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Modified INDO Calculations of the Electronic Structure of Organic Molecules. I. Electronic Excitation Energies of Some Carbonyl Compounds and Conjugated Dienes

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The semi-empirical valence-shell SCF MO theory (the INDO method) by Pople *et al.* has been modified for the purpose of calculating the electronic excitation energies of organic compounds. All the necessary one-center parameters have been evaluated from the valence-state ionization data of Hinze and Jaffé, combined with the Slater-Condon atomic parameters. The INDO method thus modified has been applied to carbonyl compounds and conjugated dienes. The calculated excitation energies have been found to be satisfactory in many respects.

The all-valence-electrons SCF MO theory with intermediate neglect of differential overlaps (the INDO method) proposed by Pople *et al.*[1] is currently of gaining recognition as a promising route to theoretical estimation of dipole moments and unpaired spin distributions of various molecular species. Baird and Dewar[2] have modified the INDO method in order to calculate heats of formation and molecular geometry with "chemical" accuracy. This marked success of the theory in predicting the ground-state properties of molecules now urges chemists to explore the applicability of this theory to the calculations of electronic excitation energies of organic compounds.

Along the above line, Giessner-Prettre and Pullmann[3] have already examined the INDO method in its original form and found that the calculated transition energies are generally too great compared with the observed, despite extensive configuration interaction treatments. Thus, in order to be capable of reproducing the energies in fair agreement with observation, one is now required to take due consideration of electronic correlations, which have apparently been left out of account in the original INDO approximation.

One of the best approaches to the above problem will be a procedure involving semi-empirical evaluations of the two-electron repulsion integrals from the atomic spectroscopic data. The strategy is essentially the one that has already received wide acceptance in connection with the π-electron SCF MO theory of the Parier-Parr-Pople type.[4] Recently, Bene and Jaffé[5]

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[1] a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967). b) *Idem., J. Amer. Chem. Soc.*, **90**, 4201 (1968). c) J. A. Pople and M. S. Gordon, *ibid.*, **89**, 4253 (1967). d) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968). e) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *ibid.*, **49**, 2965 (1968). f) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1 (1970). g) *Idem., ibid.*, **92**, 11(1970).

[2] a) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969). b) *Idem., J. Amer. Chem. Soc.*, **91**, 352 (1969). c) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969). d) N. Boden, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970). e) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970).

[3] C. Giessner-Prettre and A. Pullman, *Theoret. Chim. Acta* (Berl.), **13**, 265 (1969).

[4] a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953). b) J. A. Pople, *Trans. Faraday Soc.*, **149**, 1375 (1953).

have coupled this empiricism with Pople's simplest version of the all-valence-electrons SCF MO theory (the CNDO method)[6] Kato *et al.*[7] have also availed the empiricism in evaluating various integral parameters to be used in their own valence-shell theory analogous to the INDO method. In both these treatments, the transition energies obtained for various organic compounds are in satisfactory agreement with observation.

In this paper, a modification of the INDO method will be presented in order to calculate the excitation properties of conjugated compounds. All the necessary one-center parameters have been evaluated from the data for the valence-state ionization potentials and electron affinities compiled by Hinze and Jaffé,[8] in combination with the Slater-Condon atomic parameters.[1a] The procedure adopted for this parametrization is much the same as that in the MINDO method presented by Baird and Dewar.[2a] Our specific aim of the present treatment is to assess the applicability of the modified INDO theory to the calculations of electronic excitation energies of conjugated compounds, especially those of geometrical isomers. The results appear to be encouraging in most cases here investigated.

Method of Calculations

Since the INDO formulation has been described in detail by Pople *et al.*,[1a] there is no need to duplicate it here. Suffice it here to note that the Hamiltonian matrix elements for closed shell systems are given as follows:

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{\lambda}^{A} [P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - \frac{1}{2}P_{\lambda\lambda}(\mu\lambda|\mu\lambda)] + \sum_{B \neq A} (P_{BB}-Z_B)\gamma_{AB} \qquad (\mu \text{ on atom A}) \quad (1)$$

$$F_{\mu\nu} = \frac{3}{2}P_{\mu\nu}(\mu\nu|\mu\nu) - \frac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu) \qquad (\mu\ \nu, \text{ both on atom A}) \quad (2)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \qquad (\mu \text{ on atom A and } \nu \text{ on atom B}) \quad (3)$$

where P_{BB} and $P_{\mu\mu}$ are the atomic and orbital charge densities, respectively; $P_{\mu\nu}$ is the orbital bond order; Z_B is the core charge on atom B; γ_{AB} is the two-center electron repulsion integrals; $(\mu\mu|\lambda\lambda)$ and $(\mu\lambda|\mu\lambda)$ are one-center Coulomb and exchange integrals, respectively; $U_{\mu\mu}$ is the one-center core-electron attraction integral; and $\beta_{\mu\nu}$ is the core resonance integral.

In calculating the transition energies and moments, we have adopted the conventional virtual orbital approximations. The energies required to promote an electron from orbital i to virtual orbital j are given by the following expressions for singlet and triplet states, respectively:[5a]

$$\Delta^1E = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij} \quad (4)$$

$$\Delta^3E = \varepsilon_j - \varepsilon_i - J_{ij} \quad (5)$$

where ε_j and ε_i are the energies of the jth and ith molecular orbitals, and where J_{ij} and K_{ij} are the molecular Coulomb and exchange integrals. The dipole moment length for the i-j singlet-singlet transition is given by

$$M_{i-j} = 2\sum_{A}^{N}\sum_{\mu}^{A}\sum_{\nu}^{A} C_{i\mu}C_{j\mu}(\mu|\boldsymbol{r}_A|\nu) \quad (6)$$

where $\boldsymbol{r}_A$ is the coordinate vector operator of atom A.

Refinements of the transition energies by the configuration interaction treatments were not performed in the present calculations. For the geometries of the treated compounds, latest data from Ref. 9 were adopted. The solutions of the Hartree-Fock equations were required to be self-consistent to within 0.001 of all the resulting eigenvalues.

The above procedure was programmed in FORTRAN, and computations were carried out on the FACOM 230-60 Computer at the Kyoto University Computation Center.

Evaluation of Integral Parameters

One-center Parameters. The one-center integrals appropriate to the present calculations are (i) the core-electron attraction integrals, U_{ss} and U_{pp}, (ii) the Coulomb integrals, $(ss|ss)$, $(ss|xx)$, $(xx|xx)$ and $(xx|yy)$, and (iii) the exchange integrals of the types $(sx|sx)$ and $(xy|xy)$. In the framework of INDO approximations, all these energies are related with the Slater-Condon atomic parameters G^1 and F^2.[1a] The principle that we adopt for the evaluation of these one-center integrals is exactly the same as that of Pople *et al.*,[1a] except that we now follow a different semi-empirical procedure in estimating the average one-center electron repulsion integral, F^0.

For a second-row atom X with n valence electrons, the empirical electron repulsion energies may be estimated from[10]

$$g_{ss} = [E(X^-, s^2p^{n-1}) - E(X, sp^{n-1})] - [E(X, sp^{n-1}) - E(X^+, p^{n-1})] \quad (7)$$

$$g_{sp} = [E(X^-, s^mp^{n-m+1}) - E(X, s^{m-1}p^{n-m+1})] - [E(X, s^mp^{n-m}) - E(X^+, s^{m-1}p^{n-m})] \quad (8)$$

$$g_{pp} = [E(X^-, s^mp^{n-m+1}) - E(X, s^mp^{n-m})] - [E(X, s^mp^{n-m}) - E(X^+, s^mp^{n-m-1})] \quad (9)$$

where m may be 0, 1, or 2 wherever appropriate. The various g values can be evaluated from the valence-state ionization data of Hinze and Jaffé.[8] In the case

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[5] a) J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968). b) *Idem., ibid.*, **48**, 4050 (1968). c) *Idem. ibid.*, **49**, 1221 (1968). d) *Idem., idem.*, **50**, 1126 (1969).

[6] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, s129 (1965).

[7] a) H. Kato, H, Konishi, and T. Yonezawa, This Bulletin, **40**, 1017 (1967). b) H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, *ibid.*, **40**, 2761 (1967).

[8] a) J. Hinze and H. H. Jaffé, *J. Amer. Chem., Soc.*, **84**, 540 (1962). b) *Idem., J. Phys. Chem.*, **67**, 1501 (1963).

[9] A. D. Mitchell, ed., "Table of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).

[10] J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta* (Berl.), **7**, 32 (1967).

of a valence-state carbon atom, for example, the g values are 12.10, 11.72, and 11.31 eV.

At the level of the INDO approximation, the empirical repulsion energies may be related with the Slater-Condon parameters by[11]

$$F^0(s,s) = g_{ss} \tag{10}$$

$$F^0(s,p) = g_{sp} + \frac{1}{6}G^1 \tag{11}$$

and

$$F^0(p,p) = g_{pp} + \frac{2}{25}F^2 \tag{12}$$

The parameter, F^0, for each atom with the ground state configuration, s^2p^{n-2}, may then be determined by averaging the values, $F^0(s,s)$, $F^0(s,p)$ and $F^0(p,p)$ over the electron pairs involved. Namely,

$$F^0 = \frac{1}{N}[F^0(s,s) + 2(n-2)F^0(s,p) + \frac{(n-2)(n-3)}{2}F^0(p,p)] \tag{13}$$

with

$$N = 1 + (n+1)(n-2)/2 \tag{14}$$

Using the F^0 values obtained as above and the G^1 and F^2 values given in Pople's INDO paper, the various two-electron parameters can be evaluated.

$$(ss|ss) = (ss|xx) = F^0 \tag{15}$$

$$(xx|xx) = F^0 + \frac{4}{25}F^2 \tag{16}$$

$$(xx|yy) = F^0 - \frac{2}{25}F^2 \tag{17}$$

$$(sx|sx) = \frac{1}{3}G^1 \tag{18}$$

$$(xy|xy) = \frac{3}{25}F^2 \tag{19}$$

The core-electron attraction integrals for atoms from boron to fluorine are[1a)]

$$U_{ss} = -\frac{1}{2}(I_s+A_s) - \left(Z_A - \frac{1}{2}\right)F^0 + \frac{1}{6}\left(Z_A - \frac{3}{2}\right)G^1 \tag{20}$$

$$U_{pp} = -\frac{1}{2}(I_p+A_p) - \left(Z_A - \frac{1}{2}\right)F^0 + \frac{1}{3}G^1 + \frac{2}{25}\left(Z_A - \frac{5}{2}\right)F^2 \tag{21}$$

where I and A are the relevant valence-state ionization potential and electron affinity, respectively.

TABLE 1. ATOMIC PARAMETERS[a)]

	H	C	N	O	F
U_{ss}	−13.595	−52.320	−72.078	−104.841	−131.248
U_{pp}		−44.648	−63.946	− 93.819	−116.272
F^0	12.845	11.715	12.860	15.897	17.233
G^1		7.285	9.416	11.817	14.486
F^2		4.727	5.961	7.250	8.594
I_s	13.595	19.603	23.777	33.234	39.922
I_p		12.309	16.598	20.013	20.452

a) Values given in units of eV.

The one-center parameters evaluated as above for C, N, O, F atoms are listed in Table 1.

For an H atom, the parameters were $U_{ss} = -13.595$ eV and $F^0 = 12.845$ eV.

Two-center Parameters. The two-center repulsion integrals, γ_{AB}, between atoms A and B, which are R_{AB} apart, were evaluated by the Ohno approximation[12)]

$$\gamma_{AB} = 14.397[R_{AB}^2 + (\rho_A + \rho_B)^2]^{-1/2} \tag{22}$$

where

$$\rho_A = 7.199/F_A{}^0; \quad \rho_B = 7.199/F_B{}^0 \tag{23}$$

The core resonance integrals, $\beta_{\mu\nu}$, between atoms A and B were evaluated by the Wolfsberg-Helmholtz expression[13)]

$$\beta_{\mu\nu} = \frac{1}{2}k^{\omega}S_{\mu\nu}(I_\mu{}^A + I_\nu{}^B) \tag{24}$$

where $I_\mu{}^A$ was taken as the valence-state ionization potential of μ AO of atom A. The parameters, k^ω, were so chosen as to reproduce the observed spectroscopic data, namely σ–π^* and π–π^* transition energies. For these purposes, discrimination between k^σ for σ orbitals and k^π for π orbitals was necessary, as was noted by Bene and Jaffé[5a)] in their CNDO treatments of electronic spectra. The final values adopted were $k^\sigma = 1.1$ and $k^\pi = 0.9$.

Results and Discussion

The Values of k$^\sigma$ *and* k$^\pi$. Bene and Jaffé[5)] have shown in their CNDO treatments that, in order to obtain consistent spectroscopic data, the core resonance integrals $\beta_{\mu\nu}$ are necessary to be distinguished between σ and π orbitals. In order to examine whether or not

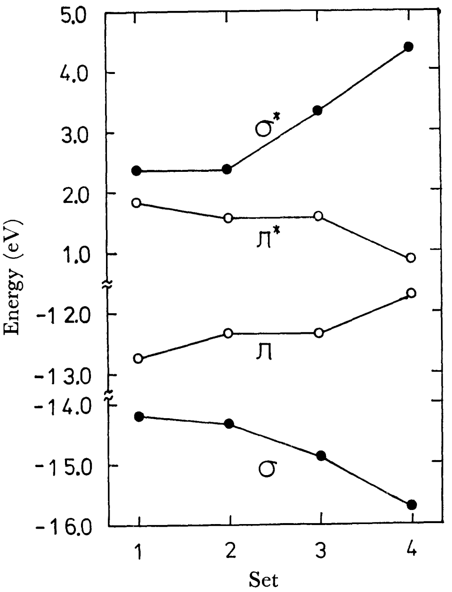

Fig. 1. Variations of the orbital energies of ethylene with the change in the resonance integral parameters used.
Set 1: $k^\sigma = 1.0$ and $k^\pi = 1.0$
Set 2: $k^\sigma = 1.0$ and $k^\pi = 0.9$
Set 3: $k^\sigma = 1.1$ and $k^\pi = 0.9$
Set 4: $k^\sigma = 1.2$ and $k^\pi = 0.7$

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[11] Equations (7)—(9) in the present work, coupled with Eq. (3.16) of Ref. la, generate Eqs. (10)—(12). $F^0(p,p')$, where p and p' are different p orbitals centered on the same atom, were assumed to be equal to $F^0(p,p)$.

[12] K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).

[13] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

this discrimination will likewise be inevitable in the present INDO treatments, we have calculated Δ^1E of the ethylene molecule for various sets of k^σ and k^π values.

Shown in Fig. 1 are the highest occupied and lowest vacant orbital energies, both σ and π, calculated with different choices of k^σ and k^π.

Figure 1 clearly shows that both the σ–σ^* and π–π^* orbital energy separations tend to increase with the increasing k^σ and k^π values. Further, both the calculated π and π^* orbital heights are almost independent of k^σ. Likewise, the σ and σ^* orbital heights are relatively insensitive to the change in k^π. It is therefore obvious that both the σ–π^* and π–σ^* energy separations are dependent on both k^σ and k^π.

On the other hand, neither molecular Coulomb nor exchange integrals, J and K, shows material change with the variation of the core resonance integral parameters, as may be seen in Fig. 2. This facilitates adequate choice of k^σ and k^π values that may reproduce the observed transition energies.

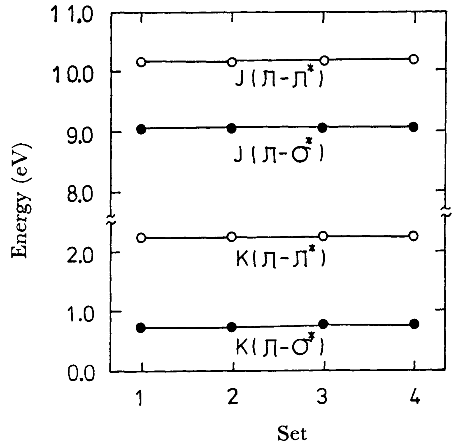

Fig. 2. Variations of the molecular repulsion integrals of ethylene with the change in the resonance integral parameters used.
The parameter sets are the same as those given in Fig. 1.

Similar analyses have been made for a few other compounds. It has been found that the parameter set $k^\sigma=1.1$ and $k^\pi=0.9$ are the most suitable to give consistent spectroscopic data in majority of cases here investigated. In the case of ethylene, the lower transition energies calculated with this parameter set were 8.27, 8.18, and 3.73 eV for the π–π^* ($^1B_{2u}$), σ–π^* ($^1A_{2u}$) and π–π^* ($^3B_{2u}$) transitions, respectively. Although these calculated values are somewhat deviated from the corresponding experimental data, 7.6, 6.4, and 4.8 eV,[3] these deviations are tolerable in view of the neglect of configuration interaction that may be important in such a highly symmetrical molecule.

Carbonyl Compounds. Formaldehyde, formic acid and formamide have been selected for test. The results obtained for lower transitions are summarized in Table 2, together with experimental data.

For each of the three compounds investigated, the calculated values of Δ^1E for both the n–π^* and π–π^* transitions have shown good agreement with the observed. Although the observed data for the triplet state excitation energies are limited, a good agreement is seen in formaldehyde. Therefore, the present parametrization seems to be satisfactory.

TABLE 2. TRANSITION ENERGIES, ΔE, AND TRANSITION MOMENT LENGTHS, M, OF CARBONYL COMPOUNDS

Type	Symmertry[a)]	Calcd		Obsd[b)]	
		ΔE, eV	M, Å	ΔE, eV	f[c)]
		Formaldehyde			
n–π^*	$^1A_2$	3.58	—	4.21	10^{-4}
σ–π^*	$^1B_2$	6.89	0.74	7.07	0.04
π–σ^*	$^1B_1$	7.75	0.65	8.18	
π–π^*	$^1A_1$	9.46	0.77	9.05	~0.1
n–π^*	$^3A_2$	3.14	0	3.12	
π–π^*	$^3A_1$	4.71	0		
		Formic acid			
n–π^*	S	4.68	0.22	5.5—5.8	
σ–π^*	S	6.87	0.27	7.4	
π–σ^*	S	7.60	0.32		
π–σ^*	S	7.64	0.70		
π–π^*	S	8.47	0.78	8.3	
n–π^*	T	4.34	0		
π–π^*	T	5.23	0		
		Formamide			
n–π^*	S	4.69	0.27	5.65	0.002
σ–π^*	S	7.24	0.56	6.80	0.06
π–σ^*	S	7.56	1.02	7.2—7.3, 7.8	0.240
π–π^*	S	7.80	0.76	8.6	~0.1
n–π^*	T	4.34	0		
π–π^*	T	5.26	0		

a) The symbols S and T denote that the excited states are singlet and triplet, respectively.
b) Observed values cited from Ref. 3.
c) Oscillator strength.

According to the present results, the second singlet-singlet transition band of the carbonyl spectra appearing at 7 to 8 eV is ascribed to a π–σ^* transition. As the assignment of this band is not entirely clear as yet,[3] no decisive assessment of the theory is permissive.

Butadiene and Glyoxal. Calculations have next been extended to butadiene and glyoxal. The electronic excitations of these compounds have already been the subject of the all-valence-electrons treatments by Kato *et al.*[7b)] It will be of particular interest to compare the results between their treatments and the present.

The results of calculations for lower energy regions are summarized in Table 3, together with the experimental data. Agreements of the calculated results with the observed data are generally good, except for the energies for the singlet π–π^* transitions of the *s-trans* conformations of both butadiene and glyoxal, in which our calculated values are a little too great. For the n–π^* transitions of glyoxal, our results are more plausible than those of Kato *et al.*[7b)]

In both treatments, the energies predicted for the n–π^* and π–π^* transitions of the *s-cis* conformers are lower than those of their *s-trans* counterparts. For the π–π^* transitions, the tendency agrees with observation.[14)] Also in the n–π^* transition of glyoxal, there is

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[14)] N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **86**, 2811 (1964).

Table 3. Transition energies, ΔE, and transition moment lengths, M, of some conjugated compounds

Conformation	Type	Symmetry[a]	Calcd[b] ΔE, eV	Calcd[b] M, Å	Obsd ΔE, eV	Obsd f
			Butadiene			
s-trans	π-σ^*	^1A_u	6.52	0.24		
	π-π^*	^1B_u	6.61(6.38)	1.38(1.37)	5.7,[c] 6.0[d]	0.53[c]
	σ-π^*	^1A_u	6.83	0.47		
	π-π^*	^3B_u	3.65(4.18)	0 (0)	3.2[e]	
	π-σ^*	^3A_u	5.75	0		
s-cis	π-π^*	$^1B_1$	6.11(6.03)	0.93(0.95)		
	π-σ^*	$^1B_2$	6.51	0.42		
	σ-π^*	$^1B_2$	6.73	0.34		
	π-π^*	$^3B_1$	3.49(4.11)	0 (0)		
	π-σ^*	$^3B_2$	5.77	0		
			Glyoxal			
s-trans	n-π^*	^1A_u	2.79(3.22)	0.37(0.062)	2.72,[f] 3.23[g]	
	n-π^*	^1B_g	4.97(5.81)	— (0)	4.50,[f] 4.33[g]	
	n-π^*	^1B_g	6.10(7.20)	— (0)		
	n-σ^*	^1B_u	7.53	1.05		
	π-π^*	^1B_u	8.37(7.27)	1.09(1.167)	7.2—7.6[f]	
	n-π^*	^3A_u	2.44(2.68)	0 (0)	2.42[f]	
	n-π^*	^3B_g	4.61(5.22)	0 (0)		
	π-π^*	^3B_u	4.82(4.59)	0 (0)		
s-cis	n-π^*	$^1B_1$	2.78(3.18)	0.34(0.065)	2.66[g]	
	n-π^*	$^1A_2$	4.58(5.68)	— (0.034)	4.43[g]	
	n-π^*	$^1A_2$	6.03(7.08)	— (0.006)		
	n-σ^*	$^1B_1$	7.47	0.98		
	π-π^*	$^1B_2$	7.77(6.94)	0.66(0.805)		
	n-π^*	$^3B_1$	2.43(2.60)	0 (0)		
	n-π^*	$^3A_2$	4.20(5.07)	0		
	π-π^*	$^3B_2$	4.50(4.50)	0		
			trans-Crotonaldehyde			
s-trans	n-π^*	S	4.31	0.30	5.87[h]	
	π-π^*	S	6.91	1.38		
	n-π^*	T	4.07	0		
	π-π^*	T	4.08	0		
s-cis	n-π^*	S	4.29	0.28		
	π-π^*	S	6.57	1.08		
	n-π^*	T	4.06	0		
	π-π^*	T	4.07	0		

a) The symbols S and T denote that the excited states are singlet and triplet, respectively.
b) The values given in parentheses are those calculated by Kato *et al.* [7b]
c) Taken from Ref. 3.
d) Taken from Ref. 16b.
e) D. F. Evans, *J. Chem. Soc.*, **1960**, 1735.
f) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).
g) Taken from Ref. 15.
h) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York (1962), p. 213.

an indication of agreement between theory and experiment, if the Δ^1E values (2.66 and 4.43 eV) of a cyclic *cis*-α-diketone[15] may be assumed to closely approximate those of the *s-cis* conformation of glyoxal.

The trend that the π-π^* excitation energies calculated for *s-trans* conformation of a conjugated compound are greater than those for its *s-cis* conformer has long been noticed.[16-18] The trend now appears to be generally true with excitations including those of the n-π^* and σ-π^* types. This generalization seems not to be

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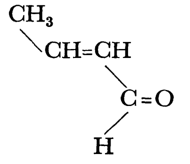
[15] N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, **72**, 5388 (1950).

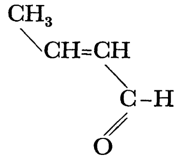
[16] a) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950). b) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

[17] M. Klessinger and W. Lüttke, *Z. Electrochem.*, **65**, 707 (1961).

[18] A. Julg and J. C. Donadini, *Compt. rend.*, **252**, 1798 (1961).

affected by the level of sophistication at which the approximations used have been laid. The π–π* and *n*–π* transition energies calculated for *trans*-crotonaldehyde (I) have been included in Table 3, as an example that may serve to reinforce the above generalization.

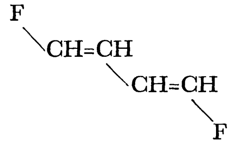

I (*s-trans*)

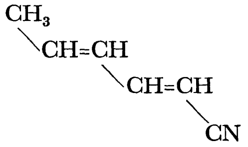

I (*s-cis*)

1,4-Disubstituted Butadienes. Butadiene derivatives that are substituted at the terminal carbon(s) have well-defined geometrical isomers, which can be separated from one another.

We here apply the present method of calculations to geometrical isomers of 1,4-difluorobutadiene (II) and sorbonitrile (III), to investigate the effect of geometrical isomerism on electronic spectra.

The reason for the choice of the F, CH_3, and CN groups as substituents is that they introduce no knotty problem of conformational multiformity with respect to the bond through which the substituents are linked with the sp^2 carbon. The butadiene framework will be assumed to be in the *s-trans* form, and various isomers will all be treated as having coplanar structure.


II (*trans,trans*)


III (*trans,trans*)

The results of calculations for low energy transitions are summarized in Table 4, together with experimental data wherever available. The energies and moment lengths for the π–π* transitions have also been calculated by the Pariser-Parr-Pople π-electron approximation (the PPP method).[4)]

Table 4. Transition energies, ΔE, and transition moment lengths, M, of butadiene derivatives

Configuration	Type	Spin-state[a]	Calcd ΔE, eV	Calcd M, Å	Calcd (PPP)[b] ΔE, eV	Calcd (PPP)[b] M, Å	Obsd ΔE, eV
			1,4-Difluorobutadiene-1,3				
cis,cis	π–σ*	*S*	5.74	0.03			
	π–π*	*S*	6.28	1.39	6.206	1.42	5.69[c]
	π–π*	*T*	3.52	0	2.965	0	
trans,cis	π–σ*	*S*	5.27	0.45			
	π–π*	*S*	6.26	1.39	6.214	1.49	5.82[c]
	π–π*	*T*	3.55	0	2.977	0	
trans,trans	π–σ*	*S*	4.82	0.38			
	π–π*	*S*	6.29	1.41	6.223	1.50	5.85[c]
	π–π*	*T*	3.56	0	2.986	0	
			Sorbonitrile				
cis,cis	π–π*	*S*	5.65	1.49	5.137	1.83	5.17[b]
	π–π*	*T*	3.51	0	2.880	0	
trans,trans	π–π*	*S*	5.74	1.62	5.200	1.93	5.28[b]
	π–π*	*T*	3.57	0	2.951	0	

a) The symbols *S* and *T* denote that the excited states are singlet and triplet, respectively.

b) Taken from Ref. 20.

c) Taken from Ref. 21.

The singlet π–π* transition energies and moment lengths calculated by the Modified INDO and the PPP methods are numerically almost equal. However, these energies are uniformly a little too great as compared with the observed values. Experimentally, the bathochromic (red) shifts are recognizable for the singlet π–π* transitions on going from the *trans,trans* to *cis,cis* isomers. The theoretical results obtained by the PPP method agree with observation,[19)] while those by the Modified INDO method partly fail to reproduce the tendency.

As for the triplet π–π* transitions, there is no experimental data available. It will only be noted here that the values of Δ^3E calculated by the present method are all greater than those obtained from the PPP calculations.

Finally, according to the results of the present treatments, the singlet π–σ* excited state of II is lower-lying than the singlet π–π* excited state. Also, the moment lengths of the transitions leading to the former excited state is sufficiently great to warrant observation in usual cases. Since such transitions were not recorded together with the π–π* transitions, the calculated values of ΔE are perhaps too small.

Conclusions

The INDO method of Pople *et al.* is useful for the calculations of the quantities concerning the electronic transitions of unsaturated compounds, provided the two-electron repulsion integrals are evaluated from the atomic spectroscopic data. In particular, discrimination between the singlet and triplet states resulting from the *n*–π* transition of carbonyl compound comes up with satisfactory accuracy. Success attained in the interpretations of the excited-state properties of molecules allows us to anticipate versatile usefulness of Dewar's MINDO method in various chemical problems.

[19)] In our separate piece of work, we have measured the lowest singlet π–π* excitation energies of a great number of 1-substituted and 1,4-disubstituted butadienes and found that the *trans* and *trans,trans* isomers have greater excitation energies and oscillator strengths than do the corresponding *cis* and *cis,cis* isomers, with no exception whatsoever. The PPP calculations have been found to give results that are in accord with all these experimental data. Details will be presented elsewhere.[20)]

[20)] T. Fueno and K. Yamaguchi, to be published.

[21)] H. G. Viehe, *Chem. Ber.*, **97**, 598 (1964).