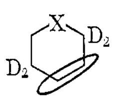
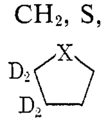
ward application of eq 1 thus cannot be made to five-membered rings.

It is noted that J_{cis} is not affected by changes in the H–C–H projection angle χ (eq 5b). The torsional angle Ψ can therefore be calculated from this equation, with A evaluated to be 9.95 from J_{cis} (7.90 Hz) and Ψ (27°) in cyclopentane. The values of Ψ obtained by this classical Karplus approach for the remainder of the series (**2**–**6**) are recorded in the last column of Table I. Only the value for cyclopentanone (34.5°) can be compared with experimental data[8] (37.4°, electron diffraction). The agreement (3°) is quite good for a quantitative Karplus-type analysis. The figures in the last column of Table I offer the best current torsional angles for five-membered rings in solution. Just as in six-membered rings,[1] the shorter C–O and C–N bonds flatten the ring slightly and the longer C–S bonds and smaller C–S–C angle pucker the ring considerably.

In six-membered rings, calculation of Ψ from eq 1 and from eq 5b should give identical results, since distortions from threefold symmetry are very small. For molecules of the type **7** (X = CH_2, S, $^+SCH_3$, Se, $SeBr_2$, $TeBr_2$),[9] the two methods indeed give essentially the same values of Ψ, in contrast to the situation in five-membered rings (Table I, last two columns). For molecules without angle strain, the methods can therefore be considered to be equivalent. Application of the Karplus approach requires the evaluation of A and demonstration that it is constant throughout a series. The R-value method is therefore to be preferred for six-membered rings, since the A factor cancels out (eq 3). For five-membered rings of the type **1**–**6**, the present work shows that the standard Karplus approach is the more reliable (Table I). For systems such as **8**, however, the A factor is strongly dependent on the electronegativity of X and neither method is quantitatively accurate. Within an homologous series of five-membered rings, qualitative trends in the R values, as originally propounded,[10] can still give a valid indication of the relative shapes of the molecules.



7



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(9) Data from J. B. Lambert, D. H. Johnson, R. G. Keske, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 8172 (1972); E. W. Garbisch, Jr., and M. G. Griffith, *ibid.*, **90**, 6543 (1968). The Karplus A = 13.28 was determined from Ψ = 58° in cyclohexane.

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(11) (a) This work was supported by the National Science Foundation (Grants GP-34259X and GP-35868X) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4); (b) NSF Trainee, 1969–1970; NDEA Fellow, 1970–1973; (c) NSF Trainee, 1969–1970.

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Ab Initio Valence Bond Calculation of Benzene

Sir:

The qualitative concepts of resonance, in particular the relative importance of specific valence bond functions, have been based almost entirely on empirical and semiempirical calculations. The first of these for aromatic hydrocarbons was the valence bond calculation on benzene done by Pauling and Wheland[1] which showed, in part, that the Kekule structure (I) of benzene is approximately four times more important than the Dewar structure (II). These workers assumed that polar structures are unimportant. More recently Craig[2] examined the question of the importance of polar structures in benzene, again using semiempirical arguments. He found the ortho singly polar structures to contribute no more than 0.5% to the ground state.

Recently, an *ab initio* valence bond program package capable of including many valence bond functions has been developed in this laboratory. The theory behind this program, which utilizes the symmetric group and Young Tableaux to handle the spin degeneracy problem, has been published elsewhere.[3–6] We have used this program to perform a "full π" VB calculation of benzene.

The fixed GTO basis of Whitten[7] was used and the calculation was done at the experimental geometry. All 1s and σ bonded electrons were included explicitly in the calculation by keeping the first 18 SCF molecular orbitals paired. The "full π" VB calculation includes 175 individual valence bond functions which in unnormalized form may be written

$$\theta_i = \mathcal{A}\Phi_i(1,\ldots,6)\Xi(7,\ldots,42)$$

where $\mathcal{A}$ is the antisymmetrizer, and

$$\Xi(7,\ldots,42) = 1a_{1g}(7)1a_{1g}(8)(\alpha_7\beta_8 - \alpha_8\beta_7)\ldots$$
$$3e_{2ga}(39)3e_{2ga}(40)(\alpha_{39}\beta_{40} - \alpha_{40}\beta_{39}) \times$$
$$3e_{2gb}(41)3e_{2gb}(42)(\alpha_{41}\beta_{42} - \alpha_{42}\beta_{41})$$

represents the 18 σ molecular orbitals which are kept doubly occupied throughout the calculation.[8]

Each of the Φ_i refers to a specific valence bond function. Chart I gives a schematic representation for the covalent and singly polar functions in terms of a representative Rumer diagram. As an example, structure I, one of the two Kekule structures, is represented by

Chart I

	I	II	III	IV
H_{ii}, au	−230.2971	−230.2838	−229.8101	−229.7185
Occupation no.	0.0622	0.0194	0.0234	0.0381

	V	VI	VII	VIII
H_{ii}, au	−230.0452	−229.7039	−230.3244	−230.1732
Occupation no.	0.098	0.0078	0.4753	0.2756

$$\Phi_K(1,\ldots,6) = p_1(1)p_2(2)p_3(3)p_4(4)p_5(5)p_6(6) \times (\alpha_1\beta_2 - \alpha_2\beta_1)(\alpha_3\beta_4 - \alpha_4\beta_3)(\alpha_5\beta_6 - \alpha_6\beta_5)$$

(1) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(2) D. P. Craig, *Proc. Roy. Soc.*, *Ser. A*, 200, 401 (1950).

(3) G. A. Gallup, *Int. J. Quantum Chem.*, **6**, 899 (1972).

(4) G. A. Gallup and J. M. Norbeck, *Chem. Phys. Lett.*, in press.

(5) G. A. Gallup and J. M. Norbeck, *Chem. Phys. Lett.*, in press.

(6) J. M. Norbeck and G. A. Gallup, *Int. J. Quantum Chem.*, in press.

(7) J. Whitten, *J. Chem. Phys.*, **44**, 359 (1965).

(8) The 18 occupied σ orbitals are listed with their respective orbital energies in ref 9.

and as a further example structure VII, one of the 24 ortho polar structures, is represented by

$$\Phi_{\mathrm{op}}(1,\ldots,6) = \mathrm{p}_2(1)\mathrm{p}_2(2)\mathrm{p}_3(3)\mathrm{p}_4(4)\mathrm{p}_5(5)\mathrm{p}_6(6) \times (\alpha_1\beta_2 - \alpha_2\beta_1)(\alpha_3\beta_4 - \alpha_4\beta_3)(\alpha_5\beta_6 - \alpha_6\beta_5)$$

In each case p_i refers to the atomic p_π orbital centered at the *i*th carbon nucleus with no delocalization or orthogonalization. This gives, in effect, a mixed MO-VB calculation which we believe is the first of its kind.

The 175 individual valence bond functions are then grouped into 22 $^1A_{1g}$ symmetry functions, among which are two covalent (I, II), six singly polar (III-VIII), 11 doubly polar, and three triply polar $^1A_{1g}$ types. Consequently, our "full π" VB calculation corresponds exactly to the "full π" MO-CI fixed basis calculation done by Buenker, Whitten, and Petke,[9] and the ground state and 21 excited $^1A_{1g}$ energies for these two calculations are identical. The ground-state energy is given in Table I.

Table I. Comparisons of Various VB Calculations

	Functions	*E*, au	(*E* − SCF), au (kcal)
Covalent (I + II)	2	−230.3026	+0.0728 (+45.7)
SCF		−230.3754	0.0 (0.0)
Ortho ionized (VII, VIII)	2	−230.3781	−0.0027 (−1.7)
Covalent and singly ionized (I–VIII)	8	−230.4373	−0.0619 (−38.8)
"Full"	22	−230.4546	−0.0792 (−49.7)

In addition to the "full π" calculation, a series of smaller calculations was done to determine the importance of specific valence bond functions. The diagonal energy obtained for each covalent and singly polar *symmetry function* is listed in Chart I. For convenience, as was noted above, we have included a representative Rumer diagram for each function type.[10]

It should be noticed that the Kekule (I) and Dewar (II) forms have a higher energy than the ortho singly polar function (VII). The importance of these polar functions is shown further in a series of smaller calculations given in Table I. If one includes the covalent functions only, the energy obtained is 45.7 kcal above the SCF. If one includes the ortho polar functions only the energy is slightly lower than the SCF. However, including functions I-VIII the calculated energy was 38.8 kcal below the SCF and 84.5 kcal below the energy obtained with just the covalent functions. The occupation numbers obtained in this last calculation are listed in Chart I. The occupation numbers show very clearly the importance of the polar valence bond functions; the Kekule function (I) is listed fourth in importance and considerably below the two ortho polar functions.

The stability and importance of the singly polar functions in this calculation appears surprising and shows a definite disagreement with the calculation done by Craig.[2] However, Weinbaum[11] showed, in the VB treatment of the hydrogen molecule, that there is approximately 20% contribution to the wave function and a 5.5 kcal lowering in the energy, when the polar function is included. An analogy can be made with this calculation in explaining the importance of the polar functions to benzene. The correct $^1A_{1g}$ functions involve structures such as VII and VIII averaged around the ring. Such averaging corresponds to roughly 33% polar and 67% covalent character in the functions of this one type. Such averaging is, of course, impossible within one function type in H_2 where there are only two electrons but obviously improves the energy calculation for benzene. Other aromatic systems, including heteronuclear molecules, admit these kinds of mixed polar-covalent structures, and it seems likely that symmetric averages of these will be found to be more stable than purely covalent functions.

Among several points of interest brought out by this study is that the energy expectation values of the Kekule and Dewar structures are closer in the *ab initio* than in the semiempirical treatments, and this puts these structures on a much more competitive basis in this calculation than in previous ones. Many studies have been given (see, for example, Pullman[12] and Coulson[13]). However, these studies are restricted to the intercomparison of Kekule and (generalized) Dewar types. Since the present study indicates that the covalent types are of relative unimportance in benzene, it is possible the same situation may apply to the larger systems and, hence, it may be necessary to reopen these questions.

Furthermore, it has been argued on the basis of simple electrostatics that the farther separated charges are in VB structures the higher energy they have. Examination of IV shows that this trend is followed here, but a more careful analysis also shows that distance cannot alone account for the large differences found, and hence other phenomena must also be involved.

Finally, it is admitted that the Kekule structures alone seem to work very well in explaining chemical stability and reactivity in aromatic systems. The effect the present results will have on the existing concepts of resonance is not known. However, further work is being carried out on benzene and other aromatic systems, which will be published shortly. It is hoped this work will help to clarify the situation.

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(9) R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).

(10) A listing of all covalent and ortho polar structures and the different symmetry functions is given in ref 2.

(11) S. Weinbaum, *J. Chem. Phys.*, **1**, 593 (1933).

(12) A. Pullman, *Ann. Chim. (Paris)*, **2**, 5 (1947).

(13) C. A. Coulson, *Proc. Roy. Soc., Ser. A*, 207, 91 (1957).

(14) NDEA Predoctoral Fellow, 1972–1973.

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Kinetics and Mechanism of Oxidative Addition of Iodine to Platinum Acetylacetonate in Nonpolar Solvents. The Photochemically Initiated Free-Radical Chain Pathway

Sir:

Some important oxidative addition reactions of coordinatively unsaturated metal complexes with simple