the stronger oxidizing nature of this last species. The oxygen–oxygen bond (stronger[13] in O_2^- than in O_2^{2-}) can have, in this case (as often in redox processes) a certain influence on the reaction rates. This hypothesis seems in agreement with the extremely low rates observed, in preliminary experiments, for reactions between nitrite and molecular oxygen whose O–O bond is certainly stronger[13] than those of its negative ions O_2^- and O_2^{2-}. Further pertinent work to elucidate this question is in progress.

Acknowledgment. This work was carried out with the financial assistance of the Italian National Research Council (CNR). Part of the kinetic data was obtained with the aid of Mr. Armando Bufo during his undergraduate research training. The calculation of the simulated chemical kinetics were performed using an IBM System 360 Model 65 computer of the "Centro di Calcolo Elettronico," CSATA, University of Bari.

Appendix

Derivation of Eq 14. By applying the stationary-state condition to the species O^{2-} involved in the autocatalytic mechanism presented in Figure 6

$$d[O^{2-}]/dt = k_a[NO_2^-][O_2^{2-}] - k_{-a}[NO_3^-][O^{2-}] - k_b[O^{2-}][O_2^-] = 0 \quad (I)$$

one obtains $[O_2^{2-}]$. The rate of disappearance of superoxide is

$$-d[O_2^-]/dt = k_b[O^{2-}][O_2^-] \quad (II)$$

Equation 14 can be derived from (II) by adding the term $k_i[NO_2^-][O_2^-]$ which expresses the contribution of the parallel "direct" reaction between NO_2^- and O_2^-.

Derivation of Eq 17. Equation 14 can be reduced (by substituting $[O_2^{2-}]$ with $([O_2^-]_0 - [O_2^-])/2$) to

$$-dt = \frac{B + Dx}{x[(Ax_0 + BC) + (CD - A)x]}dx \quad (III)$$

where $A = k_ak_b[NO_2^-]/2$, $B = k_{-a}[NO_3^-]$, $C = K_i \cdot [NO_2^-]$, $D = k_b$, $x_0 = [O_2^-]_0$, and $x = [O_2^-]$. Upon integration, the value of the integration constant can be calculated from the limiting condition $t = 0$. Equation 17 can be readily obtained by setting $\alpha = B/(Ax_0 + BC)$, $\beta = Ax_0 + BC$, $\gamma = CD - A$, and $\delta = D/(CD - A)$.

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Theoretical Studies of the Ground and Excited Electronic States of the Benzynes by *Ab Initio* Self-Consistent-Field and Configuration-Interaction Methods[1]

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Abstract: *Ab initio* self-consistent-field (SCF) and configuration-interaction (CI) calculations on *o*-, *m*-, and *p*-benzyne are reported for the molecules in a geometry constrained to be that of benzene. The results predict conclusively that the ground electronic state of *o*-benzyne is a singlet. The meta and para isomers are found to have triplet ground states in the geometries considered; however, the singlet–triplet energy separations are quite small. Electronic spectral calculations for *o*-benzyne show the existence of both n → n* and $\pi \rightarrow \pi^*$ states near the region of the experimentally observed intense absorption; also a $\pi \rightarrow$ n* transition is found at longer wavelength. An important conceptual aspect of the study is the failure of a single-determinant SCF wave function to describe adequately the weak additional bond between the dehydrocarbon atoms in the case of a singlet state. It is shown that for a proper description at least a two-determinant (CI) wave function is required both in principle and in practice.

Since the work of Roberts confirmed the intermediacy of the species *o*-benzyne (1,2-dehydrobenzene) in the amination of aryl halides by metal amides in liquid ammonia,[2] *o*-benzyne has been proposed as an intermediate in a number of reactions.[3] Generally, it is assumed that the ground state of *o*-benzyne is of singlet multiplicity, but no definitive proof of this assertion has as yet been given. In fact, the contrary assumption, that the ground state of *o*-benzyne is a triplet, has also been proposed.[4]

Several semiempirical calculations concerning the nature of the ground electronic state of *o*-benzyne have been reported recently.[5-8] Also, the correspond-

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[1] Research supported by National Science Foundation Grant No. GP-7875.

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Table I. Total Electronic Energies of the Benzynes at Each of the Different Stages of Calculation[a]

	Ortho		Meta		Para	
	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet
Single-determinant SCF	−229.0018	−229.0436	−228.9405	−229.0466	−228.9041	−229.0490
Two-determinant CI	−229.0639		−229.0435		−229.0399	
Many-determinant CI	−229.1506	−229.1240	−229.1307	−229.1331	−229.1287	−229.1342
CI core defect		−0.0114		−0.0109		−0.0123

[a] In the many-determinant CI treatments, triplet-state energies have been lowered by the amounts tabulated as triplet CI core defects; see text. (Energies are in atomic units, 1 au = 27.21 eV.)

ing meta and para isomers (1,3- and 1,4-dehydrobenzene) have been treated by Hoffmann, *et al.*[7,8] The present work is designed to supplement the existing semiempirical work and to provide a definitive answer as to the multiplicity of the ground electronic states of the three benzynes. The nature of the bonding in the three species is also discussed and electronic spectral calculations are reported for *o*-benzyne.

Method of Calculation

Full *ab initio* SCF–MO calculations (in which all electronic interactions are explicitly included) followed by large configuration-interaction calculations were carried out for each of the benzynes. The availability of electron repulsion integrals from a previous calculation on benzene[9] enabled the benzyne calculations to be carried out with a smaller expenditure of computer time than would have otherwise been possible. However, for this reason, the geometries of the three benzynes were restricted to be the same as that of the equilibrium geometry of benzene (regular hexagon, $R_{\mathrm{C-C}} = 1.393$ Å, $R_{\mathrm{C-H}} = 1.08$ Å). While this restriction is rather severe, it is still possible to obtain definitive evidence concerning the singlet–triplet separation for *o*-benzyne.

The basis set used is the same as was employed for benzene,[9] consisting of 10 s and 15 p Gaussian lobe functions for each carbon and 5 s functions for each hydrogen (180 Gaussian functions in all). These basis functions were grouped in linear combinations with fixed coefficients, reducing the effective number of basis functions to 3 s and 1 p_x, p_y, and p_z group function for each carbon and 1 s function for each hydrogen (for a total of 42 basis functions). The use of this type of basis, which is slightly more flexible than a minimal basis of atomic Hartree–Fock orbitals, has been extensively investigated previously.[9–11]

Results are obtained for each of the benzyne species at three different levels of complexity of the structure of the total wave function: (1) a single-determinant wave function (full SCF–MO treatment of both the singlet and triplet states), (2) a two-determinant wave function (configuration-interaction calculation of the single state), and (3) a many-determinant wave function (configuration-interaction treatment of both the singlet and triplet states). The total energies of the singlet and triplet states at each level of treatment are presented in Table I. A schematic representation of the changes in the singlet–triplet separation at each level of treatment is given in Figure 1. A detailed discussion of the three treatments is given in the Results section.

Results

A. Single-Determinant SCF Level. The single-determinant SCF results (orbital energies and atomic and overlap populations) are summarized in Tables II and III, in which corresponding results for benzene are included for comparison.

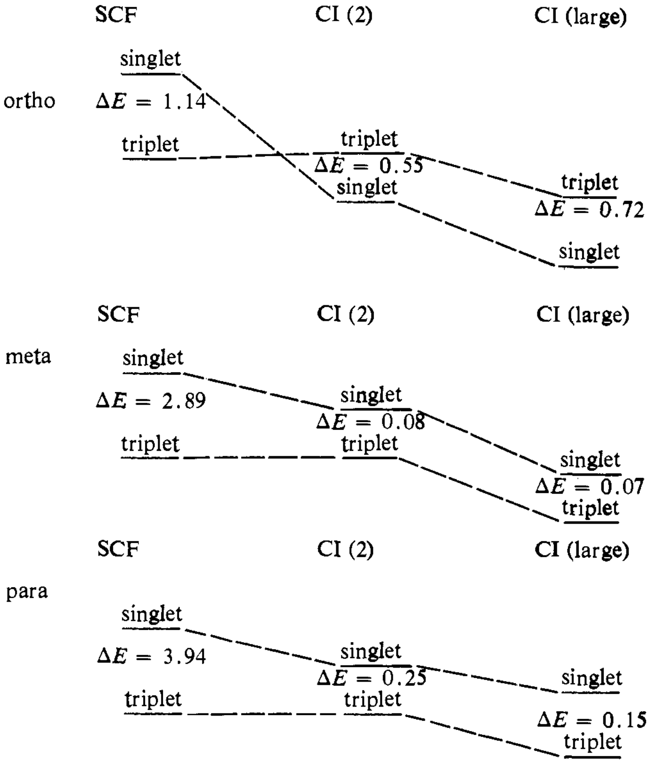

Figure 1. Diagrammatic presentation of the singlet–triplet separations for each of the three benzynes at the single-determinant SCF, two-determinant CI, and many-determinant CI levels of treatment. Singlet–triplet separations for the many-determinant treatment correspond to values obtained after triplet core energy adjustments; see text. Energies are in electron volts.

In each of the benzynes, the highest occupied orbital and the lowest unoccupied orbital are linear combinations of two lone-pair-like orbitals (n_1, n_2) which are relatively localized on the dehydrocarbons. In *o*- and *m*-benzyne the highest occupied orbital is $n_1 + n_2$ and the lowest unoccupied orbital is $n_1 - n_2$; this order is reversed for *p*-benzyne.

At the present single-determinant SCF level the ground states of all three of the benzynes are predicted to be triplets, which for *o*-benzyne is in disagreement with the aforementioned single-determinant semiempirical calculations.[5–8] However, certain other fea-

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Table II. SCF Molecular Orbital Energies for the Singlet and Triplet States of the Three Benzynes[a]

Benzene		*o*-Benzyne			*m*-Benzyne			*p*-Benzyne		
			Singlet	Triplet		Singlet	Triplet		Singlet	Triplet
		$9b_2$	+0.561*		$8b_2$	+0.548*		$9b_2$	+0.624*	
		$11a_1$	+0.550*		$12a_1$	+0.541*		$11a_1$	+0.553*	
		$3a_2$	+0.342*		$4b_1$	+0.338*		$3a_2$	+0.343*	
		$2a_2$	+0.109*		$2a_2$	+0.103*		$3b_1$	+0.125*	
		$3b_1$	+0.104*		$3b_1$	+0.010*		$2a_2$	+0.092*	
$2b_1$	−0.379	$8b_2$	−0.020*	−0.445	$7b_2$	−0.067*	−0.459	$10a_1$	−0.088*	−0.461
$1a_2$	−0.379	$10a_1$	−0.401*	−0.536	$11a_2$	−0.351*	−0.525	$8b_2$	−0.321*	−0.529
$1b_1$	−0.538	$2b_1$	−0.405*	−0.403	$1a_1$	−0.413*	−0.402	$1a_2$	−0.394*	−0.397
$10a_1$	−0.660	$1a_2$	−0.412*	−0.409	$2b_1$	−0.414*	−0.410	$2b_1$	−0.421*	−0.414
$8b_2$	−0.526	$1b_1$	−0.566*	−0.565	$1b_1$	−0.571*	−0.564	$7b_2$	−0.555	−0.549
$9a_1$	−0.526	$9a_1$	−0.582	−0.580	$10a_1$	−0.588	−0.583	$1b_1$	−0.566*	−0.565
$8a_1$	−0.626	$7b_2$	−0.611	−0.611	$6b_2$	−0.615	−0.605	$9a_1$	−0.651	−0.655
$7b_2$	−0.626	$8a_1$	−0.671	−0.667	$5b_2$	−0.671	−0.667	$8a_1$	−0 674	−0.671
$6b_2$	−0.674	$6b_2$	−0.673	−0.672	$9a_1$	−0.675	−0.668	$6b_2$	−0.688	−0.681
$7a_1$	−0.741	$7a_1$	−0.737	−0.736	$8a_1$	−0.752	−0.745	$7a_1$	−0.712	−0.706
$5b_2$	−0.848	$5b_2$	−0.845	−0.845	$4b_2$	−0.842	−0.836	$6a_1$	−0.845	−0.842
$6a_1$	−0.848	$6a_1$	−0.866	−0.864	$7a_1$	−0.872	−0.864	$5b_2$	−0.873	−0.870
$5a_1$	−1.043	$5a_1$	−1.057	−1.057	$3b_2$	−1.067	−1.056	$4b_2$	−1.050	−1.048
$4b_2$	−1.043	$4b_2$	−1.070	−1.070	$6a_1$	−1.076	−1.069	$5a_1$	−1.082	−1.076
$4a_1$	−1.173	$4a_1$	−1.203	−1.205	$5a_1$	−1.215	−1.203	$4a_1$	−1.206	−1.204
$3b_2$	−11.352	$3b_2$	−11.388	−11.387	$4a_1$	−11.394	−11.388	$3a_1$	−11.399	−11.397
$2b_2$	−11.353	$3a_1$	−11.389	−11.388	$2b_2$	−11.394	−11.388	$3b_2$	−11.399	−11.396
$3a_1$	−11.353	$2a_1$	−11.410	−11.390	$3a_1$	−11.404	−11.391	$2b_2$	−11.405	−11.396
$2a_1$	−11.354	$2b_2$	−11.410	−11.390	$2a_1$	−11.409	−11.401	$1b_2$	−11.405	−11.401
$1b_2$	−11.354	$1b_2$	−11.420	−11.415	$1b_2$	−11.428	−11.410	$2a_1$	−11.406	−11.397
$1a_1$	−11.354	$1a_1$	−11.422	−11.416	$1a_1$	−11.428	−11.410	$1a_1$	−11.406	−11.401
E_T	−230.3745	E_T	−229.0018	−229.0436	E_T	−228.9405	−229.0466	E_T	−228.9041	−229.0490

[a] Values for benzene are included for comparison. C_{2v} symmetry is used throughout (the C_2 axis interchanges the dehydro carbons). Orbitals allowed to have variable occupancy in the subsequent CI calculations are indicated by an asterisk. E_T is the total molecular energy including nuclear repulsion. (Energies are in atomic units.)

Table III. Atomic and Overlap Populations for the Benzynes Obtained from SCF (I) and Two-Determinant CI (II) Treatments[a]

		o-Benzyne			*m*-Benzyne			*p*-Benzyne		
		Singlet		Triplet	Singlet		Triplet	Singlet		Triplet
Center	Benzene	I	II	I	I	II	I	I	II	I
1	6.31	6.05	6.05	6.04	6.00	6.00	6.00	6.34	6.35	6.33
2	6.31	6.35	6.38	6.34	6.35	6.35	6.38	6.02	5.97	6.01
3	6.31	6.34	6.30	6.30	6.00	6.00	6.00	6.34	6.35	6.33
4	6.31	6.34	6.30	6.30	6.35	6.35	6.33	6.34	6.35	6.33
5	6.31	6.35	6.38	6.34	6.21	6.21	6.22	6.02	5.97	6.01
6	6.31	6.05	6.05	6.04	6.35	6.35	6.33	6.34	6.35	6.33
7	0.69							0.66	0.67	0.67
8	0.69	0.68	0.69	0.66	0.67	0.66	0.65			
9	0.69	0.67	0.68	0.68				0.66	0.67	0.67
10	0.69	0.67	0.68	0.68	0.66	0.67	0.67	0.66	0.67	0.67
11	0.69	0.68	0.69	0.66	0.55	0.55	0.54			
12	0.69				0.66	0.67	0.67	0.66	0.67	0.67
					Overlap Populations					
1–2	1.02	1.06	1.04	1.04	0.97	0.99	1.04	1.20	1.11	1.04
2–3	1.02	1.02	1.01	1.00	0.97	0.99	1.04	1.20	1.11	1.04
3–4	1.02	1.06	1.05	1.04	1.08	1.08	1.07	0.85	0.92	1.00
4–5	1.02	1.02	1.01	1.00	1.00	1.00	1.01	1.20	1.11	1.04
5–6	1.02	1.06	1.04	1.04	1.00	1.00	1.01	1.20	1.11	1.04
6–1	1.02	1.40	1.29	1.01	1.08	1.08	1.07	0.85	0.92	1.00
1–7	0.79							0.77	0.78	0.78
2–8	0.79	0.79	0.83	0.77	0.81	0.78	0.76			
3–9	0.79	0.79	0.79	0.79				0.77	0.78	0.78
4–10	0.79	0.79	0.79	0.79	0.77	0.78	0.78	0.77	0.78	0.78
5–11	0.79	0.79	0.83	0.77	0.65	0.65	0.64			
6–12	0.79				0.77	0.78	0.78	0.77	0.78	0.78

[a] Values for benzene (SCF) are included for comparison. The numbering is explained in Figure 2.

tures of the present results agree with the previous semiempirical work, as discussed below.

The ordering of the $n_1 + n_2$ and $n_1 - n_2$ orbitals, as given in Table II, agrees with that reported by Hoffmann, *et al.*,[7] for *o*-, *m*-, and *p*-benzyne, and the trend in orbital energy separations for ortho and meta agrees as well. In the para case, the separation is smaller than that reported by Hoffmann, *et al.* However, the general agreement of the two calculations can be taken as a substantiation of the semiempirical parameterization.

The qualitative trends in the bond strengths as measured by overlap populations also agree with the results of Gheorghiu and Hoffmann:[8] in singlet *o*-benzyne the bond between the dehydrocarbons is strongest, while the 1,2 and 2,3 bonds in singlet *m*-benzyne and the 1,6 and 3,4 bonds in triplet *p*-benzyne are weaker than the other carbon–carbon bonds (see Figure 2). In triplet *m*-benzyne, which in the present work is found to be the ground state of the meta isomer, the 4,5 and 5,6 bonds are weaker.

B. Two-Determinant CI Level. The singlet-state single-determinant SCF wave functions discussed in the previous section contain an inherent correlation error resulting from the assumption of double occupation of spatial molecular orbitals. This effect is particularly important in the case of the relatively weak bond involving the orbitals n_1 and n_2. For example, for *o*-benzyne, the single-determinant two-electron function describing the bond is of the form

$$\begin{aligned}\psi(1,2) &= N_1{}^2\mathcal{A}\{[n_1 + n_2]\alpha(1)[n_1 + n_2]\beta(2)\} \\ &= N_1{}^2\{[n_1(1)n_1(2) + n_2(1)n_2(2)] + [n_1(1)n_2(2) + \\ &\qquad n_2(1)n_1(2)]\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}(1/\sqrt{2}) \\ &= \psi_{\text{ionic}} + \psi_{\text{covalent}}\end{aligned}$$

where $\mathcal{A}$ is the antisymmetrization operator and N_1 is the normalization constant for the orbital $(n_1 + n_2)$. This expanded form of the wave function shows an equal weighting of ionic and covalent terms, exactly analogous to the familiar two-electron molecular orbital wave function for H_2.[12]

As in the H_2 solution of Weinbaum,[13] the ionic and covalent terms can be weighted differently by extending the form of the wave function to include two configurations, *viz.*

$$\begin{aligned}\psi(1,2) = \lambda_1 N_1{}^2\mathcal{A}\{[n_1 + n_2]\alpha(1)[n_1 + n_2]\beta(2)\} + \\ \lambda_2 N_2{}^2\mathcal{A}\{[n_1 - n_2]\alpha(1)[n_1 - n_2]\beta(2)\}\end{aligned}$$

In the present work this is accomplished for singlet states by a simple configuration interaction of the ground configuration with the doubly excited configuration $(n_1 + n_2)^2 \rightarrow (n_1' - n_2')^2$, where the $n_1' - n_2'$ orbital is taken to be the virtual orbital from the ground-state SCF solution and thus corresponds only approximately to $n_1 - n_2$.

In the case of triplet states, the appearance of ionic terms $n_k(1)n_k(2)$ is prohibited by the Pauli principle, and thus the two-determinant level of description can produce an important change in the previously calculated separation of the singlet and triplet states. It is only at the two-determinant level for the singlet that the valence-shell basis functions n_1 and n_2 are utilized completely to produce an equivalent treatment of the singlet and triplet states.

The above analysis of the correlation effect leads one to predict the relative energy lowering at the two-determinant level compared to the single-determinant treatment for *o*-, *m*-, and *p*-benzyne: para > meta > ortho, corresponding to the expected order of increasing covalent character with increasing distance between n_1 and n_2. This conjecture is borne out by the results shown in Figure 1, which shows the new ordering of states after performing the two-configuration CI calculation. It is important to note that the ordering of the states for *o*-benzyne is now reversed, with the singlet below the triplet, in agreement with the conjecture of a singlet ground state for *o*-benzyne.

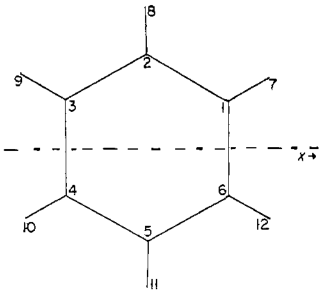

Figure 2. The numbering system used in benzene and the benzynes for the atomic and overlap populations. In the benzynes the following hydrogens are removed: ortho, 7 and 12; meta, 7 and 9; para, 8 and 11.

Energy minimization with respect to λ_1 and λ_2 gives the following ratios of coefficients for *o*-, *m*-, and *p*-benzyne

$$\begin{aligned}\text{ortho}\quad \lambda_2/\lambda_1 &= -0.46 \\ \text{meta}\quad \lambda_2/\lambda_1 &= -0.63 \\ \text{para}\quad \lambda_2/\lambda_1 &= -1.36\end{aligned}$$

In each case the ratio λ_2/λ_1 corresponds to an increase in covalent character of the bond compared to that of a single-determinant description; furthermore, the covalent character increases in the order ortho, meta, para, which is the same order as the trend in the aforementioned correlation effect. The present result thus is contrary to previous speculation that the bond in *o*-benzyne is highly ionic.[14]

C. Many-Determinant CI Level. Large-scale configuration-interaction calculations were carried out for each of the three benzynes for both the singlet and triplet states using techniques described in detail in ref 15. Molecular orbitals from the singlet SCF calculations were used to describe both the singlet and triplet states. While in principle this approach favors the singlet states, in the species involved here the SCF calculations showed a close similarity of the molecular orbitals of the singlet and triplet states. The main defect of the triplet-state description lies in the assumption of a relatively large core of orbitals which are assumed to be the same as in the singlet state. The difference in core energies can be accounted for approximately by adjusting the triplet-state energies after the CI calculation. The amount by which the triplet-state energy is adjusted is calculated by taking the difference of the single-determinant energy from the full triplet SCF calculation and the single-determinant energy resulting from a limited SCF calculation, in which the CI core orbitals are held fixed and the other orbitals are determined as linear combinations of the orbitals that are allowed to have variable occupancy in the CI calculation. Numerical values of the triplet-state energy adjustments, called triplet CI core defects, are given in Table I.

The molecular orbitals involved in the CI calculations and their symmetry properties are described in Figure 3. The final results (total energies and singlet–triplet separations) are presented in Table I and Figure 1. The

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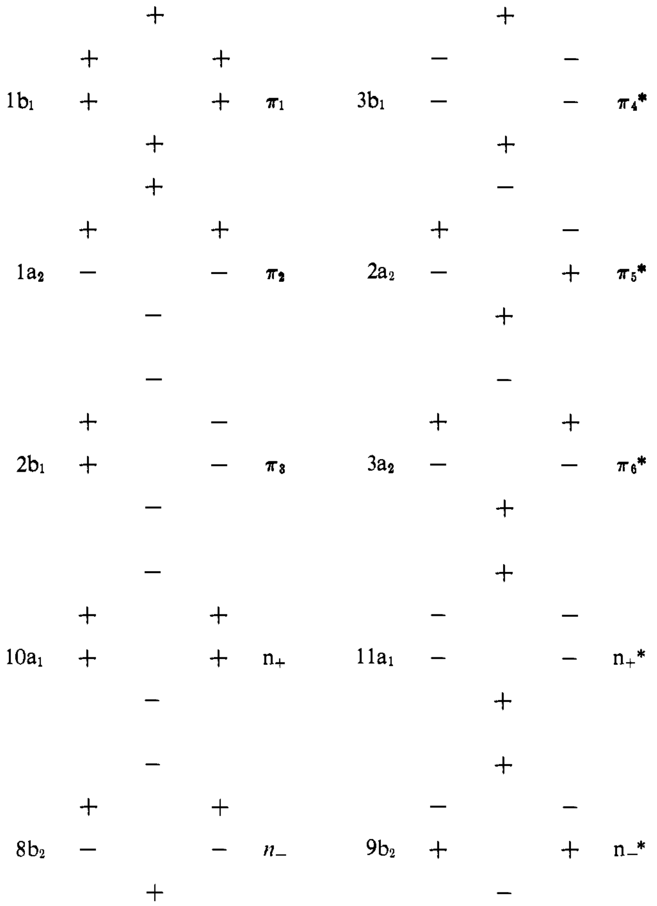

Figure 3. Symmetry properties of the molecular orbitals used in the CI calculations on *o*-benzyne (similar orbitals were employed for *m*- and *p*-benzyne).

singlet–triplet separations at the many-determinant CI level are approximately the same as at the two-determinant level, bearing out the supposition that after performing the two-configuration CI treatment of the singlet the remaining valence-shell correlation effects are essentially the same in the singlet and triplet states.

D. Population Analysis. A population analysis of the type proposed by Mulliken,[16] but not restricted to an LCAO wave function, was performed for benzene and the benzynes. The results for the overlap and gross atomic populations are presented in Table III.

Comparison of the results for the ground states of the benzynes with the corresponding results for benzene shows that in *o*-benzyne, the overlap population between the dehydrocarbons is considerably greater than in benzene, while the dehydrocarbon atoms have been depleted in electron density. The carbons adjacent to the dehydrocarbons are slightly enhanced in density, the general trend being a migration of electronic charge into the bonds between the dehydrocarbons.

In the *m*-benzyne triplet, the dehydrocarbon atoms are also considerably depleted in electron density, as is the carbon atom most distant from the dehydrocarbon atoms (center 5 in Figure 2). The atoms adjacent to the dehydrocarbons (centers 2, 4, and 6) are slightly more negative than in benzene. Here the overlap populations are all nearly equal to those in benzene.

In the *p*-benzyne triplet, the dehydrocarbon atoms are again depleted in electron density relative to benzene, as are the hydrogens, while the other carbons are slightly enhanced in density. The overlap populations are nearly equal to those in benzene, but show a tendency toward formation of two allylic fragments, as noted by Gheorgiu and Hoffmann.[8]

The effect of the two-determinant CI treatment compared to the single-determinant (SCF) treatment may be seen by comparing the results of the population analysis at the two levels of calculation. For instance, for *o*-benzyne, referring to Table III, the atomic population is seen to increase for centers 2 and 5, as well as for the hydrogens, while the atomic population for centers 1 and 6 (the dehydrocarbons) remains the same. The overlap populations for the carbon–carbon bonds all decrease, the decrease for the bond between the dehydrocarbons being significantly larger than the others. The overall effect of the two-determinant CI treatment, then, is to transfer electron density from the overlap region to a covalent distribution on the atoms, as would be expected from the analysis in section B.

E. Electronic Spectra. Experimental spectral studies which have been reported for photolytically produced *o*-benzyne[17,18] show only one very broad transient absorption in the region around 2430 Å. Tentatively, this absorption has been assigned to a $^1(n \rightarrow n^*)$ electronic transition of benzyne, the expected but unobserved $^1(\pi \rightarrow n^*)$ transition being predicted by Berry, *et al.*,[17] to lie at much longer wavelength, perhaps in the infrared region. Experimental spectral studies for the meta and para compounds have also been reported.[19,20]

In the present work the electronic spectrum is studied theoretically at the configuration-interaction level for both the singlet and triplet states of *o*-benzyne. Calculated transition energies to the low-lying excited states are given in Table IV, along with qualitative descriptions of the nature of the electronic excitations. In addition to singlet–singlet transitions from the ground state, triplet–triplet excitation energies from the lowest triplet state are also included in the table, since the possibility exists for formation of the triplet state on photolysis, even though our calculations suggest that the lowest state of *o*-benzyne is a singlet.

Before discussing the spectral results, the accuracy of the CI treatment employed here should be critically examined in the light of experience gained from previous studies of other systems.[15] The spectral treatments are restricted in three important respects. First, the basis orbitals are capable of representing only valence-shell atomic orbitals and not a more diffuse type of orbital which might be required in the accurate description of certain excited states. Second, the geometry is that of benzene. The fact that the calculations are performed for a nonequilibrium geometry of *o*-benzyne means that a calculated Franck–Condon excitation will not necessarily correspond to the band maximum observed experimentally if the molecule has first relaxed to its equilibrium geometry. The third restriction concerns the form of the virtual orbitals employed for the CI description of the ground and excited states. The virtual orbitals were taken directly from the ground-

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Table IV. Electronic Spectral Results for *o*-Benzyne

Electronic state and orbital promotion	Transition energy (calcd), eV	Wavelength, Å	Major contributions (coefficient of configuration)[a]
$^1B_2$ n → n*	6.04	2056	20 → 21 (0.84); 19 → 23 (0.37)
$^1A_1$ π, n → n*, π*	5.93	2094	18, 20 → 21, 22 (0.49); 19, 20 → 21, 23 (−0.47)
$^1A_1$ π → π*	5.41	2294	18 → 23 (0.53); 19 → 22 (0.52); 18, 20 → 21, 22 (−0.37)
$^1B_1$ π → n*	4.03	3071	18 → 21 (0.85)
$^3A_2$ π → n*	5.85[b]	2122	17 → 21 (0.60); 18, 20 → 21, 21 (0.46)
$^3A_2$ n → π*	5.50[b]	2258	20 → 23 (0.84)
$^3B_2$ π → π*	4.41[b]	2816	19 → 23 (0.58); 18 → 22 (0.57)
$^3B_2$ π → π*	3.05[b]	4081	18 → 22 (−0.64); 19 → 23 (0.57)
$^3A_2$ π → n*	2.09[b]	5945	19 → 21 (0.87)

[a] Only configurations with coefficients greater than 0.33 in magnitude are included. Configurations are described in terms of orbital promotions from the ground configuration based on MO's numbered according to increasing orbital energy; see Table II and Figure 3. [b] These are triplet–triplet excitations from the lowest triplet state (Table I).

state SCF calculation with no virtual orbital transformations employed prior to configuration interaction. All π* (a_2 and b_1) molecular orbitals, but only one n* orbital of each symmetry (a_1 and b_2), were included in the calculation; thus, the possibility exists that the description of the optimum n* orbital may be somewhat deficient. In spite of the above restrictions, there is sufficient flexibility in the treatment to give reliable information concerning the essential features of excited states arising from intravalence shell excitations. However, in those cases in which the low-lying states depart significantly from intravalence shell character, the present level of treatment would be inadequate.

The results presented in Table IV show three singlet excited states at 2294, 2094, and 2056 Å which are close to the region of the intensive observed absorption, around 2430 Å.[17,18] Although all calculated transitions are higher in energy than 2430 Å, the differences are well within the range of the theoretical uncertainty of the calculations. Likewise, there are numerous triplet–triplet transitions in the same region of the spectrum; however, as noted earlier, these transitions would be observed only if the electronic excitation occurs from the lowest triplet state of *o*-benzyne. Their existence rules out the possibility of a determination of the multiplicity of the lowest state of benzyne based solely on the agreement of calculated *vs.* observed transition energies. It should also be noted that the prediction of Berry, *et al.*,[17] that the $^1(\pi \rightarrow n^*)$ transition would probably occur at much longer wavelengths, is only qualitatively borne out by the calculation. The $^1(\pi \rightarrow n^*)$ transition is calculated to occur at longer wavelength (3071 Å), but still well into the uv region.

One of the most interesting features of the present treatment is that only the lowest singlet state at 3071 Å is well described by a simple single excitation, in this case, π → n*. All other singlet excited states involve double excitations or considerable mixing between two single excitations of the same overall symmetry. It happens that the above mixing is such that there is always a cancellation between transition moments of individual configurations to give overall oscillator strengths for the multiconfiguration wave functions which are always quite small, 0.04 in the case of the transition at 2056 Å (principally n → n*) and less than 0.01 for all other transitions. In principle, this means that the present treatment has failed to predict any intensive absorption. However, the cancellation of contributions from different configurations is a situation which is extremely sensitive to questions of detailed orbital shape and, as noted in the discussion, the almost complete cancellation may be an artifact of the highly restricted basis set which is essentially one of valence-shell atomic orbitals.

Conclusion

The present calculations predict conclusively that the ground electronic state of *o*-benzyne in the geometry of benzene is a singlet. For this species, relaxation of the geometry restriction by decreasing the distance between the dehydrocarbon atoms will favor the singlet over the triplet; hence a calculation performed at the equilibrium geometry should also yield the result that the singlet state is lower in energy than the triplet. For the meta and para isomers, the ground states are found to be triplets in the geometries considered; however, the singlet–triplet energy separations are quite small, such that calculations performed at the equilibrium geometries could very likely result in an inverted order.

An important conceptual aspect of this study is the failure of the single-determinant (SCF) wave function to describe adequately the weak additional bond between the dehydrocarbons in the case of a singlet state. In *o*-benzyne the triplet state is predicted to be lower in energy than the singlet at the single-determinant level, but the order is inverted as a result of configuration interaction. It is shown that to obtain a theoretical description of the singlet which is equivalent in principle to that of the triplet, it is necessary to allow a variable amount of ionic and covalent character in the description of the weak bond. In the present study, this is accomplished by a configuration-interaction formulation of the wave function and the results show that a simple two-determinant description is in qualitative agreement with the results of the many-determinant configuration-interaction calculations. It should be noted that the same general argument would apply to semiempirical as well as *ab initio* treatments of other systems involving weak bonds of a similar type.

The electronic spectral calculations on *o*-benzyne show several electronic transitions, notably n → n* and π → π*, close to the region of the experimentally observed intense absorption, and a π → n* transition at longer wavelength. Generally, however, most of the calculated excited states cannot be described as involving simple single excitations from the ground configuration, since considerable mixing of several excited configurations of the same symmetry is found to occur.

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Discrimination of Stereochemical Configurations of 2,4-Dichloropentane, 2,3-Dichlorobutane, and Poly(vinyl chloride) by Carbon-13 Nuclear Magnetic Resonance

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Abstract: Natural-abundance carbon-13 nuclear magnetic resonance spectra, with proton noise decoupling, have been obtained for pure *meso*- and *rac*-2,4-dichloropentane, pure *meso*- and *rac*-2,3-dichlorobutane, and two samples of poly(vinyl chloride) of different stereochemical configuration. The ^{13}C chemical shifts of the chlorinated hydrocarbon models are interpreted in terms of their rotational isomers. The sensitivity of ^{13}C shifts to stereoisomers was found to be an order of magnitude greater than that of proton shifts. Triad sequences were easily distinguished for poly(vinyl chloride), but the diad, tetrad, or pentad structures may be more difficult to extract from ^{13}C spectra than from proton spectra taken at high frequency.

Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C nmr) has provided microstructural information on a number of polymer systems.[2-4] The determination of stereochemical configurations by ^{13}C nmr has been demonstrated by Schaefer[2b] on homopolymers of poly(propylene oxide) and by Bovey[4] on homopolymers of poly(vinyl methyl ether), polystyrene, poly(methyl methacrylate) and polypropylene. Differences observed in ^{13}C chemical shifts of carbons differing only in stereochemical configuration were greater than the corresponding differences reflected by proton chemical shifts.

Stereochemical configuration in poly(vinyl chloride), PVC, has been the subject of many proton nmr investigations.[5-22] Proton nmr spectra of PVC provide diad[9]–tetrad[12,21] information from the methylene resonances and triad[9]–pentad[20-22] information from the methyne resonances. However, complexity due to proton coupling and the overlapping of the many proton chemical shifts leads to ambiguities in tacticity analyses except perhaps at 220 MHz.[21] Even here accurate quantitative analyses of pentad structures are questionable.[21-22]

In this article results are described for the investigation of PVC by ^{13}C nmr. Since *meso*- and *rac*-2,4-dichloropentane have been used as model compounds for the interpretation of proton nmr spectra of PVC,[7,10,11,23-25] these same compounds are used as models for ^{13}C studies. In addition, ^{13}C spectra have been obtained of pure *meso*- and *rac*-2,3-dichlorobutane. The stereochemical environments of these model compounds have been interpreted and related to the ^{13}C spectra of PVC samples having different amounts of syndiotacticity as indicated by ir and X-ray diffraction studies.

Experimental Section

2,3-Dichlorobutane was obtained from Aldrich Chemical Co. and 2,4-dichloropentane was prepared by the method of Pritchard.[26]

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