

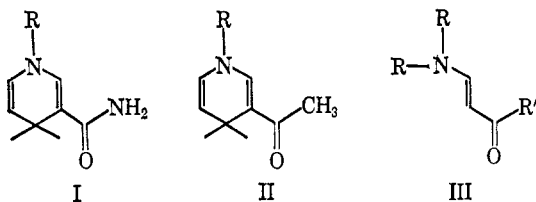
# The Electronic Structures of the Dihyronicotinamides and Related Materials

E. M. Evleth<sup>1</sup>

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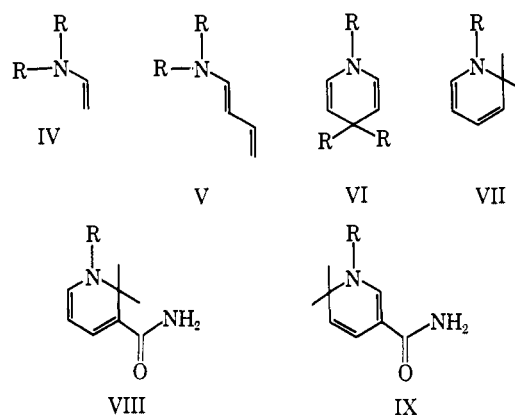
**Abstract:** The electronic structures of 1,2-, 1,4-, and 1,6-dihyronicotinamide, 1,2- and 1,4-dihydropyridine, pyrrole, 3-acetyl-1,4-dihydropyridine, aminoethylene, aminobutadiene, and aminobutadienone were estimated using the semiempirical molecular orbital configuration interaction method of Pariser, Parr, and Pople. The spectral features of these materials were compared with those calculated. The effect of the inclusion of doubly excited configurations and nonneighbor resonance parameters was investigated. It was found that the inclusion of doubly excited configurations is computationally significant. Comparison of the ground- and excited-state electron densities in 1,4-dihyronicotinamide indicated that the qualitative arguments of resonance theory have no application to spectral interpretation of this material. It was found that simple charge transfer–exciton arguments can rationalize the intensity characteristics of the materials investigated.

The primary object of this paper is to interpret the spectral properties of the dihyronicotinamides and related compounds. This study was prompted by our previous work in the spectroscopy and chemistry of the dihydropyridines.<sup>2,3</sup> Of particular interest are the known spectral features of the 1,4-dihyronicotinamides (I), the 3-acetyl-1,4-dihydropyridines (II),<sup>4–7</sup> and the 1-aminobutadienones (III).<sup>4,8–11</sup> Compounds with structures I and II exhibit electronic transitions in the 340–380-m $\mu$  region with moderate intensities ( $\epsilon$



$\leq 10,000$ ). In contrast compounds of structures III exhibit strong maxima ( $\epsilon$  20,000–30,000) in the 300-m $\mu$  region. The question arises as to why II, which conceptually has the same NC=CC=O grouping as III, exhibits a much lower intensity in the lowest electronic transition. To help with spectral interpretation and parameterization of the semiempirical molecular orbital method employed here we also have decided to investigate the electronic structures of aminoethylene (IV), 1-aminobutadiene (V), 1,4- and 1,2-dihydropyridines (VI and VII), and the 1,2- and 1,6-dihyronicotinamides (VIII and IX). In addition we will attempt to give a qualitative charge transfer perturbation inter-

pretation of the systematics of the spectral properties of compounds I–IX.



## Method of Calculation

The usual computational methods for estimating the electronic spectral features of polyatomic molecules involve the use of perturbation methods,<sup>12,13</sup> free-electron calculations,<sup>14</sup> or semiempirical molecular orbital calculations.<sup>15</sup> Of the techniques available, the self-consistent field configuration interaction (SCF-CI) methods of Pople<sup>16,17</sup> and Pariser and Parr<sup>18</sup> are the most adaptable to the computationally rapid estimation of the electronic structures of the ground and excited states of  $\pi$ -electron systems. The principal problem with the application of these methods lies in their semiempirical character, requiring parameter assignments of the various coulomb, exchange (resonance), and electron repulsion terms. This problem is well discussed in the literature<sup>19,20</sup> and no attempt is made here to

(1) Address inquiries to: Division of Natural Sciences, University of California, Santa Cruz, Calif. 95060.

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resolve the theoretical problems surrounding parameterization.

The Pariser-Parr-Pople technique is applied here in a standard fashion. The approximate self-consistent field equations of Pople are used.<sup>21</sup> Penetration integrals are neglected. Two two-centered electron repulsion integrals are computed by the method of Parr<sup>22</sup> using the Slater  $Z$  values shown in Table I. The valence state ionization potentials, one-centered electron repulsion integrals for carbon, nitrogen, and oxygen, are also listed in Table I.

Table I

Atom	Set	$I_p$ , ev	$\langle 11 11 \rangle$ , ev	$Z$
C	1	11.22	10.53	3.25
N	1	28.16	15.92	4.25
	2	25.00	15.00	4.00
O	1	17.17	15.30	4.55
	2	16.00	14.00	4.25

The calculations were tested, in certain occasions, with two different sets of parameters for nitrogen and oxygen (1 and 2). Calculations done here used the Chalvet-Bessis SCF-CI program.<sup>23</sup> This program normally uses set 1. The additional option of using any other set may be contained with the input data. Set 2 was selected on an arbitrary manner without recourse to any possible theoretical relationships<sup>24</sup> between  $I_p$ ,  $\langle 11|11 \rangle$ , and  $Z$ .

In addition to the simple parameter problem is the question of the inclusion of a resonance parameter for nonneighbor atoms. In molecules with nonstrained bond angles an individual atom may have a number of near neighbors at distances between 2 and 3 Å. Assignment of resonance parameters to "bonds" at distances other than the standard 1.3–1.5-Å region is, at very least quantitatively difficult. We have selected values of  $-0.25$  eV for bonds in the 2.30-Å region,  $-0.10$  eV in the 2.8-Å region, and 0 over 3 Å. The use of nonbonded resonance parameters is designated in the tables presenting the computed data.

The assignment of the bond resonance parameter presents a slightly different problem. Calibration of molecular orbital calculations using ethylene and benzene as standards for values of the resonance parameter in the regions of 1.34 and 1.40 Å (approximately  $-2.70$  and  $-2.40$  eV, respectively) is theoretically justifiable<sup>18,25,26</sup> for spectral correlations. Use of these parameters on larger molecules generally leads to predicted transitions at higher energies than the experimental values.<sup>27,28</sup> Nishimoto and Forster<sup>29,30</sup> have

introduced both the variation of the resonance parameter with the SCF cycling procedure (justified assuming a bond distance–bond order–resonance integral relationship) and different fundamental resonance parameters for different ring systems. There has appeared in the literature no fundamental justification for this latter procedure. It may be suspected that the larger ring systems and  $\sigma$ -bond polarizability result in a change in coulomb and resonance core and electron repulsion terms.<sup>31</sup>

The results obtained here indicate resonance parameters for C=C and C–C at  $-2.40$  and  $-2.20$  eV, respectively. The C–N resonance parameter in the area of  $-2.45$  eV also proved satisfactory. This value is higher than used for ground-state calculations<sup>32</sup> ( $-1.40$  eV) but in the range of some other spectral calculations<sup>12,24,33–36</sup> ( $-1.80$  to  $-3.00$  eV).

The final problem in the application of the SCF-CI method involves the number and type of excited states used in the construction of the configuration interaction energy matrix. The inclusion of configuration interaction is particularly important when there is a computed degeneracy in the excited states of the same symmetry type. This occurs in upper excited states of all alternate hydrocarbons computed according to conditions under which the pairing rule is obeyed.<sup>27,37</sup> Under such conditions all transitions resulting from the promotion of a single electron from occupied orbital  $i$  to an unoccupied orbital  $j'$  are degenerate with promotions  $j$  to  $i'$ . This degeneracy breaks down when the conditions of the pairing rule are not obeyed.<sup>37</sup> In this condition or in any molecular orbital calculation on a large system there will be a high density of upper excited states having energies within a range of several electron volts. These upper excited states will strongly interact according to the usual symmetry conditions to yield configurational wave functions having significant contributions from a number of basis functions. Often, however, either first or second lowest energy configurational wave function will have a high contribution (90% or more) of the function resulting from the promotion of a single electron from the highest occupied to the lowest unoccupied molecular orbital ( $1 \rightarrow 1'$ ). Under conditions where configuration interaction plays little importance it is possible that less theoretically exact methods (Hückel, perturbation techniques) may produce adequate spectral correlations for structurally related materials.<sup>38</sup>

It is presently a computational necessity to limit the number of excited states used in the configurational energy matrix of a large polyatomic molecule. The usual practice has been to include only a limited number

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of singly excited states, neglecting all doubly or higher excited states. Murrell and McEwen<sup>39</sup> and Donath<sup>40</sup> have shown that the inclusion of doubly excited configurations was of computational importance in the higher excited states of benzene. Allinger and Tai<sup>41</sup> showed that the second excited state of *cis*-butadiene is lowered significantly by the inclusion of doubly excited configurations. Recently, we have shown<sup>42</sup> that the inclusion of doubly excited configurations is also significant in calculations on pyrrole and 1,4-dihydropyridine. We have therefore done a number of calculations incorporating doubly excited configurations. Again, because of computational necessity, we have included a maximum of ten doubly excited configurations, these resulting from the promotions of two electrons from either of the two highest occupied to either of the two lowest unoccupied molecular orbitals.<sup>41</sup> The number and type of configurations used are so designated in tables reporting the results of the calculations.

The geometries were assigned in the following manner. All formal C=C bonds are given values of 1.35 Å, all C—C bonds are 1.45 Å, all C—N bonds are 1.39 Å, and all C=O are 1.24 Å. All nonring geometries were computed using the bond angles of 120°. The geometries of the cyclic compounds are assumed to be planar using the bond distances as above. In addition the C—C (sp<sup>2</sup>–sp<sup>3</sup>) bond was set at 1.50 Å. This requires the geometry of 1,4-dihydropyridine to be such that the angles to the olefinic bonds to be other than 120°. The actual geometry was estimated by assuming approximately equal distortion for the internal angles of the ring system. The result of this being that distance between the terminal carbon atoms in VI to be slightly greater than between the carbon atoms bonded to the nitrogen. The slightly distorted geometry is not particularly important, yielding only minor changes in the computed energies, dipole moments, and transition moments.

No calculations of the positions of the triplet states were done. No experimental information of such states are available to test the accuracy of such calculations.

Because of the difficulty in establishing the positions of the 0–0 transitions, all calculations will be compared with positions of the Franck–Condon maxima. In addition, literature spectra will generally be referred to without reference to the solvent used. The solvent effects may be fairly large in some of the compounds investigated but the matter of interest here is the approximate positions of the transitions.

## Results and Discussion

The computed spectral features of structures I–IX are shown in Tables II–IX. Pyrrole has also been added because of its structural relationship with 1,4-dihydropyridine. A number of calculations are reported using various parameter values.

**Aminoethylene (IV).** An examination of the reported data<sup>4,8,43,44</sup> on the aminoethylenes (IV) or enamines reveal that they absorb in the region of 230 m $\mu$  with

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moderate intensities ( $\epsilon \leq 10,000$ ), corresponding to 5.4 eV and an approximate oscillator strength of 0.2.<sup>45</sup> This transition is strongly shifted from the 160-m $\mu$  band (7.6 eV) in ethylene.<sup>46</sup> The approximate position of the ethylene band can be computed using a  $\beta_{C=C}$  of  $-2.65$  eV. As shown in Table II, calculation no. 3, the com-

**Table II.** Variation of the Computed Lowest Electronic Transition of Aminoethylene with the Resonance Parameters

Calculation no. <sup>a</sup>	Singly excited configurations <sup>b</sup>		Singly and doubly excited configurations <sup>b</sup>		Resonance parameters		
	$E_{max}$	$f$	$E_{max}$	$f$	1-2	2-3	1-3
1	5.72	0.55	5.89	0.56	-2.40	-2.45	0
2	5.39	0.50	5.57	0.51	-2.40	-2.45	-0.25
3	6.10	0.59	6.24	0.59	-2.65	-2.45	0
4			5.58	0.53	-2.20	-2.45	0
5			5.55	0.53	-2.20	-2.65	0
6			5.24	0.48	-2.00	-2.45	0
7			5.20	0.48	-2.00	-2.65	0
8 <sup>c</sup>	5.33	0.57			-2.40	-2.45	0

<sup>a</sup> Atoms number in the following manner, C(1)–C(2)–N(3), all energy values given in electron volts;  $E_{max}$  = transition energy;  $f$  = oscillator strength. <sup>b</sup> Number of configurations used: two singly, two doubly excited. <sup>c</sup> Parameter set 2 for nitrogen.

puted value of the lowest transition for aminoethylene is 6.10–6.24 eV, using  $\beta_{C=C} = -2.65$  eV and  $\beta_{C=N} = -2.45$  eV and set 1 for the coulomb parameters. The calculations predict, as expected, that the bond order of the C=C and C—N bonds would decrease and increase, respectively, in the excited state as compared to the ground state. First-order perturbation theory predicts that a lowering of the transition energy will occur if resonance parameter for the C=C and C—N bonds are made, respectively, less and more negative. However, it was observed that the bond-order change was much larger for the C=C bond than the C—N bond and thus the spectral transitions would be much more sensitive to changes in the former rather than the latter quantity. A progressive drop of  $\beta_{C=C}$  from a value of  $-2.65$  eV (calculation no. 3) to  $-2.40$  (calculation no. 1) to  $-2.20$  (calculation no. 4) to  $-2.00$  (calculation no. 6) generated a drop from 6.24 to 5.24 eV in the transition energy. The differential,  $\partial E/\partial \beta_{C=C}$  has an approximate value of  $-1.5$ . The corresponding value of  $\partial E/\partial \beta_{C=N}$  as obtained by comparing calculations 4 with 5 or 6 with 7 is approximately  $+0.5$ . Thus changes in the computed transition energy of IV are approximately three times more sensitive to changes in the C=C than the C—N resonance parameter. However, there are alternative ways of adjusting the calculation of the transition energy. First, the inclusion of doubly excited configurations (only two possible) produced a computed increase in the transition energy. However, the inclusion of a nonneighbor resonance parameter between atoms 1 and 3 plus a change in the C=C parameter yield (calculation no. 2) a transition energy near the experimental value. However, so did a change in the nitrogen coulomb and  $\langle 11|11 \rangle$  parameter (calculation no. 8).

(45) C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 108. The oscillator strength can be estimated for an isolated electronic transition from the extinction coefficient. All oscillator strengths estimated here assume a band width of 5000 cm<sup>-1</sup>;  $f_{est} = 4.32 \times 10^{-9} \times 5000 \times 1.06 \times \epsilon_{max}$ .

(46) See ref 21, p 51, for a discussion of the spectrum of ethylene.

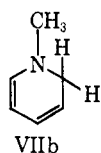
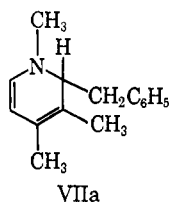
Table III. Variation of the Computed Two Lowest Electronic Transitions of *trans,trans*-Aminobutadiene with the Resonance Parameters

Calculation no. <sup>a</sup>	Singly excited configurations <sup>b</sup>		Singly and doubly excited configurations <sup>b</sup>		Resonance parameters			
	$E_{\max}$	$f$	$E_{\max}$	$f$	1-2	2-3	4-5	1-3
					3-4	2-4	3-5	
9			4.59	0.006	-2.40	-2.20	-2.45	0
10	4.32	0.91	4.99	1.01	-2.40	-2.20	-2.45	-0.25
	5.38	0.004	3.89	0.035				
11 <sup>c</sup>	4.27	1.00	4.64	0.90	-2.40	-2.20	-2.45	0
	5.78	0.001						
12			4.14	0.008	-2.20	-2.00	-2.65	0
			4.78	0.93				

<sup>a</sup> Atoms numbered in the following manner, C(1)-C(2)-C(3)-C(4)-N(5); all energy values given in electron volts;  $E_{\max}$  = transition energy,  $f$  = oscillator strength. <sup>b</sup> Number of configurations used: six singly, ten doubly excited. <sup>c</sup> Parameter set 2.

**1-Amino-1,3-butadiene (V).** The absorption spectrum of presumably all *trans*-N,N-diethyl-1-amino-1,3-butadiene<sup>8</sup> shows a broad band with a maxima in the 280-m $\mu$  region (4.4 eV) with a strong intensity ( $\epsilon$  23,500,  $f = 0.5$ ). This position is strongly shifted from the values in various *trans*-1,3-dienes, 217-228 m $\mu$  ( $\epsilon$  17,000-27,000),<sup>47</sup> *cis*-Dienes have weaker ( $\epsilon < 7000$ ) and lower energy transitions than the *trans*-dienes.<sup>48,49</sup> Table III contains four calculations done on V. In particular, calculation 10 contains a direct comparison to calculation 2. Only two computed transitions are reported here since the others are considerably higher computed energies. In calculation 10, the inclusion of doubly excited configurations generates a computed shift to higher energies of the strong (principally  $1 \rightarrow 1'$ ) transition from 4.32 to 4.64 eV while the weak 5.38-eV transition shifts to 3.89 eV. Since there is no experimental information on the position of the weak transition no judgment can be made on the adequacy of either parts of calculation 10.

**1,2-Dihydropyridine (VI).** Recently Fry has reported<sup>50</sup> the spectra of several 1,2-dihydropyridines, VIIa and VIIb. Two bands are reported for VIIa, 325



m $\mu$  (3.8 eV) and 275 m $\mu$  (4.5 eV), both having weak intensities ( $\epsilon$  4100 and 3800, respectively, corresponding to oscillator strengths of about 0.1). Only one band is reported for VIIb at 335 m $\mu$  ( $\epsilon$  2100). Table IV lists the calculations done on this material. This structure corresponds to a *cis-cis* configuration of the aminobutadiene V. As with V the incorporation of doubly excited configurations strongly affects the computed position of the weak transition in 1,2-dihydropyridine. Only the incorporation of doubly excited configurations brings both transitions near the experimental values of 3.8 and 4.4 eV. It should be noted that the presence of a phenyl group in VIIa should produce only a weak

band ( $\epsilon < 300$ ) in the 250-m $\mu$  region<sup>51-53</sup> unless there exists a conjugated impurity. The computed oscillator strengths of these transitions do not correspond to the experimental values.

**1,4-Dihydropyridine.** The ultraviolet absorption spectrum of 1,4,4-trimethyl-1,4-dihydropyridine<sup>54,55</sup> exhibits a weak transition at 270 m $\mu$  (4.6 eV,  $\epsilon$  3200,  $f = 0.07$ ) and a stronger transition at 231 m $\mu$  (5.4 eV,  $\epsilon$  7500,  $f = 0.17$ ). The spectrum of 1,4-dihydropyridine<sup>55</sup> is reported as a weak band ( $\epsilon$  1300) at 278 m $\mu$ . The calculations on this electronic system is given in Table V.<sup>42</sup> Calculations 18 and 19 give the best comparison with experiment. The inclusion of doubly excited configurations strongly affects the oscillator strength of the second electronic transition.

**Pyrrrole.** Pyrrrole is the only aromatic system under consideration. A number of SCF calculations have been done on this system.<sup>24,33,34,36,42,56</sup> We have done approximately 40 SCF-CI calculations on this structure using a wide variety of parameters, including a comparison of the Mataga-Nishimoto electron repulsion method with the Parr method. It is stated that the experimental transitions occur at 5.9, 6.8, and 7.2 eV with increasing intensities.<sup>57-59</sup> Configuration interaction effects are important in pyrrrole.<sup>42</sup> As demonstrated in Table VI the incorporation of doubly excited configurations leads to the prediction that the lowest excited state should have  $^1A_1$  symmetry. The reverse is predicted if only singly excited configurations are used. Brown and Heffernan<sup>24</sup> predict a near degeneracy of these transitions, Dahl and Hansen<sup>33</sup> (using the Mataga-Nishimoto repulsion parameters) predict the  $^1A_1$  excited state should have the lowest energy. Previous workers<sup>33,36</sup> have placed a great deal of emphasis on matching the computed transition energies and intensity sequence with the experimental values. The actual symmetries of the excited states are not known, nor are the integrated intensities. The question of the applicability of  $\pi$ -electron semiempirical calculations in the region of possible Rydberg transitions also

(51) The unconjugated "weakly" substituted benzene ring will exhibit a weak transition in the 250-m $\mu$  region corresponding to the slightly perturbed  $^1L_b \leftarrow ^1A$  transition in benzene.<sup>52,53</sup>

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**Table IV.** Variation of the Computed Two Lowest Electronic Transitions of 1,2-Dihydropyridine with the Resonance Parameters

Calculation no.	Singly excited configurations		Singly and doubly excited configurations		Resonance parameters <sup>b</sup>				
	$E_{\max}$	$f^a$	$E_{\max}$	$f$	1-2 3-4	2-3	4-5	1-3 2-4 3-5 1-5	1-4 2-5
13	4.12	0.30	4.40	0.30	-2.40	-2.20	-2.45	0	0
	6.16	0.01	4.63	0.003					
14	4.06	0.30	4.33	0.28	-2.40	-2.20	-2.45	-0.25	-0.10
	5.77	0.09	4.43	0.04					
15 <sup>c</sup>	3.82	0.27			-2.40	-2.20	-2.45	0	0
	5.72	0.022							
16			4.18	0.06	-2.20	-2.00	-2.65	0	0
			4.20	0.22					

<sup>a</sup> Atoms numbered in the following manner C(1)-C(2)-C(3)-C(4)-N(5); all energy values given in electron volts. <sup>b</sup> Number of configurations used: six singly, ten doubly excited. <sup>c</sup> Parameter set 2 for nitrogen and oxygen.

**Table V.** Variation of the Two Computed Lowest Electronic Transitions of 1,4-Dihydropyridine with the Resonance Parameters

Calculation no. <sup>a</sup>	Singly excited configurations <sup>b</sup>		Singly and doubly excited configurations <sup>c</sup>		Sym <sup>e</sup>	Resonance parameters			
	$E_{\max}$	$f$	$E_{\max}$	$f$		1-2 4-5	2-3 3-4	1-3 3-5 1-5 2-4	1-4 2-5
17	4.59	0.09	4.94	0.099	<sup>1</sup> B <sub>1</sub>	-2.65	-2.45	0	0
	6.31	0.14	5.87	0.04	<sup>1</sup> A <sub>1</sub>				
18	4.25	0.088	4.63	0.095	<sup>1</sup> B <sub>1</sub>	-2.40	-2.45	0	0
	5.98	0.108	5.24	0.017	<sup>1</sup> A <sub>1</sub>				
19	4.30	0.09	4.65	0.097	<sup>1</sup> B <sub>1</sub>	-2.40	-2.45	-0.25	-0.10
	5.61	0.13	5.07	0.026	<sup>1</sup> A <sub>1</sub>				
20			4.30	0.10	<sup>1</sup> B <sub>1</sub>	-2.20	-2.65	0	0
			4.55	0.01	<sup>1</sup> A <sub>1</sub>				
21 <sup>d</sup>	3.70	0.14				-2.40	-2.45	0	0
	5.66	0.12							

<sup>a</sup> Atoms numbered in the following manner C(Z)-C(2)-N(3)-C(4)-C(5); all energy values in electron volts. <sup>b</sup> Number of configurations used: six singly, ten doubly excited. <sup>c</sup> Sym = symmetry of the excited state. <sup>d</sup> Parameter set 2 for nitrogen.

**Table VI.** Variation of the Three Lowest Computed Electronic Transitions of Pyrrole with the Resonance Parameters

Calculation no. <sup>a</sup>	Singly excited <sup>b</sup> configurations			Singly and doubly excited configurations <sup>b</sup>			Resonance parameters		
	$E_{\max}$	$f$	Sym	$E_{\max}$	$f$	Sym	1-2 4-5	2-3 3-4	1-5
22	5.96	0.116	<sup>1</sup> B <sub>1</sub>	5.67	0.021	<sup>1</sup> A <sub>1</sub>	-2.65	-1.90	-2.45
	6.18	0.040	<sup>1</sup> A <sub>1</sub>	6.24	0.124	<sup>1</sup> B <sub>1</sub>			
	7.26	0.432	<sup>1</sup> B <sub>1</sub>	7.24	0.39	<sup>1</sup> B <sub>1</sub>			
23	5.57	0.12	<sup>1</sup> B <sub>1</sub>	5.19	0.013	<sup>1</sup> A <sub>1</sub>	-2.40	-1.90	-2.45
	5.84	0.02	<sup>1</sup> A <sub>1</sub>	5.86	0.14	<sup>1</sup> B <sub>1</sub>			
	7.02	0.46	<sup>1</sup> B <sub>1</sub>	7.09	0.40	<sup>1</sup> B <sub>1</sub>			
24	5.53	0.19	<sup>1</sup> B <sub>1</sub>				-2.40	-2.20	-2.45
	5.97	0.02	<sup>1</sup> A <sub>1</sub>						
	7.46	0.89	<sup>1</sup> B <sub>1</sub>						
25 <sup>c</sup>	5.69	0.08	<sup>1</sup> B <sub>1</sub>				-2.40	-2.20	-2.45
	5.86	0.04	<sup>1</sup> A <sub>1</sub>						
	7.25	0.07	<sup>1</sup> B <sub>1</sub>						

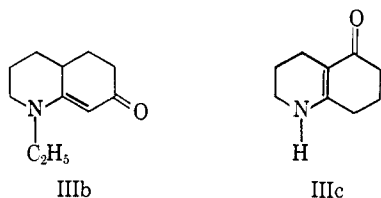
<sup>a</sup> Atoms numbered in the following manner C(1)-C(2)-N(3)-C(4)-C(5); all energy values given in electron volts,  $E_{\max}$  = transition energy,  $f$  = oscillator strength, Sym = symmetry of the excited state. <sup>b</sup> Number of configurations used: six singly, ten doubly excited. <sup>c</sup> Parameter set 2 for nitrogen.

arises. In view of the importance of doubly excited configurations demonstrated here, the sensitivity to parameter changes,<sup>60</sup> and the lack of experimental information on pyrrole we tend to view calculations on this material with some doubt. It should also be noted that the C=C and C-C resonance parameters used in calculations which most nearly matched the experimental values (no. 22) are not compatible with those used in the other calculations.

(60) We doubt whether any purpose would be served by including a larger number of calculations on pyrrole since they tend to duplicate what is already in the literature.<sup>24, 33, 38</sup>

**1-Amino-1,3-butadienone (III).** As previously mentioned the aminobutadienones (III) exhibit strong maxima in the 300-m $\mu$  region. Compound III (R = ethyl; R' = propyl) exhibits a strong transition at 307 m $\mu$  (4.1 eV,  $\epsilon$  28,000,  $f$  = 0.6) and a much weaker transition at 215 m $\mu$  (5.8 eV,  $\epsilon$  1200,  $f$  = 0.03).<sup>7</sup> The aldehyde IIIa (R = methyl, R' = H) shows a transition at 283 m $\mu$  (4.4 eV,  $\epsilon$  37,000).<sup>9</sup> The reduced hydroxyquinolines, IIIb and IIIc, have transitions at 304 m $\mu$  ( $\epsilon$  32,000) and 300 m $\mu$  ( $\epsilon$  26,000).<sup>10</sup>

Calculations on structure III are presented in Table VII. Additional coulomb and resonance parameters



for the oxygen and C=O bond were required for these calculations. The transition energies were not sensitive to changes in the value of  $\beta$  for the C=O bond from  $-2.80$  to  $-2.60$  eV. Because of the observation that the inclusion of doubly excited configurations generally raised the computed energy of the principal transition (principally  $1 \rightarrow 1'$ ) these were only included in calculation no. 26. With the maximum changes inflicted on the C=O, oxygen, and nitrogen parameters the lowest predicted transition energy was at 4.49 eV, approaching the experimental value of compound IIIa. The weak band, experimentally at 5.8 eV, was also approached by calculation no. 33. The computed  $\pi$ -dipole moments were in the region of 5–6.2 D. The experimental value of IIIa being 6.24 D.<sup>9</sup>

**Table VII.** Variation of the Two Lowest Electronic Transitions 1-Aminodienone with the Resonance and Coulomb Parameters

Calculation no. <sup>a</sup>	$E_{\max(1)}$	$f$	$E_{\max(2)}$	$f$	$\mu_{\text{calcd}}$	Parameter values <sup>b</sup>
26 <sup>c</sup>	5.26	0.77	5.74	0.06	4.99	3-4 = $-1.90$ , C=O = $-2.80$
27	5.04	0.84	7.13	0.03	5.26	3-4 = $-2.20$ , C=O = $-2.80$
28	4.90	0.82	6.62	0.05	5.18	1-3, 2-4, 3-5, = $-0.25$ + cal no. 27
29	4.78	0.86	6.80	0.05	6.17	Calcn 28 + different nitrogen parameter, set 2
30	4.53	0.84	6.25	0.06	5.55	Calcn 29 + different oxygen parameter, set 2
31	4.76	0.91	6.82	0.02	5.71	Calcn 27 + different oxygen and nitrogen parameters, set 2
32	4.72	0.93	6.68	0.02	5.88	3-4 = $-2.20$ , C=O = $-2.60$ , oxygen and nitrogen parameters, set 2
33	4.49	0.86	6.11	0.02	5.71	Calcn 32 + 1-3, 2-4, 3-5 = $-0.25$

<sup>a</sup> All energy values given in electron volts,  $E_{\max(1)}$  = first electron transition,  $E_{\max(2)}$  = second electronic transitions,  $f$  = oscillator strength,  $\mu_{\text{calcd}}$  = calculated dipole moment. <sup>b</sup> Atoms numbered in the following manner, N(1)-C(2)-C(3)-C(4)-O(5), for all calculations 1-2 =  $-2.45$  eV, 2-3 =  $-2.40$  eV. <sup>c</sup> Number of configurations used; six singly, ten doubly excited (calculation 26).

**3-Acetyl-1,4-dihydropyridine.** N-Benzyl-3-acetyl-1,4-dihydropyridine exhibits a transition of moderate intensity at 371 m $\mu$  (3.3 eV,  $\epsilon$  10,400,  $f$  = 0.2).<sup>7</sup> Calculations 37–41 all approach these values with a computed oscillator strength of approximately 0.2. A transition of moderate intensity is predicted in the 5-eV region. A sample of this material was examined and found to exhibit a weak shoulder in the 240-m $\mu$  region (5.2 eV,  $\epsilon$  4000) followed by a much stronger transition at 210 m $\mu$ , in addition to the main near-visible transition at 355 m $\mu$  (*n*-hexane)<sup>61</sup> (Table VIII).

**Table VIII.** Variation of the Two Lowest Electronic Transitions of 3-Acetyl-1,4-dihydropyridine with the Resonance and Coulomb Parameters

Calculation no. <sup>a</sup>	$E_{\max(1)}$	$f$	$E_{\max(2)}$	$f$	Parameter values <sup>b</sup>
34 <sup>c</sup>	4.23	0.20	5.15	0.006	5-6 = $-1.90$ , C=O = $-2.80$
35	3.92	0.19	5.68	0.04	5-6 = $-2.20$ , C=O = $-2.80$
36	4.02	0.19	5.40	0.05	Calcn 35 + 1-3, 1-5, 2-4, 3-5, 4-6, 5-7 = $-0.25$ ; 1-4, 2-5 = $-0.10$
37	3.46	0.24	5.39	0.11	Calcn 35 + different nitrogen parameter, set 2
38	3.45	0.24	5.38	0.11	Calcn 35 + different nitrogen and oxygen parameters, set 2
39	3.49	0.24	5.02	0.13	Calcn 36 + different nitrogen and oxygen parameters, set 2
40	3.47	0.25	5.01	0.13	Calcn 39 but with C=O = $-2.60$
41 <sup>d</sup>	3.44	0.25	5.36	0.12	Calcn 38 but with C=O = $-2.60$

<sup>a</sup> All energy values given in electron volts,  $E_{\max(1)}$  = first electronic transition,  $E_{\max(2)}$  = second electronic transition, number of configurations used, ten singly. <sup>b</sup> Atoms are numbered in the following manner, C(1)-C(2)-N(3)-C(4)-C(5)-C(6)-O(7). <sup>c</sup> Singly (ten) and doubly (ten) excited configurations included in this calculation only. <sup>d</sup> Computed dipole moments not shown, all values were between 5.1 and 6.0.

**The Dihyronicotinamides.** After having set up the parameters for all the previous calculations no changes were made for the dihyronicotinamides. N-Propyl-1,4-dihyronicotinamide is reported<sup>62</sup> to have a transition at 355 m $\mu$  (3.5 eV) of moderate intensity ( $\epsilon$  7150,  $f$  = 0.2) and a second transition at 214 m $\mu$  (5.8 eV,  $\epsilon$  10,000,  $f$  = 0.2). The calculations predict transitions at 3.47 eV (0.23) and 5.05 eV (0.11). The calculations predict that the first transition in the 1,6-dihydro compound should lie at higher energies than the 1,4 compound. This is not the case with the reduction products of 1-(2,6-dichlorobenzyl)nicotinamide and related materials.<sup>4-6</sup> In the 1,6 reduction product<sup>5</sup> a new transition does appear at 259 m $\mu$  ( $\epsilon$  7650) which is too strong to be the perturbed <sup>1</sup>L<sub>b</sub> transition of the substituted benzyl group.

The computed dipole moment of 5.9 D. for 1-benzyl-1,4-dihyronicotinamide is much larger than the experimental value of 3.89 D.<sup>63</sup> This latter value is in the region of a normal amide<sup>64</sup> and is a bit surprising considering the high dipole moment of the aminobutadienone (IIIa).<sup>9</sup>

Also shown in Table IX are the total  $\pi$ -electron energy of these three structures, computed according to the method of Pople.<sup>16</sup> The higher computed stability of the 1,4 structure must be treated with care since such values are parameter dependent and, in this case, probably reflects the fact that we used a higher value for the C-N resonance parameter than the C-C.

**The Effect of the Inclusion of Doubly Excited Configurations.** The main point that has been demonstrated

(61) The author wishes to thank Dr. H. L. Ammon for a sample of this material.

(62) H. L. Ammon, "A Study of Some Reactions of Model Compounds of DPNH in Acidic Media," Dissertation, University of Washington, 1963.

(63) G. Cilento, E. de Carvalho Fihlo, and A. C. Giora Albanese, *J. Am. Chem. Soc.*, **80**, 4472 (1958).

(64) L. M. Lee and W. D. Kumler, *ibid.*, **83**, 4586 (1961); **84**, 565 (1962).

**Table IX.** Calculation<sup>a</sup> of the Electronic Properties of 1,2-, 1,4-, and 1,6-Dihydropyridinamide

Structure <sup>b</sup>	$\mu_{\text{calcd}}$ , D.	Electronic transitions		Comments
		$E_t$ , ev	$f$	
1,6-	6.7	3.83	0.26	Total ground state $\pi$ energy = -156.9976 ev
		5.26	0.17	
		5.49	0.18	
		6.29	0.92	
1,2-	6.6	3.64	0.41	Total ground state $\pi$ energy = -157.0453 ev
		5.15	0.06	
		5.84	0.003	
		6.25	0.58	
1,4-	5.9	3.47	0.23	Total ground state $\pi$ energy = -157.239 ev
		5.05	0.11	
		5.53	0.22	
		6.44	0.76	

<sup>a</sup> Parameters used, all formal C=C bonds, -2.40 ev; all formal C—C bonds, -2.20 ev; all formal C—N bonds, -2.45 ev; C=O, -2.60 ev. Nitrogen and oxygen coulomb parameters from set 2.

<sup>b</sup> Number of configurations used, eight singly.

is that the inclusion of doubly excited configurations is computationally important. In contrast to the inclusion of singly excited configurations only the presence of doubly excited configurations generates some mixing with the ground-state wave functions. The weight of doubly excited configurations in the ground state is small, less than 2%. This is also the case for the transitions having a high weight of the  $1 \rightarrow 1'$  singly excited configuration. A comparison of the calculations incorporating singly with those incorporating both singly and doubly excited configurations shows that the computed energy of these principally  $1 \rightarrow 1'$  transitions are increased by 0.3 to 0.4 ev. Parameter adjustment will bring these into agreement with experiment. The secondary transitions have from 30 to 50% weights of doubly excited configurations and are significantly lowered compared to those calculations in which only singly excited configurations are utilized. The relative computed lowering in the energies of these transitions are variable, between 0.5 and 1.5 ev. Because there are no electric dipole matrix elements between the ground state and the doubly excited states there is a decrease in the computed oscillator strengths. Whether one considers the inclusion of doubly excited configurations significant in computing transition energies depends on one's tolerance. The net effect of the inclusion is to decrease the amount of energy separating the two lowest excited states. In the case of 1,2-dihydropyridines the inclusion of only singly excited configurations generates a separation of 1.7–2.0 ev between these states compared to less than 0.3 ev when doubly excited configurations are utilized. The experimental separation for a single known material (VIIa) is 0.7 ev. For 1,4-dihydropyridine the corresponding computed separations are 1.3–2.0 vs. 0.2–1.0 ev and are to be compared with the experimental separation of 0.8 ev. It must be mentioned that dihydropyridines are notoriously air-sensitive materials and the possibility of spectroscopic impurities cannot be ruled out.

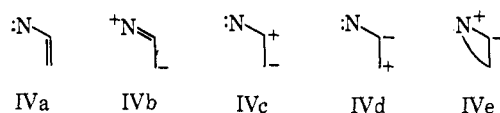
What has been established is that the inclusion of doubly excited configurations can be of importance. It is not theoretically justifiable to arbitrarily exclude these configurations unless it can be shown that they are of minor importance. Additional computations

indicate that the effects are not large on the lower excited states of indole, indene, and benzofuran.

**Effect of the Inclusion of Nonneighbor Resonance Parameters.** The inclusion of nonneighbor resonance parameters has a mild effect on the computed positions on some of the electronic transitions. For transitions having a high weight of the  $1 \rightarrow 1'$  configuration the effects are varied. In calculations pairs 1–2, 9–10, 32–33, the shifts are -0.2 to -0.35 ev. For calculation pairs 13–14, 18–19, 28–29, 35–36, and 38–39 the effects are negligible ( $\pm 0.1$  ev). For the highly mixed transitions of the same calculations the effects are from weak (-0.17) to strong (-0.77 ev). The minimal conclusion is that the inclusion of nonneighbor resonance parameters is of computational importance. This is also the conclusion of Flurry and Bell.<sup>65</sup>

**The Effect of Changes in the Coulomb Parameters.** As treated here the valence state ionization potential was changed for nitrogen and oxygen while also changing the  $\langle 11|11 \rangle$  integrals. The spectral effect of changing the valence-state ionization potential, alone, can be assessed from first-order perturbation theory using the charge densities on the atom of interest in the ground and excited states. In all the calculations done here the nitrogen atom loses additional electron density in going to the first excited state. With the 1,4-dihydropyridinamide the oxygen atom undergoes no particular electron loss or gain when the molecule is excited (*vide infra*). It is also the case with the 3-acetyl-1,4-dihydropyridine. These calculations are more sensitive to variations in the nitrogen than in the oxygen parameters.

**Charge Densities in the Ground and Excited States.** General conditioning to the qualitative rules of resonance theory produces expectations as to the role of various ionic resonance structures in the ground and excited states of molecules. The case of aminoethylene is demonstrative.



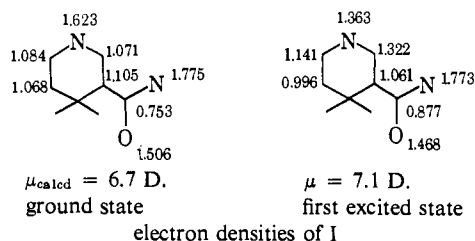
Resonance structures

1.	N	1.868	N	1.625
2.	C	0.982	C	1.285
3.	C	1.150	C	1.090
	ground state		first excited state	
	computed electron densities			

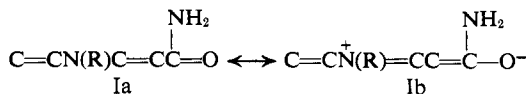
The traditional resonance arguments might only consider IVa and IVb as having principal importance in the ground and first excited state of IV. Although the ground-state electron density of IV might be interpreted in this way the excited state cannot. The loss of electron density of atom 3 and gain by atom 2 indicate that all structures must play a part and that IVb cannot even play a dominant part in the excited state.

The case for the lack of the applicability of resonance arguments to spectral interpretation is also shown in the case of the 1,4-dihydropyridinamide (I).

(65) R. L. Flurry, Jr., and J. J. Bell, *J. Am. Chem. Soc.*, **89**, 525 (1967).



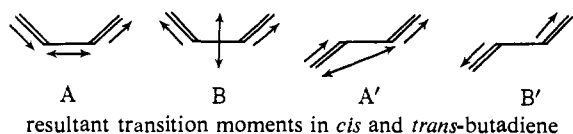
The argument has been put forth<sup>66</sup> that the solvent or substrate spectral characteristics in I can be explained in terms of resonance structures of type Ib playing an important role in the excited state of I. The resonance argument is not substantiated by the molecular orbital calculation. It must be stressed that the ground-



state dipole moment of 3.89 D. is not reproduced by the calculation and only a slight increase in the dipole moment is predicted in going to the first excited state. However, what increase is predicted is done so without any increase in the electron density at the oxygen atom. It is the carbon atoms attached to the nitrogen atom which undergo the greatest change in electron density. It also can be argued even from valence bond theory<sup>12</sup> that the large coulomb term in structure Ib would suppress its contribution in the ground or the lower excited states. The observed solvent and substrate spectral effect in I may reflect either total dipole moment changes or changes in localized electron densities on excitation.

**Rationalization of the Spectral Features of I-IX.** Although it has been computationally predicted that the dihydropyridines I and II undergo transitions with weaker intensities ( $f = 0.2$ ) than the aminobutadienones ( $f = 0.6$ ) no comprehensive explanation has been put forth as to why this is so. The previous resonance argument tends to disregard the "extra" ethylene group hanging off the end of the aminobutadienone in Ia. The usual fault to a purely computational approach to spectra analysis is that it fails to systematize the spectral features of structurally related materials. We will attempt to do that now.

As previously shown it is not presently possible to rationalize spectral features through the use of simple resonance arguments. The rationalization of substituted benzene spectra can be accomplished either through perturbation techniques of Petruska<sup>53</sup> and Stevenson<sup>52</sup> (free electron theory) or of Murrell<sup>12,21</sup> (charge transfer theory). In addition, the spectra of polyene structures can be rationalized within the framework of coupled oscillator theory.<sup>48</sup> The weak nature of the first electronic transition in cyclopentadiene and cyclohexadiene as compared to *trans*-butadiene can be explained by examining the net transition dipole resulting from the corrected vector addition of the individual ethylene moments.<sup>48</sup>



(66) Reference 4, pp 202, 207.

From simple exciton theory it can be shown that the dipole additions A and A' are lower energy forms than B or B'. The vector addition is much larger for A' than A and thus it is qualitatively predicted that *trans*-butadiene absorbs with a much greater intensity than does *cis*-butadiene. The corresponding transition B' is forbidden ( ${}^1A_g \rightarrow {}^1A_g$ ) and B is predicted to be strong. From the viewpoint of molecular orbital calculations the predicted strength of B is in error.<sup>42</sup> This transition is computationally forbidden within the context of additional selection rules placed on alternate hydrocarbons by the pairing rule.<sup>27,37</sup> This results because of the fact that configuration interaction plays a dominant role in this transition. However, if arguments are contained only to transitions in which the  $1 \rightarrow 1'$  configuration plays the dominant role a modified exciton-charge transfer argument can be applied to explain the intensity characteristics of compounds I-IX and to predict the direction of their transition moments. These qualitatively predicted directions of the transition moments will be compared with the computational values. Table X shows the direction

Table X. Computed Direction of the Transition Moments

Structure	Calculation no.	Direction of moment	
		$N \rightarrow V_1$	$N \rightarrow V_2$
	2	$\sqrt{-75^\circ}$	
	10	$\sqrt{-74^\circ}$	$-79^\circ$
	33	$\sqrt{-67^\circ}$	$-57^\circ$
	Any	$\sqrt{0}$	$90^\circ$
	14	$\sqrt{-44}$	$-74^\circ$
	40	$\sqrt{-24}$	$-84^\circ$
		$\sqrt{-18}$	$+55^\circ$
		$\sqrt{-50}$	$+88^\circ$
		$\sqrt{+71}$	$+61^\circ$

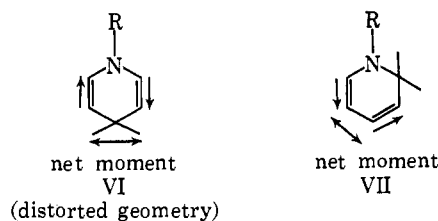
of the computed transition moments in structures I through IX for the  $N \rightarrow V_1$  and  $N \rightarrow V_2$  transitions. No experimental information from either crystal spectra or polarized fluorescence is known on any of these materials.

The principal transition moment in aminoethylene results from a weighted superposition of ethylene mo-



ment and the charge transfer moment from N to the unoccupied molecular orbitals of ethylene. The former moment is  $-90^\circ$  (according to the geometry shown in Table X). The latter moment is approximately  $-60^\circ$  resulting from the transfer of one electron from the amino to the middle of the ethylene double bond. Since the transition in aminoethylene is a weighted superposition of both the charge transfer and ethylene moments the resulting moment will be at some intermediate angle between  $-90$  and  $-60^\circ$ . This is in agreement with the actual SCF-CI calculation 2 ( $-75^\circ$ ) shown in Table X. The same argument can be applied for the  $N \rightarrow V_1$  transitions of both aminobutadiene and aminobutadienone. In these cases the charge transfer transition of the amino group is to the corresponding strong  $A'$  transition of *trans*-butadiene or butadienone. Superimposed on these exciton transitions are the charge transfer transitions between the ethylene groups or between the ethylene group and ketone group. These will result in moments for III and V still intermediate between  $-90^\circ$  and  $-60^\circ$ . Computationally these are  $-67$  and  $-74^\circ$ , respectively. Interestingly, the forbidden  $B'$  transition in *trans*-butadiene ( ${}^1A_g \rightarrow {}^1A_g$ ) is no longer forbidden in III and V. Their moments will still tend to cancel in spite of the charge transfer contributions and the observed weak ( $\epsilon$  1200) transition in III at  $215 \text{ m}\mu$  may be the perturbed forbidden transition of *trans*-butadiene.

The charge-transfer-exciton considerations for 1,2- and 1,4-dihydropyridine (VII and VI) leads to some interesting conclusions. The low energy configuration of the exciton combinations as shown below.

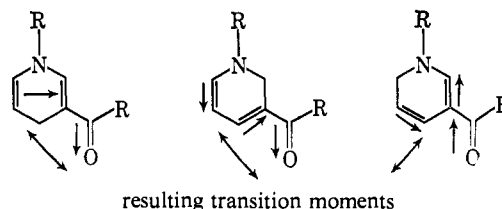


The contribution of the exciton ethylene moments to the net moment of VI will be zero unless the geometry is distorted. Due to the  $C_{2v}$  symmetry of VI there will be no charge transfer moment contribution from the amino group to the ethylenes in the  ${}^1B_1 \leftarrow {}^1A_1$  transition. Thus the direction of the net moment of this low energy transition is as shown ( ${}^1B_1 \leftarrow {}^1A_1$ ), in agreement with the computational assignment. This explanation essentially explains the weak nature of the low energy transition in 1,4-dihydropyridine ( $\epsilon$  1300–3200).

The same arguments applied to 1,2-dihydropyridine (VII) state that the low energy transition in this material is a superposition of the weak transition in the *cis*-butadienes with the charge transfer contributions. The moment in the *cis*-butadiene will be at approximately  $-30^\circ$  as shown above, or in Table X. The charge

transfer contribution will be approximately to the center of the formal C—C bond. The energy for the charge transfer band  ${}^+NH_2(CH=CH_2)^-$  is approximately 7.3 eV ( $I_p(NH_3) - A_{\text{ethylene}} - C$ ).<sup>48</sup> Because the coulomb correction  $C$  will become smaller as the system becomes larger, it is doubtful whether the charge transfer energy will change much as the amino group becomes attached to larger polyenes. The contribution of charge transfer will become less as the energy of the lowest transition of the polyene decreases. Thus the 7.6-eV transition in ethylene is shifted to 5.4 eV in IV. The corresponding 5.0-eV transition in cyclohexadiene is only shifted to 3.8 eV in VII. These arguments would lead to the conclusion that the transition moment for the  $N \rightarrow V_1$  transition in VII is dominated by the contribution from *cis*-butadiene and would remain near the  $-30^\circ$  of the latter. Computationally it is  $-44^\circ$ .

The  $N \rightarrow V_1$  transitions in I and II can be viewed as perturbations of the  $N \rightarrow V_1$  transitions in 1,4-dihydropyridine as perturbed by the C=O group. Due to the low energy of the  $N \rightarrow V_1$  of the VI the resulting moments of I and II will be dominated by the moment of the  $N \rightarrow V_1$  transition of VI. The low energy arrangement of the moments are as shown.



In this view the resulting moments in I and II will be negatively displaced from  $0^\circ$ . This is computationally supported by the calculations, these being, respectively,  $-18$  and  $-24^\circ$ . The intensity of the transitions will be dominated by the intensity of the  $N \rightarrow V_1$  transition in VI but increased by the various charge transfer contributions and a small fraction of the C=O moment. Thus the weak nature of the  $N \rightarrow V_1$  transitions in I and II ( $f = 0.2$ ) is explained by the weak nature of the  $N \rightarrow V_1$  transition in VI ( $f = 0.1$ ).

Finally, the resulting moments in VIII and IX can be viewed as combinations of the *cis*-butadiene and C=O contributions.

The qualitative arguments presented above give a reasonable explanation of the weak intensities of the transitions of I and II and the strong intensities of the substituted polyenes III, IV, and V.

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