BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3290—3293 (1972)

Comparison of the Electronic Spectra of Geometric Isomers. II. 1,2-Disubstituted Ethylenes

Takayuki FUENO and Kizashi YAMAGUCHI
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

(Received February 21, 1972)

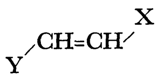
The ultraviolet absorption spectra of the *cis* and *trans* isomers of various 1,2-disubstituted ethylenes were measured in isopentane solution. Each isomer showed a single intense band assignable to the lowest π—π^* transition. For the majority of the compounds studied, both energy and oscillator strength of transition are found to be greater for *trans* isomers than for the corresponding *cis* isomers, in accord with the general trend predicted by the Pariser-Parr-Pople calculations. Existence of some anomalous cases which contradict the generalization indicates a limited validity of the usual assumption of virtual orbitals.

Despite abundant data available for the ultraviolet absorption spectra of unsaturated compounds,[1] very few comparative studies have been made on the spectra of *cis* and *trans* isomers of olefins. A study on the π—π^* transitions of *cis*- and *trans*-stilbenes revealed that the *cis* isomer shows absorption peaks in shorter wavelength regions than does the *trans*.[2] Several workers agreed in attributing the higher-energy shift of the lowest transition peak of *cis*-stilbene to its nonplanarity resulting from the *steric repulsion* between the two phenyl groups located *cis* to each other.[3-6]

We recently reported[7] that in both gaseous phase and *n*-hexane the lowest π—π^* transition energy of the majority of terminal-substituted butadienes is more or less greater for isomers bearing the substituent(s) at the *trans* placement(s). Since all these compounds are likely to be planar in structure, the observed trend must be taken as a reflection of a certain *electronic effect* of the fully conjugated chromophores. The LCMO-SCF-CI computations of the Pariser-Parr-Pople (PPP) type[8,9] showed that this electronic effect might be related with the smaller inter-frontier-orbital Coulombic repulsion J_{hl} for the isomers having more of the *trans* ethylenic moieties.

Experimental data which may be tested for the above argument are very scanty for ethylene derivatives. Walsh[10] reported that the lowest π—π^* excitation energies Δ^1E for *trans*- and *cis*-dichloroethylenes in the gaseous phase are 6.36 and 6.53 eV, respectively. Gary and Picket[11] reported that, in the same phase, the values of Δ^1E for the *trans* and *cis* isomers of butene-2 are 6.975 and 7.066 eV, respectively. Both these sets of data show that the excitation energies are smaller for *trans* isomers, in contradiction to the generalization found for the butadiene derivatives. The situation has led us to examine the electronic spectra of 1,2-disubstituted ethylenes more extensively.

We have thus undertaken to measure the ultraviolet absorption spectra of *cis* and *trans* isomers of a variety of 1,2-disubstituted ethylenes.



$$Y\diagup CH{=}CH\diagup X$$

$X = CH_3$, Cl, OCH_3, CN, or COR

$$Y = \begin{cases} CH_3 \text{ (1-substituted propenes)} \\ X \text{ (symmetrically 1,2-disubstituted ethylenes)} \end{cases}$$

It has turned out that the generalization also holds for most of the ethylene derivatives here studied. Theoretical treatments of the PPP type rationalize the observed trend. Dichloroethylene and butene-2 have been verified to be exceptions. Most likely, the usual assumption of virtual orbitals is greatly invalidated in such compounds. These results will serve as a guide in the study of the excited electronic structure of olefin isomers.

Experimental

Methyl propenyl ether (**1**),[12] 1,2-dimethoxyethylene (**9**),[13]

---

[1] For instance, H. H. Jaffé, and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y. (1962).

[2] H. Suzuki, This Bulletin, **33**, 381 (1960).

[3] H. Suzuki, *ibid.*, **33**, 379 (1960).

[4] H. H. Jaffé and M. Orchin, *J. Chem. Soc.*, 1078 (1960).

[5] D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, **87**, 5340 (1965).

[6] H.-H. Perkampus and J. V. Knop, *Theoret. Chim. Acta*, (*Berl.*), **6**, 45 (1966).

[7] T. Fueno and K. Yamaguchi, *J. Amer. Chem. Soc.*, **94**, 1119 (1972).

[8] R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[9] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[10] A. D. Walsh, *ibid.*, **41**, 35, 76 (1945).

[11] J. T. Gary and L. W. Picket, *J. Chem. Phys.*, **22**, 599 (1954).

[12] M. Farina, M. Peraldo, and G. Bressan, *Chim. Ind.* (Milan), **42**, 967 (1960).

[13] H. Baganz, K. Praefcke, and J. Rost, *Chem. Ber.*, **96**, 2657 (1963).

and 1,2-dicyanoethylene (**10**)[14] were prepared according to the methods given in the literature. They were separated into geometric isomers by means of preparative gas chromatography. Column packings used were poly(ethylene glycol). Column length (3—5 m) and operating temperature (80—150°C) were so chosen as to best suit the separation. Hydrogen was used as a carrier gas at a flow rate of 25 m*l*/min.

The *cis* and *trans* isomers of crotononitrile (**2**), crotonic acid (**4**), crotoamine (**5**) and methyl propenyl ketone (**6**) were supplied by Dr. Kobuke, Kyoto University. *trans*-Crotonaldehyde (**3**) and diethyl maleate and fumarate (**11**) were purchased and distilled.

All the geometric isomers were identified from the magnitudes of NMR coupling constants observed between the olefinic hydrogen atoms. Gas chromatography showed that all samples had an isomeric purity exceeding 95%.

The absorption spectra were measured on isopentane solutions. Isopentane was purified by passing through an alumina column of 1.5 m in length and 2 cm in diameter. Sample solutions were prepared by dissolving *ca.* 20 mg of olefin in 10 cc of isopentane. The solutions were further diluted down to *ca.* 10^{-5}M, and were degassed before observation. A quartz cell with a 1 cm path length was used. The spectra were recorded on a Cary Model 15 spectrophotometer at room temperature under an atmosphere of nitrogen gas. The extinction coefficient obtained was not corrected for possible isomeric impurities.

Method of Calculation

The LCAO–MO–CI method of the Pariser-Parr-Pople (PPP) type was used for calculating the energies and oscillator strengths of the π—π^* transitions. The integral parameters used for the present calculations were all the same as those adopted previously.[7]

All the ethylene derivatives were assumed to be coplanar. The bond lengths and angles of the various 1,2-disubstituted ethylenes were taken from the literature.[15]

The spin configurations were constructed using the SCF closed-shell virtual orbitals. The configuration interactions were treated by including lower 10 (at maximum) singly excited configurations. All computations were perfomed on a KDC–II at the Computation Center of Kyoto University.

Results and Discussion

A. Absorption Spectra. Figure 1 shows the absorption spectra of the *cis* and *trans* isomers of crotonic acid (**4**) as an example. They show a strong absorption miximum at 208 and 207 nm, respectively. Although the Franck-Condon maxima are hard to locate, these band maxima may be used for our present purposes.

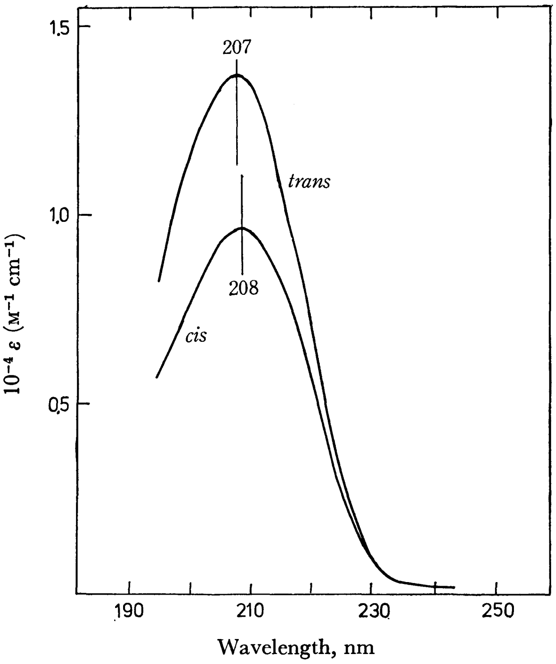


Fig. 1. Absorption spectra of *cis*- and *trans*-crotonic acids in isopentane.

The spectral data obtained are summarized in Table 1, together with those for butene-2 (**7**)[11] and dichloroethylene (**8**).[10] All the compounds show one intense band with or without vibrational structure in the wavelength region 190—250 nm. No doubt, the observed bands correspond to the lowest π—π^* excitation.

Inspecion of the experimental data given in Table 1 indicates that, except for **2**, **7**, **8**, and **11**, both energy Δ^1E and oscillator strength f of the lowest π—π^* excitation of a given 1,2-disubstituted ethylene are more or less greater for the *trans* isomer. This tendency has no direct bearing on the relative stabilities of geometric isomers; *cis*-**9** is probably more stable than its *trans* isomer,[16,17] whereas *trans*-**1** is known to be thermochemically more stable than its *cis* isomer by *ca.* 0.9 kcal/mol at ordinary temperature.[17] The exceptions **2**, **7**, **8**, and **11** will be discussed later.

The energy difference between the *cis* and *trans* isomers of **6** is large compared to those for the other carbonyl compounds, **4** and **5**. This is probably due to the concurrent effects of the configurational and conformational differences between the isomers. While α,β-unsaturated carbonyl compounds exist predominantly in the planar *s-trans* conformation, the most stable form of *cis*-**6** is the *s-cis* conformation because of the steric repulsion between the two methyl groups.[18] The *s-trans* conformation of a conjugated framework generally tends to give greater excitation energies than does the *s-cis* counterpart.[19,20]

As regards the oscillator strength, **2** is not anomalous; the *trans* isomer has a greater f value, in harmony with

---

[14] D. T. Mowry and J. N. Butler, "Organic Syntheses," Coll. Vol. 4, 486 (1963).

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

[16] T. Okuyama and T. Fueno, *J. Polymer Sci. A-1*, **9**, 629 (1971).

[17] T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969).

[18] Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, **92**, 6548 (1970).

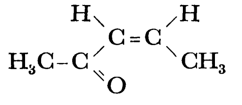
[19] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

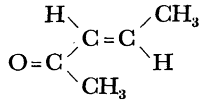
[20] N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **86**, 2811 (1964).

Table 1. Lowest singlet π—π^* transitions of 1,2-disubstituted ethylenes

Serial No	Substituents		Geometry[a]	Obsd[b]			Calcd			
	X	Y		ΔE, eV	$\lambda_{\max}$, nm	f(10^{-3} ε, $\mathrm{M}^{-1}\mathrm{cm}^{-1}$)	ΔE, eV	J_{hl}, eV	f_x	f_y
1	OCH_3	CH_3	*cis*	6.41	193		6.798	6.287	0.605	0.017
			trans	6.47	192		6.872	6.251	0.633	0.257
2	CN	CH_3	*cis*	6.17	201	0.135 (5.4)	6.105	5.680	0.804	0.014
			trans	6.14	202	0.344 (13.8)	6.183	5.625	0.819	0.391
3	CHO	CH_3	*cis*				5.646	5.604	0.917	0.0
			trans	5.87	211	0.184 (9.5)	5.698	5.544	0.937	0.200
4	COOH	CH_3	*cis*	5.97	208	0.277 (9.6)	5.819	5.670	0.921	0.0
			trans	5.99	207	0.379 (13.8)	5.859	5.604	0.942	0.201
5	$CONH_2$	CH_3	*cis*	6.12	203		6.031	5.520	0.932	0.004
			trans	6.16	201		6.064	5.492	0.961	0.152
6	$COCH_3$	CH_3	*cis*[c]	5.64	220	0.226 (8.8)	5.589	5.459	0.397	0.356
			cis				5.608	5.500	0.682	0.004
			trans	5.76	215	0.293 (11.5)	5.681	5.419	0.720	0.219
7	CH_3	CH_3	*cis*	7.07[g]		0.59[g]	6.615	5.852	0.804	0.0
			trans	6.98[g]		0.32[g]	6.669	5.809	0.813	0.339
8	Cl	Cl	*cis*	6.53[h]			7.430	6.885	0.711	0.0
			trans	6.36[h]			7.432	6.859	0.715	0.065
9	CH_3O	CH_3O	*cis*[d]				7.395	6.851	1.068	0.000
			cis[e]	6.16	201	0.384 (13.0)	7.322	6.880	0.631	0.022
			trans[d]	6.20	200	0.433 (11.3)	7.344	6.873	0.678	0.084
			trans[f]				7.308	6.903	0.398	0.171
10	CN	CN	*cis*	5.64	220		5.821	5.608	0.881	0.0
			trans	5.65	219		5.900	5.534	0.890	0.448
11	$COOCH_3$	$COOCH_3$	*cis*	6.12	203		5.736	5.702	1.149	0.0
			trans	5.94	209		5.806	5.670	1.178	0.101

a) The molecular conformation, whenever appropriate, is assumed to be *s-trans*, unless otherwise noted.
b) Measured in isopentane, unless otherwise noted.
c) *s-cis* conformation assumed (see text).
d) *s-trans,s-trans.*
e) *s-trans,s-cis.*
f) *s-cis,s-cis.*
g) Gas phase data, Ref. 11. F. H. Watson, Jr. and S. P. McGlynn, *Theoret. Chim. Acta*, (Berl.), **21**, 309 (1971), have also reported gas-phase data: ΔE=6.58 (*cis*) and 6.48 (*trans*) eV and ε=12.2×10^3 (both *cis* and *trans*).
h) Gas phase data, Ref. 10.


cis-**6** (*s-cis*)


trans-**6** (*s-trans*)

the trend for the majority of "normal" compounds. Butene-2 (**7**), however, is still anomalous.

B. Calculated Excitation Energies. Calculations of the PPP type were performed for all the compounds **1** through **11**. For all isomers of these compounds, the lowest π—π^* excitation was the only intense transition in our wavelength range of interest. In what follows, we will be concerned only with the lowest π—π^* transition. The calculated excitation energies Δ^1E are listed in Table 1.

It may be noticed in Table 1 that the Δ^1E values calculated for *trans* isomers are, without exception, greater than those for the corresponding *cis* isomers. The differences between the calculated values are *ca.* 1% the excitation energies, in rough agreement with those observed for "normal" cases. As our present problem lies in the comparison of geometric isomers, we will not concern ourselves with numerical agreement between the calculated and observed values for individual isomers.

The isomeric difference calculated for **6** is in better agreement with the observed, when the *s-cis* conformation is assumed for the *cis* isomer than when the *s-trans* conformation is assumed. Also, the calculated results for **9** are best correlated with observation, if it is assumed that the *cis* isomer is in the *s-trans,s-cis* conformation while the *trans* isomer is in the *s-trans, s-trans* conformation.

The anomaly encountened in **11** is apparently due to the twisting of the *cis* isomer around its C–C single bonds because of the steric repulsion between the methoxycarbonyl groups. The essential discord between theory and experiment for the cases **2**, **7**, and **8** cannot be interpreted from the conformational consideration. Neither can it be remedied by means of all valence-electron theories. For example, the excitation energies of **2** calculated by the INDO method[21] are 11.137 and 11.163 eV for the *cis* and *trans* isomers, respectively.

---

[21] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

By our modified INDO method,[22] they are calculated to be 6.801 and 6.833 eV. Both these calculations give a higher excitation energy for *trans*-**2**, in disagreement with observation. The disagreements in **2**, **7**, and **8** will be discussed in Subsection D.

We previously ascribed the greater excitation energies for *trans* isomers of butadiene derivatives to their smaller Coulomb repulsion J_{hl} between the highest occupied and lowest vacant π orbitals.[7] Exactly the same situation has been confirmed with th Δ^1E values calculated for ethylene derivatives. For the sake of comparison, the calculated values of J_{hl} are included in Table 1. It is our working hypothesis that J_{hl} somehow measures a relief of a molecule from intramolecular electronic repulsion upon excitation, so far as the virtual orbital approximation is not greatly in error. That *cis* isomers have greater values of J_{hl} than the corresponding *trans* isomers is obvious from the relatively small spatial separations between the substituents. Apparently, the hypothesis is invalidated in the cases of **2**, **7**, and **8**.

C. Oscillator Strengths. The oscillator strength f may be calculated from the expression

$$f = 1.085\times10^{-5}\nu(r_x{}^2+r_y{}^2) = f_x + f_y \qquad (2)$$

where ν is the frequency of transition (cm^{-1}) and r_s ($s=x$ or y) is the transition moment length (Å) in the specified direction, x or y (Fig. 2). The values of f_x and f_y calculated for isomers of various ethylene derivatives are given in Table 1.

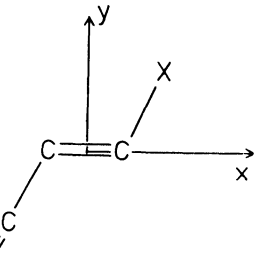


Fig. 2. Coordinate axes chosen for 1-substituted propenes.

It can be seen from Table 1 that there is little difference in the f_x value between the isomers, whereas the f_y value is considerably greater for the *trans* isomers. As a consequence, the sum f_x+f_y for a *trans* isomer is greater than that of the corresponding *cis* isomer, in agreement with observation. However, the unusually large f value reported for *cis*-**7** is hardly justifiable.

D. Ionization Potential. As has already been mentioned, the anomalous spectral features of **2**, **7**, and **8** cannot be attributed to steric strains in the *cis* isomers. A comparison of the ionization potentials of geometric isomers shows this to be the case.

Table 2 gives the observed[23] and calculated (PPP) vertical ionization potentials I_p for the *cis* and *trans* isomers of **1**, **2**, **7**, and **8**. The I_p values observed for *cis* isomers are greater than those for *trans* isomers only by a few hundredths of an electron volt. The isomeric differences calculated by assuming planar structures are found to be in good agreement with the observed. Thus, so far as the ground-state structure is concerned, nothing anomalous is perceptible for those spectroscopically anomalous olefins **2**, **7**, and **8**. If the *cis* isomers were greatly twisted in the ground state, their I_p values relative to the *trans* isomers would be more marked. For the sake of comparison, the relevant data for 1-phenyl-1-propene $C_6H_5CH{=}CHCH_3$ are included in Table 2. The isomeric difference found for this compound is as great as 0.11 eV, which should be attributed to the nonplanarity of the *cis* isomer.[24] All these results lead to the conclusion that stereostructures of the *cis* isomers of **1**, **2**, **7**, and **8** do not differ greatly, irrespective of their excitation characteristics.

Table 2. Vertical ionization potentials of some 1,2-disubstituted ethylenes

Compound	Geometry	I_p, eV Obsd[23]	I_p, eV Cacld (PPP)
1	*cis*	8.47	10.01
	trans	8.43	10.00
2	*cis*	10.21	10.66
	trans	10.20	10.65
7	*cis*	9.12[a]	10.39
	trans	9.12[a]	10.38
8	*cis*	9.83[b]	9.31
	trans	9.81[b]	9.29
1-Phenyl-1-propene	*cis*	8.44	9.78[c]
	trans	8.33	9.67

a) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

b) R. F. Lake and S. H. Thompson, *Proc. Roy. Soc.* (London), **A315**, 323 (1970).

c) The phenyl group is assumed to be rotated out of plane by 30°.[24]

Concluding Remarks

For most of the 1,2-disubstituted ethylenes the energy of the lowest singlet excitation is greater for *trans* isomers than for the corresponding *cis* isomers. Of the various ethylene derivatives studied, butene-2 (**2**), crotononitrile (**7**), dichloroethylene (**8**) were anomalous in the above respect. The oscillator strength is greater for *trans* isomers, with virtually no exceptional case. The generalization can be rationalized by the PPP calculations.

Changes in electronic population upon excitation might be drastic in some ethylene derivatives. In cases where reorganization of the electronic structure upon excitation is considerable, the virtual orbitals would no longer be capable of depicting the Franck-Condon excited states with reasonable accuracy. Anomalous spectral behaviors of the *cis* isomers of **2**, **7**, and **8** could be ascribed to this change. However, the reason for it to occur only in these particualr compounds is still unclarified.

---

[22] K. Yamaguchi and T. Fueno, This Bulletin, **44**, 43 (1971).

[23] The authors are indebted to Prof. S. Ikeda and Dr. I. Watanabe, Osaka University, for measurements of the photoelectron spectra for **1**, **2**, and 1-phenyl-1-propene.

[24] T. Fueno, K. Yamaguchi, and Y. Naka, This Bulletin, the succeeding article.