Theoretical Studies of Benzene and Its Valence Isomers

Marshall D. Newton,*[1a] Jerome M. Schulman,[1b] and Michael M. Manus[1c]

Contribution from the Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, Queens College, City University of New York, Flushing, New York 11367, and the Polytechnic Institute of Brooklyn, Brooklyn, New York 11201. Received June 7, 1973

Abstract: Calculated properties are presented for benzene (I) and its valence isomers Dewar benzene (II), benzvalene (III), and prismane (IV) based on extensive *ab initio* calculations and supplemented in some cases by semi-empirical INDO calculations. The predicted equilibrium geometries are in excellent agreement with experiment, confirming the presence of very short (1.45 Å) and very long (1.58 Å) bridgehead–bridgehead bonds in III and II, respectively. Minimal and extended basis dipole moments are shown to bracket experimental dipole moments in several polycyclic systems including III, and the magnitude predicted for Dewar benzene is <0.04 D. Vertical ionization potentials obtained by scaling the calculated orbital energies agree well with experimental data for I, and the predicted values are presented for the other isomers. INDO wave functions based on the calculated equilibrium geometries are analyzed in terms of hybrid atomic orbitals, and the latter are employed in calculating spin–spin coupling constants for the CH and single CC bonds in I–IV, through the use of empirical least-squares equations. This leads to the interesting prediction of a negative value of J_{CC} for the central bond in benzvalene (-4.0 Hz) and also for the simpler analog bicyclo[1.1.0]butane (-8.4 Hz). These predictions are also borne out b INDO perturbation theory. The other predicted J_{CC} and J_{CH} values are compared with known values in related systems, and correlations between J_{CH}, hybridization, and HC$=$C angle for olefinic CH bonds, including those in II and III, are noted.

I. Introduction

Since the early 1960's there has been a resurgence of interest[2] in the chemistry of the Kekulé benzene (I) valence isomers, Dewar benzene (bicyclo[2.2.0]hexa-2,5-diene, II), benzvalene (tricyclo[3.1.0.0²,⁶]hex-3-ene), and prismane (tetracyclo[2.2.0.0²,⁶.0³,⁵]hexane, IV).[3]

Valence isomers (I–IV) may be considered from a topological viewpoint as multigraphs[4] resulting from pairwise connections of hexagon vertices: I ≡ (12)-(34)(56) ↔ (16)(23)(45), II ≡ (14)(23)(56), III ≡ (15)-(26)(34), and IV ≡ (14)(26)(35). As indicated, all except Kekulé benzene are well described by perfect pairing, being characterized by the predominance of a single ("classical") valence bond structure.[5] Clearly an
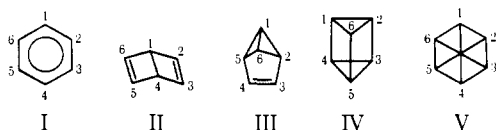
additional (nonplanar) multigraph is possible, namely that derived from the all-diagonal pairing: V, (14)-(25)(36).[4] Such a system is historically identified with the proposals of Claus and Thomsen; however, it is not obvious to what three-dimensional structure V corresponds. Some preliminary work shows that an octahedral arrangement is unstable with respect to at least

one set of nontotally symmetric distortions of the group O_h.[6]

The valence isomers (II–IV) have now all been isolated.[2] Dewar benzene and benzvalene were first obtained by irradiation of benzene. Recently, prismane has been synthesized by Katz and Acton,[7] starting from benzvalene, which they have succeeded in preparing with good yield. The isomers are also represented by a growing list of derivatives.

Concomitant with the recent synthetic achievements has been the development of three new important techniques for probing electronic structure: [13]C magnetic resonance,[8] photoelectron spectroscopy,[9] and *ab initio* molecular orbital theory, especially through the development of contracted Gaussian basis functions,[10] which has made molecules of this size accessible to calculation.

The latter two methods were brought to bear on Kekulé benzene, and despite initial concern over the validity of Koopmans' theorem, it was ultimately found[11] that the ordering of the one-electron orbital energy levels agreed with the photoelectron values.[12] In this instance Koopmans' theorem is qualitatively valid, and its quantitative use has become more wide-

(1) (a) Brookhaven National Laboratory; (b) Queens College; Alfred P. Sloan Fellow, 1971–1973; (c) Polytechnic Institute of Brooklyn.

(2) For recent reviews which discuss benzene valence isomerism see L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972); E. E. van Tamelen, *Accounts Chem. Res.*, 5, 186 (1972).

(3) There are other isomers of molecular formula C_6H_6, such as fulvene, and an additional isomer of structure $(CH)_6$, bicyclopropenyl. Although of importance in the ground and excited state potential energy surfaces, they are not considered here.

(4) A complete enumeration of $(CH)_n$ valence isomers ($n \leq 10$) is given by A. T. Balaban, *Rev. Roum. Chim.*, 11, 1097 (1966).

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(7) T. J. Katz and N. Acton, *J. Amer. Chem. Soc.*, 95, 2738 (1973).

(8) Empirical correlations between spin–spin coupling constants ($J^{13}CH$ and $J^{13}C^{13}C$) and orbital hybridizations have been discussed by, among others, N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768, 1471 (1959); J. N. Shoolery, *ibid.*, 31, 1427 (1959); K. Frei and H. J. Bernstein, *ibid.*, 38, 1216 (1963).

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(10) (a) J. L. Whitten, *J. Chem. Phys.*, 44, 359 (1966); (b) E. Clementi and D. R. Davis, *ibid.*, 45, 2593 (1966); (c) J. M. Schulman, J. W. Moskowitz, and C. Hollister, *ibid.*, 46, 2759 (1967); (d) W. J. Hehre, R. F. Stewart, and J. A. Pople, *ibid.*, 51, 2657 (1969); (e) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, 54, 724 (1971).

(11) J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, 47, 3491 (1967).

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Table I. Equilibrium Geometries for the Benzene Valence Isomers (Bond Lengths R in Å, Angles in Degrees)

Benzene (D_{6h})			Dewar benzene (C_{2v})			Benzvalene (C_{2v})			Prismane (D_{3h})		
	Equilibrium value			Equilibrium value			Equilibrium value			Equilibrium value	
Parameter	Calcd	Exptl	Parameter[a]	Calcd	Exptl	Parameter[a]	Calcd	Exptl	Parameter[a]	Calcd	Exptl
$R_{C_1C_2}$	1.39[b]	1.397[c]	$R_{C_1C_2}$	(1.523)[d]	1.523[e]	$R_{C_1C_2}$	1.52[b]	1.529[f]	$R_{C_1C_2}$	1.51[b]	1.500[g]
$R_{C_1H_1}$	1.08[b]	1.084[c]	$R_{C_2C_3}$	(1.352)[d]	1.352[e]	$R_{C_1C_6}$	1.45[b]	1.45[f]	$R_{C_1C_4}$	1.56[b]	1.585[g]
			$R_{C_1C_4}$	1.58[b]	1.58,[h] 1.597,[g] 1.63[e]	$R_{C_2C_3}$	1.52[b]	1.503[f]	∠H$_1$C$_1$C$_2$	130[b]	
			Dihedral angle (C$_2$C$_1$C$_4$C$_5$)	117[b]	117.7[h]	$R_{C_8C_4}$	(1.33)[i]	1.339[f]			
			∠H$_1$C$_1$C$_4$	121[b]	120.1[h]	Dihedral angle (C$_2$C$_1$C$_6$C$_5$)	107[b]	106[f]			
			∠H$_2$C$_2$C$_3$	134[j]	131.7[h]	∠H$_1$C$_1$C$_6$	132[k]	134[f]			
			Dihedral angle (H$_2$C$_2$C$_1$C$_4$)	178[l]		∠H$_2$C$_2$C$_3$	124[m]	124[f]			
						∠H$_3$C$_8$C$_4$	129[j]	129[f]			

[a] r_{CH} taken as 1.09 Å. After orbital hybridizations were obtained (section IVB), refinements were estimated for the equilibrium CH bond lengths (r_0), as follows: Dewar benzene, $r_{C_1H_1} = 1.085$, $r_{C_2H_2} = 1.07$; benzvalene, $r_{C_1H_1} = 1.070$ Å, $r_{C_2H_2} = 1.085$ Å, $r_{C_3H_3} = 1.075$ Å; prismane, $r_{C_1H_1} = 1.075$ Å. These refined r_{CH} values were used in the extended basis[10e] calculations (section III). [b] Ab initio optimized (STO-3G basis[10d]). [c] Reference 24. [d] Assumed from data of ref 19. [e] Reference 19. [f] Reference 21. [g] Reference 22. [h] Reference 20. [i] Assigned the ethylene value.[27] [j] INDO[17] optimized and adjusted as described in the text. The uncorrected values are 137 and 132° for Dewar benzene and benzvalene, respectively. [k] Ab initio optimized (STO-3G[10d]) and adjusted as described in text. The uncorrected value is 136°. [l] Distorted out-of-plane in the endo sense. [m] INDO[17] optimized.

spread through the scaling of ab initio orbital energies[13] or, alternatively, reparametrization of semiempirical molecular orbital theory.[14] For Kekulé benzene the principal outcome of interest was the confirmation that the highest σ electron is more readily removed than the lowest π electron. Other electronic properties of Kekulé benzene, such as the quadrupole moment and field gradients, have also been calculated with some success.[15]

The time seems ripe, then, to apply ab initio molecular orbital methods to Dewar benzene, benzvalene, and prismane.[16] The present paper gives predicted values for equilibrium geometries, vertical ionization energies of the valence electrons, and dipole moments (of II and III). Then, using the ab initio determined molecular geometries and the valence orbital hybridizations, [13]CH and [13]C–[13]C spin–spin coupling constants are calculated.

We begin in section II with the results of the geometry studies. Since there are many independent parameters in the lower symmetry isomers, we have utilized a combination of ab initio theory, semiempirical INDO theory,[17] intuition based on known analogs, and previous computational experience with regard to the errors inherent in these levels of calculation.[18] Section III presents the scaled ab initio orbital energies, which are the predicted photoelectron ionization energies. In section IV the calculated dipole moments, hybridizations, and [13]CH and [13]C–[13]C spin–spin coupling con-

stants are given. Finally, section V contains a discussion and summary of the results.

II. Determination of Equilibrium Geometries

The optimal geometries of I–IV were obtained by using the ab initio STO-3G[10d] method for the most important parameters, with the remaining parameters obtained by a combination of INDO calculations and experimental data for structural analogs, most often substituted benzene valence isomers. At the time these calculations were carried out, the literature contained no structural data for any of the unsubstituted isomers II–IV, and only in the case of II were there data for substituted isomers.[19,20] (Shortly after completion of the calculations new data for III[21] and derivatives of II and IV[22] became available, and these data compare well with our predictions given in Table I.) Particular ab initio consideration was given to optimizing dihedral angles and bond lengths associated with the bridgeheads, since at these positions the effect of strain on structure is apt to be most strongly felt. Parameters further removed from the bridgeheads were assumed close to their values in related systems.

The STO-3G method usually gives equilibrium CC and CH bond lengths of hydrocarbons accurate to within 0.01 Å,[18] including strained systems such as cyclopropane[18b] and bicyclo[1.1.0]butane.[23] We note, however, that a somewhat larger error (-0.03 Å) was obtained for the interbridgehead distance in bicyclo[2.1.0]pentane.[23] Bond angles of the HCC and CCC kind are usually predicted to within 2° in the STO-3G basis.[18] The INDO method is reliable for HCC angles but less so for bond lengths.[18a] Accordingly, it was

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(23) M. D. Newton, unpublished work.

only used for a few HCC angles. The details for the particular benzene valence isomers follow.

A. Benzene. Optimization of the CC and CH bond lengths for D_{6h} benzene furnished 1.39 and 1.08 Å, respectively, in good agreement with the experimental values,[24] 1.397 and 1.084.

B. Dewar Benzene. The independent geometrical parameters of Dewar benzene (C_{2v}) can be taken to be the three CC bond lengths, the framework dihedral angle (between cyclobutene planes), the two unique CH bond lengths, and the three angular degrees of freedom of the CH bonds ($H_1C_1C_4$, $H_2C_2C_3$, and the dihedral angle $H_2C_2C_1C_4$).

As a first step in the optimization process, the parameters available from electron diffraction studies of hexamethyl Dewar benzene[19] and perfluoro Dewar benzene[20] were assumed, and the CH bond angle parameters were optimized at the INDO level. The HCC angles at the double bonds were then augmented by 3°, corresponding to the amount by which the ethylene HCC angle is underestimated by INDO theory.[18a] (The same was done for the olefinic HCC angle of benzvalene (III).) The CH bond lengths, ultimately refined (footnote *a*, Table I) using hybridization data presented in section IVB, were taken to be 1.09 Å (the same was done for prismane and benzvalene). Successive *ab initio* optimization of the C_1C_4 bond length, the framework dihedral angle, and the bridgehead HCC angle, followed by a reoptimization of the dihedral angle, led to the final geometry given in Table I.

The predicted C_1C_4 bond distance is 1.58 Å, which agrees well with the electron-diffraction values for C_6F_6,[20,22] but is appreciably shorter than the electron-diffraction value for $C_6(CH_3)_6$,[19] 1.63 Å. The dihedral angle between cyclobutene planes and the HCC angles are very similar to the corresponding angles in perfluoro Dewar benzene.[20] We also note that the calculated HCC angle of the vinyl moiety (134°) is the same as the microwave value reported for cyclobutene (133.5).[25] The vinyl CH bond in Dewar benzene is calculated to have a preference for a slight out-of-plane deformation (~2°) in the endo direction.

C. Benzvalene. The independent parameters of benzvalene (C_{2v}) were taken to be the four unique CC bond lengths, the framework dihedral angle ($C_2C_1C_6C_5$), and the unique CH bond angles. The CH bond lengths were assigned the value 1.09 Å (*vide supra*).

The initial carbon–carbon distances for C_1C_2, C_1C_6, and C_3C_4 were those of bicyclobutane[26] and ethylene,[27] while for the C_2C_3 bond 1.54 Å was used, based on the norbornadiene structure.[28] HCC angles were optimized at the INDO level, and then consecutive *ab initio* optimization of the C_1C_6 central bond, the dihedral angle, and the $H_2C_2C_6$ angle was carried out. The latter angle was diminished by 5°, since the STO-3G basis exaggerates[23] the corresponding bicyclobutane angle (128°)[26] by this amount. Finally, the C_1C_2 and C_2C_3 bond lengths were simultaneously optimized by

quadratic interpolation. Table I shows excellent agreement between our calculated values and the microwave data of Suenram and Harmony.[21]

D. Prismane. Since in D_{3h} prismane there are only three independent parameters, aside from the CH length, again taken as 1.09 Å, the entire optimization could be carried out by the *ab initio* method. Starting with bond lengths appropriate to cyclopropane[29] (C_1C_2) and cyclobutane[30] (C_4C_4), and an assumed HC_1C_2 angle of 131°, based on INDO calculations, we first optimized the C_1C_2 distance and then simultaneously optimized the C_1C_4 distance and HCC angle by quadratic interpolation. The resulting distances are similar to unpublished data for hexamethylprismane.[22]

III. Orbital Energies and Predicted Ionization Potentials

In this section we present the calculated orbital energies (ϵ) of the occupied and lowest unoccupied orbitals.[31] The values given are for the extended Gaussian basis denoted 4-31G[10e] (referred to as EBMO in our previous studies).[32] The same ordering is obtained for the occupied orbitals at the STO-3G[10d] minimal basis set level. Experience has shown that for the case of the so-called "double-ζ" basis sets, multiplication by a factor of *ca.* 0.9 converts these orbital energies into vertical ionization energies with good success.[13] Thus, for bicyclo[1.1.0]butane[32a] we have found the following values for -0.9ϵ (in eV), with the experimental ionization energies[33] in parentheses: 8.48 (9.14); 10.67, 11.33 (11.23); 12.62 (12.87); 14.20, 14.28 (14.51, 14.85); 17.04 (16.86); 19.19, 19.25 (18.91); 22.80 (22.1). The maximum deviation is seen to be ~0.6 eV, with typical values being ~0.2-0.3 eV. The highest occupied orbital in bicyclobutane corresponds largely to the central bond.

The valence ionization potentials for the benzenes (I–IV), obtained from scaling the ϵ values by the factor -0.9, are given in Table II, along with their symmetry designations. For benzene, the only case for which experimental values are known, agreement is as good as in the bicyclobutane case. We also note the excellent agreement between the present ϵ values and the recent near-Hartree–Fock results of Ermler and Kern[15b] (see footnote *c* in Table II).

A. Dewar Benzene. The highest occupied orbitals are largely the symmetric ($8a_1$) and antisymmetric ($5b_2$) combinations of the two double bonds (C_2C_3 and C_5C_6), the antisymmetric being higher by 0.48 eV. This situation is comparable to that in norbornadiene, where the antisymmetric orbital is higher by 0.86 eV,[34]

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(31) These results are based on the calculated geometries given in Table I, with the following exceptions. The benzvalene calculation employed partially optimized values for $R_{C_1C_2}$ (1.50 Å), $R_{C_2C_6}$ (1.46 Å), and $R_{C_2C_3}$ (1.54 Å). The Dewar benzene calculation used a framework dihedral angle of 119°. These slight departures from the ultimately determined equilibrium geometries cause differences of ≤ 0.25 eV in the predicted ionization potentials.

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(33) G. B. Ellison, private communication; K. B. Wiberg, G. B. Ellison, M. B. Robin, and C. R. Brundle, submitted for publication.

(34) As inferred from the experimental ionization potential data of P. Bischoff, J. A. Hashmall, E. Heilbronner, and V. Horning, *Helv. Chim. Acta*, **52**, 1745 (1969), and calculations reported by M. H. Palmer and R. H. Findlay, *Chem. Phys. Lett.*, **15**, 416 (1972).

Table II. Vertical Ionization Energies (eV) of the Valence Electrons

Orbital type[a]	Benzene Calcd value $(-0.9\epsilon)^{b,c}$	Exptl value[d]	Orbital type[e]	Dewar benzene Calcd value $(-0.9\epsilon)^b$	Orbital type[e]	Benzvalene Calcd value $(-0.9\epsilon)^b$	Orbital type	Prismane Calcd value $(-0.9\epsilon)^b$
$1e_{1g}(\pi)$	8.2	9.3	$5b_2(\pi)$	8.2	$4b_1(\pi)$	7.8	$3\epsilon''$	8.4
$3e_{2g}$	11.9	11.8	$8a_1(\pi)$	8.6	$10a_1{}^f$	9.2	$4\epsilon'$	10.1
$1a_{2u}(\pi)$	12.3	12.5	$7a_1{}^f$	10.5	$1a_2$	10.3	$3\epsilon'$	13.5
$3e_{1u}$	14.3	14.0	$3a_2$	11.1	$6b_2$	11.9	$4a_1'$	14.1
$1b_{2u}$	15.1	14.9	$5b_1$	11.9	$3b_1$	12.6	$3a_2''$	14.5
$2b_{1u}$	15.6	15.5	$4b_2$	13.0	$5b_2$	12.8	$2\epsilon''$	17.4
$3a_{1g}$	17.4	17.0	$6a_1$	14.0	$9a_1$	12.9	$3a_1'$	17.7
$2e_{2g}$	20.1	19.2	$3b_2$	16.2	$8a_1$	15.4	$2\epsilon'$	21.4
$2e_{1u}$	24.8	22.6	$4b_1$	16.4	$7a_1$	17.5	$2a_2''$	24.9
$2a_{1g}$	28.2	25.8	$5a_1$	16.9	$4b_2$	17.9	$2a_1''$	31.5
			$2a_2$	18.5	$6a_1$	18.5		
			$4a_1$	20.8	$2b_1$	19.3		
			$3b_1$	21.9	$3b_2$	22.8		
			$2b_2$	25.5	$5a_1$	25.2		
			$3a_1$	29.4	$4a_1$	31.1		

[a] b_2 is defined to have nodes at the atoms. [b] The calculated (EBMO) orbital energies (ϵ) have been scaled by the factor -0.9, as described in section III. [c] To allow comparison with near-Hartree–Fock results, we list the valence-level values of ϵ (in au) from ref 15b, with the present (EBMO) results in parentheses: -0.3337 (-0.3331); -0.4946 (-0.4859); -0.4979 (-0.5008); -0.5872 (-0.5855); -0.6187 (-0.6175); -0.6427 (-0.6353); -0.7081 (-0.7104); -0.8230 (-0.8204); -0.0138 (-1.0132); -1.1487 (-1.1526). [d] Reference 14 and references cited therein. [e] b_2 is defined to be antisymmetric with respect to the plane containing the bridgehead atoms and the twofold axis. [f] Primarily a bridgehead–bridgehead bonding orbital.

both molecules having similar framework dihedral angles ($118°^{20}$ and $115°,^{28}$ respectively).

The next lowest bonding orbital lies ~ 2 eV below $8a_1$ and corresponds roughly to the long bond between the bridgeheads. Its ionization energy is between those calculated[23] for the highest filled orbitals of cyclopropane (10.2 eV) and cyclobutane (10.6). The lowest unoccupied orbitals can be viewed as the symmetric ($6b_1$) and antisymmetric ($4a_2$) combination of localized π^* orbitals, with the antibonding C_1C_4 σ^* orbital lying considerably higher.

B. Benzvalene. The highest occupied orbital of benzvalene (7.8 eV) is the π bond linking C_3 and C_4. The penultimate orbital, $10a_1$, corresponds to the bridgehead–bridgehead bond and, as expected,[32a,35] contains little s character. The lowest unoccupied orbital of benzvalene is the π^* orbital ($2a_2$) at $+0.18$ au, with the bridgehead σ^* orbital again appreciably higher.

C. Prismane. The highest occupied orbitals of prismane are most readily interpreted by analogy with cyclopropane, where the highest orbitals are a degenerate pair ϵ' formed largely from in-plane, tangential 2p basis functions. The prismane $3\epsilon''$ orbitals at 8.4 eV can be identified as the antisymmetric combination of the ϵ' orbitals of each cyclopropane ring. The next highest pair in prismane $4\epsilon'$ at 10.1 eV can be described as the symmetric combination of cyclopropane tangential orbitals with an admixture of the axial p orbitals of the two rings corresponding, in part, to the side bonds (C_1C_4, C_2C_3, and C_5C_6). The lowest unoccupied σ^* orbitals come grouped closely together at $+0.25(5a_1')$, $+0.26(1a_2')$, and $+0.26(4a_2'')$ au, respectively.

IV. Dipole Moments and ^{13}CH and ^{13}C^{13}C Spin–Spin Coupling Constants

A. Dipole Moments. The STO-3G and 4-31G *ab initio* basis sets yield dipole moments which systematically

bracket the experimental values of benzvalene,[36] bicyclo[1.1.0]butane[26] and bicyclo[2.1.0]pentane,[37] thus making it likely that dipole moments in other strained ring hydrocarbons can be predicted with assuredness. The calculated values, along with the INDO values, which overestimate the experimental magnitudes by *ca.* 60%, are given in Table III. In no case is there any

Table III. Calculated Dipole Moments

Molecule	Calculated STO-3G	4-31G	INDO	Exptl
Bicyclo[1.1.0]butane	0.66[a]	0.88[b]	1.19[b]	0.68[c]
Bicyclo[2.1.0]pentane	0.18[a]	0.28[a]	0.44[a]	0.26[d]
Benzvalene	0.74[e]	0.95[f]	1.36[e]	0.88[g]
Dewar benzene	0.02[e]	0.04[f]	0.27[e]	

[a] See ref 23. [b] Reference 32a. [c] Reference 26. [d] Reference 37. [e] Based on geometry given in Table I. [f] Reference 31. [g] Reference 36.

disagreement in sign, all calculations giving dipole moments with positive ends exocyclic to the fused ring systems. The average *ab initio* value for benzvalene, 0.85 D, agrees very well with the experimental value of Suenram and Harmony, 0.88 D.[36] Our predicted magnitude for Dewar benzene, <0.04 D, suggests that the likelihood of obtaining a microwave spectrum is marginal, at best. We note that for all the benzene isomers only small atomic charges as found (as inferred from population analysis). In the STO-3G basis the carbons possess from 6.04 to 6.10 electrons and the hydrogens from 0.92 to 0.94. Similar trends are obtained from INDO calculations, where the corresponding ranges are 5.91–6.02 and 1.00–1.04 electrons.

B. Directly Bonded CH Coupling Constants. The directly bonded CH spin–spin coupling constant, J_{CH}, is

(35) J. M. Schulman and G. Fisanick, *J. Amer. Chem. Soc.*, 92, 6653 (1970).

(36) R. D. Suenram and M. D. Harmony, *J. Amer. Chem. Soc.*, 94, 5915 (1972).

(37) R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, 56, 3837 (1972).

generally believed to arise entirely from the electron-coupled Fermi-contact interaction between nuclear spins. With the assumption of an average energy denominator in a sum-over-states localized molecular-orbital formalism there results a linear dependence of J_{CH} on the per cent s character in the bonding hybrid, and indeed this has frequently been found to be the case.[8] The exact form of the linear relationship will depend upon the particular definition of per cent s character, e.g., localization of ab initio (Slater or Gaussian) or semiempirical molecular orbitals, followed by decomposition of the localized molecular orbitals into hybrid atomic orbitals,[32] or construction of bonding orbitals from hybrid atomic orbitals (orthogonal on the same center).[16b,38] Subject to this choice of definition, a measurement of J_{CH} is tantamount to a determination of CH bonding character. The present work has utilized a particularly rapid procedure, localization of INDO molecular orbitals according to the Edmiston-Ruedenberg procedure,[39] which minimizes the total interorbital contribution to the two-electron repulsion energy. The method has also been employed in our earlier work on bicyclobutane[32a] and bicyclo[1.1.1]-pentane.[32b]

Using a set of 19 cyclic and acyclic hydrocarbons which provided experimental J_{CH} values ranging from 125 to 220 Hz and the calculated INDO hybrids, we obtained the least-squares relationship[40]

$$J_{CH} = 5.70(\% \text{ s}) - 18.4 \text{ Hz} \qquad (1)$$

having a standard deviation (s.d.) of 5.7 Hz. The need for a nonzero intercept is shown by the larger s.d., 6.3, when the intercept is constrained to be zero, and it may be thought to arise from the implicit use of a universal average energy denominator for all molecules in the series as well as other deficiencies of the INDO method.

The predicted J_{CH} values for the benzene isomers, based on this equation and their calculated INDO hybridizations, are given in Table IVA. For the two known cases, benzene[41] and prismane,[7] our calculated values are within 4 and 9 ± 2 Hz, respectively, of experiment, that is, essentially on the order of the above root-mean-square error. The calculated values for the bicyclo[1.1.0]butane moiety of benzvalene, $J_{C_1H_1} = 209$ Hz and $J_{C_2H_2} = 164$ Hz, are similar to those calculated[42] for bicyclo[1.1.0]butane itself, $J_{C_1H_1} = 203$ Hz (exptl,

Table IV. Per Cent s Character and Calculated Spin-Spin Coupling Constants for CH and CC Single Bonds

Molecule	Bond (XY)	Hybridization and per cent s character Atom X		Atom Y		J_{XY} (from eq 1 or 2)
		(A)	**CH Bonds**			
Benzene	C_1H_1	$sp^{2.30}$	30.3			154 (158)[a]
Dewar benzene	C_1H_1	$sp^{2.28}$	30.5			155
	C_2H_2	$sp^{1.76}$	36.2			188
Benzvalene	C_1H_1	$sp^{1.51}$	39.8			209
	C_2H_2	$sp^{2.13}$	32.0			164
	C_3H_3	$sp^{1.97}$	33.7			174
Prismane	C_1H_1	$sp^{1.75}$	36.4			189 (180 ± 2)[b]
		(B)	**CC Bonds**			
Dewar benzene	C_1C_2	$sp^{2.76}$	26.6	$sp^{2.20}$	31.3	41.5
	C_1C_4	$sp^{4.47}$	18.3	$sp^{4.47}$	18.3	10.6
Benzvalene	C_1C_2	$sp^{2.88}$	25.8	$sp^{4.20}$	19.2	18.5
	C_1C_6	$sp^{9.01}$	10.0	$sp^{9.01}$	10.0	−4.0
	C_2C_3	$sp^{2.00}$	33.4	$sp^{2.18}$	31.3	55.0
Prismane	C_1C_2	$sp^{4.50}$	18.2	$sp^{4.50}$	18.2	10.4
	C_1C_4	$sp^{2.53}$	28.3	$sp^{2.53}$	28.3	39.7

[a] Experimental value from ref 41. [b] Experimental value from ref 7.

205 Hz[43]) and $J_{C_2H_2}(\text{exo}) = 160$ Hz (exptl, 153 Hz[43]). The calculated J_{CH} for the bridgehead of Dewar benzene is 155 Hz, considerably smaller than the bicyclobutane bridgehead values but quite close to the calculated value for Kekulé benzene (154 Hz). The magnitudes of the calculated J_{CH} values for the olefinic CH bonds in Dewar benzene and benzvalene, 188 and 174 Hz, respectively, reflect the high degree of angle strain (vide infra) at these carbons, compared to molecules like benzene and ethylene. Finally, we note that J_{CH} in prismane is much larger than in cubane (calcd, 163 Hz; exptl, 160 Hz[44]), being similar to that for the bridgehead CH bond in bicyclo[2.1.0]pentane (calcd, 178 Hz; exptl,[45] 178 Hz), a molecule which although less strained than prismane shares the common feature of fused three- and four-membered rings.

C. Directly Bonded CC Coupling Constants. The theory of the coupling constant between directly bonded carbons (A and B), $J_{C_AC_B}$, is both more complicated than for J_{CH} and more interesting, as well, since for strained rings it gives direct information on the molecular framework. The difficulties in accounting for J_{CC} arise, first, from the fact that two bonding hybrids contribute to the Fermi contact term and, second, from possibly significant orbital and spin-dipolar contributions.[46] Neglecting for the moment the contribution of the latter noncontact terms, it may be assumed within the same average energy approximation (vide supra) that $J_{C_AC_B}$ is linearly related to the product of the per cent s characters in the two bonding hybrids. Such proposed relationships have had success,[8] though the experimental data are more scarce than in the CH case.

For the present study we selected 16 known $J_{C_AC_B}$ values for singly bonded carbons and calculated their INDO hybridizations. These values are shown in Fig-

(38) (a) K. Mislow, Tetrahedron Lett., **22**, 1415 (1964); (b) J. D. Petke and J. L. Whitten, J. Chem. Phys., **51**, 3166 (1969).

(39) C. Edmiston and K. Ruedenberg, J. Chem. Phys., **43**, S97 (1965).

(40) The experimental data used in the least-squares fit consist of the known $^1J^{13}_{CH}$ values for the following set of molecules: methane, ethane, ethylene, allene, acetylene, and propyne (data cited by G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, J. Amer. Chem. Soc., **92**, 1 (1970)); toluene (N. Muller and D. E. Pritchard, J. Chem. Phys., **31**, 1471 (1959)); cyclopropane and cyclobutane (T. Yonezawa, I. Moreshima, M. Fijii, and K. Fukui, Bull. Chem. Soc. Jap., **38**, 1226 (1965)); cyclopropene, benzene, cyclooctatetraene, norbornane, norbornene, norbornadiene, nortricyclene, and quadricyclene (data cited in Table V footnotes and G. A. Olah and A. M. White, J. Amer. Chem. Soc., **91**, 3956 (1969)); bicyclo[1.1.0]butane[43] and bicyclo[2.1.0]pentane.[45] Per cent s values were obtained from INDO calculations (details will appear in a future publication) based on experimentally available geometrical parameters, supplemented, as needed, with INDO optimized CH bond angles.

(41) H. M. Hutton, W. F. Reynolds, and T. Schaefer, Can. J. Chem., **40**, 1758 (1962).

(42) Note that these calculated J_{CH} values, based on the least-squares eq 1, agree more closely with experiment than the calculated values presented in ref 32, which depended on parameters (i.e., the values of valence s orbitals at their origins) which were not fully optimized.

(43) K. Wüthrich, S. Meiboom, and L. C. Snyder, J. Chem. Phys., **52**, 230 (1970).

(44) P. E. Eaton and T. W. Cole, Jr., J. Amer. Chem. Soc., **86**, 962 (1964).

(45) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, J. Amer. Chem. Soc., **94**, 997 (1972).

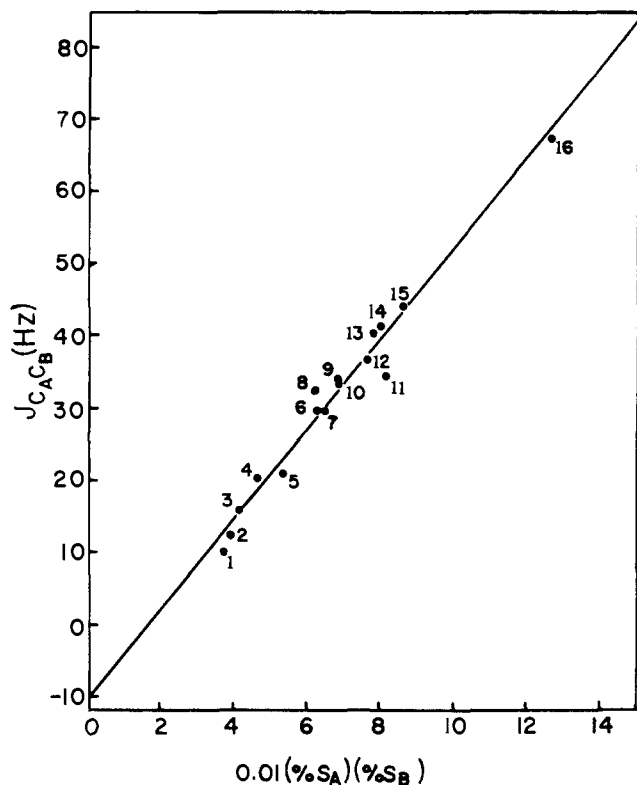(46) A. C. Blizzard and D. P. Santry, J. Chem. Phys., **55**, 950 (1971).

Figure 1. Experimental nuclear spin–spin coupling constants between singly bonded carbons in 12 hydrocarbons vs. the product of the per cent s characters in the two bonding carbon atomic hybrids obtained from localization of INDO molecular orbitals. The straight line is the least-squares fit given in eq 2. The bonds indicated by number on the figure are for: (1) cyclopropane (ref 29 and 52); (2) quadricyclene, C_1–C_2(ref 51 and a below); (3) bicyclo[2.1.0]pentane, C_4–C_5 (ref 37 and 45); (4) spiropentane, C_1–C_2 (ref 45 and b); (5) bicyclo[1.1.0]butane, C_1–C_2 (ref 26 and 45); (6) cyclobutane (ref 45 and c); (7) nortricyclene, C_3–C_4 (ref 51 and d); (8) norbornane, C_1–C_7 (ref 51 and e); (9) norbornane, C_1C_2 (ref 51 and e); (10) neopentane (see f and g); (11) ethane (see f and h); (12) bicyclo[2.1.0]pentane, C_1–C_2 (ref 37 and 4); (13) nortricyclene, C_1–C_7 (ref 51 and d); (14) quadricyclene, C_1–C_7 (ref 51 and a) (15) toluene, C_1–C_7 (see i and j); and (16) methylacetylene, C_2–C_3 (see i and k). The references indicate the sources of the experimental J_{CC} data and the geometries used in the INDO calculations. The equilibrium CH bond angles were based on INDO calculations, when not available experimentally or otherwise specified. References: (a) the following values were assigned: $r_{C_1C_2}$ = 1.50 Å, $r_{C_2C_3}$ = 1.54 Å, and $\angle H_7C_7H_{7'}$ = 110°; (b) G. Dallinga, R. K. van der Draai, and L. H. Toneman, Recl. Trav. Chim. Pays-Bas Belg., 87, 897 (1968) (the HCH angle was assumed to be 115°); (c) ref 30 and S. Meiboom and L. C. Snyder, J. Chem. Phys., 52, 3857 (1970); (d) J. F. Chiang, C. F. Wilcox, and S. H. Bauer, Tetrahedron, 25, 369 (1969); (e) ref 28a; $H_7C_7H_7'$ = 110°; $\angle H_2C_2H_2'$ = 109°, tilted 1.4° in the exo direction; (f) K. D. Summerhays and G. E. Maciel, J. Amer. Chem. Soc., 94, 8348 (1972); (g) assumed r_{CC} = 1.54 Å, all bond angles tetrahedral; (h) D. E. Shaw, D. W. Lepard, and H. L. Welsh, J. Chem. Phys., 42, 3736 (1965); (i) Frei and Bernstein, work cited in ref 8; (j) assumed benzene geometry, $R_{C_7C_1}$ = 1.52 Å, and tetrahedral methyl bond angles; (k) C. C. Costain, J. Chem. Phys., 29, 864 (1958).

ure 1, and the least-squares equation which results from these data is

$$J_{C_AC_B} = 0.0621(\% \, s_A)(\% \, s_B) - 10.2 \text{ Hz} \qquad (2)$$

with a standard deviation of 2.4 Hz. Equation 2 and the calculated INDO hybridizations for the benzene valence isomers then furnished the J_{CC} values given in Table IVB.

The most interesting result obtained is that the

coupling constant, $J_{C_1C_6}$, for the bridgehead bond of benzvalene is negative (−4.0 Hz). It is because of the small s character in the bonding hybrids that the negative intercept dominates the sign. The question arises as to whether this result is physically real. In the absence of an experimental answer, we have calculated the coupling constant independently by INDO perturbation theory, including, for completeness, the noncontact terms evaluated by the method of Blizzard and Santry.[46,47] In confirmation of the result using eq 2, we find all three contributions to be negative (Fermi contact, −8.1 Hz; spin dipolar, −1.5 Hz; orbital, −4.4 Hz).

It might be pointed out that a negative J_{CC} is also found for the central bond of bicyclobutane, a result which is not too surprising, since it is this moiety which is in question in benzvalene. Application of eq 2 to the calculated bicyclobutane C_1–C_3 hybrids[32a] gives −8.4 Hz, and INDO perturbation theory again yields three negative terms, which lead to a total value of −6.9 Hz. An experimental measurement of this bond in bicyclobutane and benzvalene would be very useful since these bonds provide an important test of these fundamental theories of the coupling constant.[48]

The remaining carbon–carbon bonds in the benzene valence isomers have J_{CC} values which fall on the upper, positive part of the least-squares line, Figure 1, and the Fermi contact term is positive and dominant. The effect of ring strain is clearly exhibited. Dewar benzene has a somewhat unusual value of J_{CC} for its central bond, 10.6 Hz being rather small for a four-membered ring.[49] Conversely, the value of J_{CC} (55.0 Hz) for the C_2C_3 bond in benzvalene is relatively high for a single bond between a saturated and a trigonal carbon atom[50] and reflects the fact that in the strained environment of benzvalene both hybrids in the bond are calculated to be ca. sp². The other single-bond J_{CC} values in Table IVB can be easily related to those in systems whose J_{CC} values are known. Thus, J_{CC} for the three-membered ring in prismane (10.4 Hz) is similar to that in quadricyclene ($J_{C_1C_2}$; calcd, 14.0 Hz; exptl,[51] 12.6) and cyclopropane itself (calcd, 13.2 Hz; exptl,[52] 10.0 Hz), while that in the side bond of benzvalene ($J_{C_1C_2}$, 18.5 Hz) is closer to the corresponding value in bicyclo[1.1.0]butane (calcd, 23.2 Hz; exptl,[45] 21.0 Hz). The values for the four-membered rings in prismane ($J_{C_1C_4}$, 39.7 Hz) and Dewar benzene ($J_{C_1C_2}$, 41.5 Hz) are close to the analogous value for the side bond in bicyclo[2.1.0]pentane (calcd, 37.1 Hz; exptl,[45] 36.7 Hz).

(47) The noncontact calculations reported here are based on the formalism of ref 46 and were carried out with a computer program supplied by Professor Santry. As a result of an Erratum published by A. C. Blizzard and D. P. Santry (J. Chem. Phys., 58, 4714 (1973)), we have repeated the least-squares fitting of their set of 15 J_{CC} values, using corrected spin-dipolar terms. This has the effect of reducing the optimal values of the parameters, $(S^2c(O))^2$ and $(\langle r^{-3}\rangle_C)^2$, by factors of 0.967 and 0.963, respectively, relative to the originally published values.[46] The theoretical values of J_{CC} for the bridgehead–bridgehead bonds in bicyclo[1.1.0]butane and its 1-cyano derivative which we communicated to M. Pomerantz and D. F. Hillenbrand, J. Amer. Chem. Soc., 95, 5809 (1973), were calculated before publication of the Erratum. The amended values of J_{CC} are −6.9, −6.2, and +22.3 Hz, respectively.

(48) Further studies of noncontact contributions to J_{CC} will be reported by J. M. Schulman and M. D. Newton in a future publication.

(49) E.g., see the examples contained in ref 45.

(50) E.g., cf. toluene, K. Frei and H. J. Bernstein, J. Chem. Phys., 48, 1216 (1963).

(51) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, J. Amer. Chem. Soc., 92, 7107 (1970).

(52) F. J. Weigert and J. D. Roberts, J. Amer. Chem. Soc., 94, 6021 (1972).

V. Discussion and Summary

The foregoing results demonstrate that the level of calculation adopted in the present study is capable of giving a good overall account of the ground state properties of benzene and its valence isomers. The calculated molecular geometries are in excellent agreement with available experimental data and indicate that the central bonds in benzvalene and Dewar benzene are respectively rather short and long compared to other carbon–carbon single bonds, although not anomalously so.

Among the important features of the predicted vertical ionization energies we note the following. The ionization energy of the $10a_1$ MO in benzvalene (9.2 eV), corresponding to the bridgehead–bridgehead bond,[53] is similar to the lowest energy IP's for ethylene (calcd, 9.2 eV; exptl,[9] 10.5 eV), bicyclo[2.1.0]pentane (calcd, 9.0 eV), and bicyclo[1.1.0]butane (calcd, 8.5 eV; exptl,[33] 9.1 eV), which also involve removal of electrons from bonds formed largely of p orbitals. The lower p character (sp[4.47]) and larger ionization energy (10.5 eV) associated with the central bond in Dewar benzene (approximately, MO $7a_1$) can be compared with similar magnitudes found for cyclopropane (sp[4.16] for the CC bonding hybrids and 10.3 eV for the IP of the highest filled MO, $1e'$; cf. the experimental[9] value of ~10.5 eV). Although the hybridization of the CC bonds in the three-membered rings of prismane (sp[4.50]) is similar to that in cyclopropane, the lowest IP of prismane (8.4 eV) is appreciably smaller than the corresponding cyclopropane value, since the $3e''$ MO of prismane is delocalized over both three-membered rings. All of the above IP's are appreciably smaller than that corresponding to ionization from the CC bond in ethane (calcd, 11.9 eV; exptl,[9] ~13 eV, based on the $3a_{1g}$ MO of D_{3d} ethane) which has the degree of p character expected of an unstrained alkane.

The charge distributions of the benzene valence isomers have been analyzed (section IV) primarily in terms of calculated dipole moments, which are in close accord with available experimental data and orbital hybridizations. We have also given detailed attention to the relationship between orbital hybridization and spin–spin coupling constants. The predicted coupling constants for directly bonded CH atoms, as obtained from the calculated per cent s character via appropriate least-squares equations, appear reasonable by comparison with known data for analogous systems. For example, Table V illustrates how the calculated J_{CH} values for the vinyl CH bonds in Dewar benzene and benzvalene fit into a monotonic sequence of J_{CH} vs. HC=C angle.[54] We have also examined the relation between J_{CC} and the per cent s character, which for

Table V. Dependence of J_{CH} and Hybridization on the HCC Angle for Olefinic CH Bonds in Cyclic Hydrocarbons

Molecule	Bond angle (HC=C), deg	J_{CH} Calcd (eq 1)	J_{CH} Exptl	Hybridization
Cyclooctatetraene	117.6[a]	145	155[b]	sp[2.49]
Benzene	120.0	154	158[c]	sp[2.30]
Norbornene	126.4[d]	170	165[e]	sp[2.02]
Norbornadiene	126.7[f]	172	172[e]	sp[2.00]
Benzvalene	128.9[g]	174		sp[1.97]
Dewar benzene	134[h]	188		sp[1.76]
Cyclopropene	149.9[i]	229	220[j]	sp[1.31]

[a] M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724 (1966). [b] H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **14**, 468 (1961). [c] Reference 41. [d] INDO optimized (and adjusted as described in section II), based on framework parameters taken from norbornadiene and norbornene (ref 28). [e] K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963). [f] INDO optimized (and adjusted as described in section II), based on framework parameters taken from norbornadiene (ref 28). [g] See Table I and ref 21. [h] See Table I. [i] P. H. Kasai, R. J. Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). [j] G. L. Closs, *Proc. Chem. Soc., London*, 152 (1962).

benzvalene leads to the interesting prediction of a negative spin–spin coupling constant. The relative importance of noncontact terms increases as the s character of a bond decreases, and their negative value for benzvalene supports the least-squares result based on s character.

The *ab initio* calculations in the present study give the correct qualitative ordering of isomer energies for I–IV,[55] including the prediction that the energy of Dewar benzene is slightly lower than that for benzvalene (calcd, 2 kcal/mol; exptl, 6 kcal/mol, based on the $C_6(CF_3)_6$ derivatives[55]); the other energy differences, however, are greatly exaggerated, even with the extended basis set, thus illustrating the difficulty of comparing *ab initio* total energies of systems which differ greatly in their amount of angle strain.[56]

(53) Although MO's are of course delocalized over many bonds in general, the MO's referred to in the following discussion can be identified as being essentially CC bonding MO's and, with the exception of cyclopropane and prismane, can also be largely associated with individual CC bonds.

(54) Similar correlations have been noted by Tori, *et al.* (Table V, footnote *e*), and P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(55) Based on experimental enthalpies given by D. M. Lemal and L. H. Dunlap, Jr., *J. Amer. Chem. Soc.*, **94**, 6564 (1972), for $(CF_3C)_6$. See also earlier data for $(CH_3C)_6$ given by J. M. Oth, *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968); and W. Adam and J. C. Chiang, *Int. J. Chem. Kinet.*, **1**, 487 (1969).

(56) We have previously shown[32] that reasonable *ab initio* strain energies can be calculated, *provided* balanced energy equations are available, which match systems of similar total strain energy against each other; *e.g.*, bicyclo[1.1.0]butane + ethane *vs.* 2-cyclopropanes. This analysis has not been pursued for the present systems, I–IV.