far obtained, there appear to be no compelling reasons to choose either alternative. Nevertheless, the results presented here provide a clear indication of anomalous behavior. When similar studies are extended to other amino acids, a fuller understanding of the underlying causes will hopefully emerge.

Electronic States of the Azoalkanes

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Abstract: The electronic spectra of *cis-* and *trans*-HN=NH have been calculated in a Gaussian-type orbital basis with limited configuration interaction, and their states have been correlated with those of the isoelectronic molecule, ethylene. Comparison of the theoretical results with the electronic spectra of *cis-* and *trans*-azoalkanes, RN=NR, observed in the region 3–10 ev, shows that the weak band in these compounds at 3.5 ev is virtually 100% $n_+ \rightarrow \pi^*$, corresponding to the lowest Berry transition of ethylene; the second component, $n_- \rightarrow \pi^*$, is predicted to come 4 and 7 ev higher in the *cis* and *trans* compounds, respectively. Inasmuch as the N → V transition is predicted to come at 11 ev, all of the transitions observed in the 5–10-ev region, weak and strong alike, are assigned as involving σ-type orbitals in either the originating or terminating molecular orbitals, or both. The interpretation of the spectra is complicated by the fact that the compounds all show effects in the 5–9-ev region due to the substitution of one alkyl group for another, although the alkyl groups themselves do not absorb in this region, effects with which the calculations on HN=NH cannot cope.

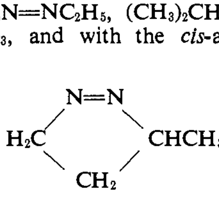
It is rather interesting to contrast the wide popularity of the azoalkanes, RN=NR, among photochemists with the almost complete lack of interest in these molecules shown by spectroscopists. Not all azo compounds have been so mistreated, for the larger azo dyes, containing phenyl and/or naphthyl groups, have been studied extensively both experimentally and theoretically; it is only the azoalkanes, the parent molecules of this class of compounds, that have been ignored. Our current interest in the azoalkanes stems originally from the rather surprising conclusions drawn from an earlier spectroscopic study of a closely related system, the alkylolefins.[1]

As discussed in that study, in the alkylolefins there is a weak singlet–singlet transition about 1 ev *below* the N → V (singlet $\pi \rightarrow \pi^*$) transition, which has been the object of numerous investigations in the past 30 years. The assignment of this low-lying "mystery band" is puzzling since, in a conventional theory with π–σ separation, there are no other singlet–singlet excitations below the $\pi \rightarrow \pi^*$ transition. Our work on this mystery band led to its assignment as a $\pi \rightarrow$ CH σ^* transition (${}^1A_g \rightarrow {}^1B_{2u}$ in ethylene) with significant s-type Rydberg character in the terminating orbital.[1] In an earlier study of the olefin spectra, Berry[2] concluded that the mystery-band excitation is CH $\sigma \rightarrow \pi^*$ (${}^1A_g \rightarrow {}^1B_{3g}$) at the obital level, just the reverse of the one quoted above.

The presence of a mystery band at 6 ev in ethylene immediately suggests that such a band might be found in this spectral region in a wide variety of other π-electron systems. Because most investigators now agree that either the originating or the terminating molecular orbital (MO) of the mystery-band transition involves σ-type orbitals, it seems clear that assignments of bands in the 5–6-ev region made using a π-electron model, which neglects explicit mention of the σ orbitals, may, in fact, be in error. There is already one example of an erroneous spectral assignment arising from this neglect of the σ orbitals in the molecular orbital description of the electronic states of an unsaturated molecule.[3] It is our aim in this paper to investigate the importance of σ orbitals in the low-lying states of azoalkanes through an experimental study of the azoalkane spectra, the assignment of these spectra aided by calculations embracing all of the electrons and by the correlation between the olefin and azoalkane excited states involving $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, and $\sigma \rightarrow \sigma^*$ excitations.

Experimental Section

If two *trans* (*cis*) protons of an ethylene molecule are imagined to be pushed into the carbon nuclei, then the isoelectronic molecule *trans-* (*cis-*) diimide, HN=NH, results. Diimide is itself of great current interest, but for other, more chemical reasons.[4] Our interest in this molecule resides in the comparison between its spectrum and that of ethylene. Actually, diimide is very reactive, and our experiments were performed instead with the *trans*-azoalkanes $CH_3N{=}NCH_3$, $C_2H_5N{=}NC_2H_5$, $(CH_3)_2CHN{=}NCH(CH_3)_2$, and $(CH_3)_3CN{=}NC(CH_3)_3$, and with the *cis*-azoalkane, 3-methyl-1-pyrazoline



The first three materials were obtained from Merck Sharp and Dohme, Montreal, Canada, and were stated to be 99% pure. Both

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[1] M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, **44**, 1803 (1966).

[2] R. S. Berry, *ibid.*, **38**, 1934 (1963).

[3] Numerous π-electron calculations have led to the conclusion that the 6-ev band of norbornadiene is the symmetry-forbidden N → V_1, $\pi \rightarrow \pi^*$ transition. Vibronic analysis, however, shows that the band is a symmetry-allowed one and is most likely an olefin mystery band involving σ orbitals as well as π: M. B. Robin and N. A. Kuebler, *J. Chem. Phys.*, **44**, 2664 (1966).

[4] S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Intern. Ed. Engl.*, **4**, 271 (1965).

the azoisobutane, a gift from Professor E. Kosower, and the 3-methyl-1-pyrazoline, a gift from Professor R. J. Crawford, were purified by gas phase chromatography (gpc). Immediately before recording the spectra, the azoalkane samples in a blackened vacuum system were subjected to repeated freeze–pump–thaw cycling at −160° for azomethane, and at −95° for the heavier azoalkanes. In addition to the above azoalkanes, we also report here the electronic spectrum of *trans*-difluorodiazine, FN=NF, obtained prepurified by preparative gpc from the Air Products and Chemicals Co.

The ultraviolet spectra were determined using a McPherson, Model 225, 1-m photoelectric spectrometer and a punched tape data system described earlier.[5] A Supersil-windowed D_2 lamp was used as the light source for the 33,000–60,000-cm^{-1} region, and microwave-powered Kr and Ar lamps were used for the region 59,000–80,000 cm^{-1}. Using a grating having 600 lines per mm blazed for 1500 A allowed the use of exit and entrance slits of 50 μ or less in all experiments. A Cary spectrophotometer, Model 14, was used for recording the spectra in the 25,000–33,000-cm^{-1} region.

Calculations

The electronic excitation energies and the corresponding transition moments and polarizations were calculated using a program[6] which first obtains a self-consistent field (SCF) ground state for the molecule of interest with all electrons included, using Gaussian-type orbital (GTO) basis functions. An extension of the program was then used to perform a limited configuration interaction (CI) among excited configurations generated from the virtual orbitals of the ground-state calculation.

Gaussian-type orbitals have the advantage that all integrals over basis functions can be evaluated easily and exactly, and the disadvantage that large basis sets are required for the adequate description of molecular wave functions. Both aspects stem from the radial dependence of the GTO function, $e^{-\alpha r^2}$, which may be compared with the Slater-type orbital (STO) radial dependence of $e^{-\alpha r}$. Specifically, the product of two GTO's on different centers is simply another GTO centered between the original two;[7] thus, the four-center integrals which plague quantum chemistry in the STO basis immediately reduce to tractable two-center integrals in the GTO basis. However, GTO's resemble the true wave functions much less than do STO's and thus require basis sets two or three times as large. This requires, however, about two orders of magnitude more computer memory, since the memory requirement is set by the number of four-center integrals to be computed, a number which increases as the fourth power of the number of basis functions. A computation in the augmented basis of Table I requires the calculation of about a quarter of a million integrals.[8]

Thus, because of the limited IBM 7094 computer memory and the large number of GTO basis functions required for an adequate description of the MO's, we cannot yet calculate the electronic states of an azo compound larger than $CH_3N{=}NH$. Moreover, since we have no azo compound smaller than $CH_3N{=}NCH_3$ on which to experiment, the experiments and theoretical calculations were necessarily performed on different molecules. At the outset, it was hoped that there would be no fundamental differences in the electronic states of diimide and the azoalkanes, at least up to the region of alkyl-group absorption, *i.e.*, 75,000 cm^{-1}. As a result of this study, it now appears that, in fact, there are important spectral differences between HN=NH and RN=NR, especially for transitions which involve σ orbitals. Thus, while the calculations and experiments are each of interest in their own right, the use of HN=NH as a model compound for calculating the electronic spectrum of RN=NR has not yielded as illuminating an interplay between theory and experiment as might have been hoped.

Table I. Exponents Used in the Energy-Minimized, Augmented, and Expanded Bases GTO Calculations on Diimide

	Energy-minimized	Augmented[d]	Expanded
N(s)	58.5697[a]	42.9800	8.2000
	6.9428	5.0990	0.3830
	0.8230	0.6047	0.0300
		0.0717	
		0.0083	
N($p_{x,y,z}$)	2.1300[b]	1.4810	0.3500
	0.3630	0.2469	0.0350
		0.0412	
H(s)	0.3800[c]	0.3800	0.0800
		0.0600	

[a] C. M. Reeves and M. C. Harrison, *J. Chem. Phys.*, **39**, 11 (1963). [b] M. C. Harrison and I. G. Csizmadia, Quarterly Progress Report No. 49 of the Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Mass., July 15, 1963, p 78. [c] J. W. Moskowitz, *J. Chem. Phys.*, **42**, 1726 (1964). [d] Reference 1, Table II, calculation C.

For purposes of calculation, *cis*- and *trans*-HN=NH were taken to have planar structures with ∠NNH = 112° 39′, *D*(N–H) = 1.021 A, and *D*(N=N) = 1.240 A, as in the published structure of HN=N=N.[9] The use of the same structural parameters for both *cis*- and *trans*-diimide is supported by the near equality of the N=N distances and NNR angles in *cis*-difluorodiazine (1.214 ± 0.005 A, 114.5 ± 0.5°)[10] and *trans*-azomethane (1.24 ± 0.05 A, 110 ± 10°),[11] the only two nonaromatic, acyclic azo compounds for which structures have been determined.

Using the distances quoted above, the energy level scheme of *trans*-diimide was calculated in the conventional "energy-minimized" Gaussian basis and in an augmented GTO basis using the exponents listed in Table I. As was mentioned before,[1,12] there are signs which suggest that in ethylene the energy-minimized basis yields excited states of unusually high energies due to a neglect of the tails of the wave functions. This was confirmed in the case of *trans*-diimide, where it was found that the lowest excited triplet state is predicted to lie *below* the singlet ground state when calculated in the energy-minimized basis, but is 2 ev above it when calculated in a basis augmented with expanded GTO's.

The augmented[1,12] ethylene GTO basis (Table I) was used throughout, except as otherwise noted, for both *cis*- and *trans*-diimide and for ethylene. This was done both for uniformity with our previous calculation on ethylene[1] and because this basis led to a pre-

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(5) R. R. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **42**, 3631 (1965).

(6) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, S. Seung, B. T. Sutcliffe, and M. P. Barnett, "Program Set for Non-Empirical Molecular Calculations POLYATOM," Program QCPE 47A of the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(7) S. F. Boys, *Proc. Roy. Soc.* (London), **A200**, 542 (1950).

(8) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

(9) E. Amble and B. P. Dailey, *J. Chem. Phys.*, **18**, 1422 (1950).

(10) R. L. Kuczkowski and E. B. Wilson, Jr., *ibid.*, **39**, 1030 (1963).

(11) H. Boersch, *Monatsh. Chem.*, **65**, 331 (1935).

(12) R. R. Hart and M. B. Robin, *Theoret. Chim. Acta*, **3**, 375 (1965).

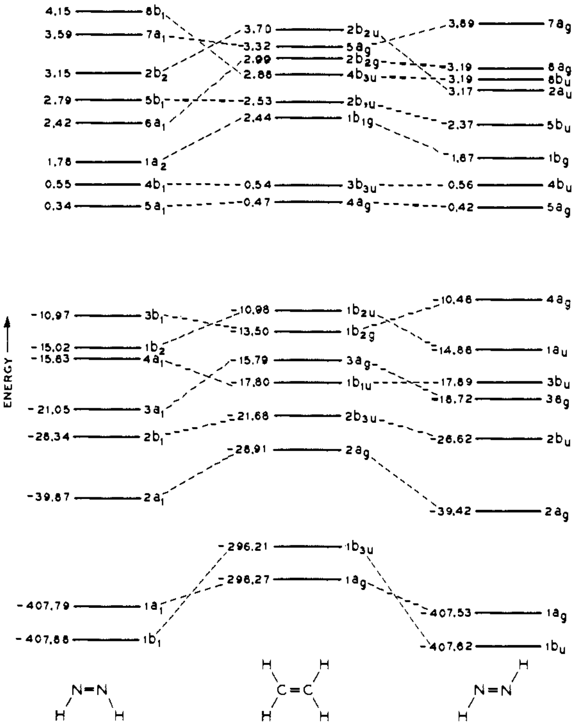

Figure 1. The SCF MO's calculated for *cis*-diimide, ethylene, and *trans*-diimide. In the ground states, all levels with negative energies (ev) are doubly filled. The drawing is not to scale. Appropriate nodal patterns are presented in Figure 3 of ref 1.

diction of the first singlet–singlet excitation of the azoalkanes in better agreement with experiment than did the other reasonable basis. This latter was the diimide augmented GTO basis, obtained from the energy-minimized diimide basis (Table I), in the same way the ethylene augmented basis was obtained from the conventional energy-minimized ethylene basis.[1,12]

Results and Discussion

As mentioned above, one of the motivations in this work was to find an absorption in the azoalkanes which is analogous to the mystery-band absorption in the olefins. Actually, as in the olefins, a weak, low-lying band is observed in the spectra of the azoalkanes (Table II), but its assignment does not appear at first to offer any mystery, for it is universally agreed that the weak transition at 28,000 cm^{-1} (3.47 ev) in the azoalkanes involves the excitation of an electron from the highest filled, nonbonding orbital, n, to the lowest empty orbital, π^*.[13-17] However, because such an n $\rightarrow$ π^* assignment for the first band of azoalkanes correlates with the CH $\sigma \rightarrow \pi^*$ Berry assignment in ethylene, and because it has been shown that the Berry CH $\sigma \rightarrow \pi^*$ and the anti-Berry $\pi \rightarrow$ CH σ^* excitations in ethylene differ but little in energy, it is a question as to which of these two excitations lies lower in azoalkanes. Moreover, since the lowest empty orbital in ethylene was computed in our scheme to be CH σ^*, and *not* π^*, it seems possible that such a situation also holds for azoalkanes, and that in diimide, an n $\rightarrow$ NH σ^* excitation would fall below the n $\rightarrow$ π^* excitation. Thus, it is seen that, pending a calculation which includes all electrons, there are three nominally reasonable choices for the assignment of the first absorption band of azoalkanes: n $\rightarrow$ π^*, n $\rightarrow$ σ^*, and $\pi \rightarrow \sigma^*$.

Table II. The First Singlet–Singlet Excitation in the Azoalkanes and Difluorodiazine

Molecule	$\nu_{\max}$, cm^{-1}	$\epsilon_{\max}$
trans-$CH_3N{=}NCH_3$	29,410	5
trans-$C_2H_5N{=}NC_2H_5$	28,170	10
trans-$C_3H_7N{=}NC_3H_7$	28,090	8
trans-$C_4H_9N{=}NC_4H_9$	27,210	13.5[a]
trans-FN=NF	>50,000	
Difluorodiazirine	29,760	~100[b]
3-Methyl-1-pyrazoline	30,860	225

[a] Private communication from E. M. Kosower and D. J. Severn. [b] R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964). The value reported here is estimated from a smoothed absorption envelope deduced from Mitsch's spectrum.

The results of our calculations on the diimides and the correlation between the SCF MO's calculated for ethylene and *cis*- and *trans*-diimide are given in Figure 1.[18] From this, one sees first that on going from ethylene to either *cis*- or *trans*-diimide, the low-lying, 1b$_{2g}$ CH bonding orbital of ethylene (doubly occupied) becomes rather destabilized, having crossed over the bonding π orbitals derived from the ethylene 1b$_{2u}$ orbital. These destabilized orbitals [3b$_1$ (*cis*) and 4a$_g$ (*trans*)] are now roughly the out-of-phase, antibonding combination of the nitrogen "nonbonding" orbitals, n$_+$, the corresponding in-phase, bonding combination, n$_-$ [4a$_1$ (*cis*) and 3b$_u$ (*trans*)], being 5 to 7 ev lower. A large interaction and splitting (approximately one-half the π–π^* splitting) of the supposedly nonbonding orbitals of the *trans* azo group, with the a$_g$ (n$_+$) combination higher than the b$_u$ (n$_-$), was predicted earlier[14] on the basis of a simple overlap consideration. The large calculated split between the "nonbonding" orbitals suggests that the orbitals are, in fact, strongly bonding and antibonding. As a result of this large split, only the electron pair in the higher n$_+$ orbital is basic, in agreement with the fact that azo compounds can be monoprotonated with ease, but not diprotonated at all.

That the orbitals heretofore described as "n" in the azo compounds are not simply nonbonding atomic orbitals (AO's) is verified not only by the very large n$_+$–n$_-$ split, but also by the fact that the "n" molecular orbital wave functions of *cis*- and *trans*-diimide have nonzero H-atom contributions. The fraction of H-atom character in the "n" molecular orbital is taken as $\Sigma_j[C_j^2 + \Sigma_{i \neq j} C_i C_j S_{ij}]$ where C_j is the coefficient of the jth hydrogen atom GTO in the "n" molecular orbital wave function, and S_{ij} is the overlap between the ith and jth GTO's. Calculations on the 4a$_g$ orbital of *trans*-diimide and the 3b$_1$ orbital of *cis*-diimide show the former to contain 3.36% H-atom character while

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(13) H. C. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(14) M. B. Robin and W. T. Simpson, *ibid.*, **36**, 580 (1962).

(15) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

(16) J. N. Murrell, "Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963.

(17) G. Kortüm and H. Rau, *Ber. Bunsenges. Physik. Chem.*, **68**, 973 (1964).

(18) The calculated orbital energies reported here for ethylene differ slightly from those given earlier[1] for the identical calculation. The difference is due to the fact that the earlier calculation was not carried through to the SCF limit. A difference in group theoretical notation will also be noticed in these figures due to an interchange of the y and z axes in the figure of this paper.

the latter contains 18.5% H-atom character. The difference in these figures reflects the stronger interaction of orbitals which are *trans* across a double bond, as is demonstrated both by the much larger size of the *trans* nmr coupling constant in olefins[19] and by the much larger n+–n− split calculated here for *trans*-diimide than for *cis*-diimide. For convenience, we will continue to call the strongly antibonding $3b_1$ and $4a_g$ molecular orbitals of *cis*- and *trans*-azoalkanes the "n" orbitals, but it must be understood that they are in fact not in the least nonbonding.

One sees from Figure 1 that, as in ethylene, the lowest empty MO's in *cis*- and *trans*-diimide are calculated to be NH σ^* ($5a_1$ and $5a_g$) and not π^* ($1a_2$ and $1b_g$). Thus, in this scheme, the originating orbital of the first electronic transition in azoalkanes is far from nonbonding and the terminating orbital would appear to be σ^* rather than π^*. Indeed, according to Figure 1, the singlet–singlet $n_+ \rightarrow \pi^*$ excitation is only the third lowest excitation in both *cis*- and *trans*-diimide. However, the estimation of excitation energies from such a molecular orbital scheme neglects Coulomb and exchange integrals as well as configuration interaction, factors which we will consider below. The solvent-induced blue-shift experiment usually used for the characterization of $n \rightarrow \pi^*$ bands[20] is of little significance here, for it depends upon the originating orbital being basic, as it is for either the $n_+ \rightarrow \pi^*$ or the $n_+ \rightarrow \sigma^*$ assignment.

It is also to be noticed that on going from ethylene to *cis*- and *trans*-diimide, though the antibonding $1b_{1g}$ π^* orbital is stabilized by 0.6 ev, the bonding $1b_{2u}$ π orbital is stabilized by approximately 4 ev. Thus, the 7.6-ev $\pi \rightarrow \pi^*$ singlet–singlet excitation of ethylene may fall at about 11 ev in the azoalkanes.

The Koopmans' theorem ionization potentials of *cis*- and *trans*-diimide, 10.97 and 10.46 ev, respectively, are in only fair agreement with an experimental value of 9.85 ± 0.1 ev, determined mass spectrometrically for HN=NH of unknown geometry.[21] The calculation also predicts a dipole moment of 3.94 D. for *cis*-diimide.

In order to predict the spectra of the diimides, it is necessary to calculate the excited configuration energies using not only the one-electron energies of Figure 1, but Coulomb and exchange terms as well, and to then mix the singly excited configurations of the same symmetry,[22] an approximation first used here in *trans*-diimide. Computation and diagonalization of the *trans*-diimide configuration interaction matrices, described in Table III, proved to be a lengthy and expensive proposition. Since our interest extends to only the two or three lowest excitations of each symmetry, in the remaining computations on *cis*-diimide and ethylene the off-diagonal configuration interaction matrix elements were taken as zero unless they involved the lowest few levels in the block. The total number of configurations considered in each symmetry block and the number of low-lying configurations connected to all other configurations is given in Table III. From these diagonalized matrices, the state energy diagrams and their correlations were constructed (Figure 2) and the major components of the multiconfigurational wave functions tabulated (Table IV). The directions of the transition moments are assigned with reference to the figure below, moments not aligned along either the *x*, *y*, or *z* axes being in the *xz* plane and inclined to the *x* axis by the angle *θ*. It is pertinent to mention that though certain orbitals which resemble AO's in their nodal and angular behavior do result from a GTO calculation, formally there are no AO's and one cannot always phrase the molecular orbital

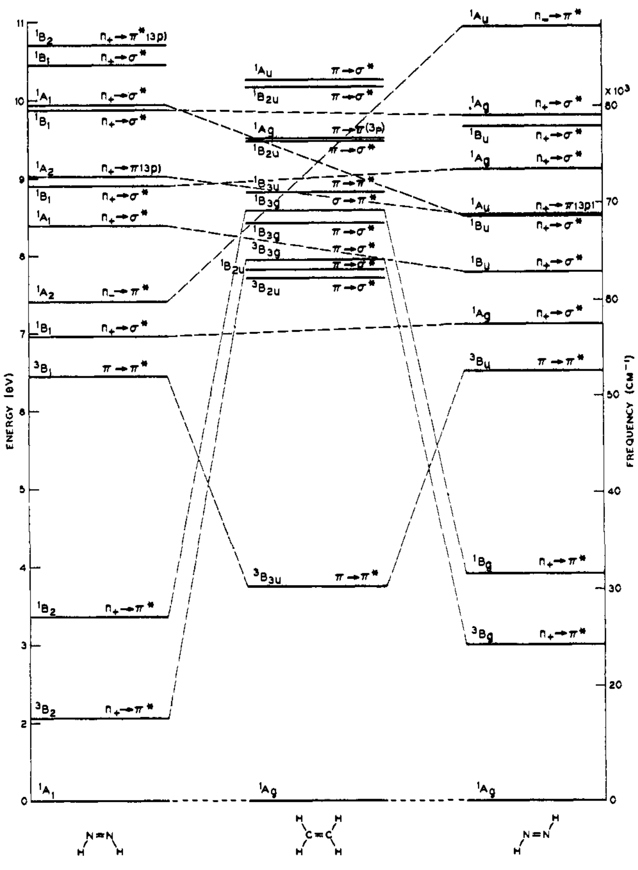

Figure 2. The state diagrams for *cis*-diimide, ethylene, and *trans*-diimide calculated in the limited configuration interaction approximation.

Table III. The Configuration Interaction Matrices

Molecule	Symmetry block	No. of configurations: In block	No. of configurations: Mixed with all others
trans-N_2H_2	A_g	5	5
	A_u	4	4
	B_g	5	5
	B_u	7	7
cis-N_2H_2	A_1	9	2
	A_2	8	2
	B_1	9	3
	B_2	6	2
C_2H_4	A_g	9	1
	A_u	4	1
	B_{2u}	5	2
	B_{3g}	5	2
	B_{3u}	6	1

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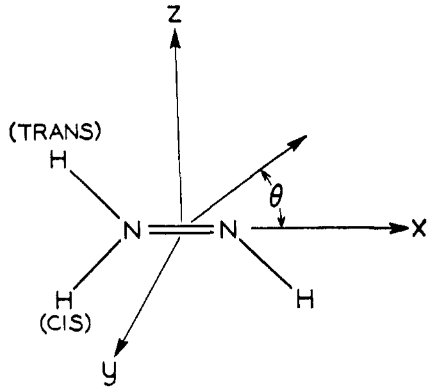
(19) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 242.
(20) M. Kasha, *Discussions Faraday Soc.*, 9, 14 (1950).
(21) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 28, 719 (1958).
(22) J. N. Murrell and L. McEwen, *ibid.*, 25, 1143 (1956).

Table IV. The Multiconfigurational Excited States Calculated for *cis*-Diimide, Ethylene, and *trans*-Diimide[a]

cis-Diimide	Ethylene	*trans*-Diimide
$^3B_2$ (2.07 ev); 0.92 ($3b_1 \rightarrow 1a_2$) − 0.40 ($3b_1 \rightarrow 2a_2$); $n_+ \rightarrow \pi^*$; 0.00 eA	$^3B_{3g}$ (7.96 ev); 0.86 ($1b_{2g} \rightarrow 1b_{1g}$) + 0.51 ($1b_{2g} \rightarrow 2b_{1g}$); $\sigma \rightarrow \pi^*$	^3B_g (3.01 ev); 0.99 ($4a_g \rightarrow 1b_g$); $n_+ \rightarrow \pi^*$; 0.00 eA
$^1B_2$ (3.36 ev); 0.93 ($3b_1 \rightarrow 1a_2$); $n_+ \rightarrow \pi^*$; 0.20 eA, y	$^1B_{3g}$ (8.59 ev); 0.84 ($1b_{2g} \rightarrow 1b_{1g}$) + 0.46 ($1b_{2g} \rightarrow 2b_{1g}$); $\sigma \rightarrow \pi^*$	^1B_g (3.92 ev); 1.00 ($4a_g \rightarrow 1b_g$); $n_+ \rightarrow \pi^*$; 0.00 eA
$^3B_1$ (6.45 ev); 1.00 ($1b_2 \rightarrow 1a_2$); $\pi \rightarrow \pi^*$; 0.00 eA	$^3B_{3u}$ (3.76 ev); 0.82 ($1b_{2u} \rightarrow 1b_{1g}$) + 0.58 ($1b_{2u} \rightarrow 2b_{1g}$); $\pi \rightarrow \pi^*$	^3B_u (6.53 ev); 1.00 ($1a_u \rightarrow 1b_g$); $\pi \rightarrow \pi^*$; 0.00 eA
$^1B_1$ (6.97 ev); 0.70 ($3b_1 \rightarrow 5a_1$) + 0.68 ($3b_1 \rightarrow 6a_1$); $n_+ \rightarrow \sigma^*$; 0.25 eA, x		^1A_g (7.12 ev); 0.80 ($4a_g \rightarrow 5a_g$) + 0.60 ($4a_g \rightarrow 6a_g$); $n_+ \rightarrow \sigma^*$; 0.00 eA
$^1A_2$ (7.41 ev); 0.91 ($4a_1 \rightarrow 1a_2$); $n_- \rightarrow \pi^*$; 0.00 eA		^1A_u (10.94 ev); 1.00 ($3b_u \rightarrow 1b_g$); $n_- \rightarrow \pi^*$; 0.26 eA, y
	$^1B_{2u}$ (7.83 ev); 0.83 ($1b_{2u} \rightarrow 4a_g$) + 0.54 ($1b_{2u} \rightarrow 5a_g$); $\pi \rightarrow \sigma^*$	
$^1A_1$ (8.40 ev); 0.74 ($3b_1 \rightarrow 4b_1$) − 0.64 ($3b_1 \rightarrow 5b_1$); $n_+ \rightarrow \sigma^*$; 0.07 eA, z		^1B_u (7.80 ev); 0.64 ($4a_g \rightarrow 4b_u$) − 0.72 ($4a_g \rightarrow 5b_u$); $n_+ \rightarrow \sigma^*$; 0.23 eA, $\theta = 81° 15'$
	$^1B_{3g}$ (8.42 ev); 0.93 ($1b_{2u} \rightarrow 2b_{1u}$); $\pi \rightarrow \sigma^*$	
	$^1B_{3u}$ (8.82 ev); 0.99 ($1b_{2u} \rightarrow 1b_{1g}$); $\pi \rightarrow \pi^*$	
$^1B_1$ (8.90 ev); −0.58 ($3b_1 \rightarrow 5a_1$) + 0.70 ($3b_1 \rightarrow 6a_1$); $n_+ \rightarrow \sigma^*$; 0.19 eA, x		^1A_g (9.14 ev); −0.58 ($4a_g \rightarrow 5a_g$) + 0.78 ($4a_g \rightarrow 6a_g$); $n_+ \rightarrow \sigma^*$; 0.00 eA
$^1A_2$ (9.02 ev); 0.99 ($3b_1 \rightarrow 2b_2$); $n_+ \rightarrow \pi$ (3p); 0.00 eA		^1A_u (8.56 ev); 1.00 ($4a_g \rightarrow 2a_u$); $n_+ \rightarrow \pi$ (3p); 0.18 eA, y
$^1B_1$ (9.88 ev); 0.82 ($3b_1 \rightarrow 7a_1$); $n_+ \rightarrow \sigma^*$; 0.06 eA, x		^1A_g (9.82 ev); 0.98 ($4a_g \rightarrow 7a_g$); $n_+ \rightarrow \sigma^*$; 0.00 eA
	$^1B_{2u}$ (9.52 ev); −0.50 ($1b_{2u} \rightarrow 4a_g$) + 0.82 ($1b_{2u} \rightarrow 5a_g$); $\pi \rightarrow \sigma^*$	
$^1A_1$ (9.94 ev); 0.66 ($3b_1 \rightarrow 4b_1$) + 0.73 ($3b_1 \rightarrow 5b_1$); $n_+ \rightarrow \sigma^*$; 0.22 eA, z		^1B_u (8.53 ev); 0.54 ($4a_g \rightarrow 4b_u$) + 0.67 ($4a_g \rightarrow 5b_u$) + 0.50 ($4a_g \rightarrow 6b_u$); $n_+ \rightarrow \sigma^+$; 0.19 eA, $\theta = 0°$
	^1A_g (9.67 ev); 0.99 ($1b_{2u} \rightarrow 2b_{2u}$); $\pi \rightarrow \pi$ (3p)	
	$^1B_{2u}$ (10.16 ev); 0.96 ($1b_{2u} \rightarrow 6a_g$); $\pi \rightarrow \sigma^*$	
	^1A_u (10.26 ev); 0.98 ($1b_{2u} \rightarrow 2b_{2g}$); $\pi \rightarrow \sigma^*$	
		^1B_u (9.68 ev); −0.55 ($4a_g \rightarrow 4b_u$) + 0.81 ($4a_g \rightarrow 6b_u$); $n_+ \rightarrow \sigma^*$; 0.16 eA, $\theta = 80° 30'$
$^1B_1$ (10.43 ev); 0.93 ($3b_1 \rightarrow 8a_1$); $n_+ \rightarrow \sigma^*$; 0.004 eA, x		
$^1B_2$ (10.71 ev); 0.92 ($3b_1 \rightarrow 2a_2$); $n_+ \rightarrow \pi^*$ (3p); 0.001 eA, y		

[a] Each excited state is listed with a symmetry label ($^3B_2$), a computed energy (2.07 ev), the coefficients of the major components of the wave function after CI [0.92 ($3b_1 \rightarrow 1a_2$)], the transition labeled according to orbital type ($n_+ \rightarrow \pi^*$), and, for the diimides, the computed transition moment dipole (0.00 eA) from the ground state and the polarization.

composition in conventional AO terms. This is especially true if the excited state is a mixture of configurations.



We first focus our attention on the lowest singlet excited states of the diimides. From Figure 2, it is seen quite clearly that the singlet excited states observed at about 28,000 cm^{-1} (3.5 ev) in both *cis*- and *trans*-azoalkanes (Table II) are to be associated with a $^1B_2$ state in *cis*-diimide calculated to come at 3.36 ev and a ^1B_g state predicted to fall at 3.92 ev in *trans*-diimide. Examination of the eigenfunctions of the $^1B_2$ configuration interaction matrix for *cis*-diimide shows that the lowest $^1B_2$ state is overwhelmingly the $n_+ \rightarrow \pi^*$ ($3b_1 \rightarrow 1a_2$) Berry excitation, though it also has a contribution from the $\pi \rightarrow \sigma^*$ ($1b_2 \rightarrow 5a_1$) anti-Berry excitation. In *trans*-diimide, ^1B_g is virtually all $n_+ \rightarrow \pi^*$ ($4a_g \rightarrow 1b_g$). One sees from Figure 2 that even though the $^1B_{2u}$ anti-Berry excited state is quite near but lower than the $^1B_{3g}$ Berry excited state in ethylene, on going to the diimides the Berry excitation, $n_+ \rightarrow \pi^*$, is lowered by about 5 ev, whereas the lowest $\pi \rightarrow \sigma^*$ anti-Berry excitation is *raised* by almost the same amount.

Most interestingly, the $n_+ \rightarrow \pi^*$ transition in FN=NF would appear to lie beyond 50,000 cm^{-1}, for it cannot be found experimentally at frequencies lower than this.

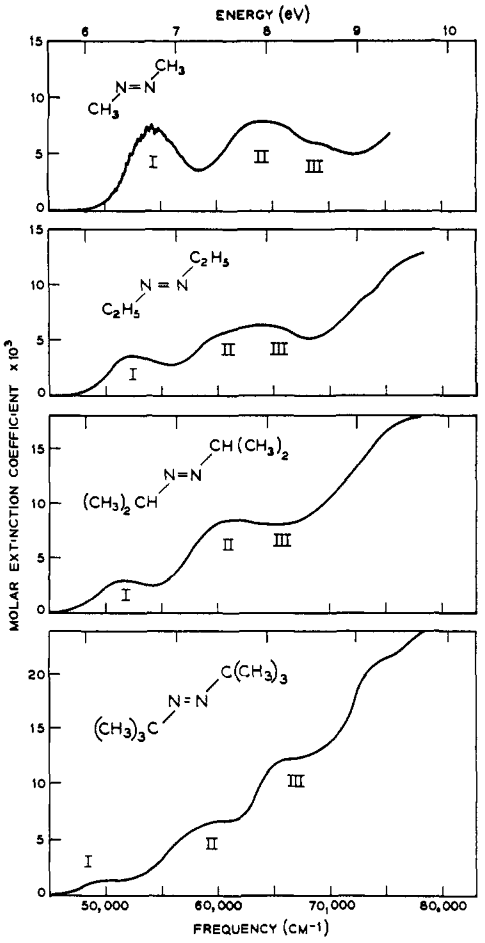


Figure 3. The electronic spectra of azomethane, azoethane, azoisopropane, and azoisobutane in the gas phase.

The shift of the diimide $n_+ \rightarrow \pi^*$ transition from 31,600 to >50,000 cm^{-1} on replacing the hydrogens with fluorine seems in every way analogous to the situation in the isoelectronic molecule formaldehyde, where the $n \rightarrow \pi^*$ band shifts successively from 31,800 to 44,500 cm^{-1} and thence beyond 51,300 cm^{-1} as first one and then both hydrogens are replaced with fluorines.

As for the $n_+ \rightarrow \pi^*$ triplets, there is no experimental evidence to show their location in the azoalkanes. However, on going from a *trans*-azoalkane to *trans*-azobenzene, the $n_+ \rightarrow \pi^*$ singlet is observed to drop from 3.55 to 2.75 ev. If the $n_+ \rightarrow \pi^*$ triplet were to behave similarly, it would come at about 2.21 ev in azobenzene. A maximum is observed in the *trans*-azobenzene magneto-optical rotation spectrum[23] at 2.29 ev, which may be due to the $n_+ \rightarrow \pi^*$ triplet. In support of a 3.01-ev excitation energy for the $n_+ \rightarrow \pi^*$ triplet state, an upper limit of 3.1 ev for this excitation in azomethane has been deduced from the observed transfer of triplet excitation energy from acetone (3.1 ev) to azomethane.[24] It is interesting to note that no luminescence from a simple azo compound has even been reported.

According to our calculations, the $n_+ \rightarrow \pi^*$ bands of *cis*- and *trans*-diimide differ in their intensity, the band being electronically forbidden in the *trans* compound, but allowed with out-of-plane polarization in the *cis* compound. Thus, it is understandable that the molar extinction coefficient, ϵ, at the wavelength of maximum $n \rightarrow \pi^*$ absorption is observed to be an order of magnitude larger in the *cis*-azoalkanes than in the *trans*-azoalkanes (Table II). By vibronic mixing, the $n_+ \rightarrow \pi^*$ band of *trans*-azoalkanes is observed to muster a transition moment of approximately 0.03 eA, which, however, is still significantly smaller than that of 0.20 eA predicted and 0.08 eA observed for the *cis*-azoalkanes. Though the borrowed $n_+ \rightarrow \pi^*$ intensity increases rapidly on phenyl substitution, so that the moment has risen to 0.18 eA in *trans*-azobenzene, the moment for the same band in *cis*-azobenzene is still larger, being 0.29 eA.

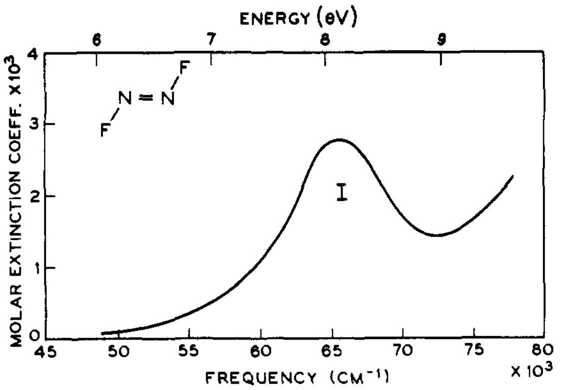


Figure 4. The electronic spectrum of *trans*-difluorodiazine vapor.

In agreement with the simpler theory of Figure 1, the configuration interaction calculation predicts the $n_- \rightarrow \pi^*$ ($^1A_1 \rightarrow {}^1A_2$) excitation to be 4 ev higher than the $n_+ \rightarrow \pi^*$ excitation in *cis*-diimide and 7 ev higher in the *trans* compound ($^1A_g \rightarrow {}^1A_u$). Contrary to the situation with the $n_+ \rightarrow \pi^*$ excitations, the $n_- \rightarrow \pi^*$ band is allowed in the *trans* molecule with out-of-plane polarization, but is forbidden in the *cis*. The opportunity for observing these $n_- \rightarrow \pi^*$ bands is slim, however, for both are weak and are predicted to fall among much stronger transitions.

Kosower and Severn[25] have recorded the first circular dichroism spectrum of an optically active azoalkane and found that the circular dichroism changes sign in the region of the $n_+ \rightarrow \pi^*$ absorption. That this apparent splitting is due to the two separate transitions, $n_+ \rightarrow \pi^*$ (3.26 ev) and $n_- \rightarrow \pi^*$ (3.82 ev), would be contrary to our calculated spectrum, and we suggest that the observed change of sign of the circular dichroism is due instead to the presence of two different *vibronic* states, each with the same $n_+ \rightarrow \pi^*$ electronic state but having accompanying vibrations of different symmetries. Professor Kosower has recently informed us that the circular dichroism spectrum of a derivative of the original azoalkane shows only one band in the $n \rightarrow \pi^*$ region.

Proceeding from the $n \rightarrow \pi^*$ transitions, the remainder of the gas phase ultraviolet spectra of the *cis*- and *trans*-azoalkanes and of difluorodiazine are shown in Figures 3–5. In interpreting the spectra of the azoalkanes, we now face exactly the problem encountered by Barnes and Simpson[26] in their work on the far-

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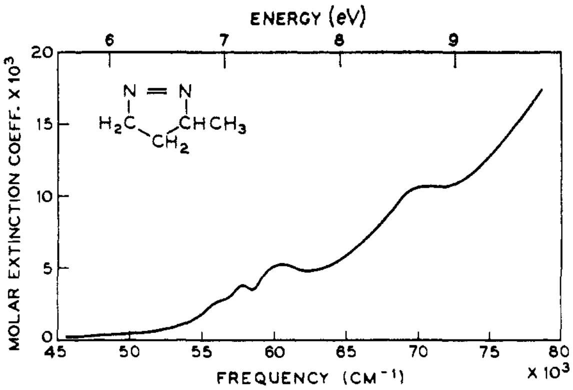

Figure 5. The electronic spectrum of 3-methyl-1-pyrazoline vapor.

ultraviolet spectra of ketones and carboxylic acids. They found that even though there is no alkyl group absorption in the 60,000–80,000-cm^{-1} region, the spectra in this region clearly show the effects of changing one alkyl group for another. Thus indirectly the alkyl groups influence the spectra in a region where they themselves have no absorption. Because of this, we expect a calculation of the spectrum of HN=NH to fall short of the mark in quantitatively explaining the spectrum of RN=NR, especially at higher energies. The one hope in such a situation is to *qualitatively* relate the predicted states of HN=NH to the states deduced from the study of a series of compounds in which the HN=NH molecule is substituted first with CH_3, then C_2H_5 and so on. In this way regularities will be revealed and bands which are badly overlapped and not at all obvious in one compound may appear in another, though in fact present in both. We have approached the interpretation of the *trans*-azoalkane spectra from this direction, but as we have only the one *cis* compound, 3-methyl-1-pyrazoline, which contains the azo group in a strained ring, it has not been possible to get as far with the *cis* spectrum as with the *trans*.

According to Figure 2, the second lowest transition in the singlet manifold of *trans*-diimide is predicted to be a forbidden $^1A_g \rightarrow {}^1A_g$ excitation with an energy of 7.12 ev. The excited state wave function for this excitation is composed of 64.2% $4a_g \rightarrow 5a_g$ ($n_+ \rightarrow \sigma^*$) and 35.5% $4a_g \rightarrow 6a_g$ ($n_+ \rightarrow \sigma^*$), the former being the singlet excitation predicted to come lowest according to Figure 1. Kortüm and Rau[17] report that solutions of unpurified azomethane in hexane show a weak band (ϵ 60) at 43,000 cm^{-1} (5.33 ev). We have also observed this band in the vapor phase spectrum of various azomethane samples, but have found that on repeated freeze–pump–thaw cycling, this band diminishesr apidly to reveal a much weaker band at 44,100 cm^{-1} (5.48 ev). This second peak appears with a constant intensity as the purification proceeds and thus may be assigned as the forbidden $^1A_g \rightarrow {}^1A_g$ band of *trans*-azomethane. A corresponding absorption could not be found in any of the other azoalkanes.

We see from the diagram for *trans*-diimide (Figure 2) that in the region 7–10 ev there are predicted three allowed $^1A_g \rightarrow {}^1B_u$ bands (7.80, 8.53, and 9.68 ev), the second of which is nearly degenerate with the lowest $^1A_g \rightarrow {}^1A_u$ excitation. The experimental spectra of the *trans*-azoalkanes (Figure 3) do show three strong bands in this region (6.33, 7.44, and 8.25 ev), and we have assigned them as the first three $^1A_g \rightarrow {}^1B_u$ excitations, labeled I, II, and III. The interpretation of the spectra beyond 50,000 cm^{-1} is aided considerably by certain regularities in the spectra. Thus, in band I, the frequency of the absorption maximum decreases in a regular way by 4000 cm^{-1} on going from azomethane to azoisobutane, but, more interestingly, the intensity drops by more than a factor of 5 in the same series. Band II also decreases in frequency by 4000 cm^{-1} in the series, its intensity decreasing only slightly, however. The intensity lost in band I appears in band III, which is barely visible in azomethane, but most prominent in azoisobutane.

There are obviously several alternate ways in which one can assign band III; the assignment presented here seems to us to be the one which is most "regular" in view of the behavior of bands I and III on alkyl substitution. Thus, we see band III as a weak but distinct feature in azomethane, growing in intensity in azoethane and azoisopropane, so as to fill in the valley at 68,000 cm^{-1}, and in azoisobutane, finally becoming one of the stronger features in the spectrum, having shifted 3000 cm^{-1} to lower frequency in the process.

The first of the $^1A_g \rightarrow {}^1B_u$ excitations is predicted to fall at 7.80 ev in *trans*-diimide and is probably the band I observed in the azoalkanes at about 6.3 ev. In the past, the assignment of band I was uncertain,[14,17] for it seemed that one could argue as effectively for an $n_+ \rightarrow \sigma^*$ ($4a_g \rightarrow 4b_u$) assignment as for an $n_- \rightarrow \pi^*$ ($3b_u \rightarrow 1b_g$) assignment. The GTO calculation shows that the first allowed band in *trans*-diimide is of the $n_+ \rightarrow \sigma^*$ type, the excited state wave function being composed primarily of the $4a_g \rightarrow 4b_u$ and $4a_g \rightarrow 5b_u$ excitations, with only much smaller amounts of other ^1B_u configurations. Though the $\pi \rightarrow \pi^*$ ($1a_u \rightarrow 1b_g$) upper state is also of symmetry ^1B_u, its coefficient is less than 0.09 in each of the ^1B_u states I–III.

Band I of *trans*-difluorodiazine, centered at 8.06 ev, is 1.8 ev higher than the corresponding absorption in *trans*-azomethane. Such large shifts to higher frequencies are not unexpected in the spectra of fluorochemicals in the vacuum ultraviolet region, especially when the fluorine is an integral part of the chromophoric group, as it is here.

Band II of *trans*-azoalkanes at 7.5 ev was earlier thought to be the $\pi \rightarrow \pi^*$, $^1A_g \rightarrow {}^1A_u$ excitation of the aliphatic *trans* azo group.[14,17] In view of the fact that the present calculation places $^1A_g \rightarrow {}^1A_u$ at 12 ev, it is natural to assign the observed band II as the second lowest $^1A_g \rightarrow {}^1B_u$, $n_+ \rightarrow \sigma^*$ excitation. The character table shows that, in the C_{2h} point group of *trans*-diimide, transitions from the ^1A_g ground state are allowed to both ^1A_u and ^1B_u upper states. Ordinarily, one would correctly presume that excitations to ^1A_u would be much weaker than those to ^1B_u because the former are out-of-plane polarized and so will necessarily have smaller transition moments than the in-plane polarized excitations to ^1B_u. Surprisingly, the calculations of *trans*-diimide predict very nearly the same transition moment length for the nearly degenerate $^1A_g \rightarrow {}^1A_u$ and $^1A_g \rightarrow {}^1B_u$ band II excitations (Table IV). Our feeling here is that the predicted moment for the out-of-plane polarized $^1A_g \rightarrow {}^1A_u$ transition in *trans*-HN=NH is probably a good one for RN=NR as well, but that the in-plane polarized $^1A_g \rightarrow {}^1B_u$

excitation may be much stronger in RN=NR than is predicted for HN=NH, and is therefore more likely the correct assignment of the strong band of azoalkanes at 7.5 ev. We will meet this in-plane intensity problem again and again as we proceed through the spectrum.

The assignment of band III as the third ${}^1A_g \rightarrow {}^1B_u$ excitation is most uncertain, for it falls close to the region of possible alkyl group absorption and cannot be found with certainty in all of the azoalkanes investigated here. A spectroscopic study of the perfluoroazoalkanes would be of great help here in determining the origin of band III.

Comparison of Figures 2 and 3 shows that the calculation has put the three ${}^1A_g \rightarrow {}^1B_u$ excitations in *trans*-diimide about 1.5 ev higher than they are observed in *trans*-azoalkanes. One guesses from earlier experiences with olefins that a large part of this discrepancy may be due to an alkyl red shift brought on by substitution of the diimide hydrogen atoms by alkyl groups. A more disturbing feature than the energy disagreement, however, is the disagreement between observed and calculated transition moments. As listed in Table IV, all of the symmetry-allowed, in-plane polarized $n_+ \rightarrow \sigma^*$ excitations in both *cis*- and *trans*-diimide have predicted transition moments of 0.26 eA or less. On the other hand, we are equating these transitions with observed spectral bands having transition moments of approximately 1 eA. Once again it is easy to suggest that our neglect of the alkyl groups has resulted in σ molecular orbitals which are too compact to give the observed transition moment lengths, but we cannot demonstrate this, and the intensity disagreement must cast some doubt on the ${}^1A_g \rightarrow {}^1B_u$ assignments proposed here.

In line with the above suggestion that the alkyl groups have an appreciable effect on the intensity of the ${}^1A_g \rightarrow {}^1B_u$ bands, it is to be noted (Figure 3) that the over-all intensity in the spectral region free of alkyl group absorption does increase on going from azomethane to azoisobutane, the over-all transition moment increasing by a factor of 4. Because our calculation does not include the alkyl group, we cannot comment on the gradual redistribution of intensity in the ${}^1A_g \rightarrow {}^1B_u$ bands as the alkyl groups are changed from methyl to *t*-butyl except to note that the explanation may lie with the extensive interaction demonstrated here between the ${}^1B_u$ configurations (Table IV).

The first ${}^1A_u$ state in *trans*-diimide (8.56 ev) is predicted to fall among the ${}^1B_u$ states discussed above. This state is 99.9% $n_+ \rightarrow \pi(3p)$ ($4a_g \rightarrow 2a_u$), where $\pi(3p)$ is the π *bonding* molecular orbital composed of in-phase 3p orbitals. Unlike $n_+ \rightarrow \pi^*$, $n_+ \rightarrow \pi(3p)$ is symmetry allowed and has a predicted transition moment of 0.18 eA, with out-of-plane polarization. Such a band would be too weak to observe among the stronger ${}^1A_g \rightarrow {}^1B_u$ transitions, being only about one thirtieth as intense.

In going over to *cis*-diimide from the *trans* isomer, the three lowest ${}^1A_g$ excited states of the *trans* compound become the three lowest ${}^1B_1$ states of the *cis*. Unlike the ${}^1A_g \rightarrow {}^1A_g$ transitions of the *trans* molecule, the ${}^1A_1 \rightarrow {}^1B_1$ transitions of *cis*-diimide are allowed, having a polarization along the N=N line. However, like their ${}^1A_g$ counterparts, the ${}^1B_1$ configurations are strongly mixed. It is interesting to note that the three lowest ${}^1B_1$ states of *cis*-diimide differ by 0.15 ev or less in energy from their ${}^1A_g$ counterparts in *trans*-diimide, a rather remarkable prediction considering the very large shifts involved in going from ethylene to either *cis*- or *trans*-diimide.

The GTO calculation also predicts that on going from *trans*- to *cis*-diimide, the first three ${}^1B_u$ states of *trans*-diimide are raised in energy and are transformed into the first three ${}^1A_1$ excited states of *cis*-diimide. The transition ${}^1A_1 \rightarrow {}^1A_1$ is allowed with an in-plane polarization perpendicular to the N=N line. It is interesting to note that the eigenfunctions of the ${}^1A_1$ configuration interaction matrix for *cis*-diimide are very similar to those of the ${}^1B_u$ block of *trans*-diimide (Table IV). Because the wave functions of the ${}^1B_u$ states of *trans*-azoalkanes appear to be so similar to those of the corresponding ${}^1A_1$ states of the *cis*-azoalkanes, one might well expect in *cis*-azoalkanes a redistribution of intensity as the alkyl groups are changed, comparable to that reported here for the ${}^1A_g \rightarrow {}^1B_u$ transitions of the *trans*-azoalkanes.

Since the ${}^1A_1 \rightarrow {}^1A_2$ ($n_- \rightarrow \pi^*$) transition predicted to come at 7.41 ev in *cis*-diimide is forbidden, it appears that the strong absorption centered at 7.3 ev in the spectrum of 3-methyl-1-pyrazoline is to be assigned as the lowest ${}^1A_1 \rightarrow {}^1B_1$ ($n_+ \rightarrow \sigma^*$) excitation. This band is predicted to come at 6.97 ev with an intensity nearly that of the ${}^1A_g \rightarrow {}^1B_u$ bands of the *trans*-azoalkanes. The next allowed transition in *cis*-diimide is predicted to be a ${}^1A_1 \rightarrow {}^1A_1$ excitation at 8.40 ev, with a rather low intensity due to a fortuitous cancellation of the moments of the configurations in the configuration interaction wave function. Though this predicted energy correlates nicely with the band centered at 8.7 ev in the spectrum of 3-methyl-1-pyrazoline, the observed band is not a weak one, having a molar extinction coefficient of approximately 10,000. If the ${}^1A_1 \rightarrow {}^1A_1$ assignment is correct for the 8.7-ev band, then the very large difference between the observed and predicted transition moments (*ca.* 1 *vs.* 0.07 eA) points out again the inadequacy of neglecting the alkyl groups in the azoalkane higher excited-state wave functions.

In both the ${}^1A_g \rightarrow {}^1A_g$ and ${}^1A_g \rightarrow {}^1B_u$ bands of *trans*-diimide and the ${}^1A_1 \rightarrow {}^1B_1$ and ${}^1A_1 \rightarrow {}^1A_1$ bands of *cis*-diimide, on going from the lowest energy transition of a given symmetry to higher ones, the terminating orbital in the transition is composed increasingly of GTO's with smaller and smaller exponents, and therefore larger and larger radii. Thus, it appears that these bands are the first few members of Rydberg series converging on the ionization potential of the n_+ molecular orbital. As expected for symmetry-allowed Rydberg transitions, the predicted transition moments decrease as the size of the terminating orbital increases.

On going from ethylene to the diimides, a most dramatic shift is predicted for the singlet and triplet $\pi \rightarrow \pi^*$ excitations ($1b_2 \rightarrow 1a_2$, *cis;* $1a_u \rightarrow 1b_g$, *trans*). The ever popular ${}^3B_{3u}$ state of ethylene at 3.65 ev is moved upward to approximately 6.5 ev in both *cis*- and *trans*-diimide, while the ${}^1B_{3u}$ state at 8.8 ev in ethylene is moved to 12 ev in both diimides. Since the GTO–CI calculation places the ethylene $\pi \rightarrow \pi^*$ singlet approximately 1 ev too high, our suggestion is that the azoalkane $\pi \rightarrow \pi^*$ singlet falls at 11 ev. An earlier investigation[14] of the spectrum of azoisopropane concluded that the strong band centered at 1640 A (7.56 ev) was the singlet $\pi \rightarrow \pi^*$ excitation, because it fell so close to the 1630-A $\pi \rightarrow \pi^*$ band of ethylene and also because it had an intensity appropriate for $\pi \rightarrow \pi^*$ excitation. If our calculations are even only qualitatively correct, it must now be realized that the relatively low-lying excitations involving σ orbitals can have transition moments (*ca.* 1 eA) as large as that for the $\pi \rightarrow \pi^*$ excitation (1.06 eA), and that the first strong band in a simple π-electron chromophore is not necessarily the N → V band.

It is interesting to note that, in spite of the predicted drastic rearrangement of levels on going from ethylene to *trans*-diimide, the singlet anti-Berry excitation is predicted to remain slightly below the N → V band, just as is found in ethylene.

The prediction that the azo group $\pi \rightarrow \pi^*$ excitation falls at 12 ev is a surprising one and is worthy of further research. In an attempt to ascertain whether or not the 12-ev value was a peculiarity of our basis, the singlet–singlet $\pi \rightarrow \pi^*$ excitation energy for *trans*-diimide was calculated in the conventional energy-minimized basis and also in an expanded (3221) basis (Table I). In spite of the large variation in basis functions, the predicted $\pi \rightarrow \pi^*$ excitation remained in the 11.5–12.5-ev region in these calculations. That there is a large difference in the $\pi \rightarrow \pi^*$ excitation energies of multiply bonded carbon and nitrogen is supported by the fact that the lowest $\pi \rightarrow \pi^*$ band of N_2 (12 ev) is observed to be much higher than the corresponding band in HC_2H (6 ev). If indeed these indications of the unusually high $\pi \rightarrow \pi^*$ excitation energy in the azo group prove true, then the usual ideas about the corresponding excitation in the isoelectronic keto group falling somewhere in the 55,000–68,000-cm^{-1} (7–8.5-ev) region may be in error.[26]

According to the calculations, the singlet $\pi \rightarrow \pi^*$ excitations in *cis*- and *trans*-diimide differ by only 0.115 ev, the corresponding triplets being only 0.074 ev apart. This near-coincidence of $\pi \rightarrow \pi^*$ levels is probably related to the fact that *cis*- and *trans*-diimide differ only in the positions of hydrogen atoms in the nodal plane of the π-electron system. The $\pi \rightarrow \pi^*$ transition moments for *cis*- and *trans*-diimide are also predicted to be very similar, differing by less than 1%.

The earlier assumption[14] that band II of the azoalkanes at 7.5 ev was to be associated with the $\pi \rightarrow \pi^*$ band of alkylolefins at 7.2 ev was supported by the pronounced similarities in the spectra of *trans*-azobenzene and *trans*-stilbene. In view of our new $\pi \rightarrow \pi^*$ assignment in azoalkanes, these similarities once again appear puzzling, and we have no explanation as yet.

The $\pi \rightarrow \pi^*$ assignment of the weak band at 3.85 ev in the diazirines $R_2C{-}N{=}N$, by Lau,[27] seems most improbable according to our calculations on *cis*-diimide, and we agree instead with Hoffmann,[28] who assigned this band as $n_+ \rightarrow \pi^*$ on the basis of an extended Hückel theory calculation. A vibronic analysis of this band by Robertson and Merritt[29] revealed that it contains two electronically allowed origins separated by 220 cm^{-1}. Though Robertson and Merritt suggest a splitting of the n orbitals by this amount, it is to be noted that, if this interval really were the n_+–n_- split, one of the two transitions would be electronically forbidden and would have zero intensity at the origin, contrary to the observation. A theoretical calculation of the states of diazirine is now in progress.

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