III. Computational Considerations

In ab initio calculations Gelfand states, a set $\{|G\rangle\}$ of orthonormal configuration state functions that are symmetry adapted to the unitary group U(N), have proved to be a useful basis in which to solve the full N-electron Schrodinger Hamiltonian. These same states can also be used as a basis for the valence bond model if the configurations are restricted to those containing only singly occupied orbitals.[9] An example of such a subset, the 5 Gelfand states that span the VB space of benzene, is shown in Figure 1.

A comparison between the full Schrodinger Hamiltonian

$$\mathcal{H} = \sum_i\sum_j h_{ij}\hat{E}_{ij} + \tfrac{1}{2}\sum_i\sum_j\sum_k\sum_l V_{ijkl}(\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}) \qquad (2)$$

and eq 1c shows that the VB Hamiltonian, like the set of con-

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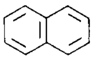
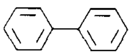
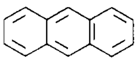
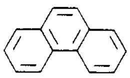
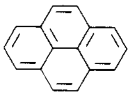
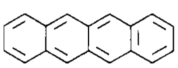
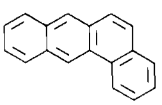
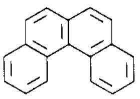
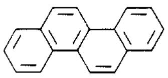
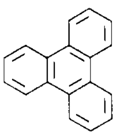
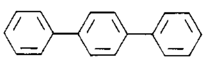
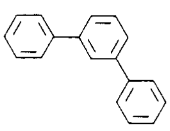
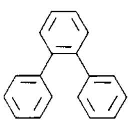
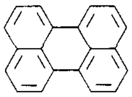
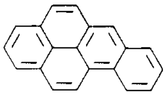
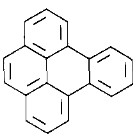
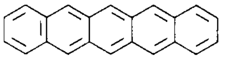
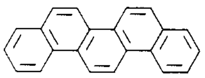
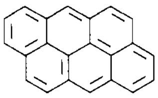
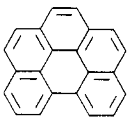
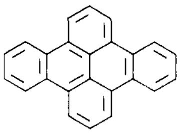
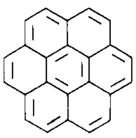
Table II

molecule		sites	energy^a
benzene		6	-8.605 54
naphthalene		10	-15.039 91
biphenyl		12	-17.917 40
anthracene		14	-21.450 49
phenanthrene		14	-21.522 50
stilbene		14	-20.669 07
pyrene		16	-25.132 56
naphthacene		18	-27.858 18
benz[*a*]anthracene		18	-27.944 52
benzophenanthrene		18	-27.993 12
chrysene		18	-27.994 97
triphenylene		18	-28.039 38
p-terphenyl		18	-27.232 84
m-terphenyl		18	-27.229 42
o-terphenyl		18	-27.235 96
perylene		20	-31.603 19
benz[*a*]pyrene		20	-31.592 04
benz[*e*]pyrene		20	-31.651 32
pentacene		22	-34.266 52
picene		22	-34.470 83
benz[*b*,*cd*]pyrene		22	-35.193 45
benz[*ghi*]perylene		22	-35.284 75
dibenz[*fg*,*op*]-naphthacene		24	-38.168 81
coronene		24	-38.950 98

^{a} In units of the exchange parameter *J*.

figuration state functions, is simply a truncated version of the one used in ab initio calculations. For this reason any ab initio technique developed to solve eq 2 can also be applied to the valence bond model. One particularly powerful tool is the Graphical Unitary Group Approach (GUGA) of computing only nonzero matrix elements.[1-3] This method is based on the observation that $\langle G'|\mathcal{H}|G\rangle$ has a simple underlying structure. In the VB model this structure is even simpler and leads to a fast, efficient algorithm.[17] As with all CI-type calculations though, the number of configurations grows quite quickly and at some point calculations become computationally impractical. In Table I we show the size of the Hamiltonian matrix as a function of the number of π centers. Calculations with 24 π sites (208 012 configurations) probably represent the feasible limit of our program as currently implemented. While some improvement of our code is possible, it seems doubtful that these changes would allow us to examine significantly larger systems.[18] At present, ab initio calculations with a million configurations are considered state of the art.[19]

Using GUGA, we have calculated the exact (VB) ground-state energies of all singlet benzenoid hydrocarbons with up to 20 sites, selected 22 site molecules, and the 24 site molecules dibenz[*fg*,*op*]naphthalene and coronene. In addition we include stillbene, which is not strictly benzenoid by our definition, for comparative purposes. The results of these calculations are presented in Table II. It can be seen immediately that VB energies depend strongly on molecular size; larger molecules have consistently lower energies than smaller molecules. However, there are significant differences in energy, up to about 1 eV, between molecules with the same number of sites. We address the relationship between molecular structure and VB energy in the next section.

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[17] Because Gelfand states are orthonormal, several well-established diagonalization methods designed specifically for large systems can be used. See, for example: Cullum, J.; Willoughby, R. A. *J. Comp. Phys.* **1981**, *44*, 329. Davidson, E. R. *J. Comp. Phys.* **1975**, *17*, 87. For an alternative approach based on the nonorthogonal Rumer basis, see: Ramasesha, S.; Soos, Z. G. *Int. J. Quantum Chem.* **1984**, *25*, 1003.

[18] Finding the lowest eigenvalue to 1 part in 10^{-5} of coronene took 29 iterations and almost 3 h of CPU time on a CDC Cyber 205. On a VAX 11/780 type machine we estimate that this calculation would have required over 100 h of CPU time.

[19] While calculations with up to two million configurations are rumored, the largest published CI we know of is by the following: Saxe, P.; Fox, D. J.; Schaefer, H. F., III, *J. Chem. Phys.* **1982**, *77*, 5584.

[20] Coulson, C. A.; Streitweiser, A., Jr.. *Dictionary of π-Electron Calculations*; W. H. Freeman: San Francisco, 1965.

Table III

molecule	VB	Hückel[a]	$\Delta E/\Delta E_{\text{benzene}}$	
	$\Delta E/\mathrm{J}$	$\Delta E/\beta$	VB	Hückel
benzene	1.10554	2.0000	1.000	1.000
naphthalene	2.03991	3.68324	1.845	1.842
biphenyl	2.41740	4.38338	2.187	2.192
stilbene	2.66907	4.87784	2.414	2.440
anthracene	2.95049	5.31371	2.669	2.657
phenanthrene	3.02250	5.44825	2.734	2.724
pyrene	3.63256	6.50546	3.286	3.253
m-terphenyl	3.72942	6.76584	3.373	3.383
p-terphenyl	3.73284	6.77233	3.376	3.386
o-terphenyl	3.73596	6.77756	3.379	3.389
naphthacene	3.85818	6.93082	3.490	3.465
benz[*a*]anthracene	3.94452	7.10125	3.568	3.551
benzophenanthrene	3.99312	7.18749	3.612	3.594
chrysene	3.99497	7.19223	3.614	3.596
triphenylene	4.03938	7.27447	3.654	3.637
benz[*a*]pyrene	4.59204	8.22200	4.154	4.111
perylene	4.60319	8.24531	4.164	4.123
benz[*e*]pyrene	4.65132	8.33605	4.207	4.168
pentacene	4.76652	8.54402	4.314	4.272
picene	4.97083	8.94323	4.496	4.472
benz[*b,cd*]pyrene	5.19345	9.25288	4.698	4.626
benz[*ghi*]perylene	5.28475	9.42507	4.780	4.713
dibenz[*fg,op*]naphthacene	5.66881	10.16439	5.128	5.082
coronene	5.95098	10.57184	5.383	5.286

[a] All Hückel results except dibenz[*b,cd*]pyrene and dibenz[*fg,op*]-naphthacene are from ref 20.

IV. Discussion

The simplest way to focus on the energetic stability of aromatic π-systems is to define the valence bond *resonance energy* to be (the negative of) the difference between the calculated VB energy of a molecule and the energy expectation value of a single Kekulé structure (i.e., a covalent spin-pairing in which each electron is singlet paired to an electron on a nearest-neighbor site). A closely related concept is available through Hückel theory: the resonance energy is defined to be the total energy, found by assigning electrons to the lowest available MO's, minus 2β for each isolated double bond. In Table III we compare the VB and Hückel estimates of the resonance energy of the molecules in Table II.

In the last two columns of Table III the VB and Hückel resonance energies have been divided by the corresponding value for benzene to cancel out the unknown parameters J and β. The agreement between the numbers in these two columns is quite startling, extending down to the exact isomer differences in the sequences *m*-terphenyl, *p*-terphenyl, *o*-terphenyl and naphthacene, benz[*a*]anthracene, benzophenanthrene, chrysene. Both VB and Hückel theory are highly approximate theories with very different assumptions. In the VB model electrons are completely correlated while in Hückel theory electrons move completely independently in molecular orbitals. Nevertheless both theories make essentially the same prediction for resonance energy which leads one to hope that this property is sufficiently independent of the details of the model to be accurately predicted by approximate theories.

If there is any systematic difference between the predictions of VB and Hückel theory in Table III, it may be that Hückel theory seems to predict less resonance energy for large molecules as compared to small ones, relative to VB theory. This point may be of importance in assessing the stability of very large (essentially infinite) π-electron polymers. Traditionally such polymers (for example, polyacetylene) have been studied via band theory with a tight binding approximation[21] which makes the same approximations as Hückel theory. Recently, a transfer matrix technique has been developed to allow approximate VB calculations to be made on long-chain polymers,[22] and several families of polymers have been argued to be asymptotically stable.[22,23]

Table IV

family	molecule	aromatic stabilization energy per site[a]
polyacenes	benzene[b]	0.0682
	naphthalene[b]	0.0648
	anthracene	0.0616
	naphthacene	0.0596
	pentacene	0.0584
polyphenanthrenes	phenanthrene[b]	0.0667
	chrysene[b]	0.0672
	picene	0.0677
fragments	pyrene	0.0675
	triphenylene	0.0697
	benz[*a*]pyrene	0.0672
	perylene	0.0677
	benz[*e*]pyrene	0.0701
	dibenz[*b,cd*]pyrene	0.0673
	benz[*ghi*]perylene[b]	0.0715
	dibenz[*fg,op*]naphthacene[b]	0.0718
	coronene[b]	0.0739

[a] In units of J. [b] Exact coverings for the graphite lattice.

Although the definition of resonance energy used in Table III gives an overall picture of the stability of π-electron systems, Dewar[24] has pointed out with reference to calculations of resonance energy at the SCF level that if we want to focus on the extra stability conferred specifically by aromatic *rings*, the above definition must be amended. Butadiene does not have twice the energy of ethylene, so there is an interaction energy between adjacent double bonds having nothing to do with aromatic stabilization. The same sorts of arguments have been made by Hess and Schaad[25] with reference to Hückel calculations.

To attempt to assess the relative aromatic character of the molecules in Table II, we have computed in Table IV an aromatic stabilization energy, or as it is sometimes called a Dewar resonance energy. We have done this an simply as possible by assigning the VB resonance energy of butadiene, -0.2320508 J, to be the interaction energy between each adjacent pair of double bonds. By comparing larger conjugated alkenes it would in principle be possible to assign values to higher order interactions involving triples, ..., etc., of double bonds, but these higher order terms are fairly small. In Table IV we present the total VB energy reduced by the contribution of the isolated double bonds and the contribution of the bond–bond interactions, divided by the number of sites in the molecule, for several series of compounds. This quantity should represent the average stabilization of each site of the molecule due to its participation in an aromatic π-system, and it should correlate with the resistance of the aromatic system to chemical attack which would destroy the aromatic character. Of course, a molecule may have a highly reactive site while still having a large average stabilization, but this factor cannot be investigated without calculations of bond orders and charge densities.

Table IV focuses on three classes of molecules. The *polyacenes* show an aromatic stabilization per site which decreases with chain length. This is related to the fact that the number of Kekulé structures for this class of molecules increases only linearly with chain length.[26] We therefore predict that long polyacene polymers will not be easy to prepare. On the other hand, the *polyphenanthrenes* (benzene and naphthalene are also the first two members of this family) show an aromatic stabilization per site which grows with chain length, which is related to the fact that

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here the number of possible Kekulé structures grows exponentially with chain length.[23] Recent calculations show that long-chain polymers of this family should be significantly stable,[22,23] and recent experimental work, though not fully characterizing the products, indicates that wider polymers of this family may exist.[27] The last group of molecules in Table IV compares several fragments which can be cut from the graphite (infinite 2-dimensional hexagonal) lattice. Those fragments identified with an asterisk can be shown to provide upper bounds to the energy per site of graphite[28] since they can be repeated to cover the whole lattice. The most stable fragments seem to be those having the highest proportion of corrugated (polyphenanthrene-like) edge and the least zigzag (polyacene-like) edge. This may be related to the way in which edge erosion occurs in graphite.[26,29]

The results for our two largest molecules, coronene and dibenz[*fg,op*]naphthacene, give us a chance to compare two "rules of thumb" for estimating the stability of conjugated benzenoid hydrocarbons. One rule states simply that the maximum stability for molecules with a given number of carbon atoms is attained when the perimeter of the molecule is minimized (i.e., when the H/C ratio is minimized).[30] For 24 carbon atoms the minimum perimeter is that of coronene. On the other hand, the ideas of Clar[31] lead one to conclude that the most stable molecules will be those which are most fully "benzenoid" (i.e., for which one can draw Clar structures with as many circles as possible). For 24 carbon atoms this rule predicts dibenz[*fg,op*]naphthacene (4 circles) to be more stable than coronene (3 circles).[32] In this view the central hexagon of coronene is essentially a hole which does not contribute to the aromaticity. As can be seen from Tables II and IV, both the raw valence bond energies and the Dewar-type aromatic stabilization energies here favor the minimum perimeter rule. In fact, the computed VB energy of coronene currently provides the best rigorous upper bound to the VB energy of the graphite lattice.[28]

Acknowledgment. We thank Florida State University for providing us with a grant of computer time on their Cyber 205. Special thanks also go to Dr. Kenneth Flurchick of ETA Systems, Inc. for his assistance with the coronene calculation.

Registry No. Benzene, 71-43-2; naphthalene, 91-20-3; biphenyl, 92-52-4; anthracene, 120-12-7; phenanthrene, 85-01-8; stilbene, 588-59-0; pyrene, 129-00-0; naphthacene, 92-24-0; benz[*a*]anthracene, 56-55-3; benzophenanthrene, 65777-08-4; chrysene, 218-01-9; triphenylene, 217-59-4; *p*-terphenyl, 92-94-4; *m*-terphenyl, 92-06-8; *o*-terphenyl, 84-15-1; perylene, 198-55-0; benz[*a*]pyrene, 50-32-8; benz[*e*]pyrene, 192-97-2; pentacene, 135-48-8; picene, 213-46-7; benz[*b,cd*]pyrene, 191-26-4; benz[*ghi*]perylene, 191-24-2; dibenzo[*fg,op*]naphthacene, 192-51-8; coronene, 191-07-1.

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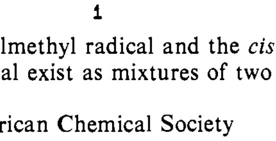
Cycloalkylmethyl Radicals. 5. 6- to 15-Membered Rings: EPR Studies of Ring Conformations and Stereodynamics[1]

K. U. Ingold*[2] and J. C. Walton*[3]

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada, and Department of Chemistry, The University, St. Andrews, Fife, Scotland KY16 9ST, U.K. *Received November 12, 1986*

Abstract: Cycloalkylmethyl radicals having 7- to 15-membered rings (excluding cyclotetradecylmethyl) have been generated and examined by EPR spectroscopy. All the cycloalkylmethyl radicals from the 9-membered ring upward show two distinguishable conformers, though there may be additional conformers present with cyclodecylmethyl and cyclopentadecylmethyl radicals. All the cycloalkylmethyl radicals from the 10-membered ring upward have one conformer, the quasi-equatorial, QE, with an H_β hfs in the range 27.7–32.0 G at 140 K and one conformer, the quasi-axial, QA, with an H_β hfs in the range 38.3–40.4 G at 140 K. The QE and QA conformers have been assigned to species in which the $CH_2^\bullet$ group occupies "outer-edge" and "corner" sites, respectively, in the preferred conformations of the cycloalkanes. The EPR results indicated that the preferred conformations of the C_9, C_{10}, C_{11}, C_{12}, C_{13}, and C_{15} rings were [333], [2323], [335], [3333], [346], and [33333], respectively. Arrhenius parameters for ring-atom site exchange in the cycloalkylmethyl radicals have been determined from the exchange broadening in the EPR spectra. These EPR barriers are compared with literature data on cycloalkane free energy barriers measured by NMR and enthalpic barriers estimated by force field and related methods.

The $C_\alpha H_2^\bullet$ group in cycloalkylmethyl radicals, **1**, provides a novel and useful conformational "spin probe" that can be monitored by EPR spectroscopy.[4-7] This probe yields both the preferred conformation of the $C_\alpha H_2^\bullet$ group with respect to the C_β–H_β bond and, more interestingly, information regarding ring conformations and even, in suitable cases, information regarding the dynamics of interconversion of ring conformers. For example,



1

both the cyclohexylmethyl radical and the *cis*-(4-methylcyclohexyl)methyl radical exist as mixtures of two conformers, one

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(1) Issued as NRCC No. 27590. Part 4: Reference 4.

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0002-7863/87/1509-6937$01.50/0 Published 1987 by the American Chemical Society