

# Ab Initio Calculations on Large Molecules Using Molecular Fragments. Configuration Interaction Calculations on the Ground and Lower Excited States of Carbazole<sup>1</sup>

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**Abstract:** The energies and wave functions for the ground state and  ${}^1,{}^3A_1(4b_1 \rightarrow 5b_1)$ ,  ${}^1,{}^3A_1(3a_2 \rightarrow 4a_2)$ ,  ${}^1,{}^3B_2(3a_2 \rightarrow 5b_1)$ , and  ${}^1,{}^3B_2(4b_1 \rightarrow 4a_2)$  excited electronic states of carbazole have been calculated using a configuration interaction (CI) procedure based on the molecular orbitals from a ground state SCF calculation. Franck-Condon transition energies from the ground state were calculated and compared to experimentally and other theoretically determined transition energies. Also calculated were dipole moments and charge and bond order matrices for the various states, oscillator strengths for allowed transitions, and configuration interaction estimates of ionization potentials and electron affinities. Agreement with experimentally observed ordering of states is observed. Calculated transition energies were found to be larger than experimentally observed, but an excellent linear mapping of the calculated and observed transition energies is observed. Dipole moment trends and calculated oscillator strengths are also seen to be in good agreement with available experimental data, and substantial insight into the nature of electronic transitions and solvent and N-alkylation effects upon transitions is obtained through examination of charge and bond order matrices.

## I. Introduction

Recently carbazole and carbazole-containing systems have attracted much attention, with the photophysical properties being of particular interest.<sup>2-9</sup> Most of these studies have been concerned with various polymers of carbazole. However, any attempt to understand the excited state interactions which influence photophysical processes necessarily requires knowledge concerning the nature of the electronic states of the monomeric chromophore units themselves. This theoretical study was undertaken to obtain a description of the ground and low-lying excited electronic states of the carbazole molecule, including excitation energies, electronic structure, polarization of transitions, and other properties of interest.

Several spectroscopic studies have been carried out to investigate the nature of the excited states of carbazole. For example, Pinkham and Wait<sup>10</sup> have studied the vapor-phase spectrum of carbazole and have assigned the two lowest lying electronic transitions. Bree and Zwarich<sup>11</sup> have studied the spectra of carbazole single crystals and carbazole dissolved in fluorene crystal and assigned the vibrational modes and the lowest lying excited electronic state. This study was extended by Chakravorty and Ganguly,<sup>12</sup> who assigned the second electronic transition. The solution spectra of carbazole has been studied by Johnson,<sup>13</sup> who has assigned five electronic states, the four lowest singlets and the lowest triplet.

From a theoretical point of view, no ab initio configuration interaction (CI) studies have been reported prior to the current studies. However, several other types of theoretical studies have been carried out. For example, there have been semiempirical studies by Pinkham and Wait<sup>10</sup> and Mataga et al.<sup>14</sup> Also, Liberman and Batra<sup>15</sup> have studied the electronic structure of carbazole using the self-consistent-field (SCF) scattered wave method. Batra et al.<sup>16</sup> have studied the electronic structure of carbazole using ab initio SCF-LCAO-MO methods. In their studies, SCF calculations were done on the ground state and on each of the low-lying excited electronic states. Further comment on these SCF results is postponed until the discussion section.

In the present treatment of carbazole, the wave functions and energies of the ground and low-lying excited electronic states have been obtained from a CI procedure, based on orthonormal molecular orbitals from a SCF calculation on the

ground state of the molecule. Using these wave functions and energies, various quantities of interest have been calculated. Specifically, Franck-Condon transition energies, oscillator strengths for the allowed transitions and dipole moments were calculated. The results of these calculations are compared to experimental and other theoretical results. Ionization potentials and electron affinities were also calculated and are compared to experimental and other theoretical values. Bond-order and population analyses were done for each state and, in conjunction with MO electron density plots, the nature of the experimentally observed red shift of certain transitions of carbazole in hydrogen bonding solvents and on N-alkylation is examined.

## II. Theory

The SCF portion of these calculations used the molecular fragment procedure.<sup>17</sup> The basis functions are normalized, floating spherical Gaussian orbitals (FSGO), defined by

$$G_i(r) = (2/\pi\rho_i^2)^{3/4} \exp\{-(r - \mathbf{R}_i)^2/\rho_i^2\} \quad (1)$$

where  $\rho_i$  is the orbital radius and  $\mathbf{R}_i$  is the location of the FSGO relative to some origin. The nonlinear parameters were optimized prior to the SCF in calculations on "molecular fragments". The details of the molecular fragment procedure can be found elsewhere.<sup>17</sup>

The CI portion of these calculations uses a procedure given by Whitten and Hackmeyer.<sup>18</sup> Wave functions and energies are generated by a multistep procedure. The initial wave functions,  $\{\Psi_j^{(1)}\}$ , for the  $M$  electronic states of interest are expressed as linear combinations of configurations,  $\{\phi_k^{(1)}\}$ , called parents, which are expected to be important contributors to at least one of the  $M$  states,

$$\Psi_j^{(1)} = \sum_k C_{kj}^{(1)} \phi_k^{(1)}, j = 1, 2, \dots, M \quad (2)$$

where the  $\phi_k$  are antisymmetrized products of orthonormal molecular spin orbitals. Additional configurations,  $\{\phi_k^{(2)}\}$ , are then generated analytically by forming single or double excitations from the parent configurations subject to an energy threshold criterion,

$$\left\{ \frac{|\langle \phi_k^{(2)} | H | \Psi_j^{(1)} \rangle|^2}{|\langle \phi_k^{(2)} | H | \phi_k^{(2)} \rangle - \langle \Psi_j^{(1)} | H | \Psi_j^{(1)} \rangle|} \right\} > \delta \quad (3)$$

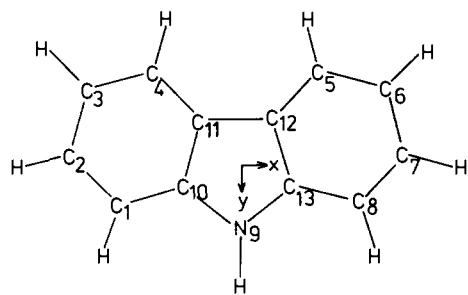


Figure 1. The coordinate axes and atomic numbering scheme used for carbazole.

for at least one  $j$  of the original  $M$  parent states.  $\delta$  is a numerical threshold value, typically  $10^{-2}$  to  $10^{-5}$ , and  $H$  is the non-relativistic Hamiltonian,

$$H = \sum_i [-\frac{1}{2}\nabla_i^2 - \sum_j Z_j/r_{ij}] + \sum_{i<j} r_{ij}^{-1} \quad (4)$$

The total wave function for each state is then expanded to include the new set of configurations,  $\{\phi_k^{(2)}\}$ , as well as the parent configurations, and the Hamiltonian matrix is diagonalized to obtain the energies  $E_j$  and the improved CI wave functions  $\Psi_j$ . The CI wave functions thus obtained are then defined to be the new parent set  $\{\Psi_j^{(1)}\}$ , and the procedure is repeated one or more times until the addition of configurations has negligible effect on the energy of the state  $E_j$ . The details of the procedure can be found elsewhere.<sup>18</sup>

### III. Results and Discussion

**A. SCF Calculations.** The SCF calculation was done on the ground electronic state ( $^1A_1$ ) of carbazole, which has  $C_{2v}$  symmetry. The molecular geometry used in this calculation was the same as used by Batra et al.<sup>16</sup> in their SCF calculations on carbazole. The coordinate axes and atomic numbering scheme are shown in Figure 1. The basis orbitals used in this calculation were taken from the planar  $\text{CH}_3$  and planar  $\text{NH}_3$  fragments, previously optimized and tested in other systems.<sup>19</sup> Such a procedure provides 78 FSGO, contracted to 65 orbitals for the SCF study.

The total energy<sup>20</sup> and molecular orbital (MO) ordering and energies obtained in this calculation for the 15 highest occupied and nine lowest unoccupied molecular orbitals are given in Table I. Also given, for comparison purposes, are the analogous data from two earlier studies. The study of Batra et al.<sup>16</sup> was an ab initio SCF study using 148 atom-centered Gaussian orbitals, contracted to 74 orbitals for the SCF calculation. The study by Liberman and Batra<sup>15</sup> used the SCF scattered wave approach.<sup>21</sup> Electron density plots from the current study for the  $b_1(\pi)$  (excluding the  $1b_1(\pi)$ ) and  $a_2(\pi)$  molecular orbitals are shown in Figure 2.

In comparing the results of the current SCF calculation to those of Batra et al.,<sup>16</sup> several points should be noted. For example, the total energy calculated by Batra et al. is  $\sim 59$  hartrees lower in energy than that of the present calculation. However, most of this energy difference is accounted for by the fact that Batra et al.<sup>16</sup> used two atom-centered Gaussian functions to represent the  $1s$  orbital, while the current calculation used only one such function. To estimate this more quantitatively, it should be noted that adding a second  $1s$  function to the  $\text{CH}_4$  fragment basis lowered the total energy by  $\sim 3.8$  hartrees,<sup>22</sup> but the extra Gaussian had only minor effects when the fragment was used in calculations on larger molecules, e.g., the rotation barrier in ethane was essentially the same whether one or two Gaussians were used for the  $1s$  orbital.<sup>22</sup>

In the present calculation, the MO eigenvalues are also shifted upward (i.e., are more positive), compared to those of

Table I. Total Energy, Molecular Orbital Ordering and Energies from Ground State SCF Calculations on Carbazole, and Comparison to Other Studies<sup>d</sup>

MO No.	MO symmetry	MO energies		
		Current study <sup>e</sup>	Batra, et al. <sup>16f</sup>	Liberman and Batra <sup>15c</sup>
53	19b <sub>2</sub>	0.8815		
52	18b <sub>2</sub>	0.7187		
51	21a <sub>1</sub>	0.6957		
50	6a <sub>2</sub> ( $\pi$ )	0.6264		
49	7b <sub>1</sub> ( $\pi$ )	0.5660		
48	5a <sub>2</sub> ( $\pi$ )	0.3729		
47	6b <sub>1</sub> ( $\pi$ )	0.3646		
46	4a <sub>2</sub> ( $\pi$ )	0.3084		-0.43
45	5b <sub>1</sub> ( $\pi$ ) <sup>a</sup>	0.2545		-0.45
44	4b <sub>1</sub> ( $\pi$ ) <sup>b</sup>	-0.1309	-0.3438	-0.54
43	3a <sub>2</sub> ( $\pi$ )	-0.1376	-0.3559	-0.56
42	2a <sub>2</sub> ( $\pi$ )	-0.2056	-0.4130	-0.58
41	3b <sub>1</sub> ( $\pi$ )	-0.2405	-0.4512	-0.59
40	2b <sub>1</sub> ( $\pi$ )	-0.3168	-0.5191	-0.60 (20a <sub>1</sub> )
39	20a <sub>1</sub>	-0.3561	-0.5378	-0.60 (17b <sub>2</sub> )
38	1a <sub>2</sub> ( $\pi$ )	-0.3570	-0.5429	-0.63 (2b <sub>1</sub> ( $\pi$ )) (17b <sub>2</sub> )
37	17b <sub>2</sub>	-0.3719	-0.5621	-0.64 (16b <sub>2</sub> ) (1a <sub>2</sub> ( $\pi$ ))
36	19a <sub>1</sub>	-0.4019	-0.5680	-0.64 (19a <sub>1</sub> )
35	16b <sub>2</sub>	-0.4113	-0.5740	-0.65 (1a <sub>2</sub> ( $\pi$ ))
34	1b <sub>1</sub> ( $\pi$ )	-0.4538	-0.6398	-0.67 (15b <sub>2</sub> ) (18a <sub>1</sub> )
33	15b <sub>2</sub>	-0.4607	-0.6483	-0.67 (18a <sub>1</sub> )
32	18a <sub>1</sub>	-0.4655	-0.6499	-0.70 (1b <sub>1</sub> ( $\pi$ )) (1b <sub>1</sub> ( $\pi$ ))
31	14b <sub>2</sub>	-0.4830	-0.6556	-0.71 (17a <sub>1</sub> )
30	17a <sub>1</sub>	-0.4915	-0.6656	-0.73 (14b <sub>2</sub> )

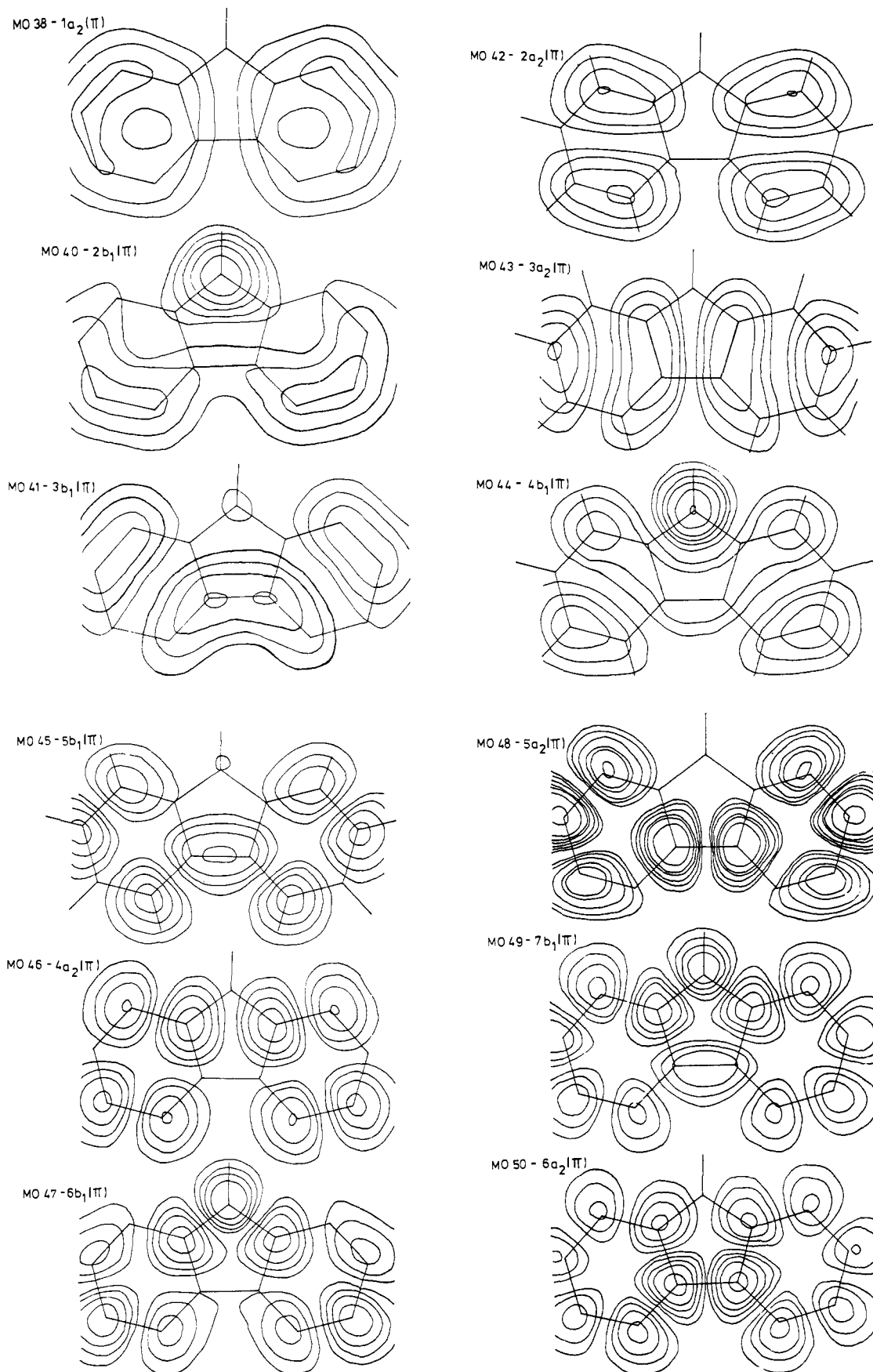
<sup>a</sup> Lowest unoccupied MO. <sup>b</sup> Highest occupied MO. <sup>c</sup> Estimated from graphical data presented in ref 15. <sup>d</sup> The nine lowest unoccupied and eight highest occupied orbitals in the current study were allowed to have variable occupancy in the CI calculations. Energies are in atomic units (see ref 20). <sup>e</sup> Total energy  $-439.393\ 298\ 55$ . <sup>f</sup> Total energy  $-498.126\ 764\ 6$ .

Batra et al.<sup>16</sup> This is a general characteristic of the molecular fragment procedure and has been discussed in detail elsewhere.<sup>19</sup> Although the MO eigenvalues are shifted upward, the shift is uniform and a linear relationship has always been found (where comparisons have been possible) between the MO eigenvalues of a suitably flexible larger basis set calculation and the present case; a linear relationship for the 31 filled valence MO's is also found between the results of Batra et al.<sup>16</sup> and the present calculation, and is given (in au) by

$$\epsilon_i^{\text{ref}} = 0.8783\epsilon_i^{\text{MF}} - 0.2297 \quad (5)$$

where  $\epsilon_i^{\text{ref}}$  and  $\epsilon_i^{\text{MF}}$  refer respectively to the MO eigenvalues of Batra et al. and the present calculation, with a standard deviation<sup>19</sup> of 0.0093 and a correlation coefficient<sup>19</sup> of 0.9984. Such a linear mapping between the orbital energies of the two basis sets indicates a quite similar balance in the MO description of the molecule.

Of the orbitals listed in Table I, the MO ordering is switched in only two places; comparing the present results to those of Batra et al.<sup>16</sup> these switches occur for MO's 37 and 38, and MO's 32 and 34. Since both calculations were made with small basis sets, a definitive assignment of the correct ordering must await the results of larger basis set calculations. However, one point should be noted. In particular, the  $1b_1(\pi)$  MO of carbazole is probably too low in the results of Batra et al.<sup>16</sup> by analogy to results on pyrrole. In that case, the MO ordering



**Figure 2.** Electron density plots for  $b_1(\pi)$  (excluding the  $1b_1(\pi)$ ) and the  $a_2(\pi)$  molecular orbitals. The contour levels are 5, 20, 50, 100, 200, 400, 800, and 1600, in units of  $5.7646 \times 10^{-5}$  electron/(bohr)<sup>3</sup>, and are in a plane 0.75 bohr above the plane of the molecule.

predicted by the molecular fragment procedure<sup>23</sup> essentially agreed with the ordering of Preston and Kaufman<sup>24</sup> (155 Gaussian basis contracted to an 80 orbital basis), while the

calculation of Clementi et al.<sup>25</sup> (95 Gaussian basis contracted to a 30 orbital basis) predicted the  $1b_1(\pi)$  MO to be too low, relative to other MO energies.

**Table II.** Energies of Carbazole Ground and Excited States from CI Treatments Based on Molecular Orbitals Determined from a Ground State SCF Calculation

Electronic state and orbital promotion	Single configuration energies	Final CI energies ( $\delta = 3 \times 10^{-4}$ )	No. of configurations	Transition energies, eV
$^1A_1$ (ground state)	-439.3993	-439.4572	439	
$^1A_1(4b_1 \rightarrow 5b_1)$	-439.1507	-439.2552	439	5.50
$^1B_2(3a_2 \rightarrow 5b_1)$	-439.1495	-439.2292	381	6.20
$^1B_2(4b_1 \rightarrow 4a_2)$	-439.1130	-439.1986	381	7.04
$^1A_1(3a_2 \rightarrow 4a_2)$	-439.0902	-439.1750	439	7.68
$^3B_2(3a_2 \rightarrow 5b_1)$	-439.2102	-439.2855	363	4.67
$^3A_1(4b_1 \rightarrow 5b_1)$	-439.2034	-439.2773	334	4.90
$^3B_2(4b_1 \rightarrow 4a_2)$	-439.1593	-439.2575	363	5.43
$^3A_1(3a_2 \rightarrow 4a_2)$	-439.1543	-439.2304	334	6.17

The current study also provides a case where detailed comparisons can be made between the results of a SCF scattered wave calculation<sup>15,21</sup> and ab initio SCF results. As noted in Table I, there are substantial differences in the MO ordering between the ab initio SCF studies and the SCF scattered wave study. As analyzed by Liberman and Batra,<sup>15</sup> the differences in MO ordering may be due to a difficulty in the  $\sigma$  vs.  $\pi$  scattered wave description. In particular, the energies of the localized molecular orbitals in the SCF scattered wave method may be shifted differently from the delocalized molecular orbitals, due to the "muffin tin" approximation. In addition, the unfilled  $5b_1(\pi)$  and  $4a_2(\pi)$  molecular orbitals have negative orbital eigenvalues. Also, as noted by Liberman and Batra,<sup>15</sup> Koopmans' theorem no longer holds for the SCF scattered wave method, and additional difficulties are encountered with electronic spectra predictions (discussed below).

**B. CI Calculations.** Using the MO's from the ground state SCF calculation, the CI wave functions and energies for the ground ( $^1A_1$ ) and  $^1,^3A_1(4b_1 \rightarrow 5b_1)$ ,  $^1,^3A_1(3a_2 \rightarrow 4a_2)$ ,  $^1,^3B_2(3a_2 \rightarrow 5b_1)$ , and  $^1,^3B_2(4b_1 \rightarrow 4a_2)$  excited electronic

states were calculated. Only the nine lowest unoccupied and the eight highest occupied MO's of Table I were allowed variable occupancy in the CI calculations. The remainder of the occupied MO's served as an unperturbed core for all electronic states, while the remainder of the unoccupied MO's were neglected.

The results of the CI calculations on the ground and excited states of carbazole are given in Tables II and III. Table II contains energetic information regarding the various states, while Table III gives information concerning the wave functions for the various states. Using the CI results, Franck-Condon transition energies from the ground to the various excited electronic states were calculated. These are compared in Table IV to the known experimental transition energies and other calculated transition energies.

Comparing the results of these calculations with experimentally determined transition energies, the calculated transition energies are seen to be too large in each case. However, although the calculated transition energies are overestimated, the order of the states agrees with the experimentally determined order, which is a feature not present in other all-valence or all-electron calculations reported to date. Furthermore, as shown in Figure 3, a least-squares fit of the experimental and calculated transition energies for the singlet states gives a linear relationship (in eV)

$$\Delta E_i^{\text{exptl}} = 0.6827 \Delta E_i^{\text{CI}} - 0.008 \quad (6)$$

where  $\Delta E_i^{\text{exptl}}$  and  $\Delta E_i^{\text{CI}}$  refer respectively to the experimental and calculated transition energies, with a standard deviation of 0.0587 and a correlation coefficient of 0.9927. This result is extremely encouraging because, not only is there a linear relationship between the experimental and calculated results, the slope of eq 6 passes approximately through the origin. Also, as shown in Figure 3, inclusion of the experimentally known and calculated  $^3B_2$  state with the singlet states gives the linear relationship (in eV),

$$\Delta E_i^{\text{exptl}} = 0.7177 \Delta E_i^{\text{CI}} - 0.252 \quad (7)$$

with a standard deviation of 0.0383 and a correlation coefficient of 0.9958. Although the linear relationship is preserved, the slope no longer passes through the origin. However, the result is not surprising, as the molecular orbitals used in the CI were determined for the ground state and would not be expected to describe triplet states as well as singlet states.

Overestimation of the calculated transition energies may be due either to the limited nature of the CI or limitations of

**Table III.** Major Contributors to the Ground and Excited State Wave Functions for Carbazole<sup>a</sup>

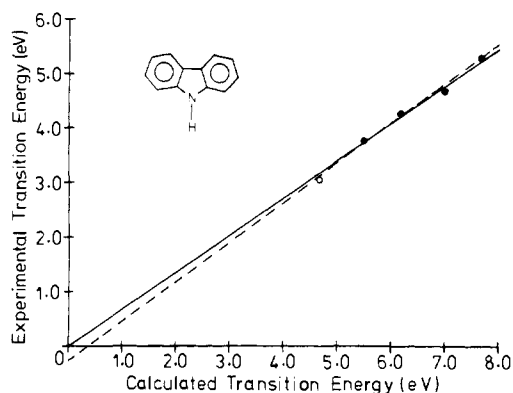
State	$A_1$ States (Configuration and Coefficient)									
	Ground	$4b_1 \rightarrow 5b_1$	$4b_1 \rightarrow 6b_1$	$3b_1 \rightarrow 5b_1$	$3b_1 \rightarrow 6b_1$	$2b_1 \rightarrow 5b_1$	$3a_2 \rightarrow 4a_2$	$3a_2 \rightarrow 5a_2$	$2a_2 \rightarrow 4a_2$	$2a_2 \rightarrow 5a_2$
$^1A_1$ (gs)	0.9567									
$^1A_1(4b_1 \rightarrow 5b_1)$		0.8882			0.1397		0.3527			0.1353
$^1A_1(3a_2 \rightarrow 4a_2)$		0.3548	0.1916			0.1374	0.7928	0.1165		0.1686
$^3A_1(4b_1 \rightarrow 5b_1)$		0.9132							0.2061	0.1769
$^3A_1(3a_2 \rightarrow 4a_2)$			0.3260	0.2477	0.1554		0.8415		0.1423	
	$B_2$ States (Configuration and Coefficient)									
	$4b_1 \rightarrow 4a_2$	$4b_1 \rightarrow 5a_2$	$3b_1 \rightarrow 4a_2$	$3b_1 \rightarrow 5a_2$	$3a_2 \rightarrow 5b_1$	$3a_2 \rightarrow 6b_1$	$2a_2 \rightarrow 5b_1$	$2a_2 \rightarrow 6b_1$		
$^1B_2(3a_2 \rightarrow 5b_1)$	0.2024	0.1861	0.1365		0.8755		0.1207	0.1300		
$^1B_2(4b_1 \rightarrow 4a_2)$	0.7567	0.1616	0.1932			0.3300	0.3853			
$^3B_2(3a_2 \rightarrow 5b_1)$	0.1588		0.1198	0.2225	0.8731		0.2236			
$^3B_2(4b_1 \rightarrow 4a_2)$	0.7888				0.2805		0.3625	0.2524		

<sup>a</sup> Only those configurations with coefficients >0.10 in magnitude in the final CI wave functions are included in the list. Configurations are described in terms of orbital promotions from the ground state configuration.

**Table IV.** A Comparison of Calculated Transition Energies and Other Properties of Carbazole with Experimental and Other Theoretical Results

Electronic state and orbital promotion	Transition energies, eV			Oscillator strength			Dipole moment, D		
	This calcn <sup>a</sup>	Other calcn	Exptl	This calcn <sup>i</sup>	Other calcn	Exptl	This calcn	Other calcn	Exptl <sup>k</sup>
<sup>1</sup> A <sub>1</sub> (gs)							2.21	1.66 <sup>b</sup>	1.7 1.9 2.2
<sup>1</sup> A <sub>1</sub> (4b <sub>1</sub> → 5b <sub>1</sub> )	5.497	5.22 <sup>b</sup> 5.23 <sup>c</sup> 4.84 <sup>d</sup> 3.45 <sup>e</sup>	3.750 <sup>f</sup> 3.804 <sup>e</sup> 3.618 <sup>g</sup>	0.056	0.13 <sup>c</sup> 0.15 <sup>d</sup> 0.10 <sup>e</sup>	0.056 <sup>f</sup> 0.090 <sup>g</sup> 0.042 <sup>j</sup>	2.87		3.1
<sup>1</sup> B <sub>2</sub> (3a <sub>2</sub> → 5b <sub>1</sub> )	6.204	6.65 <sup>b</sup> 5.68 <sup>c</sup> 5.76 <sup>d</sup> 3.76 <sup>e</sup>	4.267 <sup>f</sup> 4.505 <sup>e</sup> 4.210 <sup>g</sup>	0.51 0.10.90 <sup>d</sup>	1.02 <sup>c</sup> 0.42 <sup>e</sup>	0.15 <sup>j</sup>	2.97		3.5
<sup>1</sup> B <sub>2</sub> (4b <sub>1</sub> → 4a <sub>2</sub> )	7.037	6.88 <sup>b</sup> 6.53 <sup>c</sup> 6.16 <sup>d</sup>	4.685 <sup>f</sup>	0.45	0.58 <sup>c</sup> 0.40 <sup>d</sup>		2.10		
<sup>1</sup> A <sub>1</sub> (3a <sub>2</sub> → 4a <sub>2</sub> )	7.679	6.71 <sup>b</sup> 6.65 <sup>c</sup> 6.47 <sup>d</sup>	~5.3 <sup>h</sup>	0.30	0.67 <sup>c</sup> 0.20 <sup>d</sup>		3.03		
<sup>3</sup> B <sub>2</sub> (3a <sub>2</sub> → 5b <sub>1</sub> )	4.672	4.81 <sup>b</sup>	3.05 <sup>f</sup>				1.84		
<sup>3</sup> A <sub>1</sub> (4b <sub>1</sub> → 5b <sub>1</sub> )	4.895	4.84 <sup>b</sup>					3.84		
<sup>3</sup> B <sub>2</sub> (4b <sub>1</sub> → 4a <sub>2</sub> )	5.434	6.01 <sup>b</sup>					3.14		
<sup>3</sup> A <sub>1</sub> (3a <sub>2</sub> → 4a <sub>2</sub> )	6.171	6.41 <sup>b</sup>					2.59		

<sup>a</sup> Franck-Condon transitions from Table II. <sup>b</sup> See ref 16. The transition energies were calculated as the energy difference between ground state SCF and excited state SCF calculations. <sup>c</sup> See ref 14, approximation (a). <sup>d</sup> See ref 14, approximation (b). <sup>e</sup> See ref 10. <sup>f</sup> See ref 13. <sup>g</sup> See ref 12. <sup>h</sup> Although the transition energy to this state was not given in ref 13, the state was assigned <sup>1</sup>A<sub>1</sub> symmetry. Energy value was taken from "UV Atlas of Organic Compounds", Vol. 3, Plenum Press, New York, N.Y., 1965, p H16/6. <sup>i</sup> Computed from  $f \approx \frac{2}{3} \Delta E |R|^2$  where  $\Delta E$  and  $R$  are the calculated transition energy and transition moment, respectively, in atomic units. <sup>j</sup> See ref 11. <sup>k</sup> W. Liptay, "Modern Quantum Chemistry", Vol. 3, Academic Press, New York, N.Y., 1965, p 45.



**Figure 3.** A plot of experimental<sup>13</sup> vs. calculated (CI) transition energies. The solid circles refer to singlet states and the open circle refers to the <sup>3</sup>B<sub>2</sub> state. The solid line refers to the least squares slope determined from eq 6 of the text, and the dashed line refers to the least-squares slope determined from eq 7 of the text.

the basis set. For example, only eight filled and nine unfilled orbitals were used in the CI calculations, and important filled and/or unfilled orbitals may have been omitted. However, examination of the CI wave functions indicates that this was probably not the case. In particular, the lower filled and higher unfilled orbitals used in the CI calculations were found to make negligible contributions to any of the electronic states studied (see Table III). Thus, the overestimation of the calculated transition energies must be ascribed primarily to limitations of the basis set.

Comparing the current CI results to the SCF spectral predictions of Batra et al.<sup>16</sup> (see Table IV), the ordering of the states predicted by the two calculations is in general agreement, except for the higher-lying gs → <sup>1</sup>B<sub>2</sub> and gs → <sup>1</sup>A<sub>1</sub> transitions. Batra et al.<sup>16</sup> calculated the transition energies by taking the

energy difference between the ground state SCF and the excited state SCF calculations. Since the experimentally observed ordering is <sup>1</sup>A<sub>1</sub>, <sup>1</sup>B<sub>2</sub>, <sup>1</sup>B<sub>2</sub>, <sup>1</sup>A<sub>1</sub>, more than orbital relaxation in the excited state SCF calculations evidently is needed to obtain the experimentally observed ordering of states. Further evidence of this is shown by an analysis similar to eq 6 and 7 for the results of Batra et al.<sup>16</sup> A least-squares analysis of the experimental transition energies and the SCF transition energies calculated by Batra et al.<sup>16</sup> failed to show a significant linear relationship. For example, such an analysis of singlet states gave rise to a linear relationship with a correlation coefficient of only 0.77 with a standard deviation of 0.39.

A further comparison can be made between ab initio SCF and SCF scattered wave calculations with respect to electronic spectra predictions of both methods. In addition to the difficulties of extracting excited state energies from the SCF scattered wave method, as discussed by Liberman and Batra,<sup>15</sup> the ordering of excited states does not agree with either of the ab initio SCF methods or with the experimental ordering. For the first four excited states, Liberman and Batra<sup>15</sup> predict the states in order of increasing excitation energy as A<sub>1</sub>(4b<sub>1</sub> → 5b<sub>1</sub>), B<sub>2</sub>(3a<sub>2</sub> → 5b<sub>1</sub>), B<sub>2</sub>(4b<sub>1</sub> → 4a<sub>2</sub>), and B<sub>2</sub>(2a<sub>2</sub> → 5b<sub>1</sub>), with the two lowest B<sub>2</sub> states separated by only 0.02 eV, and the second excited A<sub>1</sub> state not appearing in this group. In addition, singlets and triplets are not identified, since the SCF scattered wave method gives only weighted averages of singlet and triplet excitation energies.<sup>15</sup> Also, as with MO eigenvalues, the SCF scattered wave transition energies are very close together; less than 1 eV separates the highest from the lowest of the above four states.<sup>15</sup>

Using the CI wave functions, the oscillator strengths for allowed transitions and dipole moments for the ground and excited states were calculated. These are compared in Table IV to the experimentally known and other calculated values. Due to the nature of the available data, quantitative compar-

isons are not possible. However, in general, there is qualitative agreement between the calculated and experimental values.

In particular, the calculated value for the oscillator strength for the first allowed transition is in excellent agreement with experimental values, and the value for the second allowed transition is larger than the first, in agreement with the experimentally observed trend. Overall, the oscillator strengths calculated here appear to fit the experimentally observed spectra (see Figure 2, ref 13). The oscillator strengths calculated here are also in general agreement with the values from the semiempirical calculations of Mataga et al.<sup>14</sup> and Pinkham and Wait,<sup>10</sup> especially "Approximation B" of Mataga et al.<sup>14</sup>

For the dipole moments, agreement between the calculated and experimental values is not quantitative, but the values calculated here do follow the experimentally observed trend.

CI energies and wave functions were also determined for some of the ionic states of carbazole. The energies of the positive  ${}^2B_1(4b_1^2 \rightarrow 4b_1)$  and  ${}^2A_2(3a_2^2 \rightarrow 3a_2)$  and negative  ${}^2B_1(5b_1)$  and  ${}^2A_2(4a_2)$  states were determined using the ground state SCF molecular orbitals and a CI calculation as described earlier. From these calculations, ionization potentials (IP) and electron affinities (EA) were calculated as the difference between the ionic state and the ground state CI energies. The calculated IP's are 3.50 eV for the  ${}^2B_1(4b_1^2 \rightarrow 4b_1)$  state and 3.84 eV for the  ${}^2A_2(3a_2^2 \rightarrow 3a_2)$  state. The experimental value for the lowest IP is 7.8 eV,<sup>26</sup> and Batra et al.,<sup>16</sup> using Koopmans' theorem, calculate a value of 8.62 eV. Thus, the IP calculated here are substantially less than the experimental value and the value calculated by Batra et al.<sup>16</sup> The calculated EA are 7.09 eV for the  ${}^2B_1(5b_1)$  state and 8.48 eV for the  ${}^2A_2(4a_2)$  state. The experimental value<sup>27</sup> for the EA is  $\sim 0$  and, thus, the value calculated here is substantially higher than the experimental value. Neither result is surprising, however. As noted earlier, the molecular orbitals are displaced upward in the molecular fragment procedure, and low values for the IP and high values for the EA are expected.

Since the manner of energy displacement in the molecular fragment procedure has been analyzed, a comparison of the IP and EA of the current study to the experimental values is appropriate only after additional analysis. Such a comparison is obtained by using eq 5 to scale the IP and EA of the current study and compare these values to the experimental values.

Scaling the  $4b_1(\pi)$  and  $3a_2(\pi)$  MO eigenvalues of the current study and using Koopmans' theorem yields respectively IP of 9.45 and 9.62 eV. Scaling the CI results yields an IP of 9.41 eV for the  ${}^2B_1(4b_1)$  state and 9.70 eV for the  ${}^2A_2(3a_2)$  state. Thus, the scaled IP are in reasonable agreement with the experimental value and the value calculated by Batra et al.<sup>16</sup>

Similarly, using eq 5 to scale the  $5b_1(\pi)$  and  $4a_2(\pi)$  MO eigenvalues of the current study and Koopmans' theorem yields respectively EA of 0.25 and 1.03 eV. Scaling the CI values yields an EA of 0.11 eV for the  ${}^2B_1(5b_1)$  state and 1.11 eV for the  ${}^2A_2(4a_2)$  state. Thus, the scaled EA for the  ${}^2B_1(5b_1)$  state is in excellent agreement with the experimental value.

Bond-order and population analyses can aid substantially in interpreting the charge distribution and its rearrangement upon electron excitation. As for single determinant wave functions, the charge and bond-order matrix can be calculated for wave functions which are sums of determinants.<sup>28</sup> Using the CI wave functions, the symmetrically orthonormalized<sup>29</sup>  $\sigma$  and  $\pi$  bond orders and populations were calculated for the electronic states of carbazole. The  $\sigma$  bond orders and populations are given in Table V, and the  $\pi$  bond orders and populations are given in Table VI. As expected, any electron redistribution upon electronic excitation was confined to the  $\pi$  system; the  $\sigma$  bond orders and populations remained essentially constant for the ground and excited states and, as such, only

**Table V.**  $\sigma$  Bond Orders and Orbital Populations for Symmetrically Orthonormalized Orbitals for Carbazole<sup>a</sup>

Bond	Bond order	Population
N <sub>9</sub> -C <sub>10</sub>	0.954	2.063
C <sub>10</sub> -C <sub>11</sub>	0.971	2.048
C <sub>11</sub> -C <sub>4</sub>	0.968	2.053
C <sub>4</sub> -C <sub>3</sub>	0.966	2.060
C <sub>3</sub> -C <sub>2</sub>	0.969	2.060
C <sub>2</sub> -C <sub>1</sub>	0.964	2.059
C <sub>1</sub> -C <sub>10</sub>	0.967	2.052
C <sub>11</sub> -C <sub>12</sub>	0.964	2.056

<sup>a</sup> The population in the bonding region between "heavy" atoms is taken as the sum of the populations of the two FSGO in that region. The atomic numbering is shown in Figure 1.

the  $\sigma$  bond orders and populations from the ground state CI are given in Table V.

As a further aid in the understanding of the electronic structure and spectra of carbazole, the nature of the molecular orbitals shown in Figure 2 can be examined. Mataga et al.<sup>14</sup> pointed out the possibility of combining  $>N-H$  with biphenyl to explain the electronic spectra of carbazole, and examination of Figure 2 and Table V show that this combination yields a fairly good description of carbazole. Strictly speaking, all the  $b_1(\pi)$  and  $a_2(\pi)$  orbitals are, by symmetry,  $\pi$  orbitals in carbazole. However, the occupied  $2b_1(\pi)$  and  $4b_1(\pi)$  orbitals show substantial electron density on the nitrogen, and could be loosely classified as nitrogen "lone pair" or "n" orbitals. The occupied  $3b_1(\pi)$  orbital shows essentially no electron density on the nitrogen and more closely resembles a  $\pi$  orbital delocalized over the biphenyl system. Similarly, the virtual  $6b_1(\pi)$  and  $7b_1(\pi)$  orbitals show substantial "hole" density on the nitrogen and could be considered as nitrogen "n\*" orbitals, while the  $5b_1(\pi)$  shows essentially no "hole" density on the nitrogen and resembles a  $\pi^*$  orbital delocalized over the biphenyl system. By symmetry, the nitrogen lone pair cannot contribute to  $a_2(\pi)$  orbitals and, thus, these orbitals are  $\pi$  orbitals that are delocalized over the biphenyl system.

Using the terminology developed above, the electronic states of carbazole can be classified according to the orbital promotion which is the dominant configuration of the state. Thus, the  ${}^1,3A_1(4b_1 \rightarrow 5b_1)$  and  ${}^1,3B_2(4b_1 \rightarrow 4a_2)$  states could be classified as "n  $\rightarrow$   $\pi^*$ " states, and the  ${}^1,3A_1(3a_2 \rightarrow 4a_2)$  and  ${}^1,3B_2(3a_2 \rightarrow 5b_1)$  states could be classified as " $\pi \rightarrow \pi^*$ " states.

As observed in Table VI, states which are predominantly "n  $\rightarrow$   $\pi^*$ " transitions show a large loss of electron density from the nitrogen lone pair and states which are predominantly " $\pi \rightarrow \pi^*$ " transitions show relatively little loss of electron density from the nitrogen lone pair. The possible exception is the  ${}^1A_1(3a_2 \rightarrow 4a_2)$  state, which is a " $\pi \rightarrow \pi^*$ " state, but shows a relatively large loss of electron density from the nitrogen lone pair. However, examination of Table III shows that this state also has a relatively large coefficient for the  $4b_1 \rightarrow 5b_1$  orbital promotion (which is a "n  $\rightarrow$   $\pi^*$ " configuration), which leads to an expected loss of some electron density from the nitrogen lone pair.

Certain bands of carbazole show a large red shift in hydrogen bonding solvents,<sup>14</sup> and upon N-alkylation,<sup>13,14</sup> while other bands are relatively unaffected. For example, Mataga et al.<sup>14</sup> have shown that the first excited singlet state of carbazole shows a large red shift and the second excited singlet state shows only a small red shift in hydrogen bonding solvents and upon N-alkylation. The spectra of Johnson<sup>13</sup> show similar results for the first two excited singlet states and, in addition, the third singlet shows a large red shift, while the lowest triplet shows only a minor red shift on N-alkylation. The two states

**Table VI.**  $\pi$  Bond Orders and Orbital Populations for Symmetrically Orthonormalized Orbitals for the Ground and Low-Lying Excited Electronic States of Carbazole from CI Treatments Based on Molecular Orbitals Determined from a Ground State SCF Calculation<sup>j</sup>

	N <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>4</sub>	C <sub>3</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>13</sub>	C <sub>12</sub>
N <sub>9</sub>	1.627 <sup>a</sup>								
	-0.174 <sup>b</sup>								
	-0.116 <sup>c</sup>								
	-0.183 <sup>d</sup>								
	-0.022 <sup>e</sup>								
	-0.012 <sup>f</sup>								
	-0.145 <sup>g</sup>								
	-0.005 <sup>h</sup>								
	-0.127 <sup>i</sup>								
C <sub>10</sub>	0.448	0.979						0.093	
	0.030	0.032						0.028	
	0.025	0.022						0.019	
	0.050	0.012						0.043	
	-0.001	0.011						-0.017	
	0.0	-0.083						-0.088	
	0.024	0.082						0.061	
	-0.007	-0.055						-0.071	
	0.041	0.044						0.071	
C <sub>11</sub>	0.187	0.542	1.024					0.033	0.390
	-0.132	-0.088	-0.007					0.026	0.063
	-0.046	-0.101	-0.066					0.005	0.102
	-0.103	-0.043	0.013					0.040	0.057
	-0.022	-0.111	-0.089					0.024	0.054
	-0.010	-0.130	-0.004					0.023	0.162
	-0.123	-0.035	-0.070					0.036	-0.047
	-0.020	-0.119	-0.018					-0.007	0.203
	-0.053	-0.019	-0.027					0.007	-0.006
C <sub>4</sub>		0.046 <sup>a</sup>	0.613	1.042					
		0.029 <sup>b</sup>	-0.066	0.045					
		0.075 <sup>c</sup>	-0.095	0.078					
		0.055 <sup>d</sup>	-0.079	0.102					
		0.064 <sup>e</sup>	-0.029	0.076					
		-0.044 <sup>f</sup>	-0.149	0.076					
		-0.027 <sup>g</sup>	-0.013	0.040					
		-0.043 <sup>h</sup>	-0.209	0.033					
		-0.043 <sup>i</sup>	0.004	0.079					
C <sub>3</sub>		0.258	0.062	0.664	1.029				
		-0.068	-0.029	-0.092	-0.068				
		-0.163	-0.031	-0.064	0.014				
		-0.063	-0.016	-0.106	-0.142				
		-0.020	-0.038	-0.091	0.041				
		-0.098	-0.024	-0.007	-0.034				
		-0.143	-0.019	-0.142	-0.022				
		-0.043	-0.054	0.027	-0.024				
		-0.175	-0.031	-0.201	-0.045				
C <sub>2</sub>		0.028	0.275	0.001	0.631	0.996			
		0.021	-0.131	0.087	-0.020	0.076			
		0.053	-0.117	0.040	-0.061	-0.078			
		0.019	-0.108	0.145	0.025	0.132			
		0.047	-0.121	0.058	-0.108	-0.119			
		0.043	-0.198	0.059	-0.071	-0.012			
		-0.026	-0.065	0.023	-0.033	-0.008			
		0.001	-0.227	0.010	-0.050	-0.017			
		-0.021	-0.026	0.051	-0.005	-0.002			
C <sub>1</sub>		0.592	0.069	0.298	0.057	0.661	1.117		
		-0.007	0.033	-0.175	-0.038	-0.109	0.009		
		-0.091	-0.046	-0.165	0.109	-0.063	0.086		
		-0.040	0.032	-0.185	0.002	-0.113	-0.026		
		-0.111	-0.007	-0.108	0.007	0.005	0.089		
		0.001	-0.036	-0.123	0.013	-0.099	0.062		
		-0.127	-0.044	-0.159	0.008	-0.020	0.049		
		0.066	-0.046	-0.160	0.021	-0.185	0.078		
		-0.175	-0.049	-0.185	-0.019	mins0.002	0.014		

<sup>a</sup> <sup>1</sup>A<sub>1</sub>(gs). <sup>b</sup> <sup>1</sup>A<sub>1</sub>(4b<sub>1</sub> → 5b<sub>1</sub>). <sup>c</sup> <sup>1</sup>A<sub>1</sub>(3a<sub>2</sub> → 4a<sub>2</sub>). <sup>d</sup> <sup>3</sup>A<sub>1</sub>(4b<sub>1</sub> → 5b<sub>1</sub>). <sup>e</sup> <sup>3</sup>A<sub>1</sub>(3a<sub>2</sub> → 4a<sub>2</sub>). <sup>f</sup> <sup>1</sup>B<sub>2</sub>(3a<sub>2</sub> → 5b<sub>1</sub>). <sup>g</sup> <sup>1</sup>B<sub>2</sub>(4b<sub>1</sub> → 4a<sub>2</sub>). <sup>h</sup> <sup>3</sup>B<sub>2</sub>(3a<sub>2</sub> → 5b<sub>1</sub>). <sup>i</sup> <sup>3</sup>B<sub>2</sub>(4b<sub>1</sub> → 4a<sub>2</sub>). <sup>j</sup> The actual values are given for the ground state, while the entries for the various excited states correspond to the difference between the excited and ground state values, i.e., a negative sign corresponds to a loss of density on going to the excited state. Diagonal and off-diagonal elements correspond to orbital populations and bond orders, respectively. The atomic numbering is shown in Figure 1.

which showed large red shifts correspond to the  ${}^1A_1(4b_1 \rightarrow 5b_1)$  and  ${}^1B_2(4b_1 \rightarrow 4a_2)$  states of this study, and the two states which showed minor red shifts correspond to the  ${}^1B_2(3a_2 \rightarrow 5b_1)$  and  ${}^3B_2(3a_2 \rightarrow 5b_1)$  states of this study. Thus, the " $n \rightarrow \pi^*$ " states show a large red shift, and the " $\pi \rightarrow \pi^*$ " states show a minor red shift in hydrogen bonding solvents and upon N-alkylation.

The experimental and current theoretical results indicate that hydrogen bonding solvents and N-alkylation of carbazole have a substantial effect on the nitrogen "lone pair", but relatively little effect on the  $\pi$  orbitals delocalized over the biphenyl system. This suggests that increased electron density on the nitrogen destabilizes the nitrogen "lone pair", and red-shifted transitions originate from this effect. Hydrogen bonding interactions would be expected to increase the electron density on nitrogen and, through hyperconjugation, N-alkylation could have the same effect. Clearly other explanations are possible, and additional work is underway in this laboratory to characterize further the electronic states and transitions in carbazole and its derivatives.

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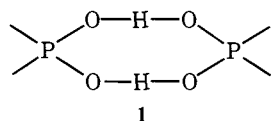
## Dimeric Structure of Di-*tert*-butylphosphinic Acid<sup>1a</sup>

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**Abstract:** The molecular structure of di-*tert*-butylphosphinic acid,  $[(CH_3)_3C]_2PO(OH)$ , as determined by single-crystal x-ray methods, is the first observed distinct dimeric  $R_2PO(OH)$  compound with two acid molecules linked through a centrosymmetric configuration, **1**. The molecule crystallizes in the monoclinic space group,  $P2_1/c$  with cell parameters  $a = 8.973$  (6) Å,  $b = 13.130$  (9) Å,  $c = 10.539$  (7) Å,  $\beta = 117.95$  (3)°, and  $Z = 4$ . The structure was solved and refined using 999 independent three-dimensional Mo  $K\alpha$  x-ray data collected with an automated diffractometer. Full-matrix least-squares refinement of 620 observations for which  $F_o > 3\sigma(F_o)$  led to  $R_F = 0.059$ . The discrete dimer which was found contains strong, 2.506 (18) Å, hydrogen bonds, in which the oxygen atoms of O-H-O are not related by a crystallographic symmetry element. The eight-membered, hydrogen bonded ring has  $I$  site symmetry and shows a small chair-conformation distortion from planarity. The P-O bond lengths are 1.521 (8) and 1.520 (6) Å which indicates that the oxygen atoms are essentially equivalent. There appear to be weak C-H...O interactions which fix the methyl group orientations to give an overall eclipsed conformation.

Monoacidic phosphorus organic compounds of the type  $(RO)_2PO(OH)$ ,  $(R)(RO)PO(OH)$ , and  $R_2PO(OH)$  show association through strong hydrogen bonding forming dimers, **1**, in nonpolar solvents<sup>2</sup> and polymeric or helical strands, **2**, in the crystalline state.<sup>3-5</sup> Unlike carboxylic acids, no distinct



1



2

eight-membered-ring dimers have been observed in the solid state; however, formation of eight-membered hydrogen bonded

rings is not uncommon. Materials such as  $K[PHO_2(OH)HF]$ ,<sup>6</sup>  $SnHPO_4$ ,<sup>7</sup>  $\beta$ -ciliatine,<sup>8</sup> and 2-aminoethanol phosphate<sup>9</sup> have been shown to form eight-membered rings of **1**, but in each of these materials further ionic or hydrogen bonding is also present. We wish to report the existence of a distinct, eight-membered-ring, dimeric  $R_2PO(OH)$  compound, di-*tert*-butylphosphinic acid,  $[(CH_3)_3C]_2PO(OH)$  ( $H[Di-BP]$  hereafter).

In recent years, the stereochemistry and binding affinities of organophosphorus compounds for specific ions have developed into a subject of wide chemical and biochemical interest.  $H[Di-BP]$  acid has acquired a special significance as an extractant in metals separations, especially the purification of