

also has a low strain energy (about 0.5 kcal mol⁻¹), in further support of the origin of the strain in angular distortion. The calculations are summarized in Table V.

Table V. Strain Energies of Dinitriles at 298.15°K, kcal mol⁻¹

Compound	Formula	ΔH_f° - (g) _{obsd}	ΔH_f° - (g) _{calcd}	[S] ^c
Cyanogen	NC-CN	73.84 ^a	73.6	0.2
Malononitrile	NC-CH ₂ -CN	63.5 ^b	51.2	12.2
Succinonitrile	NC-(CH ₂) ₂ -CN	50.11	46.3	3.8
Glutaronitrile	NC-(CH ₂) ₃ -CN	40.9 ^a	41.4	-0.5

^a Reference 16. ^b Reference 17. ^c [S] = ΔH_f° (g)[obsd - calcd].

The Strain Energy of Triethylenediamine. This molecule has a cage structure akin to that of bicyclooctane. The structure constrains the methylene hydrogen atoms into the higher energy eclipsed conformation. Hendrickson¹⁸ calculated by molecular mechanics that this strain is relieved in bicyclooctane by a slight twist of the molecule from the symmetric *D*_{3h} structure to the acentric *D*₃ structure. Other workers have suggested that the triethylenediamine molecule is similarly distorted. Although X-ray diffraction¹⁹ and spectroscopic^{19,20} studies have failed to reveal such a distortion, there is recent evidence from a quadrupole resonance experiment²¹ that the molecule may indeed be slightly distorted.

(18) J. B. Hendrickson, *Chem. Eng. News*, **39** (47), 40 (1961).

(19) G. S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, **41**, 3759 (1964).

(20) M. P. Marzocchi, G. Sbrana, and G. Zerbi, *J. Amer. Chem. Soc.*, **87**, 1429 (1965).

(21) A. Zussman and S. Alexander, *J. Chem. Phys.*, **48**, 3534 (1968).

The strain energy of triethylenediamine may be calculated by comparing the observed value of ΔH_f° (g) with that calculated by group increment or bond energy schemes. The group increment and the Allen and the Laidler schemes predict 10.8 kcal mol⁻¹ for ΔH_f° (g) of triethylenediamine. The observed value for this quantity in Table IV (21.6 kcal mol⁻¹) should be diminished by $3RT$ (in which 3 is the number of rings in the compound) since a comparison of a cyclic compound with acyclic reference compounds is involved.²² The strain energy of triethylenediamine, relative to a hypothetical acyclic reference compound, is then (in the gaseous state): ΔH_f° _{obsd} - $3RT$ - ΔH_f° _{calcd} = 21.6 - 1.8 - 10.8 = 9.0 kcal mol⁻¹.

Pitzer²³ has calculated the energy difference between the eclipsed and staggered conformations of ethane as 2.88 kcal mol⁻¹. If triethylenediamine is to be compared to a strain-free acyclic molecule, the three "eclipsed ethane" conformations must be allowed to relax to the staggered conformation. The energy release, about 8.6 kcal mol⁻¹, is significantly close to the predicted strain energy of the molecule (9.0 kcal mol⁻¹). It does not appear that there is significant strain release from this high-energy conformation, such as would occur if the molecule twists markedly.²³ Similar conclusions obtain for related bicyclooctane molecules.⁵

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(22) B. Nelander and S. Sunner, *ibid.*, **44**, 2476 (1966).

(23) K. S. Pitzer, *Discuss. Faraday Soc.*, No. 10, 66 (1951).

A Semiempirical Investigation of π - σ Excitations in Nonplanar Hydrocarbons

Frederic A. Van-Catledge

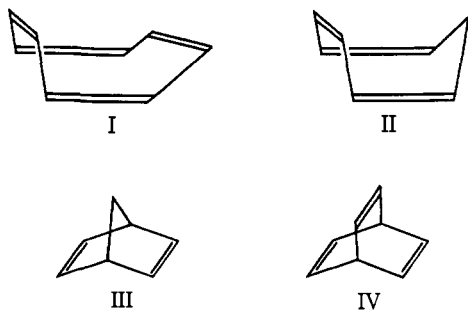
Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received October 31, 1970

Abstract: The approximate intermediate neglect of differential overlap formalism for SCF calculations (INDO) developed by Pople, *et al.*, has been modified in order to (1) obtain relative orbital energies comparable to those obtained in nonempirical calculations and (2) reproduce, using a limited CI manifold, a reasonable ordering of the lower excited states for simple hydrocarbons. To obtain the first objective, it was necessary to give up hybridization invariance, while scaling down of the electron-repulsion integrals was also required to obtain the second. The resulting scheme seems to accommodate excitations among "tight" orbitals fairly well, but does not account for excitations to Rydberg-like orbitals. Calculations carried out on cyclooctatetraene, bicyclo[2.2.2]octatriene, and bicyclo[2.2.1]heptadiene indicate that transitions best described as $\text{CH} \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ should be important in discussions of the near-ultraviolet spectra of these molecules. The conditions for the validity of the π -electron approximation are restated, and the possible consequences (in these calculations) of the INDO restrictions on the two-center electron repulsion integrals are discussed.

In attempting to account for spectral properties, one approach has been to treat nonplanar and nonconjugated unsaturated hydrocarbons as coupled ethylenic

units, with no consideration given to any effects arising from nonorthogonality of orbitals designated π and σ in the limit of infinite separation. The success of this

approach, and others akin to it, can be described at best as mixed. In the cases of cyclooctatetraene (COT, I) and cycloheptatriene (II), spectral predictions using this approach at the Pariser-Parr-Pople (PPP) level of approximation have been moderately good.¹ Likewise,



calculations on the nonconjugated systems bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, III) and bicyclo[2.2.2]octa-2,5,7-triene (barrelene, IV) would appear to be successful.^{2,3} All of these seemingly reasonable results, however, may possibly be fortuitous in the light of more recent experimental and theoretical work. Robin, *et al.*,^{4,5} have demonstrated the presence of low-lying Rydberg states in the near-ultraviolet spectrum of norbornadiene⁴ and have indicated that the valence-shell excited states in ethylene and its analogs may be higher in energy than some of the Rydberg states.⁵ These calculations included 3s-like and 3p-like functions in the basis set. The spectral studies on norbornadiene also indicate a low-lying valence-shell excited state that is obscured in the vapor phase by the lowest Rydberg state. In all, three distinct valence-shell excited states could be observed below ~ 7.5 eV. As π -electron calculations usually predict only two low-lying states,^{2,3} the presence of high-energy σ (or low-energy σ^*) orbitals is implied.

Yaris, Moscovitz, and Berry,⁶ in their semiempirical study of *trans*-cyclooctene, have shown that the methylene "rocking" mode for ethylene will permit observation of a "Rydberg-like" state in the same region as the $\pi \rightarrow \pi^*$ absorbance. The principal component of this state is $\pi \rightarrow \sigma^*$, where the σ^* orbital is best described as a C-H antibonding orbital having π_v^* symmetry. The theoretical and experimental data analyzed by these authors led them to indicate this transition as the dominant factor in determining the character of the ORD and CD spectra of *trans*-cyclooctene below 6.0 eV.

In view of these results, we felt it would be instructive to attempt to carry out a pilot semiempirical valence-shell calculation of the transition energies for exemplary molecules in each category (namely, I, III, and IV). Such a calculation should help us to understand what types of transitions might be important in the electronic spectra of these compounds. It should be borne in mind, however, that, as this is only a valence-shell

(1) F. A. Van-Catledge and N. L. Allinger, *J. Amer. Chem. Soc.*, **91**, 2582 (1969), and references cited therein.

(2) C. F. Wilcox, Jr., S. Winstein, and G. McMillan, *ibid.*, **82**, 5450 (1960).

(3) (a) N. L. Allinger and M. A. Miller, *ibid.*, **86**, 2811 (1964); (b) N. L. Allinger, J. C. Tai, and T. W. Stuart, III, *Theor. Chim. Acta*, **8**, 101 (1967).

(4) (a) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, **44**, 1803 (1966); (b) M. B. Robin and N. A. Kuebler, *ibid.*, **44**, 2664 (1966).

(5) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplin, and J. Meinwald, *ibid.*, **48**, 5037 (1968).

(6) M. Yaris, A. Moscovitz, and R. S. Berry, *ibid.*, **49**, 3150 (1968).

study, transitions involving "expanded" orbitals will be poorly described. In describing excitations we shall be using the following conventions. (1) Any orbital whose composition is $>50\%$ of the orbitals normally included in a π -electron calculation shall be called " π ." (2) An orbital that is predominantly C-C bonding shall be referred to as " σ ." (3) An orbital that is predominantly C-H bonding shall be called "CH."

Method of Calculation

We have chosen as the basis for our computational scheme the INDO formalism as outlined by Pople, *et al.*⁷ Preliminary calculations, however, led us to change the specification for the off-diagonal elements of H_{core} . Instead of using atomic β 's

$$H_{mn}^{\text{core}} = (1/2)(\beta_A^0 + \beta_B^0)S_{mn} \quad (1)$$

(m on atom A, n on atom B) as in the original INDO specification, we have found it more satisfactory to introduce an orbital dependence for β^0 by setting

$$\beta_{mn}^0 = (1/2)(E_m + E_n) \quad (2)$$

and

$$H_{mn}^{\text{core}} = S_{mn}\beta_{mn}^0 \quad (3)$$

where

$$E_m = -(I_m + A_m) \quad (4)$$

and I_m and A_m are the ionization potential and electron affinity, respectively, for orbital m . This change destroys the invariance to hybridization. We will, therefore, be working in the s-p basis. We have taken advantage of the rotational invariance of the scheme, orienting the $2p_z$ orbitals to conform to the orientations assumed for π -electron calculations. We were able, in this way, to reproduce more satisfactorily the ordering of orbitals found for ethane and ethylene in nonempirical calculations. These results are presented in Tables I and II (designated A). As can be seen, the original specification predicts the $1b_{1u}$ orbital in ethylene to be lower in energy than the $1b_{1g}$, these being π and CH bonding, respectively. In ethane, the relative energies are correct, but the proximity of the $3a_{1g}$ and $1e_g$ levels is not reproduced. Both of these discrepancies are minimized by the change we have indicated. The giving up of hybridization invariance, while aesthetically displeasing, will better facilitate comparison of these results with those of nonempirical calculations as they become available. (This problem of orbital ordering has been encountered in CNDO calculations and solved in a somewhat different manner by Jaffe.⁸)

In the original INDO specification,⁷ the repulsion integrals were taken to be dependent upon the atom pair, and not the orbitals. We have maintained this restriction, and calculated them in two ways. In calculation A these integrals were calculated using s-type STO's, as prescribed. We have found it necessary, however, to investigate the merits of using scaled repulsion integrals for calculation of transition energies. This was prompted by the fact that these calculations gave, with either specification, $\text{CH} \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$

(7) (a) J. A. Pople and D. L. Beveridge, *ibid.*, **47**, 158 (1967); (b) "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, Chapter 3.

(8) H. H. Jaffe, *Accounts Chem. Res.*, **2**, 136 (1969).

Table I. SCF Orbital Energies (au) for Ethylene

MO	7332	Unoptimized	INDO	INDO (this work)	
	Gaussian basis ^a	minimal STO basis ^b	(original)	A ^c	B ^d
2a _g	-1.0584	-1.0130	-1.3932	-1.6336	-1.6637
2b _{au}	-0.8067	-0.7815	-0.9119	-0.9491	-0.9898
1b _{nu}	-0.6604	-0.6431	-0.8293	-0.6979	-0.7318
3a _g	-0.5829	-0.5605	-0.5943	-0.4954	-0.5248
1b _{1g}	-0.5174	-0.5054	-0.4597	-0.4482	-0.4977
1b _{1u}	-0.3814	-0.3691	-0.5114	-0.4050	-0.4270
1b _{2g}	+0.1518	+0.2452	+0.2794	+0.1884	+0.0808

^a J. W. Moscowitz and M. C. Harrison, *J. Chem. Phys.*, **42**, 1726 (1965). ^b V. Kaldor and I. Shavitt, *ibid.*, **48**, 191 (1968). ^c These values were obtained using unscaled repulsion integrals. ^d These values were obtained using scaled repulsion integrals.

Table II. SCF Orbital Energies (au) for Staggered Ethane

MO	MO-SCF in	Minimal STO	INDO	INDO (this work) ^c	
	Gaussian basis ^{a,d}	basis ^{b,d}	(original) ^d	A ^d	B ^d
2a _{1g}	-1.04269	-1.04001	-1.39560	-1.68596	-1.74907
2a _{2u}	-0.85444	-0.85884	-0.96035	-1.04565	-1.11469
1e _u	-0.61912	-0.62733	-0.73810	-0.62029	-0.67887
3a _{1g}	-0.50939	-0.53607	-0.55538	-0.43258	-0.49053
1e _g	-0.50657	-0.51500	-0.46362	-0.43251	-0.50011

^a E. Clementi and D. R. Davis, *J. Chem. Phys.*, **45**, 2593 (1966). ^b R. M. Pitzer and W. N. Lipscomb, *ibid.*, **39**, 1995 (1963). ^c See footnotes c and d, Table I. ^d The same geometry was used in all calculations (see Appendix).

states significantly lower in energy than the $\pi \rightarrow \pi^*$ states of ethylene and butadiene. There is no evidence for transitions of this type at low energies in these molecules. The scaling procedure used employs the empirical relationships

$$\gamma_{AB}^{\text{emp}} = \gamma_{AB}^{\text{theo}} - S_{mn} \cdot (\Delta_A + \Delta_B)/2 \quad (5)$$

$$\Delta_A = \gamma_{AA}^{\text{theo}} - \gamma_{AA}^{\text{emp}} \quad (6)$$

$$\gamma_{AA}^{\text{emp}} = I_s - A_s \quad (7)$$

where S_{mn} and the γ 's are taken over the valence s orbitals of the atoms A and B. The justification for scaling comes from the assumption that in an NDO-type calculation we are actually working with an undefined, symmetrically orthogonalized basis set.⁹ (This type of procedure has been criticized for CNDO calculations¹⁰ by Clark and Ragle.^{10a}) A shortcoming of this type of scaling procedure is that the repulsion between basis functions is taken to be independent of the molecule under consideration. A moment's reflection will reveal that this cannot be the case. Yet, as we shall see, this modification does seem to produce state orderings in keeping with the generally accepted spectral interpretations for simple olefins. We trust that any aberrations arising from this inadequacy will be readily apparent. (An unhappy consequence of this modification is the reversal of the 1e_g and 3a_{1g} levels in ethane.) Calculations using scaled repulsion integrals shall be designated B.

All calculations were carried out using a CDC 6600 computer, programmed in FORTRAN IV. The program has options for either β specification, scaled or unscaled repulsion integrals, and orientation specifications for local coordinate systems. Within the same program, configuration interaction (CI) can be carried out over up to 100 configurations. The program auto-

matically works with those orbitals nearest the Fermi level. A check is built in to ensure that members of degenerate levels are not arbitrarily left out. Oscillator strengths are calculated in dipole length approximation, including the matrix elements coupling s and p orbitals on the same center. The effect of this inclusion will be discussed below. In the discussion of our results, we shall refer to "configuration energies" and transition energies." By the former we shall mean the excitation energy for the change in orbital occupancy $\Phi_0 \rightarrow \Phi_{i \rightarrow k}$ calculated, in virtual orbital approximation, as

$$E_{i \rightarrow k} - E_0 = \epsilon_k - \epsilon_i - J_{ik} + 2K_{ik} \quad (8)$$

The relative energies ($E_0 = 0$) of the CI wave functions shall be referred to as transition energies.

We have found it useful to have a tentative working definition of 2p π orbital. Consideration of the bond-order matrices for ethane and ethylene has led us to the following criteria. (1) The bond-order matrix element $P(i_A, \pi_A)$, where i_A is any other orbital on atom A, must be identically equal to zero. (2) The bond-order matrix element $P(s_B, \pi_A)$, where s_B is the s orbital on any neighboring (bonded) atom B, must be identically equal

Table III. Bond-Order Matrix for the CH₂ Unit of Ethylene

	H _a	H _b	C _{2s}	C _{2p_z}	C _{2p_y}	C _{2p_x}
$\theta = 0^\circ$						
H _a	0.865	-0.001	0.557	-0.424	0.697	0.000
H _b		0.865	0.557	-0.424	-0.697	0.000
C _{2s}			1.077	-0.068	0.000	0.000
C _{2p_z}				1.059	0.000	0.000
C _{2p_y}					1.341	1.000
C _{2p_x}						1.000
$\theta = 10^\circ$						
H _a	0.865	-0.001	0.557	-0.424	0.696	0.027
H _b		0.865	0.557	-0.424	0.696	0.027
C _{2s}			1.077	-0.068	0.000	0.000
C _{2p_z}				1.059	0.000	0.000
C _{2p_y}					1.133	0.022
C _{2p_x}						1.002

(9) (a) I. Fischer-Hjalmars, *Advan. Quantum Chem.*, **2**, 25 (1965); (b) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1964, pp 48 ff.

(10) (a) P. A. Clark and J. L. Ragle, *J. Chem. Phys.*, **46**, 4235 (1967); (b) P. A. Clark, *ibid.*, **48**, 4795 (1968); (c) *ibid.*, **54**, 45 (1971).

Table IV. Calculated Transition Energies (eV) for Ethylene (36 Configurations)

State symmetry ($\Phi_i \rightarrow \Phi_k$)	INDO parameterization					
	Original		A		B	
	ΔE	f	ΔE	f	ΔE	f
$\theta = 0^\circ$						
B_{3u} $1b_{1u} \rightarrow 1b_{2g}$ ($\pi \rightarrow \pi^*$)	12.92 (14.82) ^a	0.406	7.73 (9.45) ^a	0.382	7.62 (7.97) ^a	0.473
B_{2g} $1b_{1g} \rightarrow 1b_{2g}$ ($CH \rightarrow \pi^*$)	9.54 (9.54) ^a	0.000	6.44 (6.45) ^a	0.000	7.96 (7.97) ^a	0.000
B_{2g} $1b_{1u} \rightarrow 2b_{2u}$ ($\pi \rightarrow CH^*$)	14.38 (14.72) ^a	0.000	11.80 (11.79) ^a	0.000	10.32 (10.31) ^a	0.000
B_{2g} $3a_g \rightarrow 1b_{2g}$ ($\sigma \rightarrow \pi^*$)	12.20 (12.23) ^a	0.000	6.83 (6.84) ^a	0.000	8.24 (8.26) ^a	0.000
B_{2g} $1b_{1u} \rightarrow 3b_{3u}$ ($\pi \rightarrow \sigma^*$)	13.94 (13.99) ^a	0.000	10.56 (10.64) ^a	0.000	10.72 (10.74) ^a	0.000
$\theta = 10^\circ$						
B_8 $2b_1 \rightarrow 2b_2$ ($\pi \rightarrow \pi^*$) ^b			7.88 (8.70) ^a	0.350	7.17 (7.64) ^a	0.277
B_8 $1b_1 \rightarrow 2b_2$ ($CH \rightarrow \pi^*$) ^b			6.25 (7.16) ^a	0.030	8.34 (8.24) ^a	0.183
B_8 $2b_1 \rightarrow 3b_2$ ($\pi \rightarrow CH^*$)			11.69 (11.80) ^a	0.020	10.25 (10.26) ^a	0.037
B_2 $3a \rightarrow 2b_2$ ($\sigma \rightarrow \pi^*$)			6.81 (6.84) ^a	$\sim 10^{-4}$	8.20 (8.23) ^a	$\sim 10^{-4}$
B_2 $2b_1 \rightarrow 3b_3$ ($\pi \rightarrow \sigma^*$)			10.46 (10.66) ^a	0.006	10.61 (10.65) ^a	0.006

^a These parenthesized values are the configuration energies for the predominating configurations. ^b In these two states the indicated configurations are heavily mixed. The assignments are made on the basis of the more predominant configuration.

to zero. For planar and twisted ethylene, keeping both methylene groups planar, we have rotated one of them about the C-C bond through an angle θ . The bond-order matrices for a single CH₂ group with $\theta = 0$ and $\theta = 10^\circ$ are in Table III. The 10° twist is sufficient to mix the $1b_{1u}$ (π)¹¹ orbital with the $1b_{1g}$ CH bonding orbital; the resulting π orbital is $2b_1$ in the point group D_2 . Similarly the $1b_{2g}$ (π^*) orbital has mixed with the $2g_{2u}$ CH antibonding orbital (π_v^*) to give the $2b_2$ orbital of the twisted form. The twisted π and π^* orbitals are 90 and $\sim 100\%$ "pure" π orbitals, respectively, and the small $P_{i,j}$'s would lead one to speculate that this effect is of small consequence. The spectral consequences of such a distortion are, nonetheless, nontrivial.

Results

Before carrying out calculations on the molecules of interest, it was deemed appropriate to examine some relatively simple systems to obtain some insight into the possible vagaries of the various parameterizations. For ethylene and its methylated analogs we have used the "standard" bond lengths and bond angles given in the Appendix.

Ethylene. We have studied this molecule in both the planar ($\theta = 0^\circ$) and twisted ($\theta = 10^\circ$) forms. Confining our attention to the planar form for the moment, we see (Table IV) that the transition energies and orderings are highly dependent upon the parameterization. In particular, with either atomic or orbital β 's the B_{3u} state is *not* predicted to be lowest in energy. This is at variance with the semiempirical results of Yaris, *et al.*,⁶ and also the results obtained by Dunning and McKoy^{12a} by a procedure equivalent to our CI, but in a nonempirical, minimal-basis-set calculation.

(11) This molecule is taken to lie in the xy plane, the C-C bond being coincident with the x axis. In this orientation the axes of the D_2 point groups are assigned as $z = 1$, $y = 2$, and $x = 3$.

(12) (a) T. H. Dunning, Jr., and V. McKoy, *J. Chem. Phys.*, **47**, 1735 (1967); (b) M. G. Griffith and L. Goodman, *ibid.*, **47**, 4494 (1967).

These nonempirical results place the lowest states of B_{3u} , B_{2g} , and B_{2g} symmetry at 10.17, 10.44, and 10.47 eV, respectively. Introduction of scaled repulsion integrals (calculation B) reproduces the ordering of states obtained by both sets of workers, but the state correspondence is only half of the theory. Yaris, *et al.*,⁶ describe these transitions as $\pi \rightarrow CH^*$ and $\pi \rightarrow \sigma^*$, while we find them to be $CH \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$. Dunning and McKoy do not indicate the predominant configurations for their B_{2g} and B_{3g} states.^{12a} We have included in Table IV the transitions to the antibonding σ and CH orbitals. These are probably at much too high energies, since there is strong evidence that these should be Rydberg-like orbitals.^{6,13} The generally accepted spectral assignments for ethylene are as follows:¹³ the B_{3u} ($\pi \rightarrow \pi^*$) state is at 7.6 eV, while the first Rydberg-like state, B_{1u} ($\pi \rightarrow 3s$ or $1b_{1u} \rightarrow 4a_g$), comes at 7.15 eV. In calculation B we find this state at 13.90 eV for the reasons we have mentioned above. The two B_{2g} states are predicted by Merer and Mulliken to come at 7.45 ($\pi \rightarrow CH^*$) and 8.75 eV ($CH \rightarrow \pi^*$), with the B_{2g} ($\pi \rightarrow \sigma^*$) state at 7.25 eV.¹³ The state at 7.45 eV has been observed in the energy-loss spectrum of ethylene¹⁴ and is thought to be quadrupole-allowed. The early report of an additional state at 6.5 eV^{15a} has not been confirmed by more recent investigation.¹⁴⁻¹⁶ Overall, the qualitative agreement for excitations involving "tight" orbitals (no Rydberg character) is quite encouraging for calculation B.

The two sets of calculations on twisted ethylene indicate that the $CH \rightarrow \pi^*$ configuration is coupled rather strongly to the $\pi \rightarrow \pi^*$, the center of inversion being lost. If the former is the higher of the two, then our

(13) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(14) K. J. Ross and E. N. Lassette, *J. Chem. Phys.*, **44**, 4633 (1966).

(15) (a) A. Kuppermann and L. M. Raff, *ibid.*, **39**, 1607 (1963); (b) S. Trajmar, J. K. Rice, and A. Kupperman, *Advan. Chem. Phys.*, **18**, 15 (1970).

(16) J. A. Simpson and S. R. Mielczarek, *J. Chem. Phys.*, **39**, 1606 (1963).

Table V. Calculated Transition Energies (eV) for *trans*-Butadiene (100 Configurations)

State symmetry ($\Phi_i \rightarrow \Phi_j$)	— INDO parameterization —					
	— Original —		— A —		— B —	
	ΔE	f	ΔE	f	ΔE	f
A_g $1b_g \rightarrow 2b_g$ ($\pi \rightarrow \pi^*$)	13.11	0.000	8.07	0.000	7.41	0.000
	(14.31) ^a		(9.34) ^a		(7.60) ^a	
$1a_u \rightarrow 2a_u$ ($\pi \rightarrow \pi^*$)	15.80	0.000	10.07	0.000	8.90	0.000
	(16.99) ^a		(10.75) ^a		(9.06) ^a	
A_u^d $7a_g \rightarrow 2a_u$ (CH $\rightarrow \pi^*$)	8.57	0.000	5.31	$\sim 10^{-4}$	5.99	0.002
	(9.12) ^a		(5.91) ^a		(6.18) ^a	
$6a_g \rightarrow 2a_u$ (CH $\rightarrow \pi^*$)	9.97	0.003	6.18	$\sim 10^{-4}$	7.29	$\sim 10^{-4}$
	(10.63) ^a		(7.33) ^a		(7.65) ^a	
$1b_g \rightarrow 7b_u$ ($\pi \rightarrow CH^*$)	12.09	0.005	9.56	0.003	9.21	0.000
	(12.51) ^a		(10.14) ^a		(9.49) ^a	
B_g $6b_u \rightarrow 2a_u$ (CH $\rightarrow \pi^*$)	10.50 ^b	0.000	6.65 ^c	0.000	8.08	0.000
	(11.91) ^a		(11.25) ^a		(9.04) ^a	
$7a_g \rightarrow 2b_g$ (CH $\rightarrow \pi^*$)	10.26 ^b	0.000	6.92	0.000	7.78	0.000
	(12.88) ^a		(7.95) ^a		(8.16) ^a	
B_u $1b_g \rightarrow 2a_u$ ($\pi \rightarrow \pi^*$)	10.27	1.321	6.54	0.885	6.05	0.947
	(11.34) ^a		(7.65) ^a		(6.29) ^a	

^a The parenthesized values are configuration energies. ^b These two configurations are heavily mixed in this parameter set. ^c This configuration is mixed with $6a_g \rightarrow 2b_g$. ^d The oscillator strengths for states of this symmetry are identically zero if the matrix elements $\langle S_A | \hat{r} | p_A \rangle$ are neglected.

results predict that the intensity of the $\pi \rightarrow \pi^*$ state will be little altered by this deformation, but the energy will be lower. As possible confirmation of this, we point out that the observed extinction coefficients for this state in *trans*-2-butene, which is planar (6.94 eV),¹⁷ and *trans*-cyclooctene, which is nonplanar (6.32 eV),⁶ are about the same ($\sim 10,000$). This fact favors the results of calculation B. Given this result, we may now comment on the $\pi \rightarrow CH^*$ B_{3g} state. If the tentative assignment at 7.45 eV is correct,¹³ then this state will interact with the $\pi \rightarrow \pi^*$ and CH $\rightarrow \pi^*$ states, which lie above it, and move down into the 6-eV region upon twisting. This analysis is consistent with the current interpretation of the ORD and CD spectra of *trans*-cyclooctene.⁶

In regard to the π -electron approximation, the suggestion¹² that the scaling of repulsion integrals in the PPP approximation has the effect of compensating for reorganization of the σ system is borne out by our results. The lowering of the ethylene $\pi \rightarrow \pi^*$ transition energy by CI is 1.72 eV in calculation A but only 0.35 eV in calculation B. Presumably, one could find a set of repulsion integrals for which the matrix elements coupling π and σ configurations would be zero for a given molecule. These, however, would not necessarily be transferable parameters. Now a PPP calculation on twisted ethylene using the parameters of ref 1 predicts a transition energy of 7.16 eV, which compares favorably with the results of calculation B for that state energy. The deceptive aspects of this results are (1) the change in oscillator strength will not be reflected in the PPP calculation and (2) transitions of nonnegligible intensity occurring in experimentally accessible regions are not at all accounted for. This result reemphasizes the well-known, but perhaps not fully appreciated, requirement of strict planarity for the validity of the π -electron approximation.

***trans*-Butadiene.** This compound is characterized by a strongly allowed transition at 5.92 eV,¹⁷ with no evidence for forbidden or weakly allowed transitions at lower energy. Yet, both the original INDO parameterization and calculation A (orbital β 's) predict that at least one such state should exist, probably

(17) L. C. Jones and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).

CH $\rightarrow \pi^*$ (Table V). Similar results have been obtained recently in a CNDO calculation using unscaled repulsion integrals.^{10c} If such a state does exist, current evidence implies that it lies sufficiently close to the $\pi \rightarrow \pi^*$ state to be completely obscured. The states in question are of A_u symmetry and, therefore, formally allowed. Clark^{10c} found oscillator strength values of zero for these states, but our results indicate that this is a consequence of taking the dipole-length operator matrix elements in CNDO approximation. In INDO approximation the corresponding values are nonzero, indicating that these states should be observable. As such states have not yet been reported, we are inclined to favor the scaling of repulsion integrals, which gives results more in keeping with current experimental evidence.

Propene and *cis*- and *trans*-2-Butene. All of the results that are reported in the remaining parts of this paper are obtained from calculation B. Data have been obtained from calculation A, but we have not included them because of the trends noted above. In Table VI we summarize the results obtained for some methylated ethylenes. The first thing to note is that the trend toward a lower energy for the $\pi \rightarrow \pi^*$ state upon successive methylation (Woodward's rules¹⁸) is well reproduced. The reader will note that for *trans*-butene we have included calculations on a nonplanar structure. This might well serve as a model for *trans*-cyclooctene, which was studied earlier.⁶ We suggested in the discussion of the results for unsubstituted ethylene that twisting should result in a lowering of the energy of the $\pi \rightarrow \pi^*$ state by interaction with the CH (or σ) $\rightarrow \pi^*$ state, the intensity being principally carried over into the resulting state which is most like the original $\pi \rightarrow \pi^*$. In the planar *trans*-butene, the g configuration in question is actually lower in energy than the $\pi \rightarrow \pi^*$, becoming nearly degenerate with it upon twisting. The factor determining the final ordering is that the CH $\rightarrow \pi^*$ configuration at 8.01 eV interacts more strongly with the

(18) (a) R. B. Woodward, *J. Amer. Chem. Soc.*, **64**, 72 (1942); (b) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 15; (c) for a variable-electronegativity Pariser-Parr type treatment of this phenomenon, see N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 2081 (1965).

Table VI. Calculated Transition Energies (eV) for Selected Methylated Ethylenes^a

Compound	Type of excitation								
	$\pi \rightarrow \pi^*$			CH $\rightarrow \pi^*$			$\pi \rightarrow \text{CH}^*$		
	$(\Phi_i \rightarrow \Phi_k)$	ΔE	f	$(\Phi_i \rightarrow \Phi_k)$	ΔE	f	$(\Phi_i \rightarrow \Phi_k)$	ΔE	f
Propene ^f	$2a'' \rightarrow 3a''$	7.11 (7.47) ^a	0.507	$10a' \rightarrow 3a''$	7.14 (7.21) ^a	0.003	$2a'' \rightarrow 11a'$	9.65	0.002
<i>cis</i> -2-Butene ^g	$2b_2 \rightarrow 2a_2$	6.71 (6.94) ^a	0.456	$6b_1 \rightarrow 2a_2$	6.97 (7.01) ^a	0.004	$2b_2 \rightarrow 8a_1$	9.17 (9.33) ^a	0.011
				$7a_1 \rightarrow 2a_2$	7.02 (7.16) ^a	0.000			
<i>trans</i> -2-Butene ^g (planar)	$2a_u \rightarrow 2b_g$	6.78 (7.03) ^a	0.583	$7a_g \rightarrow 2b_g$	6.53 (6.61) ^{a,b}	0.000	$2a_u \rightarrow 7b_u$	9.11 (9.26)	0.000
				$6a_g \rightarrow 2b_g$	7.84 (8.01)	0.000			
<i>trans</i> -2-Butene ^g (twisted) ^c	$9a \rightarrow 8b$	6.27 (6.77) ^{a,d}	0.182	$8a \rightarrow 8b$	6.88 (6.74) ^{a,b,d}	0.336	$9a \rightarrow 9b$	9.05 (9.21) ^a	0.034
				$7a \rightarrow 8b$	7.88 (8.02) ^a	0.051			

^a The parenthesized values are configuration energies. ^b These configurations are better described as $\sigma \rightarrow \pi^*$. ^c The dihedral angle between the planes of the methylene groups was 10°. ^d These two configurations mix extensively. ^e The experimentally observed Franck-Condon maxima are 7.12 (propene), 7.04 (*cis*-2-butene), and 6.92 eV (*trans*-2-butene) from ref 16. ^f 81 configurations. ^g 100 configurations.

$\pi \rightarrow \pi^*$ than with the $\sigma \rightarrow \pi^*$. In actual fact, our suggestion regarding the distribution of intensity is not fully confirmed here. We suggest that the partitioning of oscillator strength will be highly sensitive to the dihedral angle chosen for the calculation and the inclusion of "expanded" orbitals.

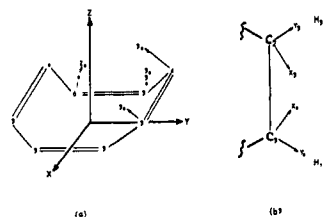


Figure 1. (a) The molecular coordinate system and p_z orbital orientation used for cyclooctatetraene (I). (b) The p_x and p_y orbital orientation used in the local σ systems for 1, 11, and 14.

The parameterization we have developed (orbital β 's, scaled repulsion integrals) seems to give a reasonable account of excitations to π^* orbitals. Excitations to CH^* and σ^* orbitals are *not* well described, owing to the "contracted nature" implicit in the undefined, symmetrically orthogonalized basis set with which we are working. If, however, we can correlate the B_{3g} ($\pi \rightarrow \text{CH}^*$) state in ethylene with the quadrupole-allowed state observed at 7.45 eV, the implication is that these states will generally be predicted at energies 2.5–3.0 eV too high. Application of such a correction to these states in the substituted ethylenes shows that they all would come *below* the $\pi \rightarrow \pi^*$ state. Finally, we trust that the reader will bear in mind the fact that the parameterization we have chosen was selected with a view toward obtaining correct *relative* orderings among non-Rydberg-like excited states. This is not the same as attempting to predict transition energies with experimental accuracy (± 0.2 eV), as is often the case in PPP calculations. We consider any tendency toward errors less than ± 1.0 eV to be a fortuitous consequence of our parameterization.

Nonplanar and Homoconjugated Systems. Cyclooctatetraene (I). For this study, the Traetteberg geometry¹⁹ was used, the local coordinates systems

being depicted in Figure 1. Examination of the bond-order matrix for this molecule shows that, by our operational definition, the $2p_z$ orbitals are by no means true π orbitals. Both of the criteria are violated and, indeed, examination of the molecular orbitals shows that the " π system" contributes in some degree, albeit sometimes small, to *all* valence-shell MO's. This result was expected, as a preliminary determination of the symmetry-adapted basis functions showed that each orbital subset (1s, 2s, etc.) contained all the irreducible representations of the point group D_{2d} . The best one can do is to identify those MO's that are primarily π in character and compare them with those arising in " π -only" calculations. In a PPP calculation the orbital ordering in terms of increasing energy is given as b_2, e, a_1, a_2, e, b_1 . If we examine our higher occupied and lower vacant MO's, we find the ordering $4b_2$ (51%), $3b_1$ ($\sim 0\%$), $7e$ (68%), $5a_1$ (85%; HOMO), $3a_2$ (97%; LVMO), $8e$ (95%), $4b_1$ (95%), $5b_2$ ($\sim 0\%$), where the percentages indicate the degree of π character in these orbitals. The $3b_1$ and $5b_2$ orbitals are predominantly CH (bonding and antibonding, respectively) in character. Their proximity to the π manifold indicates the risks of ignoring the σ system in molecules of this type. More crucial, however, is the fact that the occupied $3b_1$ level is higher in energy than $4b_2$. We would anticipate therefrom that excitations of the type $\text{CH} \rightarrow \pi^*$ will be important in describing some of the excited states.

Comparison of our current results with our own previous semiempirical calculations in π -electronic approximation¹ demonstrates the complexity of the situation. Table VII gives details of configuration energies, transition energies, and state composition. It is obvious that inclusion of the σ system changes the ordering of states markedly. More importantly, though, the assignments that one might make for the observed spectrum are now not so clear as before. The near-ultraviolet spectrum of COT can be described as a broad maximum of low intensity over the region 4.00–4.77 eV and strong end absorption with a shoulder at 6.05 eV.²⁰ In the π -electron approximation, we would

(19) M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724, 1726 (1966).

(20) N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Amer. Chem. Soc.*, **87**, 3430 (1965).

Table VII. Calculated Transition Energies (eV) for Cyclooctatetraene (99 Configurations)^a

Symmetry	PPP ^b		INDO		Contributing configuration(s)	INDO configuration energies
	ΔE	f	ΔE	f		
A ₂	4.02	0.000	4.08	0.000	5a ₁ → 3a ₂	4.25
	7.43	0.000	6.72	0.000	7e → 8e	7.83, 7.50
			7.13	0.000	7e → 8e 3b ₁ → 5b ₂ (CH → CH*)	7.83, 7.50 8.72
B ₁	6.62	0.000	6.26	0.000	4b ₂ → 3a ₂	6.77
	6.96	0.000	7.07	0.000	5a ₁ → 4b ₁ 5a ₁ → 4b ₁	6.94 6.94
					4b ₂ → 3a ₂ 3b ₁ → 3a ₂ (CH → π*)	6.77 6.44
B ₂	7.07	0.045	7.67	0.003	7e → 8e 3b ₁ → 3a ₂ (CH → π*)	7.83, 7.50 6.44
E	5.76	0.000	5.88	0.001	5a ₁ → 8e 7e → 3a ₂	6.37 6.47
	6.45	1.477	6.34	0.822	5a ₁ → 8e 7e → 3a ₂	6.37 6.47
	8.22	0.991	7.43	0.703	4b ₂ → 8e 7e → 4b ₁	8.16 8.56
			7.51	0.436	4b ₂ → 8e 7e → 4b ₁	8.16 8.56

^a See text for experimental values. ^b Taken from ref 1.

confidently assign these as an A₂ state at ~4.40 eV and an accidentally forbidden E state at ~6.5–7.0 eV. The INDO calculation, on the other hand, predicts an allowed B₂ state which is predominantly CH → π* in the same region as the now weakly allowed E state. The calculated oscillator strengths for these two states are both small, and a “hard” assignment is no longer possible. Hopefully, when we are able to extend the CI calculation, this ambiguity will be resolved.

Since the observed intensity in the A₂ state arises *via* vibronic interactions, its intensity should probably decrease upon lowering the temperature. The experimental observation,²¹ however, is that at 77°K in ethanol the apparent maximum is shifted to higher energy and is rather flat, blending quite smoothly into the strong end absorption. We would like to suggest that this phenomenon arises by a decrease in the intensity of the A₂ state which un masks the E and/or B₂ states.

Bicyclo[2.2.2]octatriene (IV). This molecule was of considerable theoretical interest² even before its synthesis,²² as no arrangement of the π orbitals is possible permitting continuous conjugation around the “barrel” (see Figure 2). We have found that it fortuitously satisfies the criteria we are using for π orbitals, but this is due to the unique symmetry of the molecule; *i.e.*, each local σ plane coincides with one of the symmetry planes appropriate to the point group of the molecule (D_{3h}). In contrast to COT (I), two irreducible representations of the point group (A₂' and A₁'') are contained only in the π subset, opening the possibility for pure π → π configurations. The orbital ordering obtained in π calculations is well documented^{22,23} as e', a₂', e'', a₁''. Interaction with the σ manifold does not change the local ordering, but the composition of the E-type orbitals is altered. This result is in keeping with the prediction of Hoffmann, *et al.*,²³ that through-

space interaction controls the π-orbital ordering. An alternate description is that the functions of appropriate symmetry (*l* = 3) to couple all three double bonds are not included in the problem and probably are too high in energy to contribute to this orbital under normal circumstances. The ordering and π percentages are 3e'' (~6%), 6a₁' (0%), 5e' (64%), 1a₂' (100%; HOMO), 4e'' (95%; LUMO), 1a₁ (100%), 6e' (~0%).

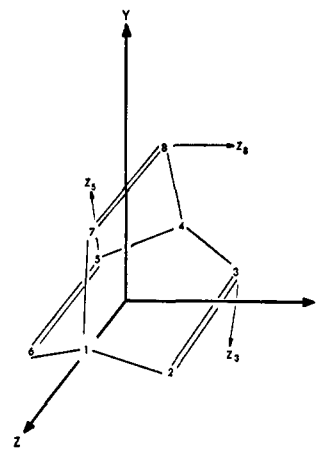


Figure 2. The molecular coordinate system and p_z orbital orientation used for bicyclo[2.2.2]octatriene (IV). The p orbitals at atoms 1 and 4 were taken parallel to the axes of the molecular coordinate system.

From CI we obtain the results presented in Table VIII for states below ~7.5 eV. We can only compare the PPP and INDO state orderings for this compound, as no definitive study has been reported of the ultraviolet spectrum of IV. Two maxima are reported¹⁹ in ethanol at 5.19 (ε 320) and 5.96 eV (ε 1120). The workers who carried out the rather elegant synthesis of this compound have fit these maxima fairly well in the π-electron approximation by what was essentially a parameter search.²² The valence-shell calculation indicates quite strongly that this compound is deserving of a more

(21) E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belg.*, 71, 845, (1962).

(22) H. E. Zimmerman, G. L. Frunewald, R. M. Paufer, and M. A. Sherwin, *J. Amer. Chem. Soc.*, 91, 2330 (1969).

(23) R. Hoffmann, E. Heilbronner, and R. Gleiter, *ibid.*, 92, 706 (1970).

Table VIII. Calculated Transition Energies (eV) for Bicyclo[2.2.2]octatriene (99 Configurations)^a

Symmetry	PPP ^b		INDO		Contributing configuration(s)	INDO configuration energies
	ΔE	f	ΔE	f		
A ₁ '			7.01	0.000	3e'' → 4e'' (CH → π*)	7.51, 7.94
A ₁ '	6.68	0.000	5.92	0.000	5e' → 4e''	6.07, 6.80
A ₂ ''	6.68	0.000	6.89	~10 ⁻⁴	5e' → 4e''	6.07, 6.80
					1a ₂ ' → 1a ₁ ''	7.26
	8.70	2.039	7.51	1.110	5e' → 4e''	6.07, 6.80
					1a ₂ → 1a ₁	7.26
E''	6.42	0.000	5.56	0.000	1a ₂ ' → 4e''	5.90
					5a' → 1a ₁ ''	6.95
			6.15	0.000	5e' → 4e''	6.07, 6.80
					1a ₂ ' → 4e''	5.90
			6.57	0.000	6a ₁ ' → 4e'' (CH → π*)	7.05
					5e' → 1a ₁ ''	6.95
			7.17	0.000	6a' → 4e'' (CH → π*)	7.05
					5e' → 4e''	6.07, 6.80
E'			7.23	0.033	3e'' → 4e'' (CH → π*)	7.51, 7.94
					3e'' → 1a ₁ '' (CH → π*)	8.40

^a See text for experimental values. ^b F. A. Van-Catledge, Ph.D. Thesis, Wayne State University, 1968.

detailed experimental investigation. Our PPP calculation, which neglects β 's between atoms in different bridges, predicts a rather simple spectrum, with no states in the region 6.7–8.7 eV. Our current results, on the other hand, infer a cluster of states in the region 6.5–7.5 eV, some of which may be reasonably described as CH → π*. Errors in the calculated transition energies on the order of 10% are not likely to alter the complexity of the problem of spectral assignments for

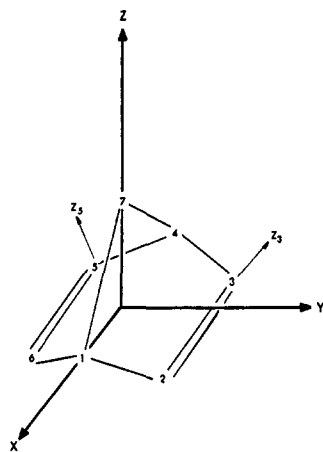


Figure 3. The molecular coordinate system and p_z orbital orientation used for bicyclo[2.2.1]heptadiene (III). The p orbitals at atoms 1, 4, and 7 were taken parallel to the axes of the molecular coordinate system.

this compound. It is clearly evident that previous attempts (including our own) to account for the spectral properties of this molecule in the PPP approximation represent a serious overextension of the formalism.^{2,3,22,24,25} An additional feature to note is that, in π -electron approximation, no states symmetric under σ_h arise. E' states would correspond to allowed CT

excitations among the double bonds. We suggest that a good probe for the E' (or E'') state would be MORD or MCD studies, provided that region of the spectrum is accessible with current instrumentation. This investigation, if carried out, might enable a hard assignment to be made regarding the CH → π* transition. Finally, as E'' states may, in principle, be observed (quadrupole allowed), the weak absorbances observed for this compound may be rationalized in a number of ways.

Norbornadiene (III). This, undoubtedly, is the most well studied of the homoconjugated systems.^{2–5} Its molecular coordinate system is shown in Figure 3. The orbital ordering obtained in the π -electron approximation is a_1, b_1, b_2, a_2 . Hoffmann has predicted that the nominally πa_1 and b_1 orbitals in 1,4-cyclohexadiene are reversed in order by interaction with the σ system.²³ Our calculations confirm the notion of extensive π - σ mixing, but the ordering ($10a_1$ vs. $7b_1$) is sensitive to the parameterization used. In calculation A Hoffmann's prediction is confirmed, while in calculation B it is not. (In either case the splitting is small.) The local ordering (calculation B) is as follows: $6b_1$ (1%), $9a_1$ (5%), $3a_2$ (2%), $5b_2$ (1%), $10a_1$ (47%), $7b_1$ (87%; HOMO), $6b_2$ (91%; LVMO), $4a_2$ (95%). As we had anticipated, the bond-order matrix precludes any π - σ separation.

The excited-state predictions in PPP approximation are A_2, B_2, A_2, B_2 , in order of increasing energy. A first-order prediction based on the coupling of two ethylenic units would predict the first A_2 state to lie below a cyclopentene state (~ 6.9 eV),¹⁷ and the first B_2 state above this.⁴ Vibronic coupling should permit observation of the low-energy state. The experimental spectrum in the vapor phase^{4b} shows distinct states at 5.95 and 6.84 eV, end absorption implying a third state at ~ 7.5 eV.¹⁶ Clearly, the first-order analysis would indicate that the state at 5.95 eV is an "extra" state, probably $\pi \leftrightarrow \sigma$ (or $\pi \leftrightarrow \text{CH}$) in nature. Our CI results for this compound (Table IX) show that the four lowest excited states do have the symmetries previously indicated, and their oscillator strengths would indicate a spectrum much like that which is observed. The principal configurations

(24) G. Giacometti and G. Rigatti, *Ric. Sci.*, **30**, 106 (1960).

(25) J. Paldus and J. Koutecky, *Collect. Czech. Chem. Commun.*, **27**, 2139 (1962).

Table IX. Calculated Transition Energies (eV) for Bicyclo[2.2.1]heptadiene (100 Configurations)^a

State symmetry	PPP ^b		INDO		Contributing configuration(s)	INDO configuration energies
	ΔE	f	ΔE	f		
A ₁			6.99	0.017	5b ₂ → 6b ₂ (CH → π*)	7.12
					3a ₂ → 4a ₂ (CH → π*)	7.49
			7.25	0.003	5b ₂ → 6b ₂ (CH → π*)	7.12
					3a ₂ → 4a ₂ (CH → π*)	7.49
A ₂	6.00	0.000	5.09	0.000	7b ₁ → 6b ₂	5.26
	7.20	0.000	6.24	0.000	10a ₁ → 4a ₂	6.28
			7.44	0.000	9a ₁ → 4a ₂ (CH → π*)	8.60
					6b ₁ → 6b ₂ (σ → π*)	8.96
B ₁			6.57	0.037	3a ₂ → 6b ₂ (CH → π*)	6.88
			7.94	0.029	5b ₂ → 4a ₂ (CH → π*)	7.94
B ₂	6.52	0.000	5.58	0.094	10a ₁ → 6b ₂	5.79
	7.71	1.201	6.51	0.230	7b ₁ → 4a ₂	6.85
			7.32	0.089	9a ₁ → 6b ₂ (CH → π*)	7.89

^a See text for experimental values. ^b Calculated using the parameters of the reference in footnote b, Table VIII.

involved are just those implied by PPP calculations. One is hardly justified, however, in describing the 10a₁ orbital as π. Explicit inclusion of the σ system results in compression of the π manifold of states and alteration of its basic nature. Also, allowed A₁ and B₁ states (CH → π*) occur quite close to the upper B₂ state. Finally, a low-resolution study of the electron-impact spectrum of this compound has shown only two peaks, one at 3.8 eV (triplet?), another at 7.4 eV.²⁶ The latter might correspond to the strong absorption at ~7.5 eV. We calculate the lowest triplet state to lie at 3.06 eV (7b₁ → 6b₂).

Discussion

The results that we have reported herein demonstrate, we feel, that π-electron calculations on nonplanar systems can lead to serious errors in spectral interpretations. First, allowed states in experimentally accessible regions of the spectra will be completely overlooked or misassigned. Second, and perhaps most important from a theoretical point of view, it is highly unlikely that a *single set of transferable parameters* will be found which can accommodate varying degrees of π-σ interaction in compounds such as the ones we have considered. Whatever the pratfalls in revising the parameterization of the INDO formalism as we have done, this evaluation is unlikely to change. Taking our lead from the now classic paper of Lykos and Parr,²⁷ we shall attempt to demonstrate why this should be so.

We begin by partitioning our basis functions into two sets, π_p and σ_q, and proceed to define molecular spin orbitals for each set as

$$\lambda_i^{\pi(1)} = \phi_j^{\pi}(1)\eta(1) \quad \phi_j^{\pi} = \sum_p C_{pj}\pi_p \quad (9)$$

$$\lambda_k^{\sigma(1)} = \phi_m^{\sigma}(1)\eta(1) \quad \phi_m^{\sigma} = \sum_q C_{qm}\sigma_q \quad (10)$$

where η(1) is the spin function, α(1) or β(1). After con-

(26) P. S. P. Wei, Ph.D. Thesis, California Institute of Technology, 1967.

(27) P. G. Lykos and R. G. Parr, *J. Chem. Phys.*, **24**, 1166 (1956).

structing the antisymmetrized wave functions for each set, (Σ) and (Π), the approximate molecular wave function may be written as

$$\Psi = \{(\Sigma)(\Pi)\}; \langle\Psi|\Psi\rangle = \langle\Sigma|\Sigma\rangle = \langle\Pi|\Pi\rangle = 1 \quad (11)$$

where the braces denote π-σ antisymmetrization. Let us assume now that the basis functions are the same undefined, symmetrically orthogonalized functions that we employ in the INDO calculation. The relationship

$$\Psi_0 = \{(\Sigma_0)(\Pi_0)\} = \Psi_0(\text{INDO}) \cdot \mathbf{U} \quad (12)$$

should hold, where U is a unitary matrix and Ψ₀ is the ground-state wave function. Now, for the excited state Ψ_{i→k} (taken, for simplicity, in single configuration approximation), we may write a similar transformation as

$$\Psi_{i\rightarrow k}(\text{INDO}) \cdot \mathbf{U} = \Psi_{i\rightarrow k} = \{(\Sigma')(\Pi')\} \quad (13)$$

In general, Σ₀ will *not* be the same as Σ' unless both the INDO MO's θ_i and θ_k satisfy the specific condition that all C_q's are zero in the expression

$$\theta(\text{INDO}) = \sum_p C_p \pi_p + \sum_q C_q \sigma_q \quad (14)$$

These are the only conditions under which π-σ separability is a valid approximation.²⁷

As pointed out by previous investigators,¹² one of the major factors necessitating the scaling of repulsion integrals in PPP calculations is compensation for the effects of σ reorganization upon excitation. Our CI results for ethylene and *trans*-butadiene are in keeping with this suggestion, but even the scaling that we have introduced does not compensate completely. A further point to note is that there seem to be the beginnings of a trend toward less lowering in energy by CI as the π system increases in length. It is not unlikely that the σ systems of large polyenes would be less sensitive to changes in π-electron configuration. This causes us to question the wisdom of using parameters derived from small, sym-

metry-determined π systems, such as ethylene and benzene, for calculations on large molecules. Griffith and Goodman^{12b} have also commented on this matter.

Consideration of the magnitude of the off-diagonal elements of the CI matrices in these calculations leads us to surmise that any aberrations in our ordering of states that might be revealed by later *ab initio* calculations will probably have their origins in the INDO-SCF correction to the difference in orbital energies for a given configuration. We cannot prove this rigorously, but the following considerations cause us to suspect that this will be the case. The INDO formalism requires the assumption of the equality

$$\begin{aligned} \gamma_{s\sigma} = \gamma_{s\pi} = \gamma_{\sigma\sigma} = \gamma_{\sigma\pi} = \gamma_{\pi\pi} = \dots = \\ \gamma_{AB} = \gamma_{ss} \quad (A \neq B) \quad (15) \end{aligned}$$

while, in fact, γ_{ss} is only a weighted average for these interactions. No serious error is likely to be introduced if all of the basis orbitals on atoms A and B contribute equally (more or less) to the MO's involved in computing the molecular-repulsion integral in question. If, on the other hand, either charge distribution includes primarily one type of orbital on an atom, the averaging process is defeated and nontrivial errors may begin to accrue. The errors we speak of are best understood if we think of comparing the INDO calculations to a less approximate calculation (specifically NDDO⁷) which gives the same difference in orbital energies. Consider, for example, the $\pi \rightarrow \pi^*$ configuration in ethylene. The correction to the difference in orbital energies, in INDO approximation, is

$$-J_{\pi\pi^*} + 2K_{\pi\pi^*} = (\gamma_{11} - 3\gamma_{12})/2 \quad 2\gamma_{12} > \gamma_{11} \quad (16)$$

where

$$\gamma_{11} = (\pi_A \pi_A | \pi_A \pi_A) \quad (17)$$

$$\gamma_{12} = (s_A s_H | s_B s_B) > (\pi_A \pi_A | \pi_B \pi_B) \quad (18)$$

The inequality in (18) will result in calculation of a lower configuration energy relative to the NDDO value. Similar arguments obtain for molecular-repulsion integrals involving interactions between s- and p-type charge distributions, particularly where the latter has an axis of symmetry differing markedly from the internuclear axis, as only $\gamma_{s\sigma}$ and $\gamma_{\sigma\sigma}$ are larger than γ_{ss} . The results of calculation A tend to confirm this analysis. Changing to the orthogonalized basis set implied in calculation B, however, should tend to suppress the differences among the repulsion integrals in the new basis, and, as a direct consequence, minimize the relative errors introduced into the calculation of configuration energies. We take some comfort from the fact that in calculation B the relative ordering of the three lower excited states for ethylene compares favorably with that obtained by Dunning and McKoy.^{12a} Further, calculations carried out in a [4s2p/2s] contracted Gaussian basis²⁸ place the ethylenic states corresponding to

our lowest three states at 7.71 (B_{3u}), 9.45 (B_{3g}), and 9.96 eV (B_{2g}), which is the same relative ordering that we have obtained.

Conclusions

On balance, this work has evolved into as much a study of the INDO formalism as a tool for theoretical predictions of spectra as it is a study of π - σ interactions. If we are compelled to give a prospectus for its utility in this regard, our attitude can best be described as "guarded hopefulness." The question is: "Can such an approximate method ever give results nearing experimental accuracy?" Further work is needed before a final answer is given, but our intuitive feeling is negative.

In regard to the specific molecules investigated, in all of these cases it would be most helpful to have available high resolution electron-impact spectra to circumvent the restrictions imposed by optical selection rules. Such data would immediately answer the question of the density of states in the 5-10 eV region and either confirm or refute the usefulness of the scheme we have employed.

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Appendix

Molecular Geometries. As some of these results may prove to be sensitive to the choice of geometries, we are summarizing the internal coordinates we have used for the molecule studied: ethane²⁹ $r(C-C) = 1.543$ Å, $r(C-H) = 1.102$ Å, $\theta(H-C-C) = 109^\circ 37'$; ethylene, propene, and *cis*- and *trans*-butene $r(C=C) = 1.334$ Å, $r(C-C) = 1.501$ Å, $r(C_{tet}-H) = 1.095$ Å, $r(C_{tri}-H) = 1.085$ Å, strict tetrahedral and trigonal angles being used; *trans*-butadiene $r(C-C) = 1.34$ Å, $r(C-C) = 1.47$ Å, $r(C-H) = 1.085$ Å, with all angles fixed at 120° ; cyclooctatetraene¹⁹ $r(C=C) = 1.3403$ Å, $r(C-C) = 1.4758$ Å, $\theta(C-C=C) = 126^\circ 8'$, $\theta(H-C=C) = 117^\circ 36'$; bicyclooctatriene³⁰ $r(C=C) = 1.337$ Å, $r(C-C) = 1.501$ Å, $r(C_1-H_1) = 1.095$ Å, $r(C_2-H_2) = 1.085$ Å, $\theta(H_1-C_1-C_2) = 113^\circ 53'$, $\theta(H_2-C_2-C_3) = 123^\circ 3'$, $\theta(C_1-C_2-C_3) = 113^\circ 53'$; bicycloheptadiene³¹ $r(C_1-C_2) = 1.522$ Å; $r(C_1-C_7) = 1.558$ Å, $r(C_2=C_3) = 1.333$ Å, $r(C_{tet}-H) = 1.095$ Å, $r(C_{tri}-H) = 1.085$ Å, $\theta(C_1-C_2=C_3) = 109^\circ 6'$, $\theta(C_6-C_1-C_2) = 102^\circ 12'$, $\theta(H_1-C_1-C_7) = 101^\circ 59'$, $\theta(H_2-C_2=C_3) = 125^\circ 27'$, $\theta(H_{7a}-C_7-H_{7b}) = 113^\circ 2'$.

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