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(42) These general remarks were prompted by the criticism of the semiempirical methods by one of the referees who calls them "simplistic". Our view is that the two methods are complementary, and one or the other or both may be chosen according to the investigator's requirements.[40,41]

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Configuration Interaction Studies on the Ground and Lower Excited States of N-Methylcarbazole

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Abstract: Ab initio calculations on *N*-methylcarbazole have been carried out using a basis set obtained from the molecular fragment technique. A self-consistent field calculation was done on the ground state, and configuration interaction studies were carried out subsequently on the ground state plus other low-lying singlet and triplet states. Several electronic structural features were derived from these studies, including ionization potentials, Franck–Condon transition energies, oscillator strengths, charge distributions, and dipole moments. The first ionization potential was found to be lowered in *N*-methylcarbazole compared to carbazole with other ionization potentials not affected greatly. The ordering of the molecular states is found to be the same as observed experimentally, and the calculated transition energies are found to be linearly related to the observed transition energies. Analysis of the changes in molecular orbital energies and charge distribution are also found to provide a satisfactory rationale for both the red shift in the absorption spectrum observed when carbazole is methylated and the changes in dipole moment in the various states.

I. Introduction

Several experimental spectral studies[1-3] previously have shown the effect of various *N*-alkyl substituents on the electronic spectra of carbazole. This effect primarily is a major red shift in transitions to the first and third excited singlet states. These results have generated interest in possible causes of the red shift, and the apparently related[4] loss of nitrogen lone pair density in the red-shifted transitions. This study was undertaken to attempt to reproduce theoretically the experimentally observed red shifts and to find a mechanism for their occur-

rence, based on observed changes in the calculated spectrum and electron distribution in the various states of the N-alkylated molecule.

A number of spectral studies have been done to characterize the low-lying excited states and π-charge densities of the ground state of carbazole and its *N*-alkyl derivatives. Witanowski et al.[3] have characterized these molecules using nitrogen-14 NMR and the linear relationship found between the observed chemical shifts and SCF-PPP-MO π-electron densities at the nitrogen in the ground states of carbazole and *N*-methylcarbazole. Johnson[1] has studied the spectra of car-

Table I. Total Energy and Molecular Orbital Ordering for the Ground States of N-Methylcarbazole and Carbazole[a]

	N-Methylcarbazole			Carbazole[4]	
(SCF) molecular orbital no.	Molecular orbital symmetry	MO energies, hartree	MO energies, hartree	Molecular orbital symmetry	(SCF) molecular orbital no.
54*	24a″ (π)	0.6267	0.6264	6a$_2$ (π)	50*
53*	30a′ (π_n)	0.5678	0.5660	7b$_1$ (π)	49*
52*	23a″ (π)	0.3735	0.3729	5a$_2$ (π)	48*
51*	29a′ (π_n)	0.3672	0.3646	6b$_1$ (π)	47*
50*	22a″ (π)	0.3085	0.3084	4a$_2$ (π)	46*
49*	28a′ (π)	0.2551	0.2545	5b$_1$ (π)	45*
48*	27a′ (π_n)	−0.1244	−0.1309	4b$_1$ (π)	44*
47*	21a″ (π)	−0.1369	−0.1376	3a$_2$ (π)	43*
46*	20a″ (π)	−0.2048	−0.2056	2a$_2$ (π)	42*
45*	26a′ (π)	−0.2395	−0.2405	3b$_1$ (π)	41*
44*	25a′ (π_n)	−0.3048	−0.3168	2b$_1$ (π)	40*
43	24a′	−0.3538	−0.3561	20a$_1$	39
42*	19a″ (π)	−0.3561	−0.3570	1a$_2$ (π)	38*
41	18a″	−0.3695	−0.3719	17b$_2$	37
40	23a′	−0.3967	−0.4019	19a$_1$	36
39	17a″	−0.4081	−0.4113	16b$_2$	35
38*	22a′ (π)	−0.4283	−0.4538	1b$_1$ (π)	34*
37	16a″	−0.4532	−0.4607	15b$_2$	33
36	21a′	−0.4542	−0.4655	18a$_1$	32
35	15a″	−0.4619	−0.4830	14b$_2$	31
34	20a′	−0.4849	−0.4915	17a$_1$	30
33	14a″	−0.5141			
32	19a′	−0.5245			
31*	18a′ (π)	−0.5273			
Total energy (SCF) −472.598 052 56 hartrees			Total energy (SCF) −439.393 298 55 hartrees		

[a] An asterisk indicates MOs which were allowed variable occupancy in the CI studies.

bazole, N-ethylcarbazole, and N-isopropylcarbazole in solution, and has assigned the three lowest singlets and the lowest triplet in each of these molecules. Zander[2] has taken the ultraviolet absorption and luminescence spectrum of N-methylcarbazole, and has assigned the four lowest excited singlet states. His study, however, did not include the spectrum of carbazole itself.

Prior to the current study, no ab initio configuration interaction investigations on N-alkylcarbazoles have been reported. A previous ab initio study[4] has, however, been done on the parent carbazole molecule using the methods of the current study, and the calculated values of observables for carbazole will be taken from the earlier study. Also, comparisons to results using other theoretical techniques are given in the earlier study.[4]

In the following sections several ab initio calculations on N-methylcarbazole will be described, including a self-consistent field (SCF) calculation on the ground state and configuration interaction studies of low-lying singlet and triplet states. A variety of electronic structural features will be discussed, including ionization potentials, Franck–Condon transition energies, charge distributions, and others, and the observed red shifts will be rationalized in terms of these properties.

II. Methodology

The SCF calculation on N-methylcarbazole utilized the molecular fragment method, the details of which may be found elsewhere.[5] The basis orbitals employed in this procedure are normalized floating spherical Gaussian orbitals (FSGO), which are defined as

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

where ρ_i is the orbital radius, and $\mathbf{R}_i$ is the location of the orbital relative to an arbitrary origin. Molecular orbitals are taken as linear combinations of the fragment orbitals,

$$\varphi_i = \sum_{A=1}^{P} \sum_{k=1}^{N_A} C_{ki}^A G_k^A \qquad (2)$$

where the G_k^A are the fragment FSGO, and the C_{ki}^A are coefficients resulting from the solution of the SCF equations. The nonlinear parameters of the FSGO were determined in previous calculations[6] on molecular fragments.

The CI calculations used a procedure reported by Whitten and Hackmeyer[7] to generate CI wave functions and energies for the M electronic states of the molecule. A set of "parent configurations" $\{\phi_k^{(1)}\}$, antisymmetrized products of orthonormal molecular spin orbitals, is chosen which is expected to contain the most important contributors to the M states. The initial wave functions $\{\psi_k^{(1)}\}$ for the states are taken as linear combinations of the parents:

$$\psi_k^{(1)} = \sum_k c_{kj}^{(1)} \phi_k^{(1)} \qquad j = 1, 2, 3, \ldots, M \qquad (3)$$

Single and double excitations from the parent configurations yield new configurations, $\{\phi_k^{(2)}\}$, which are combined, subject to an energy criterion, with the original parents to give the new total wave function for each state. The energy threshold criterion is as follows:

$$\{|\langle \phi_k^{(2)}|H|\psi_j^{(1)}\rangle|^2 / |\langle \phi_k^{(2)}|H|\phi_k^{(2)}\rangle$$
$$- \langle \psi_j^{(1)}|H|\psi_j^{(1)}\rangle|\} > \delta \qquad (4)$$

where δ is a numerical threshold value, 3×10^{-4} in the current study. (This energy criterion must be met for at least one of the original M parent states.) Having generated a new total wave function for each state, the Hamiltonian matrix is diagonalized to obtain the CI energies, E_j, and the improved wave functions, ψ_j. These wave functions then become the initial set, $\{\psi_j^{(1)}\}$, and the process is repeated until the addition of new configurations gives no appreciable change in the energies of the states. The details of this CI procedure may be found elsewhere.[7]

Table II. Important Contributing Configurations to the CI Wave Functions of the Ground and Low-Lying Excited Electronic States of *N*-Methylcarbazole[a]

State	Ground	25a'→28a'	26a'→28a'	26a'→29a'	27a'→28a'	27a'→29a'	20a''→22a''	20a''→23a''	21a''→22a''	21a''→23a''
¹A'(g.s.)	0.9559									
¹A'(27a'→28a')				0.1312	0.8470			0.1244	0.3318	
¹A'(21a''→22a'')		0.1552			0.3275	0.1597		0.1675	0.8045	0.1084
³A'(27a'→28a')					0.9183		0.1814	0.1723		
³A'(21a''→22a'')			0.3603	0.1434		0.2487			0.8292	0.1174

State	26a'→22a''	26a'→23a''	27a'→22a''	27a'→23a''	20a''→28a'	20a''→29a'	21a''→28a'	21a''→29a'
¹A''(21a''→28a')	0.1283		0.2563	0.1751	0.1133	0.1217	0.8669	
¹A''(27a'→22a'')	0.1951		0.7929	0.1477	0.3263			0.2962
³A''(21a''→28a')	0.1260	0.2215	0.1637		0.2182		0.8720	
³A''(27a'→22a'')			0.8112		0.3210	0.2344	0.2782	0.1099

[a] The configurations shown are those with coefficients $\geq |0.10|$.

III. Results and Discussion

A. SCF Calculations. The SCF calculation was done on the ¹A' ground state of *N*-methylcarbazole. The molecule has C_2 symmetry in the geometry used,[8] which is shown in Figure 1 along with the atomic numbering scheme and coordinate axes. The basis orbitals used were those from the planar CH_3, planar NH_3, and tetrahedral CH_4 molecular fragments, described in detail elsewhere.[6] This gives 83 FSGO, contracted to 70 orbitals for the SCF calculation.

The 18 highest occupied and 6 lowest unoccupied SCF molecular orbitals are listed in Table I, along with their symmetries and energies (in atomic units[9]).

A characteristic of the molecular fragment procedure is the upward shift (toward more positive values) of the calculated MO eigenvalues.[6] It is then reasonable to assume that the MO energies reported in Table I are somewhat high relative to the values which might be obtained from a calculation using a large basis set. However, this characteristic upward shift of the eigenvalues has been shown to be remarkably similar in various molecules, and linear relationships have been found between the MO energies given by the molecular fragment procedure and those resulting from calculations on the same molecule using extensive basis sets. This type of linear relationship was found for carbazole (eq 5 of ref 4) to be (in atomic units[9])

$$\epsilon_i^{ref} = 0.8783\epsilon_i^{MF} - 0.2297 \qquad \begin{array}{l} \text{corr coeff} = 0.9984 \\ \text{std dev} = 0.0093 \end{array} \qquad (5)$$

where ϵ_i^{ref} and ϵ_i^{MF} are the MO eigenvalues for the larger basis set calculation and the molecular fragment procedure, respectively.

Owing to the great similarity, it would also appear appropriate to use the above relationship obtained for carbazole to scale the MO energies for *N*-methylcarbazole to obtain approximations to the ionization potentials. Scaling the 27a' and 21a'' orbital eigenvalues in this manner and using Koopmans' theorem results in 9.22 and 9.52 eV, respectively, for the first two ionization potentials of *N*-methylcarbazole. These compare with 9.45 and 9.62 eV calculated for the first two ionization potentials of carbazole.[4] It is of interest to note that the first ionization potential of *N*-methylcarbazole has been lowered more than the second, which is consistent with the analysis of spectral shifts discussed in the following sections.

B. CI Calculations. Using the orthonormal molecular orbitals from the SCF calculation, CI wave functions and energies for the ¹A' ground state, ¹,³A'(27a'→28a'), ¹,³A''(21a''→28a'), ¹,³A''(27a'→22a''), and ¹,³A'(21a''→22a'') excited states of *N*-methylcarbazole were determined. The excited
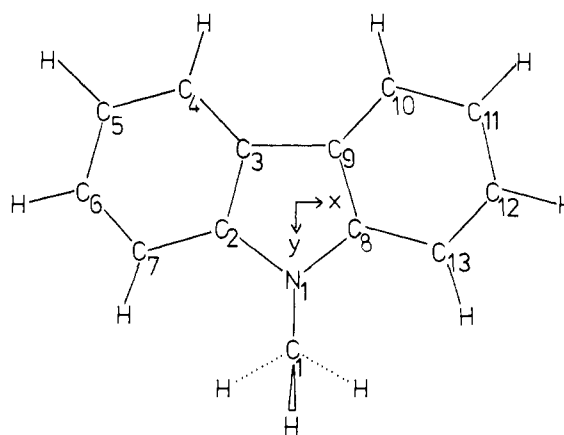

Figure 1. Depiction of *N*-methylcarbazole, including atomic numbering and coordinate axes.

states are labeled with the dominant configuration of the state, while the configurations are labeled as orbital promotions from the ground state configuration. The MOs shown with an asterisk in Table I are those which were allowed variable occupancy in the CI calculations. These include the six lowest lying unoccupied orbitals and the five highest occupied MOs, along with orbitals 31, 38, and 42. The remaining occupied MOs were kept fully occupied throughout the CI, and virtual orbitals lying higher than those shown in Table I were neglected.

Table II shows the important contributing configurations to the CI wave functions of the ground and excited states of the molecule, and gives their coefficients when these are greater than 0.10. The contributing configurations are described as orbital promotions from the ground state.

Energetic and associated information from the CI calculations is shown in Table III. This includes the final CI energies for each state, and the calculated Franck–Condon transition energies from the ground state to each of the excited electronic states. These transition energies are compared in Table IV to the experimental values of Zander.[2]

Comparing the singlet transition energies of the present calculation to the experimental results of Zander,[2] the calculated values are high in each case, as expected. A least-squares analysis, however, shows that a linear relationship is present between the sets of data, as given by (in eV)

$$\Delta E^{expl} = 0.7306(\Delta E^{calcd}) - 0.2754 \qquad (6)$$

with a standard deviation of 0.0105 and a correlation coefficient of 0.9998. This least-squares fit is shown graphically in

Table III. CI Energies, Dipole Moments, and Oscillator Strengths for the Ground and Excited States of *N*-Methylcarbazole

Electronic state and orbital promotion	Final CI energies, au	No. of configurations ($\delta\ 3 \times 10^{-4}$)	Scaled transition energies,[b] eV	Transition energies, eV	Dipole moment, D	Oscillator strength[a]
$^1A'$ (ground state)	−472.6620	451			2.208	
$^1A'(27a'\rightarrow 28a')$	−472.4651	451	3.640 (3.626)	5.358	3.310	0.054
$^1A''(21a''\rightarrow 28a')$	−472.4363	399	4.212 (4.232)	6.142	3.004	0.593
$^1A''(27a'\rightarrow 22a'')$	−472.4092	399	4.751 (4.750)	6.879	2.538	0.480
$^1A'(21a''\rightarrow 22a'')$	−472.3824	451	5.283 (5.276)	7.608	2.976	0.267
$^3A''(21a''\rightarrow 28a')$	−472.4904	355	3.136	4.669	1.824	
$^3A'(27a'\rightarrow 28a')$	−472.4867	364	3.210	4.770	3.782	
$^3A''(27a'\rightarrow 22a'')$	−472.4638	355	3.665	5.393	3.394	
$^3A'(21a''\rightarrow 22a'')$	−472.4375	364	4.188	6.109	2.358	

[a] Calculated from $f = (\frac{2}{3})\Delta E|R|^2$, where ΔE and R are the calculated transition energy and transition moment, respectively, in atomic units. [b] Scaled transition energies calculated using eq 6 are given, with observed experimental energies[2] given immediately below in parentheses.
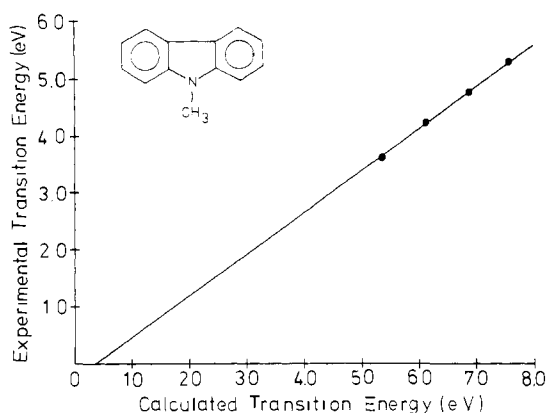

Figure 2. A plot of experimental[2] vs. calculated (CI) transition energies for singlet states in *N*-methylcarbazole. The solid line is calculated for eq 6 in the text, and the filled circles are experimentally determined points.

Figure 2, and scaled transition energies (with comparison to experimental values[2]) are given in Table III.

Linear relationships such as seen in eq 6 have now been observed for several molecules when the molecular fragment basis has been used in CI calculations as described here, including carbazole,[4] *N*-methylcarbazole (current study), pyrazine,[10] porphine,[11] magnesium porphine,[11] chlorin,[12] and magnesium chlorin.[12] Thus far, similar slopes are obtained for all molecules (0.6–0.7), and the cases examined thus far include both $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions. Of course, it is not expected that linear relationships such as these will be applicable to states where substantial Rydberg or ionic character is present.[13] However, for large molecular systems, such as discussed here, where a substantial number of low-lying valence states is expected, and about which considerable uncertainty typically exists concerning their relative location and description, it is anticipated that the procedure described here may be quite valuable. This value is emphasized further by the fact that, for most large molecular systems, more extensive CI studies using larger basis sets will not be computationally feasible.

The high values of the transition energies calculated in this study may be attributed to the nature of the CI calculations and/or the limitations of the basis set. Only 14 orbitals were allowed variable occupancy in the CI (eight filled and six unfilled), so that the CI may have been limited by the exclusion of an important MO. It might be noted that, in the earlier

carbazole studies,[4] excitations from σ-type MOs were found to be unimportant for the description of low-lying singlet and triplet states. Hence, only excitations from π-type MOs were considered in the *N*-methylcarbazole CI studies. The CI studies also indicated that the higher lying unfilled and lower lying filled orbitals made only small contributions to the states studied and, thus, it is unlikely that the CI was limited enough to cause the observed high values. A similar overestimation of the transition energies was encountered in the calculation on carbazole,[4] and was attributed to the nature of the basis set. It thus is also likely that the basis set was the cause of the high values reported in this study. However, the basis set apparently has sufficient flexibility to provide an excellent description of the relative ordering and spacing of the low-lying states.
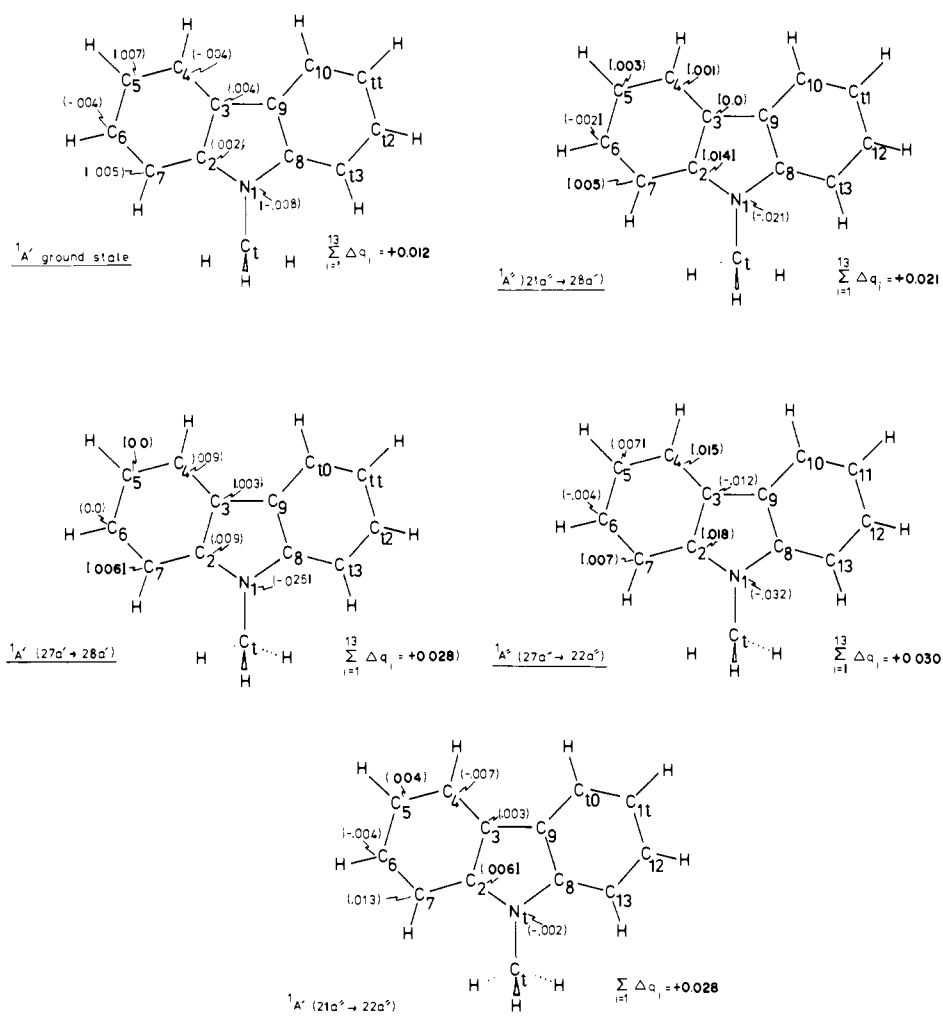
Table IV also shows calculated[4] and experimental[1,2] transition energies for carbazole and the corresponding red shifts which were calculated and experimentally observed on N-methylation of the carbazole chromophore. It should be noted that the two sets of experimental data are not from the same study. The values for carbazole are the results of photoselection experiments in a nonpolar solvent (a 7:3 ratio of 3-methylpentane to isopentane),[1] while those for *N*-methylcarbazole are from an ultraviolet absorption spectrum in heptane.[2] However, the experimental red shifts are seen to be well reproduced by the calculations, especially in view of the necessity of comparing two different experimental studies.

Bond orders and population analyses were also carried out on the σ and π systems of the ground and excited states of the molecule, to determine the degree and nature of charge redistribution upon alkylation. Table V gives the bond orders and populations for the π system. The σ system remained essentially unchanged from carbazole, and hence the σ bond orders and orbital populations have not been repeated here. Comparing the π-bond orders and orbital populations of the current study with those previously calculated for carbazole,[4] some charge redistribution is observed, and is discussed below.

It has been reported previously that a methyl substituent on a conjugated system need not be electron donating, and in calculations on benzene and toluene, Libit and Hoffmann[14] show that substitution of a methyl group on benzene depletes electron density at the carbon to which it is attached. The methyl group does, however, donate a total of 0.019 electrons into the ring in their study,[14] and has the additional effect of polarization of the ring, enhancing electron density at the ortho and para positions and depleting electron density at the ipso[15] and meta positions. In fact, it is this polarization of the π density which is the most significant effect of alkylation on the charge distribution.

Table IV. Comparison of Calculated and Experimental Transition Energy Red Shifts from Carbazole to N-Methylcarbazole

	Calcd N-methyl CBZ, eV	Calcd CBZ, eV[4]	Calcd red shift, eV	Exptl N-methyl CBZ, eV[2]	Exptl CBZ, eV[1]	Exptl red shift, eV
$^1A'$(ground state)						
$^1A_1$						
$^1A'$(27a'→28a')						
$^1A_1$(4b$_1$→5b$_1$)	5.358	5.497	0.139	3.626	3.752	0.126
$^1A''$(21a''→28a')						
$^1B_2$(3a$_2$→5b$_1$)	6.142	6.204	0.062	4.232	4.267	0.035
$^1A''$(27a'→22a'')						
$^1B_2$(4b$_1$→4a$_2$)	6.879	7.037	0.158	4.750	4.866	0.116
$^1A'$(21a''→22a'')						
$^1A_1$(3a$_2$→4a$_2$)	7.608	7.679	0.071	5.276		
$^3A''$(21a''→28a')						
$^3B_2$(3a$_2$→5b$_1$)	4.669	4.672	0.003		3.05	
$^3A'$(27a'→28a')						
$^3A_1$(4b$_1$→5b$_1$)	4.770	4.895	0.125			
$^3A''$(27a'→22a'')						
$^3B_2$(4b$_1$→4a$_2$)	5.393	5.434	0.041			
$^3A'$(21a''→22a'')						
$^3A'$(3a$_2$→4a$_2$)	6.109	6.171	0.062			

Figure 3. Changes in π-electron density for low-lying singlet states of N-methylcarbazole, compared to carbazole. Δq_i represents the change in π-orbital population at atom i in N-methylcarbazole compared to carbazole. A negative number means that a decrease in population occurred upon methylation for the particular state indicated.

The same type of substitution effects reported by Libit and Hoffmann[14] for benzene and toluene were observed in the current studies on N-methylcarbazole. In particular, the nitrogen atom showed depleted density in every electronic state (see Table V), and there was an accompanying polarization of the ring system in each state. Also, a net "donation" of electrons into the ring system from the methyl substituent occurred to varying degrees in each electronic state. Figure 3

Table V. π Bond Orders and Orbital Populations for Symmetrically Orthogonalized Orbitals in Various Electronic States of N-Methylcarbazole[a]

	N_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
N_1	1.619[b]								
	−0.192[c]								
	−0.110[d]								
	−0.190[e]								
	−0.027[f]								
	−0.025[g]								
	−0.169[h]								
	−0.003[i]								
	−0.139[j]								
C_2	0.452	0.981						0.008	
	0.025	0.039						0.029	
	0.017	0.026						0.020	
	0.049	0.019						0.043	
	0.010	0.015						0.007	
	0.003	−0.071						−0.088	
	0.016	0.098						0.070	
	0.446	−0.053						−0.071	
	0.045	0.064						0.085	
C_3	0.188	0.538	1.028					0.037	0.394
	−0.145	−0.081	−0.008					0.026	0.056
	−0.057	−0.101	−0.067					0.002	0.102
	−0.115	−0.051	0.001					0.039	0.050
	−0.017	−0.082	−0.097					−0.008	0.057
	−0.015	−0.127	−0.008					0.019	0.156
	−0.134	−0.031	−0.086					0.029	−0.065
	−0.018	−0.116	−0.024					−0.015	0.197
	−0.064	−0.029	−0.038					0.009	−0.013
C_4		0.048	0.611	1.038					
		0.022	−0.067	0.058					
		0.080	−0.097	0.075					
		0.051	−0.074	0.115					
		0.068	−0.089	0.081					
		−0.040	−0.144	0.081					
		−0.012	−0.004	0.059					
		−0.043	−0.206	0.036					
		−0.035	0.017	0.089					
C_5		0.254	0.064	0.664	1.036				
		−0.058	−0.033	−0.084	−0.075				
		−0.162	−0.039	−0.060	0.011				
		−0.057	−0.015	−0.097	−0.143				
		−0.162	−0.404	−0.060	0.030				
		−0.099	−0.033	−0.010	−0.038				
		−0.143	−0.006	−0.144	−0.022				
		−0.039	−0.053	0.027	−0.027				
		−0.175	−0.032	−0.198	−0.048				
C_6		0.027	0.274	0.001	0.630	0.992			
		0.025	−0.129	0.086	−0.021	0.080			
		0.057	−0.126	0.045	−0.066	−0.078			
		0.025	−0.106	0.146	0.023	0.132			
		0.063	−0.144	0.053	−0.071	−0.119			
		0.035	−0.194	0.052	−0.070	−0.010			
		−0.020	−0.059	0.022	−0.025	−0.008			
		0.001	−0.226	0.011	−0.051	−0.014			
		−0.025	−0.024	0.042	−0.010	0.003			
C_7		0.588	0.069	0.296	0.060	0.661	1.122		
		−0.002	0.039	−0.173	−0.042	−0.109	0.010		
		−0.089	−0.041	−0.152	0.092	−0.059	0.094		
		−0.033	0.042	−0.180	−0.001	−0.113	−0.024		
		−0.109	0.004	−0.126	0.116	−0.043	0.104		
		−0.008	−0.038	−0.120	0.007	−0.091	0.062		
		−0.138	−0.034	−0.144	0.015	−0.010	0.051		
		0.063	−0.043	−0.156	0.020	−0.181	0.079		
		−0.169	−0.051	−0.179	−0.018	0.003	0.003		

[a] Actual values are given for the ground state, while 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 in electron density in going to the excited state. Diagonal and off-diagonal elements correspond to orbital populations and bond orders, respectively. [b] ^{1}A′(ground state). [c] ^{1}A′(27a′→28a′). [d] ^{1}A′(21a″→22a″). [e] ^{3}A′-(27a′→28a′). [f] ^{3}A′(21a″→22a″). [g] ^{1}A″(21a″→28a′). [h] ^{1}A″(27a′→22a″). [i] ^{3}A″(21a″→28a′). [j] ^{3}A″(27a′→22a″).
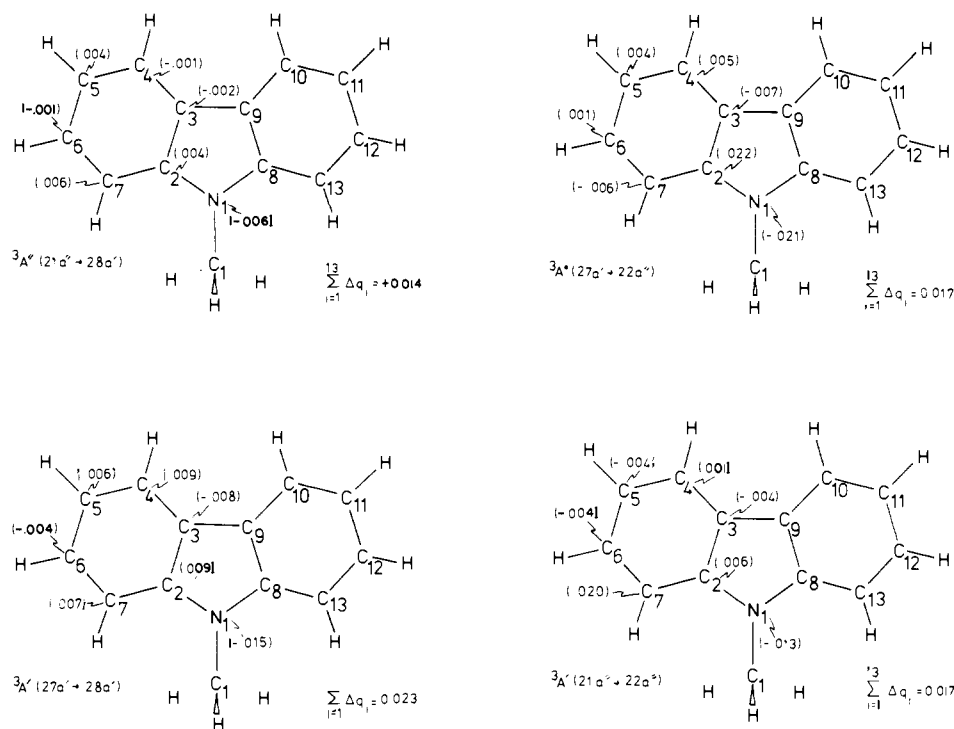
Figure 4. Changes in π-electron density for low-lying triplet states of N-methylcarbazole, compared to carbazole. Δq represents the change in π-orbital population at atom i in N-methylcarbazole compared to carbazole. A negative number means that a decrease in population occurred upon methylation for the particular state indicated.

(singlet states) and Figure 4 (triplet states) show these changes in π electronic density at each nonhydrogen nucleus in the ground and excited states when a methyl group is substituted for hydrogen on the nitrogen of carbazole.

Comparison of individual MOs in N-methylcarbazole to corresponding MOs in carbazole[4] shows that the nature of the MOs is almost identical in each case. For example, as in carbazole, two filled π orbitals (25a′ and 27a′) and two π virtuals (29a′ and 30a′) show substantial electron density or "hole" density at the nitrogen, and can be classified loosely as π-type "lone pair" orbitals ("π_n" or "π_n* " for filled or unfilled, respectively). Next, as in carbazole, the 21a″ filled MO exhibits essentially no electron density on the nitrogen, and can be termed a π orbital delocalized over the ring system. The same is true of the 28a′ and 22a′ unfilled MOs, which may be termed π* orbitals.

Using these designations for the MOs, it is then possible to classify the electronic states of the molecule according to the orbital promotion describing the dominant configuration of the electronic state. For example, the ^{1,3}A′(27a′→28a′) and ^{1,3}A″(27a″→22a″) states may be classified as π_n→π* states, and ^{1,3}A″(21a″→28a′) and ^{1,3}A′(21a″→22a″) may be classified as π→π* states.

The changes in charge distribution just described can also be seen to provide insight into the changes in dipole moment that are observed. For example, the substantial increase in dipole moment in the ^{1}A′(27a′→28a′) state can be correlated directly with the substantial shift in density from the nitrogen nucleus to the π system as a result of the 27a′→28a′ excitation. The other excitation to the 28a′ MO, i.e., forming the ^{1}A″-(21a″→28a′) state, would be expected to show a lesser change in dipole moment, since the 21a″ MO does not have density at the nitrogen. This trend is in fact observed. Similar comments apply to the four triplet states.

It is also of interest to examine whether the red shift in absorption frequency for selected states that is observed upon methylation of carbazole can be rationalized from the available data. Qualitatively, the addition of a methyl group can be

considered to provide one π orbital and two electrons (for the methyl group conformation that has been studied) that can, at least in principle, interact with the existing π system in carbazole. This interaction could be one involving charge redistribution and/or energetics, and both aspects need to be considered.

Considering charge redistribution possibilities first, we see from Figure 3 (for the singlet states) that the total charge transferred to the macrocycle π system (expressed as $\Sigma_i q_i$) is not large (∼0.02–0.03 electron), and does not vary greatly among the four excited singlet states examined. Also, except for migration of charge away from nitrogen, the changes in net charge on various atoms are generally small. Hence, while there may be subtle spectral effects that can be ascribed to charge redistribution, other effects can be expected to be more substantial contributors to the observed red shifts.

Another property to be considered, which is obviously related to the effect of adding a methyl group and the charge redistribution that occurs, is the energetic effect on molecular orbital energies. From Table I, we see that, for the four MOs (the two highest occupied and the lowest unoccupied MOs) that are the main contributors to the states examined here, there is only one that is affected substantially by methylation of carbazole. In particular, the 27a′(π_n) MO in N-methylcarbazole is raised in energy by +0.0065 hartree (∼0.18 eV) compared to carbazole, while changes in the other three MOs are an order of magnitude smaller. While MO energy differences are not the sole contributors to excitation energies, they are one of the important factors. Hence, it would be expected that, for those states in which excitations from the 27a′ MO are important contributors to the CI wave function, a red shift might be expected. Examination of Tables II and IV shows this to be the case.

Thus, the main effect of methylation of carbazole on spectral properties is seen to be selective destabilization of the highest occupied π_n MO, which results in a red shift of absorption lines that are described primarily by excitations from the 27a′(π_n) MO.

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The Vinylidene–Acetylene Rearrangement. A Self-Consistent Electron Pairs Study of a Model Unimolecular Reaction

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Abstract: As a model for a potentially important pathway for the disappearance of carbenes and nitrenes, the unimolecular rearrangement of vinylidene into acetylene has been studied using the self-consistent electron pairs (SCEP) method. SCEP provides an accurate accounting of correlation effects by yielding a wave function equivalent to a configuration expansion including all singly and doubly substituted configurations relative to one reference determinant. A double-ζ (DZ) basis set of 24 contracted Gaussian functions was used to determine the equilibrium structures of vinylidene and acetylene and the transition state for the rearrangement pathway. A larger basis set of 42 functions including polarization (DZ + P) functions was then used to determine the energetics of the reaction, and the difference in energy between vinylidene and acetylene was found to be 40 kcal/mol. Polarization functions and the inclusion of correlation effects contribute about equally to lowering the rearrangement barrier from the DZ-SCF result of 26 kcal/mol to 8.6 kcal/mol (DZ + P SCEP). Other electronic states of vinylidene were investigated, and the $^3B_2$ ($5a_1 \rightarrow 2b_2$) state was found to be the lowest excited state with a vertical excitation energy of 11 500 cm^{-1}. Finally, SCEP calculations were performed on Li$^+$–C$_2$H$_2$ in an attempt to consider rearrangement through electrostatic interaction with a positive center.
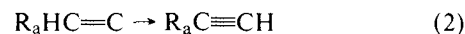
Introduction

Theoretical chemistry is in principle well suited to the study of organic free radicals and other highly reactive species. First of all, such species, while essential to any fundamental understanding or organic chemistry, tend to be very elusive in the laboratory. Theoretical methods, although often imprecise, are as well suited to evanescent species as to ordinary stable molecules. Equally important, the most intriguing unstable intermediates are usually rather small molecules, making them frequently susceptible to the more reliable of theoretical methods.[1]
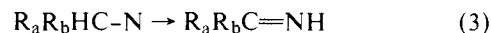
Carbenes[2] and nitrenes[3] are certainly two of the most interesting classes of organic radicals. In the present paper we consider a type of unimolecular reaction which often leads to the disappearance of carbenes and nitrenes. This is the 1,2 hydrogen shift reaction,[4] which for carbenes takes the form

$$R_aR_bHC-CR_c \rightarrow R_aR_bC=CR_cH \qquad (1)$$

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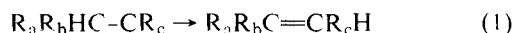
and for vinylidenes

$$R_aHC=C \rightarrow R_aC\equiv CH \qquad (2)$$

The reaction analogous to eq 1 for nitrenes is

$$R_aR_bHC-N \rightarrow R_aR_bC=NH \qquad (3)$$

The existence *at all* of the species on the left-hand side of eq 1–3 of course requires some barrier between reactants and products. Otherwise these types of carbenes and nitrenes would immediately convert to the more thermodynamically stable products on the right-hand side. However, the magnitude of these barriers (or activation energies) is of crucial importance, as it provides a measure of just how unstable these species are. Since one of the primary goals of much current experimental research is to elucidate reaction pathways, it is also important to have firm theoretical predictions of the transition state geometries for reactions such as 1–3.

The simplest prototypes for eq 1–3 are eq 4–6.

$$CH_3CH \rightarrow CH_2=CH_2 \qquad (4)$$